Structure of Transition Metal Carbides*

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Synopsis

Crystal structure of binary and ternary carbides of transition metals and electronic structure of some simple carbides and nitrides are reviewed; the carbide precipitation from steels is also discussed. Various carbide structures are classified into some groups and types according to the mode of metal atom arrangement, and each of them is described in detail. Although there are many types in the carbide structures, only three types are observed as for the metal atom arrangement in carbon environment. The bonding nature between metal and carbon atoms is considered to be responsible for the occurrence of the three types. The electronic structure is described, especially on NaCl type carbides and nitrides. A brief description is given for the crystallographic aspects of the carbides precipitated from steels.

I. Introduction

Elements in the group IVa (Ti, Zr, Hf), Va (V, Nb, Ta), VIa (Cr, Mo, W), VIIa (Mn) and VIII (Fe, Co, Ni) in the periodic table are typical transition metal elements playing important roles in science and industry. They react with carbon under appropriate conditions to form carbides. The precipitation of such carbides is known to strongly affect the properties of steel. Some carbides are also useful as refractory and tool materials. Because of their importance many studies have been carried out for a long time in the field of metallurgy and metallurgical engineering. Recently, it was found that most of the carbides become superconductive when their mother metals are superconductors, and attentions have been attracted to their low temperature properties.

Generally speaking, the transition metal carbides have the following properties:

- i. Large hardness and brittleness
- ii. High melting point
- iii. Good electrical and thermal conductivity
- iv. Non-stoichiometric composition (for some carbides).

The properties i and ii suggest the nature of atomic bonding to be covalent or ionic and the properties iii and iv the nature to be metallic. In fact, we cannot consider the transition metal carbides to be simply covalent, ionic or metallic crystals; the carbides have the three characters in identical degrees. This is different from the carbides of normal metals and of semiconductors, in which the bonding nature is covalent (for instance, SiC) or ionic (for instance, CaC₂). The hybrid nature of transition metal carbides makes it difficult to interpret their properties on the basis of electron theory, and only a few trials have been made in a simple case.

The determination of crystal structure is the basis of solid state research. Many carbide structures have

been determined by means of X-ray diffraction. Especially, Westgren and his associates have made great contributions. Like nitrides, borides and hydrides of metals, the carbides are interstitial compounds. In 1931 Hägg¹⁾ proposed the famous rule connecting the structures of interstitial compounds with radius ratio of the non-metal to metal atom, saying that if the ratio does not exceed a certain value, approximately 0.59, the lattice of metal atoms are simple, *i.e.*, cubic or hexagonal close packed, both of which having co-ordination number of 12; if it exceeds this value, complex structures arise. In 1948 Goldschmidt²⁾ made a survey on the carbide structures in alloy steels. About twenty years have passed since his survey. Many carbides have been found and their structures determined. Progress of the theory and technique of X-ray diffraction has contributed to the structure determination. Introduction of neutron diffraction and electron diffraction has also made great contributions. The first application of electron diffraction to the carbide study was done by one of us in 1950.³⁾ Furthermore, electron microscopy associated with selected area diffraction opened the door to the morphology and structure of sub-microscopic carbides dispersed in steels. Therefore, it seems to be worthy to summarize the results of carbide studies so far done, in order to serve metallurgists who study the carbides in steels, by describing their crystal and electronic structures. The description of the mode and mechanism of carbide precipitation from steels is not our chief aim and only a part of this paper is devoted for this purpose.

II. X-Ray, Electron and Neutron Diffractions and the Carbide Structure Determination

X-ray diffraction is the most general method for the structure determination. General procedure to determine the structure of a crystal is to take X-ray diffraction patterns of a single crystal of known composition and to determine its crystal system, space group and unit cell dimensions. Number of formula units in the unit cell is determined by density measurement. Diffraction intensities from various lattice planes are measured and the Patterson-Fourier method is applied to determine atomic co-ordinates in the unit cell. Sometimes, especially for a crystal with simple structure, the trial and error method is applied to test the correctness of an assumed structure. In the case of carbide crystals, however, it is not always possible to obtain single crystal specimens appropriate in size (about 0.1 mm in diameter) and the structure deter-

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mination must be done only by using powder specimens. This is a hard problem for a crystal with complex structure except a case where the diffraction data happen to be similar to those of a crystal with known structure. Carbide specimens for X-ray studies are generally produced by heating or melting homogeneous mixtures of metal and carbon powders in hydrogen gas or in vacuum, or by carburizing metals with carbon monoxide or hydrocarbon gas. The electrolytic separation method is also useful to examine carbides precipitated in steels.

In X-ray diffraction, the contribution of carbon atom to the reflection intensity is small relative to that of metal atom because of the weak scattering power of the former. Therefore, the determination of carbon atom positions is rather hard in X-ray diffraction. On the contrary, since the ratio of scattering amplitude of carbon atom to that of metal atom for electrons is two to four times as large as the corresponding ratio for X-rays, the carbon atom positions can rather easily be determined in electron diffraction. The fact that only a small amount of specimen (thinner than 1 000 Å) is necessary and that single crystalline diffraction patterns can easily be obtained makes it favourable to study the carbide by electron diffraction. Especially, structural studies of carbides finely dispersed in steels can only be done with selected area diffraction method. In addition to this, the electron diffraction has a merit that the electronic states of interstitial atoms in crystals can be determined for some kinds of carbides and nitrides by a rather crude measurement of low order reflection intensities.⁴⁾ In X-ray diffraction the determination of the electronic state of constituent atoms can only be done by a quite precise intensity measurement,^{5),6)} and in neutron diffraction it is impossible, if only the nuclear scattering is concerned. However, the interaction between incident electrons and a crystal lattice is so strong that it gives rise to the multiple scattering of electrons, so that the dynamical effect must always be taken into consideration to analyse the diffraction patterns. Specimen films for electron diffraction can easily be produced by carburizing thin metal films or by applying the electrolytic separation method. The thin foil technique in electron microscopy has successfully been applied to get informations about a relationship between the crystal shape and the structure and about lattice relationships between precipitated carbides and a matrix. In our laboratory, a direct reaction of metal atoms produced by the vacuum-arc evaporation method with amorphous carbon films and cleaved graphite films has been used to produce carbide films.⁷⁾⁻⁹⁾ This method has an advantage that carbides, even if they are only stable at very high temperatures, can easily be produced with a simple device.

Neutron diffraction is the most powerful method to determine the carbon atom positions in crystals. This is because the scattering lengths of carbon and metal nuclei are in the same order of magnitude and the reflection intensities are contributed in the same degree concerning the carbon and metal atoms. However, a quite large amount of specimen (capsule size : about

20 mm in diameter) is necessary since the scattering power of atom for neutrons is only one tenth of that for X-rays, and it is difficult to use single crystalline carbide specimens because of the difficulty in producing large crystals.

As described above, each of X-ray, electron and neutron diffractions has its advantages as well as disadvantages. Accordingly, the structural study of carbides should be done by appropriately applying the above three methods. It seems to be best to use X-rays for the determination of metal atom positions and electrons or neutrons for the determination of carbon atom positions.

III. Various Types in Carbide Structures

Various types of structures are found in the transition metal carbides ; some have simple structures and some complex ones. In this article, the structures are classified in the following ways :

Metal atoms take—	
Simple structures	
BCC group	body centered cubic (bcc) arrangement
FCC group	face centered cubic (fcc) arrangement
HCP group	hexagonal close packed (hcp) arrangement
SH group	simple hexagonal (sh) arrangement
Modified group	modified forms of fcc, hcp or sh arrangement
Complex structures	
M ₃ C ₂ type	M represents one or more metallic elements
M ₃ C type	"
M ₅ C ₂ type	"
M ₇ C ₃ type	"
M ₂₃ C ₆ type	"
M ₃ W ₉ C ₄ type	" (W: tungsten)
M ₆ C type	M represents two or more metallic elements.
Other types	

For the simple structures, the classification is made according to the mode of metal atom arrangement in a unit cell, so that each group contains various structure types. For the complex structures, on the other hand, such grouping is impossible and the classification is made according to the chemical formula.

In Table 1 single carbides hitherto found are arranged according to the periodic table. Carbides whose existence has not been fully confirmed are put in parentheses. We can find from this table that some correlations exist between the carbides and their mother metals. Ti, Zr and Hf produce FCC group carbides and V, Nb and Ta produce FCC and HCP group carbides. The melting points of these carbides are higher than those of the corresponding mother metals. Mo and W produce FCC, HCP, SH and modified group carbides, which are stable up to temperatures comparable with the melting points of their mother metals. Cr and Mn form the carbides with complex structures whose thermal stability is about the same order as that of their mother metals. Fe, Co and Ni form the carbides with the simple and complex structures and all the carbides are metastable. Based on these facts we divide the carbide formers in the following five classes :

Class 1 metals : Ti, Zr, Hf

Table 1. Single carbides of transition metals and their positions in the periodic table
(Carbides whose existence has not fully been confirmed are shown in parentheses.)

IVa		V a		VI a		VIIa		VIII						
Class Ti Zr 1 Hf		Class V Nb 2 Ta		Class 4 Cr Mo Class 3 W		Mn		Class 5 Fe, Co, Ni						
Simple structures	TiC		VC		V ₂ C		(CrC)		(Fe ₄ C)		ε · Fe ₂₃ C			
	ZrC		NbC		Nb ₂ C		α · MoC _x β · Mo ₂ C γ · MoC η · MoC _x γ' · MoC		Co ₂ C		ε · Ni ₃ C			
	HfC		Ta ₆₄ C		TaC		β · W ₂ C α · W ₂ C WC		FCC		HCP			
	Group		FCC		BCC		FCC		HCP		SH		Mod.	
Complex structures	Cr ₂₃ C ₆		Mn ₂₃ C ₆		Mn ₇ C ₃		Fe ₇ C ₃		Fe ₅ C ₂		M ₂₃ C ₆			
	Cr ₇ C ₃		Mn ₅ C ₂		Mn ₃ C		Fe ₃ C		Co ₃ C		M ₇ C ₃			
	Cr ₃ C ₂		Mn ₄ C		Mn ₈ C ₃						M ₅ C ₂			
			Mn ₇ C ₃		Mn ₇ C ₂						M ₃ C			
											M ₃ C ₂			
											Others			

V. Structure of FCC Group Carbides

The structure of FCC group carbides is shown in

Fig. 1. Structure of $Ta_{64}C$

- (a) Unit cell of bcc Ta containing a carbon atom. Open circles represent Ta atoms and crosses octahedral interstices which are at the face and edge centers of the lattice. One of the interstices is occupied by the carbon atom represented by the filled circle.
- (b) Unit cell of $Ta_{64}C$, which is tetragonal with dimensions $a \leq 4a_0$ and $c \geq 4a_0$. The carbon atoms take an ordered arrangement.

Fig. 2, where the large open circles represent metal atoms and the small filled ones the octahedral interstices formed by the metal atoms. If the composition is MC, all the octahedral interstices are occupied by carbon atoms and the structure becomes NaCl type, and if the composition is M_4C and only the body center site is occupied, the structure becomes perovskite type. No case has been found to take ZnS type structure.

1. NaCl Type Carbides

NaCl type carbides are formed by the class 1, 2 and 3 metals. The carbides of class 1 and 2 metals exist in a wide range of the chemical composition and they are non-stoichiometric. Table 3 shows their crystallographic data. The lattice parameter increases with carbon content, whose maximum is almost 50at% C, as shown in Fig. 3. All the carbides are very stable and the melting points are much higher than those of the mother metals. In general, the chemical formula can be written as MC_x ($x \leq 1$), so that, if $x < 1$, some of the octahedral interstices are left vacant.

In the V-C system, existence of two carbide phases, δ and ϵ , have been reported by Alyamovskii *et al.*¹³⁾ Al-

Fig. 2. Structure of FCC group carbides. Large open circles represent metal atoms and small filled ones the octahedral interstices to be occupied by carbon atoms. In the case of NaCl type carbides with stoichiometric composition, all the interstices are occupied, but in the case of understoichiometric composition, some of the interstices are left vacant.

Table 3. Crystallographic data of the NaCl type carbides of class 1 and 2 metals

Carbide	Composition range (at% C)	Metal lattice		Carbon atom		Structure type	Remarks	Melting point
		Type	Lattice parameter ($\text{\AA}$)	Position*	Distribution			
TiC	33 to 50	fcc	$a_0 = 4.296$ (32 at% C) to 4.326 (48.9 at% C)	Oct.	Random	NaCl (B1)		3 150°C
ZrC	35 to 50	fcc	$a_0 = 4.677$ (35 at% C) to 4.696 (50 at% C)	Oct.	Random	NaCl (B1)		3 235°C
HfC	37 to 50	fcc	$a_0 = 4.614$ (37 at% C) to 4.631 (50 at% C)	Oct.	Random	NaCl (B1)		2 890° $\pm 150^\circ\text{C}$
VC	δ : 38.6 to 44.1 ϵ : 44.1 to 47.9	fcc	$a_0 = 4.118$ to 4.141 $a_0 = 4.154$ to 4.165	Oct.	Random and order	NaCl (B1) and superstructure	VC _{0.89} : ordered cubic VC _{0.85} : ordered hex.	2 800°C
NbC	41.8 to 49.7	fcc	$a_0 = 4.433$ (41.8 at% C) to 4.470 (49.7 at% C)	Oct.	Random	NaCl (B1)		3 600°C
TaC	41.5 to 49.5	fcc	$a_0 = 4.410$ (41.5 at% C) to 4.456 (49.5 at% C)	Oct.	Random	NaCl (B1)		3 750°C

* Oct. means that the carbon atom is at the octahedral interstice. The same abbreviation is used in the following tables.

though δ and ε take the same NaCl type structure, the lattice parameter discontinuity occurs at the composition of 44.1at% C, and δ carbide exists in the range from VC_{0.63} to VC_{0.78}, while ε exists in the range from VC_{0.79} to VC_{0.92}. The lattice parameter discontinuity suggests that some kind of structural rearrangement takes place in a narrow composition range. It has also been reported that VC phase of more than 47.9 at% C (VC_{0.92}) can be formed at high temperatures but decomposes during cooling.

It has been considered that the carbon atoms occupy the octahedral interstices with equal probability in understoichiometric NaCl type carbides, since superstructure reflections had not been observed. Recently, however, de Novion *et al.*¹⁴⁾ and Froidevaux and Rossier¹⁵⁾ found in VC_{0.89} that the carbon vacancies take an ordered array to form a cubic superlattice with parameter $a=8.3340$ Å, which is twice of the original cube edge length. The space group is $P4_332$ or $P4_132$. Figure 4 shows the ordered arrangement of carbon vacancies for the ideal composition V₈C₇. More recently, Lye *et al.*¹⁶⁾ and Venables¹⁷⁾ have shown that in

Fig. 3. Lattice parameter variation of the NaCl type carbides formed by the class 1 and 2 metals with carbon content.

VC_{0.85} a vacancy ordering leads to the formation of a hexagonal superlattice and a resulting domain structure. Unlike VC_x, such a vacancy ordering could not be detected in TiC_x, except at a particularly low carbon to metal ratio.¹⁸⁾

The mechanical properties of MC_x carbides, particularly TiC_x and VC_x, have been extensively studied by Hollox *et al.* using single crystals produced by the floating zone technique.^{19),20)} TiC becomes ductile above about 900°C and VC above about 1 200°C. The slip occurs in the system $\{111\}-\langle 110 \rangle$ like fcc metals and this is different from the case of NaCl, whose slip system is $\{110\}-\langle 110 \rangle$.

