

# Na čem stojí budoucnost?

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## **Abstrakt**

*Budoucnost je nezbytně ovlivněna svými historickými základy i současnou situací. Nutnost uchování kontinuity a potřeba snadnějšího vyhledávání dostupných informačních zdrojů vyžaduje digitalizaci pramenů z "předpočítačové éry".*

*Současný uživatel dává přednost vyhledávání informací v elektronické podobě a mnoho „klasických“ papírových nedigitalizovaných a do databází nezpracovaných informačních zdrojů mu tak uniká. Informační technologie, zejména nástroje pro zpracovávání a vyhledávání informací, procházejí prudkým vývojem. Kvalita vědeckotechnických publikací periodických i neperiodických se však také mění. Řada odborných časopisů změnila svůj profil i charakter. Články bývají stručnější a s chudším faktografickým vybavením. Došlo k zániku či fúzi řady časopisů. V důsledku klesající institucionální finanční podpory publikační činnosti v mnoha odborných časopisech převažuje reklamní inzerce nad vlastním odborným obsahem. Vedle nových forem a možností publikování se objevují i nová omezení přenosu informací. Firmy mnohem přísněji než dříve utajují jakékoliv zmínky o svém know-how, proto nabývají na významu patentové databáze. V akademické sféře se publikační činnost zaměřuje především na publikování výsledků nejrůznějších grantů. Globalizace podnikání logicky vyžaduje i globalizaci databází. Dnešní databáze zpravidla neobsahují velice cenné informace z lokálních národních či regionálních konferencí apod., jejichž získávání a zpracování nelze zajistit centrálně a neobejde se bez spolupráce s lokálními partnery. Fulltextové databáze musejí lépe pokrývat zdroje z neanglických pramenů. V praxi se stále více uplatňují systémy knowledge managementu. Ani budoucnost se neobejde bez základního článku – informačního střediska a informačního pracovníka.*

## **Abstract**

*The future is necessarily influenced by its historical foundations and the present state. The necessity for preservation of continuity and need of easier search of available information sources requires digitisation of sources from "pre-computer era". Contemporary user prefers search of information in electronic form and he is therefore unaware of many "classical" paper non-digitised sources that are not included in databases. Information techniques, particularly tools for information processing and searching, undergo a turbulent development. Quality of periodical and non-periodical scientific and technical publications, however, changes as well. Many professional journals have changed their profile and character. Articles are nowadays more concise and contain less factographic accessories. Many journals were also discontinued or they merged with other titles. Due to decreasing institutional financial support of publication activities many professional journals contain nowadays more publicity advertisements than professional articles. Along with new forms and possibilities for publication there appear new limitations of information transfer. The companies nowadays conceal much more strictly any references about their know-how, that's why importance of patent information becomes more significant. In academic sphere publication activities focus primarily on publishing of results of various grants. Globalisation of business logically requires also globalisation of databases. The existing databases usually do not contain very valuable information from local, i.e. national or regional conferences, etc., acquiring and processing of which cannot be made centrally and cannot be realised without collaboration with local partners. Fulltext databases must ensure better coverage of non-English sources. Knowledge management systems assert themselves more and more in practice. The future cannot do without the basic chain link – information centre and information specialist.*

**Motto:**

*“If I have seen further than others, it is by standing upon the shoulders of giants.*

*„Viděl-li jsem dále nežli jiní, pak proto, že jsem stál na ramenech gigantů.“*

*Isaac Newton*

Obáváme se, že navzdory nevídanému rozmachu informačních technologií nemusí mít dnešní Newtonové dostatečně dobrý rozhled a přehled. K těmto obavám nás vedou níže uvedené skutečnosti:

### Změny nosičů informací

Není sporu o tom, že budoucnost má své kořeny v minulosti, jelikož přítomnost je neuchopitelná, neboť i dnešek je pro budoucnost minulostí. Povinností každé generace je předat další generaci zděděné dědictví, pokud možno rozšířené o nová bohatství. V kontextu informačních činností jsou tímto zděděným bohatstvím znalosti zpracované do formy informací, které můžeme nazvat „archivem vědomostí lidstva“. Zde jsme nejen svědky, ale i přímými účastníky tohoto procesu uchovávání znalostního a informačního bohatství pro budoucnost. Na jedné straně se množství informací neustále zvyšuje, na druhé straně se nesmírným tempem rozvíjejí i technologie pro zpracování, uchovávání a šíření těchto informací. Formy záznamu informací se po tisíciletí vyvíjely a měnily, zmiňme jen letmo první malby pračlověka v jeskyních, uzlové písmo, hliněné desky s hieroglyfy, záznamy na papyru, ručně psané a krásně iluminované knihy středověku a donedávna knihtisk, který toto dědictví dokázal ve veliké míře převést do podoby doposud nejpoužívanějšího nosiče informací všeho druhu – do knih.