Class 3 and 4 metals produce NaCl type carbides called α -MoC_x, β -W₂C and CrC (uncertain). Unlike the carbides of class 1 and 2 metals, they are stable only at very high temperatures. Crystallographic data are shown in Table 4.

α -MoC_x has been produced by heating a mixture of β -Mo₂C and carbon at 1 800° to 2 500°C²¹⁾ or by quenching molten carbide.²²⁾ The carbide transforms probably to η -MoC_x during cooling.²²⁾ Rudy *et al.*²³⁾ have reported that α -MoC_x is Mo₃C₂ (40.0 to 40.8at% C) with lattice parameter $a_0=4.281$ Å. Recently, in our laboratory, α -MoC_x films have been successfully produced by the direct reaction of evaporated molybdenum with amorphous carbon kept at

Fig. 4. Structure of VC_{0.89} (V₈C₇). Carbon vacancies represented by broken circles make an ordered array in the cubic lattice with dimension $a = 2a_0$. The vacancies exist at the corners of the cube and the centers of the hatched planes. Metal and carbon atoms are not shown to avoid the complexity.

Table 4. Crystallographic data of the NaCl type carbides of class 3 and 4 metals

Carbide	Composition range (at% C)	Metal lattice		Carbon atom		Structure type	Remarks	Stability
		Type	Lattice parameter (Å)	Position*	Distribution			
(CrC)	—	fcc	$a_0=3.62$	—	—	NaCl (B1)		Stable above 2 200°C
α -MoC _x ($x=0.54$)	—	fcc	$a_0=4.221$	Oct.	Random	NaCl (B1)	or α -Mo ₃ C ₂ (40.0 to 40.8 at% C), $a_0=4.281$ Å	Stable above 2 200°C
β -W ₂ C	—	fcc	$a_0=4.222$	Oct.	Random	NaCl (B1)		Stable between 2 350° and 2 800°C

room temperature as well as 1 600°C.⁹⁾ Careful analysis of electron diffraction intensity from the film leads to a conclusion that the composition range is rather narrow and almost MoC_{0.54}. It was also found that the carbide transforms to β-Mo₂C by heating at temperatures higher than 600°C in a wet hydrogen stream. β-W₂C is the carbide isomorphous with α-MoC_x. Trials to produce β-W₂C by quenching molten carbide have not been successful.²⁴⁾ In our laboratory β-W₂C films could be produced by using the direct reaction of evaporated tungsten with amorphous carbon film.⁹⁾

Epprecht²⁵⁾ has reported the existence of cubic carbide (NaCl type?), CrC, which are stable at temperatures above 2 000°C. However, its existence has not been confirmed. Bloom and Grant²⁶⁾ have denied CrC.

NaCl type carbides of the class 1 and 2 metals are completely soluble one another and make a continuous solid solution. They are also soluble with NaCl type nitrides of the class 1 and 2 metals to produce carbonitrides with the same type of structure. However, they dissolve limited amounts of chromium, molybdenum and tungsten. Table 5 shows the solubility limits taken from the Pearson's books.^{27), 28)}

2. Perovskite Type Carbides

Pinsker and Kaverin²⁹⁾ reported that a cubic carbide of iron, probably perovskite type, Fe₄C, were formed, when evaporated iron films were carburized by carbon monoxide gas. The lattice parameter was *a*₀=3.875 Å. Its existence, however, has not been confirmed. No other report has been published on the existence of perovskite type carbide in the binary metal-carbon systems.

In the ternary metal-carbon systems many perovskite type carbides are known to exist. Examples are AlMn₃C and AlFe₃C. The chemical formula is generally expressed as AB₃C, where *A* is non-transition metals such as Al, Zn, Ga, In, Sn, *etc.* and *B* the transi-

tion metals such as Cr, Mn, Fe, Co, Ni, *etc.* Crystallographic data are shown in Table 6 for AlFe₃C and lattice parameters of various perovskite type carbides are tabulated in Table 7 (p. 271).²⁸⁾ The space group is *Pm3m*. *A* atoms occupy the corners of the unit cell and *B* atoms occupy the face center sites as shown in Fig. 5. The proportion of *A* atoms to *B* atoms can vary in a limited range. The perovskite type carbides are ferromagnetic and their Curie points vary with composition. Zn_{0.93}Mn_{3.07}C becomes ferrimagnetic at temperatures lower than -40°C and the magnetic transformation is accompanied by a structural transformation from cubic to tetragonal.³⁰⁾ At -196°C the tetragonal unit cell dimensions are *a*=3.921 and *c*=3.899 Å with axial ratio *c/a*=0.9947.

3. Other Carbides

Cubic ternary carbides with formula AB₃C_x (*x*<1), where *A* is nontransition metals and *B* is Fe, Co and Ni,

Fig. 5. Structure of perovskite type carbide, AB₃C. *A* atoms (open circles) exist at the corners of the cubic cell and *B* atoms (double circles) at the face centers. A carbon atom (filled circle) is at the body center position and surrounded by the six *B* atoms forming an octahedron.

Table 5. Solid solubility of Cr, Mo and W into the NaCl type carbides of class 1 and 2 metals

	TiC	ZrC	HfC	VC	NbC	TaC
Cr	25 mol%Cr ₃ C ₂ at 1 725°C	—	—	20 to 25 at%Cr	—	—
Mo	75 at%Mo	20 mol%Mo ₂ C at 1 500°C	>90 mol%Mo ₂ C	25 mol%Mo ₂ C at 1 500°C	6 mol%Mo ₂ C	40 mol%Mo ₂ C at 1 500°C
W	47 mol%WC at 1 700°C	20 mol%WC at 1 500°C, >35 mol%WC at 2 100°C	~40 mol%WC at 2 000°C	12 mol%WC at 1 500°C, >20 mol%WC at 2 100°C	15 mol%WC at 1 500°C, 30 mol%WC at 2 100°C	17 mol%WC at 2 100°C

Table 6. Crystallographic data of AlFe₃C

Carbide	System	Structure type	Lattice parameter (Å)	<i>M</i> *	Space group	C atom position	Remarks
AlFe ₃ C	Cubic	E ₂ (perovskite)	3.758	1	<i>Pm3m</i>	Oct.	Ferromagnetic

Atom positions: origin at center (*m3m*).
3Fe at 3(*c*), 1Al at 1(*a*), 1C at 1(*b*).
3(*c*): $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; $0, \frac{1}{2}, \frac{1}{2}$, 1(*a*): 0, 0, 0, 1(*b*): $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

* *M* indicates the number of formula units in a unit cell. The same notation is used in the following tables.

have been found to exist.^{31),32)} In Table 8, they are shown including their lattice parameters. Although the metal atoms are known to take the fcc arrangement, superstructure reflections appear in the diffrac-

tion patterns. True structures have not yet been established.

Co₂Mn₂C is tetragonal with axial ratio $c/a=1.00$. Crystallographic data are shown in Table 9.³³⁾ The arrangement of metal atoms is similar to that in the ordered alloy CuAu and the carbon atom occupies the body center position. The carbide is ferromagnetic.

Table 7. Lattice parameters of various perovskite type carbides

Carbide	Lattice parameter (Å)	Remarks	Magnetic Curie pt. (°C)
(Fe ₄ C)	3.875		
AlFe ₃ C	3.758	At 15.7 at% C	
AlMn ₃ C	3.869		15 to 250
AlTi ₃ C	4.156		
Co ₃ GeC _{0.25}	3.61		
Co ₃ InC _{0.75}	3.86		
Co ₃ SnC _{0.7}	3.78		
Co ₃ ZnC _{~1.0}	3.73		
Fe ₃ GeC _{0.45}	3.66		
Fe ₃ InC _x	3.88		
Fe ₃ SnC _{1.0}	3.86		
Fe ₃ ZnC _x	3.81		
GaMn ₃ C	3.884	At 18 at% Ga, 62 at% Mn	390
GeMn ₃ C _{1.0}	3.87		390 to <584
GeNi ₃ C _{0.15}	3.58		
InNi ₃ C _{0.5}	3.79		
InTi ₃ C	4.199		
Mn _{3.15} Sn _{0.85} C	3.967		
Mn ₃ ZnC	3.9249	*	40 to 448
Ni ₃ ZnC _{0.7}	3.66		
Ti ₃ TiC	4.209		

* Mn_{3.07}Zn_{0.93}C at -196°C is tetragonal with $a=3.921$, $c=3.899$, $c/a=0.9947$.

Table 8. Lattice parameters of cubic ternary carbides

Carbide	Lattice parameter (Å)	Remarks
AlCo ₃ C _{0.59}	3.70	
AlNi ₃ C _x	3.62	$x=0.29$ (subcell?)
Co ₃ GaC _x	3.647	fcc
Co ₃ MgC _x	3.82	(Subcell?)
Fe ₃ GaC _x	3.74	fcc
GaNi ₃ C _x	3.597	fcc
~MgNi ₃ C	3.73	At 23 at% Mn, 9 at% C. fcc.

VI. Structure of HCP Group Carbides

HCP group carbides are formed from the class 2, 3 and 5 metals. The metals in the first two classes form M₂C type carbides, which exist in a rather narrow range of composition and are stable up to very high temperatures. The crystallographic data are shown in Table 10. The lattice parameters increase with carbon content but the axial ratio remains almost constant. Contrary to the above, the class 5 metals produce metastable carbides.

1. Various Structure Types

In Fig. 6, open circles represent metal atoms form-

Fig. 6. Structure of HCP group carbides. Large open circles represent metal atoms forming a hcp structure and small filled circles the octahedral interstices. A layer is formed by the metal atoms at (0, 0, 0) and equivalent positions (A sites) and B layer is formed by the metal atoms at (2/3, 1/3, 1/2) and equivalent positions (B sites). Two c layers are formed by the octahedral interstices at (1/3, 2/3, 1/4), (1/3, 2/3, 3/4) and their equivalent positions (c sites), and each lies halfway between the A and B layers. One-third or half of the c sites is occupied by carbon atoms in the HCP group carbides, depending on the chemical composition.

Table 9. Crystallographic data of tetragonal, pseudocubic Co₂Mn₂C

Carbide	System	Lattice parameter (Å)	Axial ratio	M	Space group	Remarks
Co ₂ Mn ₂ C	Tet.	$a=3.79$ $c=3.79$	$c/a=1.00$	1	P_4/mmm	Ferromagnetic

Atom positions: origin at center (4/mmm).
1Mn at 1(a), 1Mn at 1(c), 2Co at 2(e), 1C at 1(d).
2(e): $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, 0, \frac{1}{2}$, 1(d): $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, 1(c): $\frac{1}{2}, \frac{1}{2}, 0$, 1(a): $0, 0, 0$.

Table 10. Crystallographic data of the *HCP* group carbides

Carbide	Composi- tion range (at% C)	Metal lattice			C atom		System	Type	Lattice parameters	Space group, <i>M</i>	Thermal stability
		Type	Lattice parameters (Å)	Axial ratio, c_0/a_0	Posi- tion	Distribu- tion					
V_2C	33.3 to 33.9	hcp	$a_0=2.884$ to 2.904 $c_0=4.568$ to 4.588	1.584 to 1.580	Oct.	Random	Hex.	$L'3$	$a=a_0, c=c_0$	$M=1$	—
Nb_2C	30.7 to 33.3	hcp	$a_0=3.126$ to 3.128 $c_0=4.965$ to 4.972	1.588 to 1.590	Oct.	Random Order	Hex.	$L'3$ $\varepsilon\text{-Fe}_2N$	$a=a_0, c=c_0$ $a=\sqrt{3}a_0,$ $c=c_0$	$P6_3/mmc$ $P312, M=3$	Up to $3\,080^\circ\text{C}$
Ta_2C	29 to 33.3	hcp	$a_0=3.101$ to 3.104 $c_0=4.933$ to 4.940	1.591	Oct.	Random Order	Hex. Ortho.	$L'3, C6$ $\zeta\text{-Fe}_2N$	$a=a_0, c=c_0$ $a=c_0, b=2a_0,$ $c=\sqrt{3}a_0$	$M=1$ $Pbcn, M=4$	Up to $3\,500^\circ\text{C}$
$\beta\text{-Mo}_2C$	31 to 33.75	hcp	$a_0=2.997$ to 3.012 $c_0=4.727$ to 4.736	1.577 to 1.572	Oct.	Random Order	Hex. Ortho.	$L'3$ $\zeta\text{-Fe}_2N$	$a=a_0, c=c_0$ $a=c_0, b=2a_0,$ $c=\sqrt{3}a_0$	$M=1$ $Pbcn, M=4$	Up to $\sim 2\,400^\circ\text{C}$
$\alpha\text{-W}_2C$	26 to 35	hcp	$a_0=3.001$ $c_0=4.736$	1.578	Oct.	Random Order	Hex. Ortho.	$L'3$ $\zeta\text{-Fe}_2N$	$a=a_0, c=c_0$ $a=c_0, b=2a_0,$ $c=\sqrt{3}a_0$	$M=1$ $Pbcn, M=4$	Up to $2\,880^\circ\text{C}$
$\varepsilon\text{-Fe}_{2-3}C$	(25 to 33.33)	hcp	$a_0=2.752$ $c_0=4.353$	1.582	Oct.	Order	Hex.	$\varepsilon\text{-Fe}_3N$	$a=\sqrt{3}a_0,$ $c=c_0$	$P6_322, M=3$	Below 370°C
Co_2C	—	Pseu- do- hcp	—	—	Oct.	Order	Ortho.	Co_2N	$a=4.469$ $b=4.426$ $c=2.910$	$Pnmm, M=2$	Below 450°C
$\varepsilon\text{-Ni}_3C$	—	hcp	$a_0=2.628$ $c_0=4.306$	1.639	Oct.	Order	Trig.	$\varepsilon\text{-Ni}_3C$	$a=\sqrt{3}a_0,$ $c=3c_0$	$R\bar{3}c, M=9$	Below 430°C

ing the hcp structure with unit cell dimensions a_0 and c_0 . The structure can be represented by a stacking of close packed hexagonal layers of metal atoms as *ABAB*. . . , if the atoms at the positions (0, 0, 0) and (2/3, 1/3, 1/2) are denoted by *A* and *B*, respectively. In this structure octahedral interstices are formed at the positions (1/3, 2/3, 1/4) and (1/3, 2/3, 3/4), which lie halfway between the neighbouring two metal layers. The small filled circles in Fig. 6 show them. They are the sites for the carbon atoms and are denoted by *c*. The *c* sites form a simple hexagonal lattice with parameters $a=a_0$ and $c=\frac{1}{2}c_0$. The number of *c* sites are equal to the number of metal atoms. If all the *c* sites were occupied by carbon atoms, the compound would have the formula MC, but actually only half or one-third of them is occupied in the case of the *HCP* group carbides, and the difference in the mode of occupation causes various structure types as described below.

L'3 Type

When carbon atoms are randomly distributed among the *c* sites, the structure is called to be *L'3* type. The unit cell dimensions are the same as those formed by the metal atoms, *i.e.*, $a=a_0$ and $c=c_0$. Previously, all the *HCP* group carbides were considered to be *L'3* type, since the carbon atom positions could not be determined by X-ray method. However, recent studies

have shown that the *L'3* type structure is rather rare.