Tento relativně ustálený stav posledních staletí se ovšem prudce změnil příchodem výpočetní techniky, a zejména pak rozšířením osobních počítačů a internetu. Kdosi již před časem řekl, že „od nynějška do budoucnosti budou hrát hlavní roli informace elektronické, a vše, co nebude elektronické, jakoby přestalo existovat.“ Zatím se tato prognóza ještě zcela nenaplnila, ale stupeň jejího naplnění je již značný.

### Elektronická skleróza

S nově vznikajícími informacemi z tohoto pohledu tolik problémů není, protože už v naprosté většině vznikají přímo elektronicky, nebo jsou vzápětí do elektronické formy převedeny. Horší je to s informacemi o znalostech z „předpočítačové éry“. Ty opravdu jakoby přestávají existovat, jednoduše proto, že naprostá většina uživatelů dnes upřednostňuje elektronické vyhledávání informací. Paradoxně se tak dostáváme do situace, kdy na jedné straně zápolíme s přemírou informací, ale na druhé straně se dopouštíme „objevování Amerik“ či „vynalézání bicyklu“ jen proto, že nemáme k dispozici v elektronické podobě prameny z „předpočítačové éry“ a proto je neznáme. Většina dokumentů z doby přibližně před šedesátými léty minulého století, tj. před masovým nástupem výpočetní techniky a elektronických databází, se tak dostala do zóny jakési „elektronické sklerózy“. Jako příklad uvádíme namátkou vybraný článek z roku 1948, který svým vybavením předčí dnešní běžné odborné texty – viz Příloha. Obrovské množství podobných článků se dnes nachází právě v zóně „elektronické sklerózy“.

### Digitalizace minulosti jako nepřetržitý proces

Řešení se zdá být samozřejmé a technicky poměrně jednoduché a zvládnutelné – provést digitalizaci těchto starších pramenů. Toto triviální řešení má však velice podstatný háček – finance. Jakkoliv je objem těchto neelektronických pramenů již konečný a nijak neroste, jde přece jen o objem značný, jehož digitalizace si vyžádá nemálo úsilí a času, ale také především peněz. Bez vyřešení této finanční otázky nemůžeme předat dalším generacím toto bohatství, které jsme zdědili od generací předchozích. Současně se bude prohlubovat jakási degenerace historické paměti s mnohými důsledky, které dnes ani nedokážeme plně domyslet.

Dalším problémem budoucnosti jsou důsledky akcelerovaného vývoje zejména výpočetní a telekomunikační techniky pro uchování „archivu vědomostí lidstva“ za situace, kdy se přibližně po 5 letech mění dominantní způsob uchování informací i běžné nosiče k tomu používané. Ne tak dávno to byly děrné štítky a pásky, pak magnetické pásky, diskety nejprve obří, pak menší a 3,5 palcové, dnes dožívající CD-ROMy a DVD a nastupující disky na bázi Blue ray či hologramů atd. Nikdo přitom neví, jaký nosič se stane standardem za 10 let. A obrovské a narůstající objemy dat bude nutno znovu a znovu přenášet na nové paměťové nosiče.

### Zpracovávání a vyhledávání informací

S problematikou uchování a zpracování informací rovněž úzce souvisí formát, do kterého jsou data zpracovávána a v kterém jsou uchovávána. Stále častěji se setkáváme například s informacemi zpracovanými ve formátu XML (eXtensible Markup Language), který významně usnadňuje automatizaci zpracování obsahu informace a tím otevírá cestu k webu nové generace - sémantickému webu. Formát, který popisuje obsah informačního zdroje (bibliografické údaje, anotaci, klíčová slova atd.), se musí přizpůsobovat nástrojům pro vyhledávání informací, jelikož v souladu s vývojem informačních technologií se dynamicky mění i technologie a techniky pro vyhledávání informací. Proto byly vyvinuty a stále se vyvíjejí nové standardy pro zpracování informačních zdrojů do databází. Otázkou je, jak dlouho se s těmito standardy bude pracovat, než se vynalezne standard nový, kompatibilnější, univerzálnější, jednodušší, schopný importovat data zapsaná ve „starších“ formátech pomocí jednoduché konverze, či dokonce integrovat a propojovat data různých formátů.