$\varepsilon\text{-Ni}_3C$ Type

When the chemical formula is M_3C , one third of the *c* sites is occupied by carbon atoms. In Fig. 7, when the first carbon layer consists of atoms on c_1 sites, the second layer of atoms on c_2 and the third layer of atoms on c_3 , the stacking order of the hexagonal carbon layers is $c_1c_2c_3$. . . and the carbon atoms form a trigonal lattice with dimensions $a'=\sqrt{3}a_0$ and $c'=\frac{2}{3}c_0$. Therefore, the stacking order in the carbide can be expressed by $c_1Ac_2Bc_3Ac_1Bc_2Ac_3B$. . . as a combination of the carbon layers with the metal ones. The resulted structure, belonging to the space group $R\bar{3}c$, is trigonal with dimensions $a=\sqrt{3}a_0$ and $c=3c_0$. The structure is shown in Fig. 8.

$\varepsilon\text{-Fe}_3N$ Type

If, in Fig. 7, the c_3 sites are not occupied by carbon atoms but left vacant, the stacking order of the hexagonal carbon layers becomes $c_1c_2c_1c_2$. . . , so that the carbide structure is hexagonal with lattice parameters $a=\sqrt{3}a_0$ and $c=c_0$ and the stacking order $c_1Ac_2Bc_1Ac_2B$. . . This structure belongs to the space group $P6_322$ and is called $\varepsilon\text{-Fe}_3N$ type. Figure 9 depicts the structure.

$\varepsilon\text{-Fe}_2N$ Type

In Fe-N system nitrogen atoms begin to occupy

Fig. 7. Basal plane projection of the structure of *HCP* group carbides. Large filled circles (*A* sites) are at the height of $\frac{1}{4}c_0$ and large open circles (*B* sites) at the height of $\frac{3}{4}c_0$. Small circles are carbon atoms, whose heights vary according to the structure type. Following table shows their heights and the resulting unit cell dimensions. Broken lines indicate the hcp metal lattice and full lines the hexagonal superlattice with $a = \sqrt{3}a_0$.

Structure type	Notation of sites and height			Unit cell dimensions
	c_1 : ●	c_2 : ⊙	c_3 : ○	
ϵ -Ni ₃ C	0	$\frac{1}{2}c_0$	$\frac{3}{2}c_0$	$a = \sqrt{3}a_0, c = 3c_0$
ϵ -Fe ₃ N	0	$\frac{1}{2}c_0$	Vacant	$a = \sqrt{3}a_0, c = c_0$
ϵ -Fe ₂ N	0	$\frac{1}{2}c_0$	0	$a = \sqrt{3}a_0, c = c_0$
C6	0	0	0	$a = a_0, c = c_0$

randomly the c_3 sites in the first carbon layer of the structure of ϵ -Fe₃N with increasing nitrogen content and finally all the c_3 sites are occupied at the extreme composition corresponding to Fe₂N. The resulted structure is called ϵ -Fe₂N type, which has the stacking order $c_{1,3}Ac_2Bc_{1,3}Ac_2B \dots$. The space group and the lattice parameters are *P*312 and $a = \sqrt{3}a_0, c = c_0$, respectively. Figure 10 shows the structure.

C6 Type (Anti-CdI₂ Type)

In M_2C carbides, if all the c sites in the first carbon layer are occupied and all the c sites in the second layer are left vacant, the structure is called *C6* or anti-CdI₂ type. The stacking order becomes $c_{1,2,3}ABc_{1,2,3}AB \dots$. The structure is trigonal with space group and lattice parameters *P*3m1 and $a = a_0, c = c_0$. The distance between *A* and *B* layers is smaller than the distance

Fig. 8. Structure of ϵ -Ni₃C. Half of the unit cell is shown. Heavy lines indicate the unit cell. Large open circles represent nickel atoms taking the hcp arrangement and small filled circles carbon atoms. Not all the nickel atoms are shown in the figure.

Fig. 9. Structure of ϵ -Fe₃N type carbides. Large open circles are metal atoms taking the hcp array and small filled circles represent carbon atoms at c_1 and c_2 sites.

Fig. 10. Structure of ϵ -Fe₂N type carbides. Large open circles represent metal atoms taking the hcp array and small filled circles carbon atoms at c_1, c_3 and c_2 sites. Not all the metal atoms are shown.

between *B* and *A*. The structure is shown in Fig. 11.

Co₂N Type

In the structures of ϵ -Fe₂N and *C6* types, the number

Fig. 11. Structure of C6-anti CdI_2 type carbides. Large open circles represent metal atoms taking the hcp array and small filled circles carbon atoms.

of occupied c sites was different in the first and the second carbon layers. When they are made equal, the following two orthorhombic structures are derived.

As shown in Fig. 12 (a), when carbon atoms line up on the parallel straight lines with the interval of $\sqrt{3}a_0$ and occupy only c_I sites in the first layer and only c_{II} sites in the second layer, the stacking sequence becomes $c_I A c_{II} B c_I A c_{II} B \dots$, and the unit cell becomes hexagonal with dimensions $a' = 2a_0$ and $c' = c_0$. However, since the carbon atom arrangement has lost the hexagonal symmetry, the true structure is orthorhombic with space group and lattice parameters $Pnmm$ and $a = \sqrt{3}a_0$, $b = c_0$, $c = a_0$. This is called Co_2N type and the structure is shown in Fig. 12 (b). Actually, the metal atoms as well as the carbon atoms are displaced from the ideal positions to make a pseudo-hexagonal arrangement.

$\zeta\text{-Fe}_2\text{N}$ Type

When the carbon atoms occupy half of the c sites in a zig-zag way in each layer as shown in Fig. 13 (a), the stacking order becomes $c_I A c_{II} B c_I A c_{II} B \dots$. The hexagonal unit cell dimensions are $a' = 4a_0$ and $c' = c_0$. However, since the carbon atom arrangement loses the hexagonal symmetry, the true structure is orthorhombic with space group $Pbcn$ and lattice parameters $a = c_0$, $b = 2a_0$ and $c = \sqrt{3}a_0$. The unit cell is twice as large as that of Co_2N . The structure is called $\zeta\text{-Fe}_2\text{N}$ type and depicted in Fig. 13 (b). It should be added that in $\zeta\text{-Fe}_2\text{N}$ iron atoms are displaced slightly from the ideal hcp positions owing to the orthorhombic arrangement of nitrogen atoms. In the M_2C carbides, however, such atomic displacements have not been detected.

2. Carbides of Class 2 and 3 Metals

Bowman *et al.*³⁴⁾ studied the structure of V_2C by neutron diffraction and reported that the structure is $L'3$ type. Terao³⁵⁾ studied Nb_2C films by electron diffraction and found the structure to be $\varepsilon\text{-Fe}_2\text{N}$ type. For Ta_2C , a neutron diffraction work due to Bowman *et al.*³⁴⁾ has shown the structure to be C6 type, where the layer distance between B and A was $0.5074c_0$ and the

Fig. 12 Structure of Co_2N type carbides
 (a) Basal plane projection
 (b) Perspective view

distance between A and B was $0.4926c_2$. The difference is caused by the insertion of carbon layers between B and A but not between A and B. Recently, we have found by electron diffraction that Ta_2C takes $L'3$ and $\zeta\text{-Fe}_2\text{N}$ types as well as C6.³⁶⁾

Parthé and Sadagopan³⁷⁾ showed by neutron diffraction that the structure of $\beta\text{-Mo}_2\text{C}$ is $\zeta\text{-Fe}_2\text{N}$ type,

Fig. 13. Structure of ζ -Fe₂N type carbides
 (a) Basal plane projection
 (b) Perspective view

and this was confirmed by electron diffraction studies by Kikuchi,³⁸⁾ who used single crystalline carbide films. He also found that $L'3$ type appears. Butorina *et al.*³⁹⁾ have reported from the electron diffraction study of carburized tungsten films that α -W₂C takes C6 type structure. In our laboratory, the following results have been obtained.³⁸⁾ When α -W₂C films are synthesized at temperatures lower than 600°C by cementation of evaporated films, the structure is $L'3$ type, when synthesized between 700° and 800°C, the structure is ε -Fe₂N type, and when synthesized at temperatures higher than 900°C, the structure is ζ -Fe₂N type.

As described above, the M₂C carbides can take various structures differing one another only in the way of distribution of carbon atoms among the octahedral interstices. At present it is not clear that what type appears under what condition. However, the result of α -W₂C seems to suggest that ζ -Fe₂N type is most stable and $L'3$ type least. In V₂C any ordered structure has

not been found but it may be possible for carbon atoms to take an ordered arrangement in the carbide crystals heat-treated appropriately.

HCP group carbides of class 2 and 3 metals may be soluble each other, although very few reports have been published. HCP group carbides make solid solutions with HCP group nitrides to form HCP group carbonitrides. Examples are Fe₂(C, N), Co₂(C, N), Mn-(C, N), Ni-(C, N), Ta₂(C, N) and CrMo(N, C).⁴⁰⁾ Pickering⁴¹⁾ has reported that (CrMo)₂(C, N) has an hcp structure with lattice parameters $a_0 = 2.884$ and $c_0 = 4.551$ kX with axial ratio $c_0/a_0 = 1.578$ and the extreme composition would be very near Cr₂C, although Cr₂C does not exist in the Cr-C binary system.

In the case of molybdenum carbides, a lattice relationship between β -Mo₂C and α -MoC_x has been determined by electron microscopic observation and selected area diffraction of the carbides formed on graphite single crystal films.^{9),38)} It is

$$(10.0)_{\beta\text{-Mo}_2\text{C}} // (110)_{\alpha\text{-MoC}_x}, [00.1]_{\beta\text{-Mo}_2\text{C}} // [001]_{\alpha\text{-MoC}_x}$$

Here, hcp indices were used instead of the true orthorhombic ones. This lattice relationship is interesting, because the close packed atomic planes are not parallel each other but less close packed ones are parallel.

3. Carbides of Class 5 Metals

The iron carbide in the HCP group is isomorphous with ε nitride of iron, Fe₂₋₃N, and written here as ε -Fe₂₋₃C, although the carbide is sometimes written as Fe₂C, Fe_{2.4}C or Fe₃C. This was synthesized by Hofer *et al.*⁴²⁾⁻⁴⁴⁾ in the first time with the cementation of Fischer-Tropsch synthetic iron catalyst by carbon monoxide gas. Jack⁴⁵⁾ synthesized carbonitride, ε -Fe₂₋₃(C, N). ε -Fe₂₋₃C is known to precipitate from martensitic carbon steels at the first stage of tempering.⁴⁶⁾ The carbide can also be synthesized by carburizing iron powder or films with carbon monoxide gas at temperatures lower than 250°C.⁴⁷⁾ According to our electron diffraction result,⁴⁸⁾ ε -Fe₂₋₃C crystal is divided in several domains with respect to the regular array of carbon atoms. The carbide is ferromagnetic⁴²⁾⁻⁴⁴⁾ and transforms to Fe₅C₂ (χ -carbide of iron) at 380°C in vacuum.⁴⁸⁾ Recently, Barton and Gale⁴⁹⁾ studied an iron catalyst extracted after use in the Fischer-Tropsch process. The substance, in which the iron atoms form an approximately hexagonal close packed array, is monoclinic with cell dimensions $a = b = 2.794$, $c = 4.360$ Å and $\gamma = 120.92^\circ$. It was assumed to be a carbide with small amounts of associated oxygen and the structure was discussed on the basis of the chemical formula Fe₂C.

Co₂C is produced by carburizing cobalt with carbon monoxide gas at temperatures below 550°C.⁵⁰⁾ The structure was determined to be Co₂N type by X-ray study due to Clark and Jack⁵¹⁾ and confirmed by our electron diffraction study.⁵⁰⁾ The carbide is metastable and decomposes to metal and carbon at 450°C in vacuum.

ε -Ni₃C*^(p.276) was first studied by Jacobson and Westgren⁵²⁾ with X-ray powder method. We succeeded in

producing the carbide by the cementation of evaporated poly- and single crystalline nickel films with carbon monoxide gas at temperatures lower than 450°C and determined the structure by electron diffraction.⁵³⁾ The structure was described in the section **VI-1, ϵ -Ni₃C Type**. It was also found that there exists a kind of one dimensional disorder with respect to the carbon layer stacking. The carbide is metastable and decomposes to metal and carbon at 430°C in vacuum. The ordered arrangement persists until the decomposition.

4. H-Carbides in Ternary Systems

Jeitschko *et al.*⁵⁴⁾ studied the structure of *H*-phase in ternary metal-carbon systems. The composition is $M'_{2+y}M_{4-y}C_{2-x}$ ($y \sim 2x$), where *M* stands for a transition metal and *M'* a non-transition metal. The ideal composition is $M'M_2C$ and $AlCr_2C$ is a typical *H*-carbide. Its crystallographic data is shown in Table 11 and the structure is depicted in Fig. 14 (p. 277), where open circles represent Al atoms, double circles Cr atoms and filled small circles C atoms. The structure was determined with single crystals. In this structure metal atoms take the hcp arrangement with the stacking order of $AB'ABA'B \dots$. Here, the prime indicates non-transition metal layers. Carbon atoms exist

at the octahedral interstices formed by the transition metal atoms. Therefore, the structure can be expressed by the stacking sequence as $cAB'AcBA'BcAB' \dots$, and the lattice parameters are $a=a_0$ and $c=3c_0$. In Table 12, lattice parameters for various *H*-carbides are listed.²⁸⁾

VII. Structure of SH Group Carbides

SH group carbides are formed with the class 3 metals, Mo and W, and have a stoichiometric composition MC. The crystallographic data are shown in Table 13. Figure 15 is the structure, where the close packed hexagonal layers of metal atoms (open circles) stack in the order of $AAA \dots$ to make a simple hexagonal array. Possible positions for carbon atoms are the center of every trigonal prism formed by metal atoms and are represented by small filled circles. Since there are two such positions, *b* and *c* sites, in every unit cell, half of the possible sites is occupied by carbon atoms. The axial ratio is $c_0/a_0=1$ in the ideal simple hexagonal structure, but it is less than 1 in the actual *SH* group carbides.

In the structure of WC, three proposals have been made for the stacking order of carbon layers. They were $bbbb \dots$, $bcbcb \dots$ and random stackings. Recently, Butorina⁵⁵⁾ by electron diffraction, and Parthé

Table 11. Crystallographic data of the *H*-carbide, $AlCr_2C$

Carbide	System	Structure type	Lattice parameters (Å)	<i>M</i>	Space group	C atom position
$AlCr_2C$	Hex.	<i>H</i> -carbide	$a=2.86_0$ $c=12.8_2$ $c/a=4.48_8$	2	$P6_3/mmc$	Oct. (due to Cr)

Atom positions: origin at center ($\bar{3}m1$).

2Al at $2(d)$, 4Cr at $4(f)$ with $z=0.086$, 2C at $2(a)$.

$4(f): \frac{1}{3}, \frac{2}{3}, z; \frac{2}{3}, \frac{1}{3}, \bar{z}; \frac{2}{3}, \frac{1}{3}, \frac{1}{2}+z; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}-z$, $2(d): \frac{1}{3}, \frac{2}{3}, \frac{3}{4}; \frac{2}{3}, \frac{1}{3}, \frac{1}{4}$, $2(a): 0, 0, 0; 0, 0, \frac{1}{2}$.