### Změna kvality odborných publikací

Další charakteristikou vývoje informačních činností v době poměrně nedávné je i změna kvality vědeckotechnických publikací periodických i neperiodických. Řada odborných časopisů změnila svůj profil i charakter. Články bývají stručnější a s chudším faktografickým vybavením. Došlo k zániku či fúzi řady časopisů. V důsledku klesající institucionální finanční podpory publikační činnosti v mnoha odborných časopisech převažuje reklamní inzerce nad vlastním odborným obsahem. Vedle nových forem a možností publikování se objevují i nová omezení přenosu a sdílení informací. Firmy mnohem přísněji než dříve utajují jakékoliv zmínky o svém know-how, proto nabývají na významu například patentové databáze. V akademické sféře se publikační činnost zaměřuje především na publikování výsledků nejrůznějších grantů, přičemž často důvodem k publikování nebývá snaha podělit se o významné dosažené vědecké výsledky, nýbrž nutnost splnit podmínku grantu ohledně publikování výsledků grantového projektu. Stručně a zjednodušeně řečeno – určitá inflace informací se projevila i v poklesu kvality odborných textů.

### Globální spolupráce

Nelze nezmínit další novou črtu dnešní společnosti, která nutně ovlivní budoucí vývoj - globalizaci. Svět se postupně zmenšil natolik, že jakýkoliv druh lidské činnosti je dnes prakticky prováděn v globálních souvislostech. Globalizace podnikání logicky vyžaduje i globalizaci nakládání s informacemi a tedy mj. i globalizaci databází. Dnešní databáze, byť „mezinárodní“, zpravidla dosud neobsahují mnohdy velice cenné informace z lokálních národních či regionálních zdrojů, např. seminářů, konferencí apod., jejichž získávání a zpracování nelze zajistit centrálně a které se tudíž neobejde bez spolupráce s lokálními partnery. Budoucnost proto mají databáze globální – se vskutku globálním obsahem a globálně budované. Mezinárodní bibliografické i fulltextové databáze jsou dnes postaveny převážně na angličtině. Do budoucna bude nutno lépe pokrývat zdroje z neanglických pramenů. Právě snaha o zapojení „lokálních zpracovatelů“ do budování mezinárodních databází představuje jeden z úkolů řešených v rámci projektu MŠMT „Integrovaný informační a knihovnický systém pro rozvoj hutního průmyslu“, na kterém spolupracují Informetal, informační středisko hutního podniku Mittal Steel Ostrava a technická knihovna VÚHŽ Dobrá.

### Integrace informačních zdrojů

Globalizaci databází je možno chápat nejen jako výše uvedený problém zpracovávání lokálních zdrojů v rámci jedné tématicky zaměřené oblasti, ale samozřejmě také jako integraci či propojování různých databází s různými informačními zdroji (www stránky, firemní literatura, elektronické knihy aj.). Najít co nejvíce relevantních informací na jednom místě s použitím jediného dotazu je směrem, kterým se budoucnost vyhledávání informací ubírá. Proto vznikají databázová centra, jednotná informační brána, různé oborově zaměřené informační portály apod., které nabízejí přístup k „širokému sortimentu“ informačních zdrojů z jednoho místa. I zde nabývají na významu metadata, a do budoucna zde najdou i své místo technologie pro sémantický web.

### Knowledge management

Pro zvládnutí narůstajícího objemu informací, uchovávání a sdílení know-how s využitím moderních informačních technologií se ve firemní praxi stále více uplatňují systémy knowledge managementu. Tomuto tématu je věnována další samostatná přednáška v sekci Management informací a znalostí ve firmě. Při všech úvahách se nesmí samozřejmě zapomenout na základní článek – na informačního pracovníka a na informační střediska. Neboť i v budoucnu bude nutno při práci s odbornými a vědeckými informacemi oddělovat zrno od plev ať již při zpracovávání informačních zdrojů do databází tak i při jejich vyhledávání. Tímto oddělováním máme na mysli především výběr kvalitního informačního zdroje, ve kterém nepřevažuje reklama nad obsahem, a kvalitní zpracování jeho obsahu, neboť jen skutečně relevantní záznam je při vyhledávání informací k užítku.

### Závěr

Na čem tedy stojí budoucnost? Především na nás, na zdravém rozumu a na naší schopnosti pojmenovat podstatné problémy a vyvodit z toho jednoznačné cíle pro budoucnost. Důležité je nejen najít řešení těchto problémů, ale dokázat je i prosadit. Jinak hrozí, že rozhledna pro budoucí potenciální Newtony neporoste a že výhled z ní bude omezen jejími drolicími se základy.

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Ukázka odborného článku z časopisu z r. 1948,  
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# IRON AND STEEL INSTITUTE PAPERS

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## The Structure of Carbides in Alloy Steels

By H. J. Goldschmidt, M.Sc., A.Inst.P.

### Part I—GENERAL SURVEY

#### SYNOPSIS

The present paper is the first of a series giving an account of X-ray work on carbides liable to occur in alloy steels, especially high-speed steels. It is mainly concerned with the structures of carbides formed by iron, chromium, tungsten, and molybdenum, but these are considered as part of a broader systematic survey of carbide-forming tendencies of alloying elements and their relation to crystal structure.

A brief account is given of the relevant metal-carbon systems. The carbide structures are described and discussed, and an attempt is made to correlate them with their stability in the presence of given elements.

IN the course of X-ray investigations on alloy steels carried out for Messrs. William Jessop and Sons, Ltd., over a number of years, the nature of the carbides liable to occur in a variety of steels has been elucidated, and attempts have been made to correlate their structure and phase assemblies in a systematic fashion. The object of the present account is to present some of the results of this survey. A number of specific problems arising will be discussed, centred around the systems iron-chromium-tungsten-carbon and iron-chromium-molybdenum-carbon, and data presented to permit the ready identification of carbides found in a given steel from their diffraction patterns. In spite of some outstanding researches on individual carbides, *e.g.*, that of Westgren's school, and the more recent work at the Cavendish Laboratory (*e.g.*, cementite structure), many gaps in our knowledge still remain, and if this investigation helps to point out and to fill some of these, it will have achieved its purpose.

It is not intended to deal with the structure of the primary steel phases (austenite, martensite, ferrite), except where they are closely bound up with the carbides.

In practice the quaternary system iron-chromium-tungsten-carbon, with molybdenum as alternative to tungsten, was given particular attention, since this covers a large number of steels and alloys of the most diverse properties, notably high-speed steels. It is found that by investigating seemingly quite unrelated alloys, in different regions of this system (*e.g.*, low chromium-molybdenum steels, high-speed steels, tungsten carbide hard-metal materials, ferro-

chromes), considerable assistance is derived from one group of alloys in solving the characteristics of another. Further alloy elements, especially the strong carbide-forming ones like niobium, vanadium, and titanium, have to be given additional consideration, but even in this case the iron-chromium-tungsten (molybdenum)-carbon system forms a valuable starting point, if the broader view is taken that the compounds occurring in this system are not tied to the special chemical composition, but rather stand as representatives of certain structure types, which fall into one systematic scheme; the cubic carbide structure, *e.g.*, of NbC, although not represented in the present quaternary system, nevertheless forms an integral part of this scheme.

The present investigation will therefore fall into the following main sections:

- (1) A brief review of data on metal-carbon binary and ternary systems formed by the chief steel-alloying elements: general discussion of carbide relationships (structures).
- (2) The iron-chromium-tungsten (molybdenum)-carbon system: experimental results and discussion.
- (3) Effect of certain additional elements.

#### THE METAL-CARBON BINARY SYSTEMS

The only steel-alloying elements to be dealt with are those covering the part of the periodic table

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between the fourth and eighth group and the fourth and sixth row, *i.e.* :

Ti	V	Cr	Mn	Fe	Co	Ni	(Cu)
Zr	Nb	Mo	[Ma	Ru	Rh	Pd	Ag]
(Hf)	Ta	W	[Re	Os	Ir	Pt	Au]

The rare and noble metals shown in the square brackets may be discarded except for noting that silver, palladium, rhodium, ruthenium, gold, platinum,

iridium, and osmium all form purely graphitic systems with carbon; but there is evidence to show that rhenium, if obtainable in commercial quantities, would promise to be of very considerable interest as an alloying element (Eggers<sup>1</sup>).