Table 12. Lattice parameters of various *H*-carbides

Carbide	Lattice parameter (Å)			Carbide	Lattice parameter (Å)		
	<i>a</i>	<i>b</i>	<i>c/a</i>		<i>a</i>	<i>b</i>	<i>c/a</i>
$AlCr_2C$	2.86 ₀	12.8 ₂	4.48 ₈	$InHf_2C$	3.30 ₇	14.73	4.45 ₅
$AlNb_2C$	3.10 ₃	13.8 ₃	4.46 ₄	$PbHf_2C$	3.35 ₈	14.47	4.30 ₈
$AlTa_2C$	3.07 ₅	13.8 ₃	4.49 ₈	$SnHf_2C$	3.31 ₂	14.3 ₉	4.34 ₄
$AlTi_2C$	3.04	13.60	4.47	$TlHf_2C$	3.32 ₂	14.6 ₃	4.40 ₃
AlV_2C	2.91 ₃	13.1 ₄	4.51	$InNb_2C$	3.17 ₂	14.37	4.530
$CdTi_2C$	3.09 ₉	14.41	4.65 ₃	$InTi_2C$	3.13 ₂	14.06	4.49 ₀
$GaCr_2C$	2.88 ₆	12.61 ₆	4.37 ₀	$InZr_2C$	3.34 ₇	14.91	4.45 ₅
$GeCr_2C$	2.95 ₄	12.08	4.09 ₁	$SnNb_2C$	3.24 ₅	13.77	4.24 ₃
$FeHf_2SC_2$	3.36 ₅	11.99	3.56 ₅	$PbTi_2C$	3.20 ₉	13.81	4.30 ₂
$\sim GaMo_2C$	3.01 ₇	13.18	4.369	$PbZr_2C$	3.38 ₄	14.67	4.33 ₃
$GaTa_2C$	3.10 ₄	13.57	4.37 ₁	STi_2C	3.21 ₀	11.20	3.48 ₅
$GaTi_2C$	3.06 ₄	13.30 ₅	4.34 ₂	$\sim SZr_2C$	3.39 ₆	12.11	3.56 ₅
$GaNb_2C$	3.131	13.56 ₅	4.33 ₂	$SnTi_2C$	3.16 ₃	13.67	4.323
$\sim GaV_2C$	2.93 ₈	12.84	4.37 ₀	$SnZr_2C$	3.34 ₇	14.5 ₉	4.35 ₉
$GeTi_2C$	3.07 ₉	12.93	4.19 ₉	$TlTi_2C$	3.15 ₈	13.98	4.42 ₆
GeV_2C	3.00 ₁	12.25	4.08 ₃	$TlZr_2C$	3.36 ₃	14.79	4.39 ₈

* In order to avoid a confusion with orthorhombic Ni_3C , we call the hexagonal nickel carbide ϵ - Ni_3C .

and Sadagopan⁵⁶⁾ by neutron diffraction determined the structure to be $P\bar{6}12-D_{3h}^1$ type with the stacking order of $AbAbAb \dots$. WC has been considered to be stable at about 2 600°C but recent investigations suggest that it becomes metastable above 1 325°C.⁵⁷⁾

The molybdenum carbide corresponding to WC is γ -MoC⁵⁸⁾ but the carbon atom positions have not yet been determined. The carbide is stable only at elevated temperatures but can be stabilized by an addition

of tungsten. A ternary carbide $(\text{Mo}_{0.5}\text{W}_{0.5})\text{C}$ is known to be isomorphous with WC.⁵⁹⁾

VIII. Structure of Modified Group Carbides

In Mo-C system there are two kinds of carbides with modified order of metal layer stacking. They are η -MoC_x(HCP- D_h^1 or Mo_3C_2) and γ' -MoC(hexagonal γ' or hexagonal). Table 14 shows their crystallographic data.

η -MoC_x has the stacking order of $ABCACB \dots$ and contains six molybdenum atoms in a unit cell. The chemical formula and the carbon atom positions have not fully been established, but Rudy *et al.*⁶⁰⁾ have proposed a formula Mo_3C_2 . Kovalskii and Semenovskaya⁶¹⁾ reported that γ' -MoC_x could be produced by hot-pressing of molybdenum and lamp-black under high temperatures and pressures (1 750°C, 600 kg/cm²) and that η -MoC_x converted to β -Mo₂C by annealing at 750°C under a considerable pressure. In our laboratory, η -MoC_x were found to be formed by heating α -MoC_x films with intense electron beam irradiation in an electron microscope or by successive deposition of molybdenum onto α -MoC_x films.³⁸⁾ η -MoC_x is considered to be a modification of α -MoC_x having the stacking order $ABC \dots$.

γ' -MoC has the stacking order $AABBAABB \dots$ and contains six molybdenum atoms in a unit cell.⁵⁸⁾ Although its chemical composition and carbon atom positions have not fully been established, the structure can be considered to be a modification of γ -MoC having the stacking order $AAA \dots$.

Fig. 14. Structure of *H*-carbide, AlCr_2C . Open circles represent Al atoms and double circles Cr atoms. They make an hcp arrangement. Small filled circles are carbon atoms at the octahedral interstices formed by the six Cr atoms. Heights of the atoms are shown in the right side of the figure.

Fig. 15. Structure of *SH* group carbide. Large open circles represent metal atoms (*A* sites) and small filled circles the center of trigonal prisms formed by the metal atoms (*b* and *c* sites), which are possible sites for carbon atoms.

Table 13. Crystallographic data of the *SH* group carbides

Carbide	Compo- sition (at% C)	Metal lattice			C atom		System	Type	Lattice parameters	Space group, <i>M</i>	Thermal stability
		Type	Lattice parameters (Å)	<i>c</i> ₀ / <i>a</i> ₀	Posi- tion*	Distri- bution					
γ -MoC	—	sh	<i>a</i> ₀ =2.898 <i>c</i> ₀ =2.809	0.969	Prism	—	Hex.	WC (<i>Bh</i>)	<i>a</i> = <i>a</i> ₀ <i>c</i> = <i>c</i> ₀	$P\bar{6}m2$ <i>M</i> =1	Stable up to 2 650°C
WC	50	sh	<i>a</i> ₀ =2.906 <i>c</i> ₀ =2.837	0.975	Prism	Order	Hex.	WC (<i>Bh</i>)	<i>a</i> = <i>a</i> ₀ <i>c</i> = <i>c</i> ₀	$P\bar{6}m2$ <i>M</i> =1	Stable up to 1 325°C (or 2 720°C)

* Prism means that the carbon atom is at the center of trigonal prism formed by the metal atoms. The same abbreviation is used in the following tables.

Table 14. Crystallographic data of modified group carbides

Carbide	Compo- sition	Metal lattice			C atom position	<i>M</i>	System	Space group	Remarks
		Stacking order	Lattice parameters (Å)	<i>c/a</i>					
γ -MoC _{<i>x</i>}	—	<i>ABCACB...</i>	<i>a</i> =3.013 <i>c</i> =14.64	4.859	Oct.	2 as Mo ₃ C ₂	Hex.	<i>P6₃/mmc*</i>	γ -Mo ₃ C ₂ or γ -MoC
γ' -MoC	—	<i>AABB...</i>	<i>a</i> =2.932 <i>c</i> =10.97	3.742	Oct. and prism	4	Hex.	<i>P6₃/mmc**</i>	Metastable

* γ -MoC_{*x*}: atom positions as Mo₃C₂, origin at center ($\bar{3}m1$).
2Mo at 2(*b*), 4Mo at 4(*f*) with *z*=0.083, 1C at 2(*a*), 1C at 4(*f*) with *z*=0.667 (random).
4(*f*): $\frac{1}{3}, \frac{2}{3}, z$; $\frac{2}{3}, \frac{1}{3}, \bar{z}$; $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}+z$; $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}-z$, 2(*b*): 0, 0, $\frac{1}{4}$; 0, 0, $\frac{3}{4}$, 2(*a*): 0, 0, 0; 0, 0, $\frac{1}{2}$.
** γ' -MoC: atom positions,
4Mo at 4(*f*) with *z*=0.125, 4C: not established.

Table 15. Crystallographic data of Cr₃C₂

Carbide	System	Structure type	Lattice parameters (Å)	<i>M</i>	Space group	C atom position	Remarks
Cr ₃ C ₂	Ortho.	<i>D5₁₀</i>	<i>a</i> =5.53 <i>b</i> =2.827 <i>c</i> =11.48	4	<i>Pnma</i>	Prism	m.p.: 1 820°±20°C

Atom positions: origin at $\bar{1}$.
4Cr at 4(*c*) with *x*=0.030, *z*=0.406, 4Cr at 4(*c*) with *x*=0.175, *z*=0.770, 4Cr at 4(*c*) with *x*=0.850, *z*=0.930,
4C at 4(*c*) with *x*=0.092, *z*=0.204, 4C at 4(*c*) with *x*=0.228, *z*=0.952.
4(*c*): $x, \frac{1}{4}, z$; $\bar{x}, \frac{3}{4}, \bar{z}$; $\frac{1}{2}-x, \frac{3}{4}, \frac{1}{2}+z$; $\frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z$.

IX. Structure of M₃C₂ Type Carbide

For M₃C₂ type carbide there is only Cr₃C₂, which is stable up to 1 820°C. The structure is orthorhombic *D5₁₀* type with space group and lattice parameters *Pnma* and *a*=5.53, *b*=2.827, *c*=11.48 Å, respectively. Hellbom and Westgren⁶²⁾ determined metal atom positions with single crystals. Later, Meinhardt and Krisement⁶³⁾ determined carbon atom positions with neutron diffraction of powder specimens, which had been prepared from a mixture of chromium oxide and carbon heated in a hydrogen stream at 1 600°C. Table 15 shows the crystallographic data and Fig. 16 depicts the structure, in which Cr atom arrangement is shown by co-ordination polyhedra having the shape of trigonal prism containing a carbon atom at its center. In the structure, the prism whose axis is in the *a-c* plane is connected with the neighbour by sharing an edge to form a trail running along *b*-axis through the corner and face center of the lattice. The prism whose axis is parallel to *b*-axis plays a role to connect the trails of prisms.

X. Structure of M₃C Type Carbides

Mn₃C, Fe₃C, Co₃C and Ni₃C belongs to the M₃C type. A representative carbide is cementite, Fe₃C. The structure is orthorhombic *DO₁₁* type belonging to the space group *Pnma*. The crystallographic data are shown in Table 16. Iron atom positions were determined by Westgren⁶⁴⁾ with single crystal specimens and later refined by Lipson and Petch,⁶⁵⁾ who also determined carbon atom positions. Recently, the

Fig. 16. Structure of Cr₃C₂. The structure is considered to be built of trigonal prisms formed by Cr atoms, each of which contains a carbon atom at its center. The prisms having the axes in the *a-c* plane are connected each other to make trails running along *b* axis through the corner and the center of *a-c* plane of the lattice. The prisms having the axes parallel to *b*-axis connect the trails of prisms. Not all the prisms are shown in the figure to avoid complexity.

atom positions were further refined with neutron diffraction of powder samples.^{66)–68)} As shown in Fig. 17, six iron atoms form a co-ordination polyhedron with a shape of trigonal prism and each prism shares an edge with a neighbouring prism to form a trail of prisms. The carbon atom exists at the center of each prism. Once, the carbon atom was assumed to lie at the center of octahedron^{69),70)} but this is not accepted now.

Mn₃C⁷¹⁾ is a stable carbide but others are not stable and decompose to metal and carbon by heating at temperatures lower than about 500°C. The existence of Co₃C was found by Meyer⁷²⁾ and later one of the present authors succeeded in producing it by carburizing evaporated cobalt films with town gas.⁵⁰⁾ Kohlhaas and Meyer⁷³⁾ reported that a nickel carbide could

Table 16. Crystallographic data of M_3C type carbides

Carbide	System	Structure type	Lattice parameters ($\text{\AA}$)*	M	Space group*	C atom position	Remarks
Mn_3C	Ortho.	DO_{11}	$a=5.080$ $b=6.772$ $c=4.530$	4	$Pnma$	Prism	Stable between 950° and 1050°C
Fe_3C	Ortho.	DO_{11}	$a=5.0890$ $b=6.7433$ $c=4.5235$	4	$Pnma$	Prism	Stable below about 550°C
Co_3C	Ortho.	DO_{11}	$a=5.033$ $b=6.731$ $c=4.483$	4	$Pnma$	Prism	Stable below 480°C

Atom positions for Fe_3C , origin at $\bar{1}$.

8Fe at $8(d)$ with $x=0.186\pm 2$, $y=0.063\pm 2$, $z=0.328\pm 2$; 4Fe at $4(c)$ with $x=0.036\pm 2$, $z=0.852\pm 4$;

4C at $4(c)$ with $x=0.89\pm 2$, $z=0.45\pm 1$.

$8(d)$: x, y, z ; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; $\bar{x}, \frac{1}{2}+y, \bar{z}$; $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$; $4(c)$: $x, \frac{1}{4}, z$; $\bar{x}, \frac{3}{4}, \bar{z}$;

$\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; $x, \frac{1}{2}-y, z$; $\frac{1}{2}+x, y, \frac{1}{2}-z$. $\frac{1}{2}-x, \frac{3}{4}, \frac{1}{2}+z$; $\frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z$.

* Sometimes the structure is expressed based on the space group $Pbnm$ with the axis transform $a \rightarrow b$, $b \rightarrow c$ and $c \rightarrow a$.

Fig. 17. Structure of M_3C type carbide. There are trails of trigonal prisms formed by metal atoms in the structure. Each prism contains a carbon atom at the center and shares an edge with neighbouring prism.

Table 17. Lattice parameters of some alloy cementites

Carbide	Lattice parameters ($\text{\AA}$)		
	a	b	c
$(Cr, Fe)_3C$	5.062 to 5.075	6.714 to 6.711	4.504 to 4.512
$(FeMn)_3C$ (almost Fe_2MnC)	5.04	6.73	4.51

with Pd_5B_2 , whose structure has been determined by Stenberg⁷⁴⁾ with single crystal specimens. The identification of Mn_5C_2 was made by Stenberg⁷⁴⁾ and that of Fe_5C_2 was made by Sénateur *et al.*⁷⁵⁾ They compared their X-ray powder pattern intensities with the calculated ones on the basis of Pd_5B_2 structure. The crystallographic data are shown in Table 18. Figure 18 shows the structure. Two trigonal prisms formed by metal atoms, each in the opposite orientation, are connected by sharing an edge and the two prisms are connected with respective neighbouring prisms to form a trail of double prisms. Each prism contains one carbon atom at the center.

Mn_5C_2 ⁷⁴⁾ is a stable carbide. Fe_5C_2 ⁷⁵⁾ is the carbide previously called Hägg carbide, percarbide or χ -carbide of iron with a formula $Fe_{20}C_9$ (30.5 to 32.1 at% C),⁷⁶⁾ and the structure was assumed to be orthorhombic or hexagonal on the bases of indexing of X-ray powder patterns. The structural resemblance of Fe_5C_2 with cementite Fe_3C was studied by Sénateur and Fruchart.⁷⁷⁾ Fe_5C_2 is metastable and decomposes to Fe_3C and carbon at 500°C by heating in vacuum.⁴⁸⁾ It can be produced by carburizing iron at about 350°C,⁷⁸⁾ iron nitride at about 450°C,⁷⁹⁾ or by heating ϵ - $Fe_{2-3}C$ at temperatures higher than 380°C.⁴⁸⁾ There are some discussions about the appearance of Fe_5C_2 at the tempering of martensitic steel but, at present, no direct evidence has been presented for its precipitation. As an alloy carbide, $(Fe, Mn)_5C_2$

be produced by heating nickel powder in hydrocarbon gas at 260°C for about 200 hr and identified with orthorhombic Ni_3C by comparing its X-ray diffraction patterns with those of cementite, although he did not give lattice parameters. According to them, Ni_3C is metastable and decomposes to nickel and carbon at 420° to 500°C in vacuum.

Iron atoms in cementite can be replaced by chromium and manganese atoms to produce $(Fe, Cr)_3C$ and $(Fe, Mn)_3C$. The replacement makes the lattice parameters change slightly. Table 17 lists the lattice parameters.²⁷⁾

XI. Structure of M_5C_2 Type Carbides

In M_5C_2 type there are Mn_5C_2 and Fe_5C_2 . They are monoclinic with space group $C2/c$ and isomorphous

Table 18. Crystallographic data of M_5C_2 type carbides

Carbide	System	Structure type	Lattice parameters ($\text{\AA}$)	M	Space group	C atom position	Remarks
Mn_5C_2	Monocl.	Pd_5B_2	$a=11.66$ $b=4.573$ $c=5.08$ $\beta=97^\circ45'$	4	$C2/c$	Prism	Stable up to 1050°C
Fe_5C_2	Monocl.	Pd_5B_2	$a=11.56$ $b=4.573$ $c=5.058$ $\beta=97^\circ44'$	4	$C2/c$	Prism	Stable below about 500°C

Atom positions for Pd_5B_2 , origin at $\bar{1}$ on glide-plane, c ; unique axis, b .
8Pd at $8(f)$ with $x=0.0958$, $y=0.0952$, $z=0.4213$, 8Pd at $8(f)$ with $x=0.2127$, $y=0.5726$, $z=0.4213$,
4Pd at $4(e)$ with $y=0.5727$, 8B at $8(f)$ with $x=0.106$, $y=0.311$, $z=0.077$
 $8(f)$: $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) + x, y, z; \bar{x}, \bar{y}, \bar{z}; \bar{x}, y, \frac{1}{2}-z; x, \bar{y}, \frac{1}{2}+z.$
 $4(e)$: $0, y, \frac{1}{4}; 0, \bar{y}, \frac{3}{4}.$

Fig. 18.
Structure of M_5C_2 type carbide. Two trigonal prisms formed by metal atoms and mutually in the opposite orientation (A and B) are connected by sharing an edge, and the connected prisms are further connected with respective neighbours to form a trail. Each prism contains a carbon atom at the center.

Table 19. Crystallographic data of M_7C_3 type carbides

Carbide	System	Structure type	Lattice parameters ($\text{\AA}$)	M	Space group	C atom position	Remarks
Cr_7C_3	Trig.	Closely related to Ru_7B_2	$a=14.01$ $c=4.532$ $c/a=0.324$	8	$P31c$	Prism	Stable below 1782°C
Mn_7C_3	Ortho.	Closely related to Ru_7B_2	$a=4.546$ $b=6.959$ $c=11.979$	4	$Pnma$	Prism	Stable below 1100°C
Fe_7C_3	Ortho.	Closely related to Ru_7B_2	$a=4.540$ $b=6.879$ $c=11.942$	4	$Pnma$	Prism	Metastable magnetic Curie pt. $250^\circ \pm 3^\circ\text{C}$

Atom positions for Ru_7B_2 (hex. $a=7.469$, $c=4.713 \text{ \AA}$, $M=2$, $P6_3mc$), origin on $6_3(3m)$.
6Ru at $6(c)$ with $x=0.456_3$, $z=0.318$; 6Ru at $6(c)$ with $x=0.121_3$, $z=0.000$; 2Ru at $2(b)$ with $z=0.818$;
6B at $6(c)$ with $x=0.18_7$, $z=0.58_0$.
 $6(c)$: $x, \bar{x}, z; x, 2x, z; 2\bar{x}, \bar{x}, z;$ $2(b)$: $\frac{1}{3}, \frac{2}{3}, z; \frac{2}{3}, \frac{1}{3}, \frac{1}{2}+z.$
 $\bar{x}, x, \frac{1}{2}+z; \bar{x}, 2\bar{x}, \frac{1}{2}+z; 2x, x, \frac{1}{2}+z.$

is known.⁸⁰⁾ It has the lattice parameters $a=11.62$, $b=4.56$, $c=5.05$ Å and $\beta=97.63^\circ$.

XII. Structure of M_7C_3 Type Carbides

Cr_7C_3 , Mn_7C_3 and Fe_7C_3 belong to the M_7C_3 type. The crystallographic data are shown in Table 19 (p. 280). Although Cr_7C_3 is hexagonal and Mn_7C_3 and Fe_7C_3 are orthorhombic, the two structures are closely related each other and can be derived from the structure of Ru_7C_3 , which has been determined by Aronsson⁸¹⁾ with single crystal specimens.

Figure 19(a) shows the basal plane projection of the Ru_7B_3 structure. Octahedra formed by six ruthenium atoms exist at each corner of the hexagonal unit cell with dimensions a_0 and c_0 and two tetrahedra exist at each center of trigonal prisms made by the lattice points.

The tetrahedra take mutually opposite orientations with respects to c_0 axis. Boron atoms exist between the octahedron and tetrahedron to connect them and each boron atom itself is surrounded by six ruthenium atoms making a distorted trigonal prism.

In the structure of Cr_7C_3 ,^{82),88)} one-fourth of the octahedra formed by Cr atoms rotates by 180° around the c_0 axis to form a hexagonal lattice with parameters $a=2a_0$ and $c=c_0$, as shown in Fig. 19 (b). In the structure of Mn_7C_3 ,⁸⁴⁾ or Fe_7C_3 ,^{84),85)} half of the octahedra formed by Mn or Fe atoms rotates by 180° around the c_0 axis to form a hexagonal lattice with parameters $a=2a_0$ and $c=c_0$, as shown in Fig. 19 (c). This structure, however, can be reduced to an orthorhombic lattice with dimensions $a=c_0$, $b=a_0$ and $c=\sqrt{3}a_0$ as indicated by full lines in the figure. Thus, the two

Fig. 19.
Basal plane projection of M_7C_3 type carbides

(a) Structure of Ru_7B_3 . The octahedron (*A* type) formed by metal atoms (large circles) exists at the corner of the unit cell and the tetrahedra mutually in the opposite orientation with respect to c_0 axis exist at the centers of prisms formed by the lattice points. Non-metal atoms (small circles) exist between the octahedra and the tetrahedra, and each is surrounded by the six metal atoms forming a distorted trigonal prism.

(b) Structure of Cr_7C_3 . One-fourth of the *A* type octahedra rotate around c_0 axis by 180° to become the *B* type octahedra. The cell edge length becomes twice of the original one.

(c) Structure of Mn_7C_3 . Half of the *A* type octahedra rotate around c_0 axis by 180° to become the *B* type octahedra. The cell edge length becomes twice of the original one, but this unit cell can be reduced to orthorhombic as shown by the full lines.

carbide structures can be considered to be different kinds of superstructures of Ru_7B_3 . A carbon atom is surrounded by six metal atoms forming a distorted trigonal prism.

Cr_7C_3 and Mn_7C_3 are well known stable carbides. Fe_7C_3 is a newly found carbide, whose properties have not yet been made clear except its magnetic Curie point being $250^\circ \pm 3^\circ C$.⁸⁵⁾ Eckstrom and Adcock⁸⁶⁾ found the carbide in a catalyst charge of a fluidized-bed hydrocarbon synthesis plant. The carbide was also found among the reaction products from high pressure and high temperature synthesis of diamond, when iron was added as solvent for carbon.⁸⁷⁾ It has not yet been possible to produce the carbide in laboratories using accepted methods of carbide synthesis. The chemical formula and the structure were identified by comparing its X-ray powder patterns with those of Cr_7C_3 and Mn_7C_3 .

In the ternary system, $(Fe, Cr)_7C_3$, which is isomorphous with Cr_7C_3 , has been known to appear in annealed steels.^{88), 89)} The lattice parameters are $a=13.87$ and $c=4.46 \text{ \AA}$, which increase with chromium content.

XIII. Structure of $M_{23}C_6$ Type Carbides

The $M_{23}C_6$ type carbides have been found for chromium and manganese. The structure is complex cubic and contains four formula units in a unit cell with dimensions of about $10.6 \text{ \AA}$. The crystallographic data are shown in Table 20. The structure of $Cr_{23}C_6$ was determined by Westgren⁹⁰⁾ with single crystal specimens and the structure of $Mn_{23}C_6$ by Westgren⁹¹⁾ and by Öhman.⁹²⁾ As shown in Fig. 20, cubo-octahedra formed by metal atoms exist at the corner and face center positions of the cubic lattice, while cubes exist at the body and edge center positions.

Table 20. Crystallographic data of $M_{23}C_6$ type carbides

Carbide	System	Structure type	Lattice parameters (Å)	<i>M</i>	Space group	C atom position	Remarks
$Cr_{23}C_6$	Cubic	$D8_4$	$a=10.659$	4	$Fm\bar{3}m$	Deca.*	Peritectic temp. $1518^\circ C$
$Mn_{23}C_6$	Cubic	$D8_4$	$a=10.585$	4	$Fm\bar{3}m$	Deca.*	Peritectic temp. $1025^\circ C$

* Deca. means that the carbon atom is at the center of decahedron formed by metal atoms. The same abbreviation is used in the following tables.

Atom positions for $Cr_{23}C_6$: origin at center ($m\bar{3}m$).

48Cr at 48(h) with $x=0.165$, 32Cr at 32(f) with $x=0.385$, 8Cr at 8(c), 4Cr at 4(a), 24C at 24(e) with $x=0.275$.
48(h): $\{0, x, x; x, 0, x; x, x, 0; 0, x, \bar{x}; \bar{x}, 0, x; x, \bar{x}, 0; 0, \bar{x}, \bar{x}; \bar{x}, 0, \bar{x}; \bar{x}, \bar{x}, 0; 0, \bar{x}, x; x, 0, \bar{x}; \bar{x}, x, 0; x, x, x; x, \bar{x}, \bar{x}; \bar{x}, x, \bar{x}; \bar{x}, \bar{x}, x; \bar{x}, \bar{x}, \bar{x}; \bar{x}, x, x; x, \bar{x}, x; x, x, \bar{x}\}$
32(f): $\{0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0\} +$
24(e): $\{0, 0, 0; 0, x, 0; 0, 0, x; \bar{x}, 0, 0; 0, \bar{x}, 0; 0, 0, \bar{x}\}$
8(c): $\{\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}, \frac{3}{4}\}$
4(a): $\{0, 0, 0\}$

Fig. 20. Structure of $M_{23}C_6$ type carbide. Cubo-octahedra formed by metal atoms (48 (h) position), each of which contains a metal atom (open circle, 4(a) position) at the center, exist at the fcc lattice points. Cubes formed by metal atoms (32(f) position) exist at the edge and body center positions of the lattice. Eight metal atoms (open circles, 8(c) position) exist at the centers of $1/8$ sublattice to connect the cubo-octahedra and cubes. Carbon atoms (filled circles, 24(e) position) exist between the cubo-octahedra and the cubes to connect them and each is surrounded by eight metal atoms forming a decahedron. Not all the coordination polyhedra are shown in the figure.

The arrangement is easily understood, if, in the NaCl type, we replace Na^+ by the cube and Cl^- by the cubo-octahedron. Besides, metal atoms exist at each center of one-eighth sublattices. The carbon atom exists between the cube and cubo-octahedron to connect them and each is surrounded by eight metal atoms forming a decahedron, as indicated by thin lines in the figure.

In ternary systems, some carbides are known to have the M_{23}C_6 type structure. They are listed in Table 21.²⁷⁾ All the carbides are stable and frequently precipitate in alloy steels subjected to appropriate heat treatments.

Table 21. Various M_{23}C_6 type alloy carbides and their lattice parameters

Carbide	Lattice parameter (Å)
$\text{Fe}_{21}\text{Mo}_2\text{C}_6$	10.56
$\text{Fe}_{21}\text{W}_2\text{C}_6$	10.54
$(\text{Cr}, \text{Fe})_{23}\text{C}_6$	10.59
$(\text{Cr}, \text{W})_{23}\text{C}_6$	10.66
$(\text{Cr}, \text{Fe}, \text{Mo})_{23}\text{C}_6$	10.66
$(\text{Cr}, \text{Fe}, \text{Mo}, \text{W})_{23}\text{C}_6$	10.67
$(\text{Cr}, \text{Fe}, \text{Mo}, \text{V}, \text{W})_{23}\text{C}_6$	10.58

XIV. Structure of M_6C Type Carbides

M_6C type carbides are the double carbide and appear in ternary metal-carbon systems. The standard chemical formulae are $\text{A}_3\text{B}_3\text{C}$, $\text{A}_4\text{B}_2\text{C}$ and $\text{A}_2\text{B}_4\text{C}$, where A stands for V, Cr, Mn, Fe, Co, Ni, etc. and B for Ti, Zr, V, Nb, Ta, Mo, W, etc. Sometimes, $\text{A}_3\text{B}_3\text{C}$ and $\text{A}_4\text{B}_2\text{C}$ are called η_1 -carbide and $\text{A}_2\text{B}_4\text{C}$ η_2 -carbide. The carbides are stable and have the large cubic unit cell with dimension of 11 to 12 Å, which contains sixteen formula units. Typical M_6C carbides are $\text{Fe}_3\text{W}_3\text{C}$ and $\text{Fe}_4\text{W}_2\text{C}$ for η_1 -carbide and $\text{Co}_2\text{W}_4\text{C}$ for η_2 -carbide. The structure of η_1 was determined by Westgren⁹¹⁾ and that of η_2 by Kislyakova.⁹³⁾ The latter structure was confirmed later by Kiessling.⁹⁴⁾ The crystallo-

graphic data are shown in Table 22 for $\text{Fe}_3\text{W}_3\text{C}$. Figure 21 depicts the structure, where octahedra formed by W atoms exist at the corners and face centers of the unit cell and further at the centers of four cubes out of eight ones subdividing the unit cell. Therefore, the arrangement of octahedra are the same as that of carbon atoms in the diamond structure. Furthermore, tetrahedra formed by Fe atoms exist at the body and edge centers and the four remaining centers of the one-eighth sublattice. Thus, the arrangement of tetrahedra is also diamond-like. The structure of $\text{Fe}_3\text{W}_3\text{C}$ can, therefore, be regarded as the one formed by mutually interpenetrating two diamond-like lattices, each lattice point of which being occupied by the octahedron or tetrahedron. Remaining sixteen iron atoms exist between the tetrahedra as shown by open circles and connect them. Sixteen carbon atoms take the positions between the octahedra as shown by filled circles and each is surrounded by six tungsten atoms forming a somewhat distorted octahedron. In the structure of $\text{Fe}_4\text{W}_2\text{C}$, excess iron atoms replace randomly tungsten atoms forming the octahedra. The structure of η_2 -carbide, $\text{Co}_2\text{W}_4\text{C}$, is similar to that of $\text{Fe}_3\text{W}_3\text{C}$ and excess tungsten atoms replace cobalt atoms connecting the tetrahedra formed by cobalt atoms.