The binary diagrams are shown in summary form in Fig. 1 as far as data are available. In the following pages brief notes are given on each system, proceeding

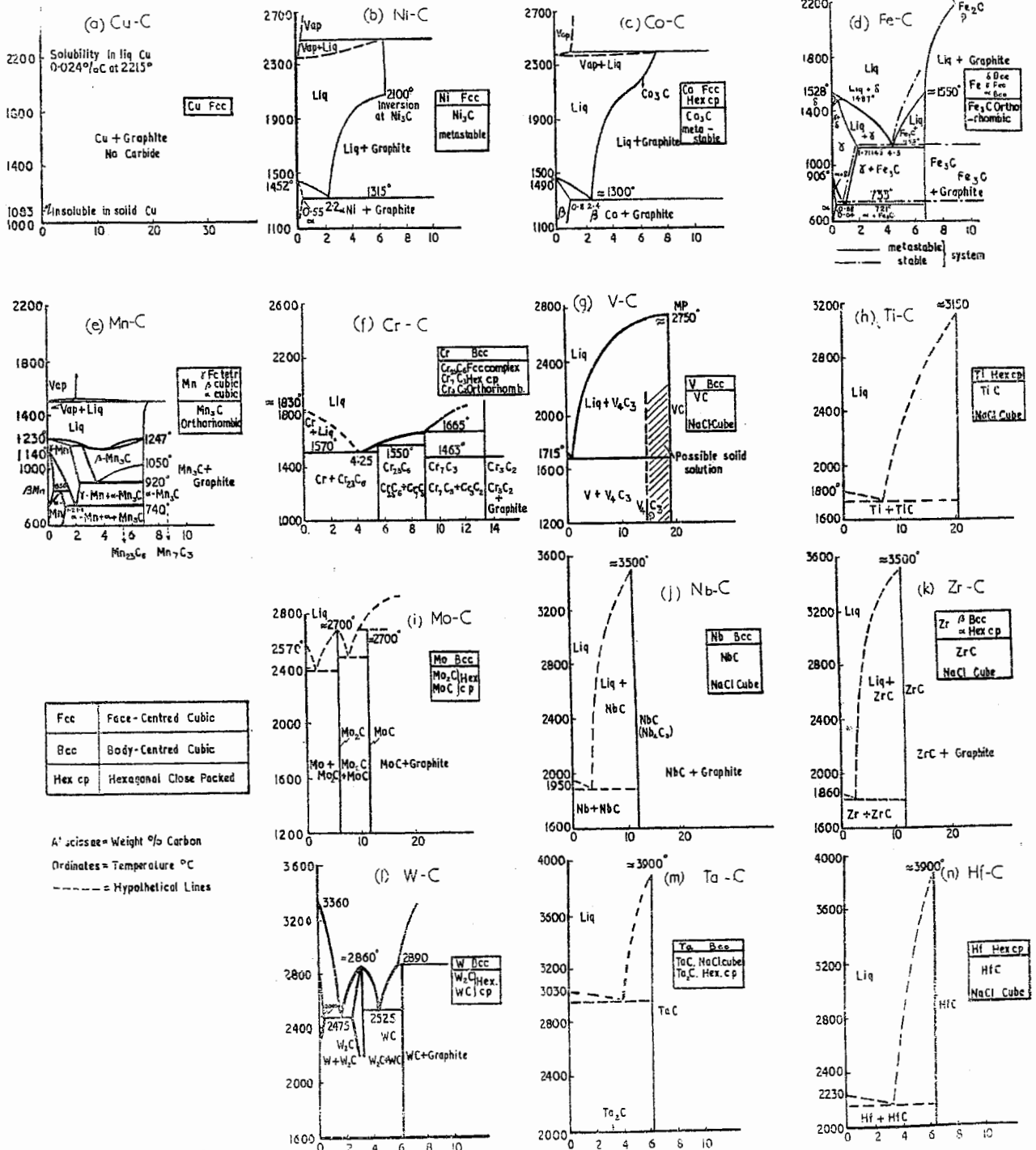


Fig. 1—Binary metal-carbon systems arranged according to the periodic table, with notes on structures of carbides and the parent metals

in order from the weakest to the strongest carbide-formers. Table I summarizes the chief data on simple carbides, *i.e.*, their compositions, melting points, densities, hardnesses, crystal structures, lattice dimensions, and heats of formation.

#### Copper-Carbon (Fig. 1 (a))

Copper forms no stable carbide, being in direct equilibrium with graphite at all temperatures. The existence of a metastable carbide has been suggested by Briner and Senglet,<sup>2</sup> which can be preserved by rapid quenching of the melt from 1600° C. Berthelot has synthesized two very unstable carbides  $\text{Cu}_2\text{C}_2$  and  $\text{CuC}_2$ , which decompose spontaneously. In liquid copper, traces of carbon are dissolved (approximately 0.02% C at 1700° C.); there is no solubility of carbon in solid copper.