Very many M_6C type carbides have been reported and they are listed in Table 23 together with their lattice parameters.^{27),28)}

XV. Structure of $\text{M}_3\text{W}_9\text{C}_4$ Type Carbides

In the W-Co-C system, there is a carbide phase called χ . Schönberg⁹⁵⁾ determined its composition to be $\text{Co}_3\text{W}_9\text{C}_4$, which had been assumed to be $\text{Co}_3\text{W}_{10}\text{C}_4$, and established the structure. The carbide is hexagonal with lattice parameters of equal a and c value, 7.826 Å. The unit cell contains two formula units. The crystallographic data and the structure are shown in Table 24 and Fig. 22, respectively (p. 285). In the structure there are trigonal prisms formed by tungsten atoms and somewhat distorted octahedra formed by 5W and 1Co atoms in the average. The latter are attached

Table 22. Crystallographic data of M_6C type carbide, $\text{Fe}_3\text{W}_3\text{C}$

Carbide	System	Structure type	Lattice parameters (Å)	M	Space group	C atom position	Remarks
$\text{Fe}_3\text{W}_3\text{C}$	Cubic	$E9_3$	$a=11.06$	16	$Fd\bar{3}m$	Oct.	η_1 - M_6C

Atom positions: origin at $\bar{4}3m$, at $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ from center ($\bar{3}m$).

48W at 48(f) with $x=0.195$; 32Fe at 32(e) with $x=0.825$; 16Fe at 16(d); 16C at 16(c).

$$\begin{aligned}
 48(f): & \begin{cases} x, 0, 0; \bar{x}, 0, 0; \frac{1}{4}+x, \frac{1}{4}, \frac{1}{4}; \frac{1}{4}-x, \frac{1}{4}, \frac{1}{4}; \\ 0, x, 0; 0, \bar{x}, 0; \frac{1}{4}, \frac{1}{4}+x, \frac{1}{4}; \frac{1}{4}, \frac{1}{4}-x, \frac{1}{4}; \\ 0, 0, x; 0, 0, \bar{x}; \frac{1}{4}, \frac{1}{4}, \frac{1}{4}+x; \frac{1}{4}, \frac{1}{4}, \frac{1}{4}-x. \end{cases} \\
 32(e): & \left(0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0\right) + \begin{cases} x, x, x; x, \bar{x}, \bar{x}; \bar{x}, x, \bar{x}; \bar{x}, \bar{x}, x; \\ \frac{1}{4}-x, \frac{1}{4}-x, \frac{1}{4}-x; \frac{1}{4}-x, \frac{1}{4}+x, \frac{1}{4}+x; \frac{1}{4}+x, \frac{1}{4}-x, \frac{1}{4}+x; \frac{1}{4}+x, \frac{1}{4}+x, \frac{1}{4}-x. \end{cases} \\
 16(d): & \frac{5}{8}, \frac{5}{8}, \frac{5}{8}; \frac{5}{8}, \frac{7}{8}, \frac{7}{8}; \frac{7}{8}, \frac{5}{8}, \frac{7}{8}; \frac{7}{8}, \frac{7}{8}, \frac{5}{8} \\
 16(c): & \frac{1}{8}, \frac{1}{8}, \frac{1}{8}; \frac{1}{8}, \frac{3}{8}, \frac{3}{8}; \frac{3}{8}, \frac{1}{8}, \frac{3}{8}; \frac{3}{8}, \frac{3}{8}, \frac{1}{8}.
 \end{aligned}$$

to the prisms. Two of eight carbon atoms exist at the center of each tungsten prism and the rests at the center of each octahedron. Carbides having the same structure have been found in W-Mn-C⁽⁹⁵⁾ and W-Ni-C⁽⁹⁶⁾ systems as shown in Table 25.

XVI. Structures of Other Type Carbides

1. Carbides in Mn-C System

There are several unidentified carbide phases in the Mn-C system.

Mn₇C₂ is stable at temperatures between 850° and 1 000°C, but the formula is uncertain. According to

Picon and Flahaut⁽⁹⁷⁾ it is Mn₈C₃ and rhombohedral with hexagonal lattice parameters $a=13.90$, $c=4.55$ Å, $c/a=0.327$. Bouchaud and Fruchart,⁽⁹⁸⁾ however, reported that it is Mn₁₅C₂ and hexagonal. They also reported on Mn₇C₃,⁽⁹⁹⁾ which is orthorhombic with lattice parameters $a=4.546$, $b=6.959$, $c=11.979$ Å and belongs to the space group *Pnma*.

Picon and Flachaut's works^(97),100) indicate the existence of tetragonal Mn₄C ($a=7.66$, $c=10.57$ Å, $c/a=1.38$), hexagonal Mn₆C₂ ($a=5.48$, $c=6.71$ Å, $c/a=1.224$; unstable) and triclinic Mn₈C₃ ($a=11.06$, others were not given). Mn₄C was obtained in alloys melted at 1 350° to 1 400°C and ferromagnetic. Ac-

Fig. 21.
Structure of γ_1 -carbide, $\text{Fe}_3\text{W}_3\text{C}$. Octahedra formed by W atoms (48(f) position) exist at the fcc lattice points and the centers of four 1/8 sublattices. Tetrahedra formed by Fe atoms (32(e) position) exist at the edge and body centers of the lattice and at the centers of the rest four 1/8 sublattices. Fe atoms (open circles, 16(d) position) exist between the tetrahedra to connect them. Carbon atoms (filled circles, 16(c) position) exist between the octahedra to connect them and each is surrounded by six W atoms forming a slightly distorted octahedron. Not all the coordination polyhedra and the atoms are shown in the figure.

Table 23. Various M_6C type carbides and their lattice parameters

γ_1 -carbide	Lattice parameter (Å)	γ_2 -carbide	Lattice parameter (Å)	γ -carbide	Lattice parameter (Å)
$\text{V}_3\text{Zr}_3\text{C}$	12.12	$\text{Fe}_2\text{Mo}_4\text{C}$	11.26	$\text{Zn}_3\text{Ti}_5\text{C}$	11.55 ₈
$\text{Cr}_3\text{Nb}_3\text{C}$	11.49	$\text{Co}_2\text{Mo}_4\text{C}$	11.25	$\text{Zn}_3\text{Hf}_5\text{C}_x$	11.95 ₇
$\text{Mn}_3\text{Mo}_3\text{C}$	11.13	$\text{Co}_2\text{W}_4\text{C}$	11.21 ₀	ZnZr_2C_x	11.16 ₀
$\text{Mn}_3\text{W}_3\text{C}$	11.13	$\text{Ni}_3\text{Mo}_4\text{C}$	11.25	ZnNb_2C_x	11.74 ₆
$\text{Fe}_3\text{Mo}_3\text{C}$	11.14	$\text{Co}_2(\text{Ti}, \text{Ta})_4\text{C}$	11.51	$\text{RuZr}_2(\text{C}, \text{N}, \text{O})$	12.30
$\text{Fe}_3\text{W}_3\text{C}$	11.06	$\text{Ni}_2(\text{Ti}, \text{Nb})_4\text{C}$	11.58	$\text{Ni}_5\text{W}_6\text{C}$	10.87 ₃
$\text{Fe}_4\text{W}_2\text{C}$	11.10	$\text{Ni}_2(\text{Ti}, \text{Ta})_4\text{C}$	11.52	$(\text{Cr}, \text{Fe}, \text{Mo})_6\text{C}$	11.08
$\text{Co}_3\text{W}_3\text{C}$	11.01	$\text{CoNb}_2(\text{C}, \text{N}, \text{O})_x$	11.64	$(\text{Fe}, \text{W}, \text{Mo}, \text{G}, \text{V})_6\text{C}$	11.04 ₄
$\text{Co}_4\text{W}_2\text{C}$	11.03			$(\text{Mo}, \text{Fe})_6\text{C}$	12.00
$\text{Ni}_3\text{Mo}_3\text{C}$	11.05			$(\text{Fe}, \text{Mo}, \text{Nb}, \text{Ta})_6\text{C}$	11.09
$\text{Ni}_3\text{W}_3\text{C}$	11.17			$(\text{Fe}, \text{Mo}, \text{Ti})_6\text{C}$	11.08
$(\text{V}, \text{Fe})_3\text{Ta}_3\text{C}$	11.54			$(\text{Fe}, \text{Mo}, \text{V})_6\text{C}$	11.09
$(\text{V}, \text{Co})_3\text{Ta}_3\text{C}$	11.56			$(\text{Fe}, \text{Mo}, \text{W})_6\text{C}$	11.09
$(\text{V}, \text{Ni})_3\text{Ta}_3\text{C}$	11.56			$(\text{Fe}, \text{Nb}, \text{Ta}, \text{W})_6\text{C}$	11.11
$(\text{V}, \text{Ni})_3\text{Nb}_3\text{C}$	11.50			$(\text{Fe}, \text{Ti}, \text{W})_6\text{C}$	11.08
$(\text{Cr}, \text{Fe})_3\text{Ta}_3\text{C}$	11.40			$(\text{Fe}, \text{W}, \text{V})_6\text{C}$	11.06
$(\text{Cr}, \text{Co})_3\text{Ta}_3\text{C}$	11.40				
$(\text{Cr}, \text{Ni})_3\text{Ta}_3\text{C}$	11.35~11.44				
$(\text{Cr}, \text{Cu})_3\text{Ta}_3\text{C}$	11.52				
$\text{FeCr}_2\text{W}_3\text{C}$	11.07				
$(\text{Fe}, \text{Cr})_4\text{W}_2\text{C}$	11.05				

Table 24. Crystallographic data of χ -carbide, $\text{Co}_3\text{W}_9\text{C}_4$

Carbide	System	Structure type	Lattice parameters (Å)	M	Space group	C atom position	Remarks
$\text{Co}_3\text{W}_9\text{C}_4$	Hex.	—	$a=7.826$ $c=7.826$ $c/a=1.000$	2	$P6_3/mmc$	Prism and oct.	χ -carbide

Atom positions: origin at center ($\bar{3}m1$).

$3\text{Co}+3\text{W}$ at $6(h)$ with $x=0.890$, $3\text{Co}+3\text{W}$ at $6(h)$ with $x=0.555$, 12W at $12(k)$ with $x=0.205$, $z=0.075$,

2C at $2(c)$, 6C at $6(g)$.

$12(k)$: $x, 2x, z$; $2\bar{x}, \bar{x}, z$; $x, \bar{x}, z$; $\bar{x}, 2\bar{x}, z$; $2x, x, \bar{z}$; $\bar{x}, x, \bar{z}$;
 $\bar{x}, 2\bar{x}, \frac{1}{2}+z$; $2x, x, \frac{1}{2}+z$; $\bar{x}, x, \frac{1}{2}+z$; $x, 2x, \frac{1}{2}-z$; $2\bar{x}, \bar{x}, \frac{1}{2}-z$; $x, \bar{x}, \frac{1}{2}-z$.

$6(h)$: $x, 2x, \frac{1}{4}$; $2\bar{x}, \bar{x}, \frac{1}{4}$; $x, \bar{x}, \frac{1}{4}$; $\bar{x}, 2\bar{x}, \frac{3}{4}$; $2x, x, \frac{3}{4}$; $\bar{x}, x, \frac{3}{4}$.

$6(g)$: $\frac{1}{2}, 0, 0$; $0, \frac{1}{2}, 0$; $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

$2(c)$: $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$; $\frac{2}{3}, \frac{1}{3}, \frac{3}{4}$.

Fig. 22.

Structure of χ -carbide, $\text{Co}_3\text{W}_9\text{C}_4$.

In the structure there are trigonal prisms formed by W atoms and slightly distorted octahedra formed by 5W and 1Co atoms in the average. Both the prisms and the octahedra contain carbon atoms at their centers.

Table 25. Lattice parameters of some χ -carbides

Carbide	Lattice parameters (Å)		
	a	c	c/a
$\text{Co}_3\text{W}_9\text{C}_4$	7.826	7.826	1.000
$\text{Ni}_3\text{W}_9\text{C}_4$	7.818	7.818	1.000
Mn-W-C	7.756	7.756	1.000

cording to Kuo and Perrson¹⁰¹⁾ Mn_4C is a carboxide $\text{Mn}_4(\text{C}, \text{O})$.

2. $\text{Fe}_6\text{W}_6\text{C}$

Umanskii and Cebotarev¹⁰²⁾ reported that $\text{Fe}_6\text{W}_6\text{C}$ has a structure similar to η_1 -carbide, $\text{Fe}_3\text{W}_3\text{C}$. Leciejewicz¹⁰³⁾ studied the carbide with X-ray and neutron diffraction and determined the structure, which is cubic with lattice parameter $a=10.934$ Å, $M=8$ and belongs to the space group $Fd\bar{3}m$. The atomic arrangement is similar to that in $\text{Fe}_3\text{W}_3\text{C}$ but carbon atoms are at the centers of undistorted octahedra formed by tungsten atoms.

3. β -Mn Type Ternary Carbides

Jeitschko *et al.*¹⁰⁴⁾ studied the structure of a ternary carbide $\text{Al}_2\text{Mo}_3\text{C}$ which had been prepared from a

mixture of aluminum, molybdenum and carbon powders heated rapidly to 1500°C and then cooled. The carbide is cubic and has a structure similar to β -Mn. The crystallographic data are shown in Table 26. Table 27 lists the carbides isomorphous with $\text{Al}_2\text{Mo}_3\text{C}$.^{28), 105)} π phase in Re-W-C studied by Kuz'ma *et al.*¹⁰⁶⁾ has the same structure.

4. Fe_2MoC or M_aC_b

Dyson and Andrews¹⁰⁷⁾ reported that M_aC_b , which had been found by Kuo¹⁰⁸⁾ in alloy steels, was actually Fe_2MoC , based on fluorescent and carbon analysis of extracted residue from heat treated Mo-Cr steel. Analysing the X-ray powder patterns and selected area electron diffraction patterns, they concluded that Fe_2MoC is orthorhombic with lattice parameters $a=16.27_6$, $b=10.03_4$, and $c=11.323$ Å and belongs to the space group $P222_1$. However, the atom positions have not been established.

5. ψ -(Cr, Fe)₂C

Goldschmidt¹⁰⁹⁾ has reported on a FCC group carbide with lattice parameter $a=3.6183$ Å formed in a steel containing 6%Cr, 1%C quenched from 1250°C . He presumed the carbide to be $(\text{Cr}, \text{Fe})_2\text{C}$.

Table 26. Crystallographic data of β -Mn type carbide, $\text{Al}_2\text{Mo}_3\text{C}$

Carbide	System	Structure type	Lattice parameter (Å)	<i>M</i>	Space group
$\text{Al}_2\text{Mo}_3\text{C}$	Cubic	Like β -Mn	6.866 at Al-poor boundary	4	$P4_132$

Atom positions: origin at 3.

12Mo at 12(*d*) with $x=0.206$, 8Al at 8(*c*) with $x=0.061$, 4C at 4(*a*).12(*d*):

$$\begin{aligned} & \frac{1}{8}, x, \frac{1}{4}+x; \frac{3}{8}, \bar{x}, \frac{3}{4}+x; \frac{7}{8}, \frac{1}{2}+x, \frac{1}{4}-x; \frac{5}{8}, \frac{1}{2}-x, \frac{3}{4}-x; \\ & \frac{1}{4}+x, \frac{1}{8}, x; \frac{3}{4}+x, \frac{3}{8}, \bar{x}; \frac{1}{4}-x, \frac{7}{8}, \frac{1}{2}+x; \frac{3}{4}-x, \frac{5}{8}, \frac{1}{2}-x; \\ & x, \frac{1}{4}+x, \frac{1}{8}; \bar{x}, \frac{3}{4}+x, \frac{3}{8}; \frac{1}{2}+x, \frac{1}{4}-x, \frac{7}{8}; \frac{1}{2}-x, \frac{3}{4}-x, \frac{5}{8}. \end{aligned}$$

8(*c*):

$$\begin{aligned} & x, x, x; \frac{3}{4}-x, \frac{3}{4}-x, \frac{3}{4}-x; \frac{1}{2}+x, \frac{1}{2}-x, \bar{x}; \frac{1}{4}-x, \frac{3}{4}+x, \frac{1}{4}+x; \\ & \bar{x}, \frac{1}{2}+x, \frac{1}{2}-x; \frac{1}{4}+x, \frac{1}{4}-x, \frac{3}{4}+x; \frac{1}{2}-x, \bar{x}, \frac{1}{2}+x; \\ & \frac{3}{4}+x, \frac{1}{4}+x, \frac{1}{4}-x. \end{aligned}$$

4(*a*):

$$\frac{3}{8}, \frac{3}{8}, \frac{3}{8}; \frac{7}{8}, \frac{1}{8}, \frac{5}{8}; \frac{5}{8}, \frac{7}{8}, \frac{1}{8}; \frac{1}{8}, \frac{5}{8}, \frac{7}{8}.$$

Table 27. Lattice parameters of some β -Mn type carbides

Carbide	Lattice parameter (Å)
$\text{Al}_2\text{Mo}_3\text{C}$	6.866
$\text{Al}_2\text{Nb}_3\text{C}$	7.06 ₅
$\text{Al}_2\text{Ta}_3\text{C}$	7.03 ₉
$\text{Re}_2\text{W}_3\text{C}$	6.85 ₉

6. W_5C_3

It has been suggested that W_5C_3 , whose structure could be isotype with W_5Si_3 , might exist.⁵⁷⁾ The carbide is stable only above 2540°C. It could be β - W_2C .

XVII. Carbon Environment

As described in the previous sections, there are so many types in the carbide structure, but if we pay an attention to a carbon atom and its surrounding metal atoms in the crystal, all the structures can be put in the following three categories.

(1) Octahedral type: The carbon atom exists at the center of octahedron formed by six metal atoms. This type includes *BCC*, *FCC* and *HCP* group carbides and M_6C type double carbides. γ - MoC_x also belongs to this type.

(2) Prism type: The carbon atom exists at the center of trigonal prism formed by six metal atoms. This type includes *SH* group carbides, M_3C_2 , M_3C , M_5C_2 , and M_7C_3 type carbides. Except the *SH* group carbides, they have the complex structures. In general, their thermal stability is lower than that in the octahedral type.

(3) Decahedral type: The carbon atom exists at the center of decahedron formed by eight metal atoms. This type includes only M_{23}C_6 type carbides.

Fig. 23. Comparison of carbon environments in the octahedral, prism and decahedral type carbides

- (a) α - W_2C (oct.)
- (b) WC (prism)
- (c) ϵ - Fe_{23}C (oct.)
- (d) Fe_3C (prism)
- (e) Cr_3C_2 (prism)
- (f) Cr_{23}C_6 (deca)

Interatomic distances are shown in the figure in Å unit. Arrow indicates the orientation of coordination polyhedron in the structure.

In the structure of γ' - MoC and $\text{M}_3\text{W}_9\text{C}_4$ type carbides, some carbon atoms exist at the centers of octahedra and some at the centers of trigonal prisms, so that these carbides are considered to be a transitional type form prism to octahedral.

The occurrence of the above three types in the carbon environment is considered to come from the difference in the nature of atomic bonding in the carbides. In order to investigate the difference a comparison was made for the carbon environments in different types of carbides formed by the same metal. Figure 23 (a)–(f) shows the carbon environments in α - W_2C (oct.), WC (prism), ϵ - Fe_{23}C (oct.), Fe_3C (prism), Cr_3C_2 (prism) and Cr_{23}C_6 (deca.). If we compare, for instance, α - W_2C and WC , it can be seen that the interatomic distance between metal and carbon is smaller for the octahedral type than for the prism type and the average

interatomic distance between metals is larger for the octahedral type than for the prism type. Table 28 shows the average metal-metal and metal-carbon distances in the co-ordination polyhedra for the carbides mentioned above. As can be seen in the sixth row, the increase of metal-metal distances caused by the carbide formation is largest for the octahedral type, while in the seventh row, the size of the interstices, in other words, the radius of carbon atom, r_c , is smallest in the octahedral type and largest in the decahedral type. Further, r_c is smaller than the tetrahedral covalent radius of carbon atom (0.77 Å) for the octahedral type, nearly equal or slightly larger for the prism type and larger for the decahedral type. Since the metal-metal bonding and the metal-carbon bonding are considered to be mainly responsible for the cohesion in the carbide and the carbon-carbon bonding may be less important because of the large carbon-carbon distance, and since we can consider that larger the interatomic distance, weaker the atomic bonding, we may presume that the metal-carbon bonding is stronger than the metal-metal bonding in the octahedral type, they are comparable in the prism type and the metal-carbon bonding is weaker than the metal-metal bonding in the decahedral type.

Hägg's rule (section I) applies to almost all the interstitial compounds but there are some cases in which the rule does not hold, for instance, the carbides of class 5 metals with simple structure. This is because the rule is only concerned with the atomic radius and not with the bonding nature which influences the atomic radius. The fact that the carbon atom radius is mutually different in the octahedral, prism and decahedral types seems to suggest the bonding nature between the metal and carbon atoms being different one another.

XVIII. Electronic Structure of Carbides

The bonding in the transition metal carbides is expected to arise from simultaneous contributions of metallic, covalent and ionic bonding to cohesive energy, but on account of such intermediate bonding characters it is difficult to establish an accurate model

of the electronic structure and there remain so many obscure points to be solved. Several attempts have been done to determine the electronic structure, especially, for the FCC group carbides and nitrides. In what follows, a description is given not only for the carbides but also for the nitrides owing to their similarities in the structure and the bonding character. A review on the electronic structure of the interstitial compounds was made by Mekata *et al.*¹¹⁰⁾ in connection with the magnetic properties.

The attempts to establish the electronic structure have been done in the following ways of approach: approach from the ionic bonding model, from the covalent bonding model and from the metallic bonding model. The first is concerned with the charge distribution between the metal and non-metal atoms, the second with the bonding character between the constituent atoms and the third with the band structure of the compounds. Since almost all the works have been done for the NaCl type compounds, the following description is limited to the NaCl type carbides and nitrides with stoichiometric composition, unless otherwise noted.

1. Resonating Bonds

As described in the section XVII, we can assume the following three kinds of interatomic bonding in the carbides and nitrides: metal-metal (M-M), metal-non-metal (M-X) and non-metal-non-metal (X-X). Among them the X-X bonding may be less important than the others and is disregarded here. The M-X bonding is considered to be responsible for the non-metallic nature such as large hardness and brittleness and the M-M bonding for the metallic nature such as electrical conductivity, which is as large as that of mother metals.

Pauling¹¹¹⁾ suggested that the nature of M-X bonding is essentially covalent. A typical covalent bonding is seen in the structure of diamond, where four localized and directed orbitals due to sp^3 hybridization make strong tetrahedral bonds with neighbouring four carbon atoms. Thus, each carbon atom is at the center of tetrahedron. In the case of carbides, however, the

Table 28. Comparison of the interatomic distances in the co-ordination polyhedra for the octahedral, prism and decahedral type carbides

Carbide			α -W ₂ C	WC	ε -Fe ₂₋₃ C	Fe ₃ C	Cr ₃ C ₂	Cr ₂₃ C ₆
Type			Oct.	Prism	Oct.	Prism	Prism	Deca.
Average distance between metal atoms	d_{M-M}	(Å)	2.97	2.89	2.73	2.62	2.68	2.59
Average distance between metal and carbon atoms	d_{M-C}	(Å)	2.09	2.20	1.93	2.03	2.05	2.10
Distance between metal atoms in bcc metal	d	(Å)	2.741		2.482		2.498	
d_{M-M}/d			1.08	1.05	1.10	1.06	1.07	1.04
$r_c = d_{M-C} - \frac{d}{2}$			(Å)	0.72	0.83	0.69	0.79	0.85

sp^3 hybrids are not appropriate, since the carbon atom is surrounded by six metal atoms forming an octahedron. Therefore, he assumed that the four valence electrons are in $(2s, 2p)$ orbitals and the carbon atom makes four covalent bonds with the six metal atoms through a resonance in six directions. The bonding electrons for the metal atoms are assumed in (d, s, p) orbitals.

Based on the Pauling's idea, Rundle¹¹²⁾ determined the bond order for the M-X bonding from the analysis of interatomic distances between metal and non-metal atoms in various carbides and nitrides with the help of the Pauling's empirical relation. The orbitals for the three valence electrons of nitrogen atom were assumed to be the mutually orthogonal $2p_x, 2p_y$ and $2p_z$ and those for the four valence electrons of carbon atom to be the mutually orthogonal and hybridized $2s-2p_x, 2p_y$ and $2p_z$, while the hybridized d^2sp^3 orbitals oriented octahedrally were taken for the bonding electrons in metal atoms. He concluded that σ -type bonds are formed between the metal and non-metal atoms with the bond order $1/2$ in the nitrides and $2/3$ in the carbides, and the larger bond order in the carbides, which comes from the contribution of $2s$ electrons to the M-X bonding, is responsible for the larger hardness of the carbides, in general, than that of nitrides. For the M-M bonding d_z orbitals were assumed.

Hume-Rothery¹¹³⁾ considered that the bond order $1/2$ or $2/3$ arises from a nitrogen or carbon atom being necessary to get $1/2$ or $2/3$ electron from each of the surrounding metal atoms in order to fill up the $2p$ shell. Krebs¹¹⁴⁾ proposed an idea that the M-X bonding orbitals are not σ -type but π -type formed between the three $2p$ orbitals of non-metal atom and the three d_x orbitals of metal atom.

2. Band Theory

Extending the concept of resonating bond, Bilz¹¹⁵⁾ made a band theory of the NaCl type carbides and nitrides. At first he took a hypothetical M_6X molecule, that is to say, a non-metal atom and its surrounding six metal atoms, out of the crystal and presumed a probable energy band when only the M-X interaction was acting. Next, he presumed an energy band when only the M-M interaction was working in the crystal. Interporating both bands, he obtained an energy *vs.* density of states curve possible for the NaCl type carbides and nitrides. This is shown in Fig. 24(a). In his treatment, the valence electrons in the carbon atom are assumed to be in the state of $(2s)(2p)^3$ and the spherically symmetric $2s$ orbital combines with each of the s orbitals of the surrounding six metal atoms to form a non-localized σ -type bond with the bond order $1/6$. The $X(2s)$ band in the figure corresponds to this M-X bonding. The three $2p$ orbitals combine with the d^2sp^3 hybrids of metal atoms with the bond order $1/2$. The corresponding energy band is designated as M-X in the figure. The M-M band is due to the M-M interaction associated with the d_z orbitals and the M-X (anti) band corresponds to the anti-bonding states of the M-X interaction. In this treatment, unlike the Rundle's interpretation, the bond

order $2/3$ for the carbides comes from the bond order $1/6$ for the $(2s)_X-(s)_M$ bonding and the $1/2$ for the $(2p)_X-(d^2sp^3)_M$ bonding.

Bilz further tried to determine the band structure by solving the one-electron Schrödinger equation under the tight binding approximation. Assuming (in the Slater and Koster scheme) the values of the two center integrals for the metallic d, s, p and non-metallic $2p$ orbitals, he obtained an energy band *vs.* density of states curve as shown in Fig. 24(b). The calculated curve fairly resembles Fig. 24(a), showing that the previous estimation is correct. Corresponding to the fact that the compounds are electrical conductor, the band overlapping is observed in the figure. The Fermi levels for TiC and TiN are also indicated. The former is below the energy level at the minimum density of states and the latter is above it.

Recently, Ern and Switendick¹¹⁶⁾ calculated the band structure of TiC, TiN and TiO with augmented-plane-wave (APW) method of Slater. The results are reproduced in Fig. 25(a) and (b) for TiC and TiN, respectively. Their energy band *vs.* density of states curves agree qualitatively with the Bilz's, except the $2s$ band being separated from the others. The Fermi levels are at the level of the minimum density of states for TiC and above for TiN. More recently, Lye and Logothetis¹¹⁷⁾ calculated the energy band for TiC according to the tight binding approximation in order to interpret the optical reflectivity. Their curve was somewhat different from the previous ones, but the reason of the discrepancy has not been clarified.

Although the exact band structure has not yet been established, some properties of the carbides and nitrides

Fig. 24. Schematic energy *vs.* density of states curves for NaCl type carbides and nitrides due to Bilz

- (a) Estimated curve
- (b) Calculated curve

Fig. 25. Energy vs. density of states curves due to Ern and Switendick

- (a) TiC
(b) TiN

can be interpreted in connection with the band model. For instance, the concentration of conduction electrons estimated from the Hall coefficient is almost zero for TiC and ZrC with total eight valence electrons per formula unit, and almost one for TiN and VC with total nine valence electrons per formula unit.¹¹⁸⁾ More recent experiments on the electrical resistivity and the Hall coefficient for TiC gave about 0.08 electrons per formula unit to the conduction electron concentration.¹¹⁹⁾ In a carbonitride, $\text{TiC}_{1-x}\text{N}_x$, the concentration of conduction electrons increases with increasing x or with increasing the total number of valence electrons in the crystal.¹²⁰⁾ These facts can be explained from the band model as follows. The non-conductive band can contain eight electrons and it overlaps slightly with the conduction band. Then, electrons beyond eight, as in the case of TiN and $\text{TiC}_{1-x}\text{N}_x$, will go into the conduction band to behave as the conduction electrons.

3. Electronic State of Constituent Atoms

Previously, the atoms in the carbides and nitrides have been assumed to be neutral. However, there is no positive reason why the atoms should be neutral. It is rather natural to consider that the atoms are in ionized states, since the electronegativity differs between metal and non-metal atoms.

Two types of theory have been proposed on the electronic state of constituent atoms in connections with the magnetic properties of some ferro- and ferrimagnetic interstitial compounds. The donor type theory assumes that the non-metal atom donates its valence electrons to the unfilled d band of metal atoms, and the acceptor type theory assumes that the non-metal atom accepts electrons from the d band of metal atoms. In order to test which theory is appropriate, Wiener and Burger¹²¹⁾ measured the magnetic moments of the perovskite type nitrides, Fe_4N , Fe_3NiN and Fe_3PtN . A

satisfactory explanation was possible when the nitrogen atom was assumed to donate its three valence electrons to the neighbouring iron atoms at the fcc positions. Frazer¹²²⁾ also supported the donor type theory on the basis of the analysis of magnetic scattering intensity in neutron diffraction of Fe_4N . In addition to these, if the non-metal atom were positively ionized, its size became considerably smaller than that of the neutral atom. This seemed to be favourable to explain the fact that the slip system of the NaCl type compounds such as TiC and VC is $\{111\} - \langle 110 \rangle$ like fcc metals but not $\{110\} - \langle 110 \rangle$ type like NaCl.^{19),20)}

The most direct and reliable way to determine the electronic state of the constituent atoms is to measure the X-ray diffraction intensities precisely, since the low order reflection intensities are influenced by the electronic state of atoms in crystals. Recently, efforts have been done successfully for some kinds of nitrides. Elliott¹²³⁾ measured the diffraction intensity from Fe_4N and reported that the nitrogen atom is in the state of N^{-3} . Kuriyama *et al.*¹²⁴⁾ measured the diffraction intensity from Mn_4N , isomorphous with Fe_4N , and found the nitrogen atom in the state of $\text{N}^{0 \text{ to } -1}$. For almost stoichiometric VN with NaCl type structure, Hosoya *et al.*¹²⁵⁾ recently have reported that the electronic state can be expressed as $\text{V}^{+2}\text{N}^{-2}$ or $\text{V}^{+3}\text{N}^{-3}$.