#### Nickel-Carbon (Fig. 1 (b))

The stable system is between nickel and graphite, there being virtually no solubility in solid nickel. However, as indicated in Fig. 1 (b), liquid nickel dissolves up to 6.4 wt.-% of carbon (atomic composition  $\text{Ni}_3\text{C}$ ), a value approached between the eutectic point and 2100° C., above which it is maintained over a wide range of temperatures (Ruff and Martin<sup>3</sup>). This would indicate the formation of  $\text{Ni}_3\text{C}$  molecules already in the liquid. The metastable nickel carbide  $\text{Ni}_3\text{C}$  has been found by Briner and Senglet<sup>2</sup>; according to them, it is relatively stable above 1600° C. and below 300° C. It is necessary to cool rapidly out of the liquid from 2000° to 1000° C. in order to obtain the carbide. Bahr<sup>4</sup> and Schmidt<sup>5</sup> obtained  $\text{Ni}_3\text{C}$  by carburizing nickel at 250° C., but the compound already decomposes between 380° and 420° C. Morrogh and Williams,<sup>6</sup> in their recent work on graphite formation in cast irons, studied the nickel-carbon and cobalt-carbon systems and also concluded the existence of metastable nickel (and cobalt) carbide, which permits the formation of nodular graphite by undercooling. Additions such as calcium silicide can stabilize the carbide.

X-ray analysis of  $\text{Ni}_3\text{C}$  by Jacobson and Westgren<sup>7</sup> gave a hexagonal close-packed structure. This structure is, however, in conflict with that reported later by Kohlhaas and Meyer,<sup>8</sup> according to whom  $\text{Ni}_3\text{C}$  possesses the orthorhombic cementite structure ( $\text{Fe}_3\text{C}$ ). The cementite structure is considered as much more probably the correct one, on the grounds of periodic classification. The hexagonal structure of Westgren and Jacobson may have corresponded to a second form of primary nickel, analogous to hexagonal cobalt, which is only rendered stable by some carbon in solid solution. In fact, sputtered or electrolytic nickel is apt to take the hexagonal structure (Bredig and Bergkamp<sup>9</sup>), with lattice dimensions  $a = 2.66$  kX,  $c/a = 1.61$ , which is almost the same as the values given by Westgren and Jacobson for  $\text{Ni}_3\text{C}$ :  $a = 2.646$  kX,  $c/a = 1.636$ .

#### Cobalt-Carbon (Fig. 1 (c))

The stable system, a eutectic one, is between cobalt and graphite. Solid cobalt dissolves 0.82% of carbon at 1300° C., 0.33% at 1000° C., and 0.1% after slow cooling, according to Boecker,<sup>10</sup> while

Hashimoto<sup>11</sup> observes a solubility of up to 1.1% of carbon at the eutectic temperature (approximately 1315° C.). A point on which there appears to be no information and which is worth investigating is whether higher solubility exists in the cubic than in the hexagonal form of the metal. A metastable carbide, of probable formula  $\text{Co}_3\text{C}$ , has been reported by Schenck and Klas,<sup>12</sup> while Ruff and Keilig<sup>13</sup> also concluded the existence of  $\text{Co}_3\text{C}$  molecules in the liquid. Liquid cobalt dissolves variable amounts of carbon, the maximum value being reported at 7.4 wt.-% of carbon (28 at.-%); the accuracy of this must be questioned, but again the value is significantly near  $\text{Co}_3\text{C}$ . However, the carbide appears to be highly unstable. Morrogh and Williams<sup>6</sup> also affirm the existence of cobalt carbide and found it slightly more stable than  $\text{Ni}_3\text{C}$ . Meyer<sup>14</sup> prepared  $\text{Co}_3\text{C}$  and determined its structure, finding it to be isomorphous with cementite. The lattice dimensions of  $\text{Ni}_3\text{C}$ ,  $\text{Co}_3\text{C}$ , and  $\text{Fe}_3\text{C}$ , are given in Table I.

A carbide  $\text{Co}_2\text{C}$  has been reported by Bahr and Jessen,<sup>15</sup> and its existence has been confirmed in a recent paper by Hofer and Peebles.<sup>16</sup> It has been prepared by carburization of cobalt powder at 218° C. and is unstable. The latter authors give its diffraction pattern, which differs from that of  $\text{Fe}_3\text{C}$  (Jack,<sup>18</sup> *see below*), but the structure is not solved.