As described in section II, electron diffraction method can also be applied to determine the electronic state of constituent atoms in crystals, if reflections appear in the low angle range of $\sin \theta / \lambda \leq 0.2 \text{ \AA}^{-1}$, where θ is the Bragg angle and λ the wavelength. Using this fact, the present authors could determine the electronic state of the carbon atom in $\beta\text{-Mo}_2\text{C}$ to be almost C^{-1} . Very recently, detailed analysis of the electron diffraction intensity was carried out for some iron nitrides, Fe_4N , $\epsilon\text{-Fe}_2\text{N}$ and $\zeta\text{-Fe}_2\text{N}$.¹²⁶⁾ The electronic structure of Fe_4N can be expressed as $\text{Fe}^0(\text{Fe}^{+\frac{1}{3}})_3\text{N}^{-1}$, that is to say, the iron atom at the corner site of the unit cell is neutral, the iron atom at the face center site is in the state of $\text{Fe}^{+\frac{1}{3}}$, and the nitrogen atom at the body center site is in the state of N^{-1} . The X-ray result due to Elliott described above is not correct. The present electronic structure is different from the previous models based on the magnetic moment data but can explain the magnetic moment distribution determined by Frazer equally well. Magnetic moment data are not sufficient enough to establish the electronic structures of crystals. For the other iron nitrides, $\epsilon\text{-Fe}_2\text{N}$ and $\zeta\text{-Fe}_2\text{N}$, the electronic structures are about $(\text{Fe}^{+\frac{3}{2}})_2\text{N}^{-3}$ and about $(\text{Fe}^{+\frac{3}{2}})_2\text{N}^{-\frac{3}{2}}$, respectively.

In Table 29, the electronic states of atoms in the interstitial compounds, hitherto determined, are tabulated. The results show that the non-metal atom is in the negatively ionized state, or at least, not positively, in the case of the compounds of the octahedral type. Since the experimental facts support the acceptor type theory, the results of magnetic moment measurements should be interpreted on a different basis. Furthermore, since the band structure calculations have been made on the assumption of neutral atoms, recalculations are necessary to obtain more refined

Table 29. Electronic states of atoms in some interstitial compounds

Compound	Structure type	Non-metal atom position	Method*	Electronic state
Mn ₄ N	Cub. perovskite	Oct.	X.D.	N ⁰ to -1
Fe ₄ N	Cub. perovskite	Oct.	X.D.	N ⁻³
			E.D.	Fe ⁰ (Fe ^{+1/3}) ₃ N ⁻¹
VN	Cub. NaCl	Oct.	X.D.	V ⁺² N ⁻² or V ⁺³ N ⁻³
ε-Fe ₂ N	Hex. ε-Fe ₂ N	Oct.	E.D.	About (Fe ^{+3/2}) ₂ N ⁻³
ζ-Fe ₂ N	Ortho. ζ-Fe ₂ N	Oct.	E.D.	About (Fe ^{+3/4}) ₂ N ^{-3/2}
β-Mo ₂ C	Ortho. ζ-Fe ₂ N	Oct.	E.D.	Almost C ⁻¹

* X.D.: X-ray diffraction.

E.D.: electron diffraction.

band structures.

A comment seems to be necessary on the ionization of atoms in the carbides and nitrides. The compounds are not the pure ionic crystals but have an intermediate bond character among the covalent, ionic and metallic bonds. The atomic ionization means that the electrons donated from the metal atoms are somewhat localized around the non-metal atom to give the non-metal atom the negatively ionized character and to the metal atom the positively ionized character. Therefore, the whole number may not always appropriate to represent the ionized state of the constituent atoms.

4. Effect of Non-stoichiometry

As was seen in the section V-1, NaCl type carbides can exist in a wide range of chemical composition and the formula is expressed by MC_x ($x \leq 1$). When $x < 1$, carbon vacancies are produced in the crystal and the various physical properties are affected by them. For instance, the carbon vacancies scatter electrons, so that the intrinsic resistivity increases with decreasing x , and also they cause a large residual resistivity. In TiC_x, the intrinsic resistivity has been found to increase from $70 \pm 10 \mu\Omega \text{ cm}$ for $x=1$ with decreasing x at the rate of $16 \mu\Omega \text{ cm}$ per a unity of x .¹¹⁹⁾ The vacancy can be regarded to have an effective charge, whose amount was estimated to be greater than $1e$ in TiC.¹¹⁹⁾ Therefore, the bond character may be changed around the vacancy, resulting in the change of mechanical properties with vacancy concentration.¹²⁷⁾

5. Electronic State in Various Types of Compounds

In the above, the electronic structure was mainly concerned with the FCC group compounds. For the other octahedral type compounds, for instance, the HCP group compounds, the M-X and M-M interactions may be similar to those in the FCC group compounds, since both the groups have the same non-metal environment and the metal atoms take the close packed array.

In the case of the prism and decahedral type compounds, nothing is known about the electronic structure. In these compounds, although the bonding nature may be essentially covalent, the nature of the M-M interaction as well as the M-X interaction seems to be different from the case of the octahedral type. The M-X bonds are not in simple directions,

so that it is too hard to make orbitals appropriate for the valence electrons in the non-metal atom from 2s and 2p orbitals. The experimental determination of the electronic state of the constituent atoms has not yet been performed but, as seen in section XVII, the radius of carbon atom in the prism and decahedral type compounds is near or slightly larger than the covalent radius of carbon atom. This might suggest the atoms to be neutral.

XIX. Carbides Precipitation from Steels

The tempering of quenched steels have been known to be divided into the following four stages. The first stage (80° to 150°C) is the decomposition of martensite, the second (200° to 300°C) is the decomposition of retained austenite, the third (200° to 500°C) is the precipitation and growth of cementite and the forth, which is only observed in alloy steels, is the conversion of cementite into alloy carbides.

The carbide precipitated in the first stage is ε-Fe₂₋₃C.⁴⁶⁾ Pitsch and Schrader¹²⁸⁾ showed that the precipitated ε-Fe₂₋₃C is fibrous and dispersed finely in the matrix. The carbide is long along [11.0] and the lattice relationships are $[11.0]_{\epsilon}/[100]_{\alpha}$, $[\bar{1}\bar{1}.1]_{\epsilon}/[010]_{\alpha}$ and $[1\bar{1}.1]_{\epsilon}/[001]_{\alpha}$, where the hcp indices were used for ε-carbide. Iron atoms in ε-carbide is considered to be replaced by chromium atoms by a considerable amount and this may make the carbide stabilize.¹²⁹⁾ The kind of carbide precipitated at the second stage has not been established. The precipitation of Fe₅C₂ during tempering is under discussion, but Sato and Nishizawa¹³⁰⁾ could not find the carbide in tempered steels. Cementite precipitated at the third stage is initially needle-like or feathery in shape and becomes round with duration of tempering. The lattice relationships with matrix ferrite obey the relation^{131),132)}: $(001)_{\text{Fe}_3\text{C}}// (211)_{\alpha}$, $[001]_{\text{Fe}_3\text{C}}//[0\bar{1}1]_{\alpha}$ and $[100]_{\text{Fe}_3\text{C}}//[1\bar{1}1]_{\alpha}$. Iron atoms in cementite can be replaced by other kinds of metal atoms. Therefore, the cementite precipitated from steels may be thought to be (Fe, Mn, . . .)₃C. At the forth stage, precipitated carbides depends on the kind and amount of alloying element as well as temperature and time of tempering. Recently, Tanino¹³³⁾ made a review on the mode and mechanism of carbide precipitation from alloy steels. In the following, a brief description is given about the precipitated carbides.

1. FCC Group Carbide Precipitation

Tanino and Nishida¹³⁴⁾ studied the precipitated carbide from vanadium containing steel (5%V, 0.018%C) quenched and then aged at 600°C by means of the thin foil technique in electron microscopy and identified the carbide to be V_4C_3 (more exactly $V_4(C, N)_3$). The carbide precipitation is responsible for the secondary hardening of the vanadium-containing steel. The precipitated V_4C_3 is very thin and rectangular in shape with the surface (100) and the edges parallel to [110] and $[1\bar{1}0]$, respectively. The lattice relationships with ferrite matrix are $(100)_{V_4C_3} // (100)_\alpha$, $[010]_{V_4C_3} // [011]_\alpha$ and $[001]_{V_4C_3} // [0\bar{1}1]_\alpha$. The coherency between the atomic planes $(100)_{V_4C_3}$ and $(100)_\alpha$ is excellent with a misfit of only 2%, while the misfit percent along the direction perpendicular to the plate is as large as 44%. These facts were considered to make the carbide crystal platelet in shape. The same conclusion has been obtained by Raynor *et al.*¹³⁵⁾ with a high purity 2%V, 0.2%C steel quenched and aged at 500° to 700°C.

Precipitation of other FCC group carbides from ferrite matrix has not yet been fully studied. Seal and Honeycombe¹³⁶⁾ studied the effect of tantalum and niobium addition to certain vanadium-containing steels on their secondary hardening and found the precipitation of fine NbC and TaC particles besides V_4C_3 . Kuo¹³⁷⁾ has reported that TiC threads with 300 Å in diameter and 200 Å in length were formed in a 0.5%Ti, 0.5%C steel tempered at 650°C.

According to Silcock,¹³⁸⁾ NbC precipitated from austenitic steels aged at 650° to 950°C is platelet in shape and appears on dislocations and stacking faults. The lattice relationship with austenite matrix is $\langle 100 \rangle_{NbC} // \langle 100 \rangle_\gamma$. The NbC particles are frequently rhombohedral platelets with their straight edges perpendicular to $\langle 111 \rangle$ directions and the plane of the platelets is frequently {110}.

2. HCP Group Carbide Precipitation

The secondary hardening of a molybdenum-containing steel is caused by the precipitation of β -Mo₂C. According to Irani and Honeycombe,¹³⁹⁾ Raynor *et al.*,¹³⁵⁾ and Tanino *et al.*,¹⁴⁰⁾ β -Mo₂C precipitated at temperatures in the range 500° to 700°C is needle-like and long along [11.0] direction. The lattice relationships with the ferrite matrix are $(00.1)_{\beta-Mo_2C} // (110)_\alpha$, $[11.0]_{\beta-Mo_2C} // [001]_\alpha$ and $[1\bar{1}.0]_{\beta-Mo_2C} // [1\bar{1}0]_\alpha$, when the hcp indices are used for β -Mo₂C. The misfit percent is 5% along [11.0] direction and much larger along other directions. This is considered to be one of the reasons why the carbide grows needle-like.

In tungsten-containing steels, the precipitation of α -W₂C is responsible for the secondary hardening. The precipitated carbide is needle-like as β -Mo₂C.¹⁴¹⁾

V₂C, Nb₂C and Ta₂C do not seem to precipitate from alloy steels. Irvine *et al.*¹⁴²⁾ stated that Cr₂C precipitated in a finely dispersed state from tempered chromium-containing steels. However, it can be (Cr, Mo)₂(C, N) studied by Andrews and Hughes,¹⁴³⁾ since Cr₂C does not exist in the Cr-C binary system.

3. SH Group Carbide Precipitation

Kuo¹⁴⁴⁾ reported that MoC and WC were precipitated from molybdenum-containing and tungsten-containing steels, respectively, but detailed studies seem to have not been carried out.

4. M₇C₃ Type Carbide Precipitation

In chromium-containing steels, the precipitated M₇C₃ type carbide is (Fe, Cr)₇C₃, which grows at the expense of (Fe, Cr)₃C and disappears with the appearance of (Fe, Cr)₂₃C₆. (Cr, Fe)₇C₃ is rod-like in shape initially and changes to spherical particles with crystal growing.¹²⁹⁾ McCann and Ridal¹⁴⁵⁾ observed in a 9%Cr steel tempered isothermally at 650°C thin layer-like M₇C₃ precipitates in the ferrite matrix. The carbide became long thin lath, needle and platelet in shape at the latter stage of transformation.

5. M₂₃C₆ Carbide Precipitation

In chromium-containing steels with high Cr/C atom ratio, (Cr, Fe)₂₃C₆ precipitates as spherical particles.¹⁴⁶⁾ In molybdenum-containing steels, the precipitated M₂₃C₆ type carbide has also a spherical shape and its composition is considered to be Fe₂₁Mo₂C₆.^{141), 147)} A M₂₃C₆ type carbide is also formed in an austenitic steel aged at high temperatures or in a long time of duration.¹⁴⁸⁾

6. M₆C Type Carbide Precipitation

In the Fe-Mo-C system, a M₆C type carbide precipitated has compositions Fe₃Mo₃C and Fe₄Mo₂C, and has a high solubility for Cr, W, V, *etc.* The carbide is polyhedral in shape and grows as large as 2 000 to 3 000 Å.¹⁴⁹⁾ The lattice relationships with ferrite¹⁴⁰⁾ are $(100)_{M_6C} // (100)_\alpha$, $[010]_{M_6C} // [010]_\alpha$. The M₆C particle is considered to be surrounded by {111} planes.¹³³⁾

7. Fe₂MoC or M_aC_b Precipitation

Irvine and Pickering¹⁴¹⁾ reported that M_aC_b might appear after the precipitation of β -Mo₂C or M₂₃C₆ in molybdenum-containing steels but details have not been known. Dyson and Andrews¹⁰⁷⁾ found M_aC_b precipitated from Cr-Mo steel after tempering for a period of time up to 1 000 hr at 550° to 700°C.

XX. Summary and Conclusions

In this article the crystal and electronic structures of transition metal carbides were described together with the carbides precipitated from steels. At first, the crystal structures were classified into various groups and types according to the mode of metal atom arrangement and the description was made for each of them. Then, from the observation of carbon environment in the structure, the various structures were put in the three categories: octahedral, prism and decahedral types. The difference in the carbon environments is expected to arise from the difference in the bonding nature between metal and carbon atoms. The electronic structures of the carbides and nitrides were described, especially on the FCC group compounds.

Finally, the crystallographic aspects of the carbide precipitation from steels were described.

The carbide studies can be divided into two categories. One is to study the nature of carbide itself and the other is to study the carbides precipitated from steels associated with the mode and mechanism of precipitation. As was seen in the previous sections, there are so many transition metal carbides but they have common characters: hard, brittle and electro-conductive. This must be interpreted on the basis of electron theory. At present, however, such kind of studies is in an unsatisfactory stage. This is due to the lack of reliable experimental results. In fact, there are very many obscure points on the nature of carbides. We have only fragmental knowledges on the nature of very limited kinds of carbide and are very far from the point of full understanding. One of the reasons of the delay in carbide studies comes from the difficulty in producing specimens suitable for experiments, especially good single crystals. The development of the carbide studies is considered to depend mainly on the progress of specimen preparation technique. If this difficulty is overcome, extensive studies, experimental and theoretical, would make possible the carbides not only to be used as tool and refractory materials but also as materials for other purposes.

In this article, the carbide precipitation was reviewed only on the crystallographic aspects. This kind of study has made a great progress after the application of electron microscopy and electron diffraction. However, the mode and mechanism of carbide precipitation and the effect of precipitation on the mechanical properties have not yet been studied sufficiently enough. Extensive studies are necessary and they will contribute to the development of more excellent steels.

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