#### Iron-Carbon (Fig. 1 (d))

The iron-carbon system, iron-graphite (strictly the equilibrium one), and the "metastable" system involving cementite, do not require description here. Cementite  $\text{Fe}_3\text{C}$  is always the prevalent carbide in plain carbon and low-alloy steels. The existence of iron percarbide  $\text{Fe}_2\text{C}$ , having been suggested by Hägg,<sup>17</sup> has recently been re-affirmed by Jack,<sup>18</sup> who found it to possess a small range of composition, *i.e.*, from 30.5 to 32.1 at.-% of carbon, and who also determined its structure. This is probably orthorhombic, with four  $\text{Fe}_{20}\text{C}_9$  molecules. The cell dimensions are:

$$a = 9.04 \text{ kX}, b = 15.66 \text{ kX}, c = 7.92 \text{ kX}.$$

Jack obtained  $\text{Fe}_2\text{C}$  by the action of carbon monoxide on iron nitrides below 500° C., above which  $\text{Fe}_3\text{C}$  is formed.  $\text{Fe}_2\text{C}$  is also metastable.

It is of interest in this connexion to note the liquid solubility of carbon in iron (*see Fig. 1 (d)*). Above the melting point of cementite (approximately 1550° C.) the liquid solubility for carbon gradually increases from 25 to a maximum of 33 at.-% of carbon at 2200° C., indicating the formation in the liquid of molecular aggregates, first of  $\text{Fe}_3\text{C}$  and then of  $\text{Fe}_2\text{C}$ .

The structure of  $\text{Fe}_3\text{C}$  has originally been determined by Westgren and Phragmen<sup>19</sup> and Hendricks,<sup>20</sup> and has been re-determined by Lipson and Petch.<sup>21</sup> Its unit cell is shown in Fig. 6; it is orthorhombic and contains four molecules (16 atoms). The cell dimensions are<sup>21</sup>:

$$a = 4.5144 \text{ kX}, b = 5.0787 \text{ kX}, c = 6.7297 \text{ kX}$$

Hume-Rothery, Raynor, and Little<sup>22</sup> slightly modified these values, while Petch<sup>23</sup> further discussed the structure and affirmed that its composition does not deviate from  $\text{Fe}_3\text{C}$ . A further discussion on cementite will follow later.



The unit cells of  $\text{Fe}_3\text{C}$  and  $\text{Fe}_2\text{C}$ , both orthorhombic, show a simple relationship, as follows :

$$\begin{aligned} a_{\text{Fe}_3\text{C}} &\approx 2 \times a_{\text{Fe}_2\text{C}}; \\ b_{\text{Fe}_3\text{C}} &\approx 3 \times b_{\text{Fe}_2\text{C}}; \\ c_{\text{Fe}_3\text{C}} &\approx 1 \times c_{\text{Fe}_2\text{C}} \quad (\text{though slightly elongated}); \end{aligned}$$

so that six  $\text{Fe}_3\text{C}$  cells stacked together form a region similar to, but slightly smaller than, one of  $\text{Fe}_2\text{C}$ . This volume contains eight more iron atoms in  $\text{Fe}_2\text{C}$  and twelve more carbon atoms. This excess in the number of atoms is almost exactly accounted for by the difference in equivalent volumes, viz. :

In  $\text{Fe}_3\text{C}$ : 96 atoms (72 iron, 24 carbon); volume occupied 924 kX<sup>3</sup>.

In  $\text{Fe}_2\text{C}$ : 96 atoms (64 iron, 32 carbon); volume occupied 934 kX<sup>3</sup>.

The increased carbon content in  $\text{Fe}_2\text{C}$  therefore involves no major expansion or contraction from  $\text{Fe}_3\text{C}$ , and the transition can probably take place in the presence of excess carbon without major change in structure.

#### Manganese-Carbon (Fig. 1 (e))

Figure 1 (e) shows the manganese-carbon binary system, according to Vogel and Döring.<sup>24</sup> Manganese forms at least one stable carbide  $\text{Mn}_3\text{C}$ , which is claimed to exist in two forms,  $\alpha$ - and  $\beta$ - $\text{Mn}_3\text{C}$ . The high-temperature  $\beta$  form possesses a high solubility for manganese;  $\alpha$ - $\text{Mn}_3\text{C}$  is isomorphous with cementite and completely intersoluble with it (Jacobson and Westgren<sup>7</sup>). The latter authors also quote Öhman's

findings of two further carbides, i.e.,  $\text{Mn}_{23}\text{C}_6$  and  $\text{Mn}_7\text{C}_3$ , analogous to and of the same crystal structure as  $\text{Cr}_{23}\text{C}_6$  and  $\text{Cr}_7\text{C}_3$ . This was confirmed in an important paper by Öhman.<sup>25</sup>

The three allotropic forms of manganese dissolve carbon up to the following limits, according to Vogel and Döring<sup>24</sup>:

$\gamma$ -manganese: 2.0% carbon at 920° C.  
 $\beta$ -manganese: 0.4% carbon at 850° C.  
 $\alpha$ -manganese: 1.3% carbon at 740° C.

It may be seen from Fig 1 (e) that the high-temperature form of  $\text{Mn}_3\text{C}$  ( $\beta$ ) and  $\gamma$ -manganese possess a considerable mutual solubility. It is questioned, however, whether the presumed " $\beta$ - $\text{Mn}_3\text{C}$  solid solution" does not correspond to Westgren's carbide  $\text{Mn}_{23}\text{C}_6$ ; a re-determination of this important system is desirable.

Liquid manganese dissolves carbon up to the composition  $\text{Mn}_3\text{C}$ , similar to the observations on iron-carbon, cobalt-carbon, and nickel-carbon. Again the formation in the liquid of molecular aggregates of  $\text{Mn}_3\text{C}$  seems probable.

#### Chromium-Carbon (Fig. 1 (f))

The existence of the three carbides  $\text{Cr}_{23}\text{C}_6$ ,  $\text{Cr}_7\text{C}_3$ , and  $\text{Cr}_3\text{C}_2$ , is firmly established through Westgren and Phragmen's work.<sup>26</sup> Earlier work includes that by Moisson,<sup>27</sup> Ruff and Föhr,<sup>28</sup> and Arnold and Read.<sup>29</sup> A carbide  $\text{Cr}_5\text{C}_2$  reported by Ruff and Föhr probably corresponds to  $\text{Cr}_7\text{C}_3$ .  $\text{Cr}_{23}\text{C}_6$  forms a eutectic system

Table I  
DATA ON BINARY CARBIDES

Carbide of:	Formula	Melting Point (approx.), °C.	Density	Hardness	Crystal Structure	Lattice Dimensions, kX	Heat of Formation <sup>23</sup> K cal./mol. at 20-25° C. 1 atm.- $\Delta$ H
Nickel	$\text{Ni}_3\text{C}^*$	..	..	..	Orthorhombic, cementite-type <sup>8</sup> (Hex. c.p.) <sup>7</sup>	$\left. \begin{aligned} a &= 2.646 \\ c/a &= 1.636 \end{aligned} \right\}$	+ 9 approx.
Cobalt	$\text{Co}_3\text{C}^*$	..	..	..	Orthorhombic, cementite-type		..
Iron	$\text{Fe}_3\text{C}$	1650	7.67	840 Brinell <sup>22</sup>	Orthorhombic	$\left. \begin{aligned} a &= 4.52 \\ b &= 5.08 \\ c &= 6.73 \\ a &= 4.5144 \\ a &= 5.0787 \\ b &= 6.7297 \\ c &= 9.04 \\ a &= 15.66 \\ b &= 7.92 \end{aligned} \right\}$	+ 2.5 approx. †
	$\text{Fe}_2\text{C}$	..	..	..	Orthorhombic <sup>13</sup>		..
Manganese	$\text{Mn}_3\text{C}$	1520	..	..	Orthorhombic, cementite-type	$\left. \begin{aligned} a &= 10.564 \\ a &= 13.87 \\ c &= 4.53 \\ a &= 10.638 \\ a &= 13.98 \\ c &= 4.523 \\ a &= 2.821 \\ b &= 5.52 \\ c &= 11.46 \\ a &= 4.30^{24} \\ \text{or } a &= 4.152^{23} \\ a &= 4.3189^{25} \\ \text{or } a &= 4.3251^{25} \end{aligned} \right\}$	- 23 ± 2
	$\text{Mn}_{23}\text{C}_6$	..	..	..	Cubic (complex), <sup>7</sup> as $\text{Cr}_{23}\text{C}_6$		..
	$\text{Mn}_7\text{C}_3$	..	..	..	Hexagonal (as $\text{Cr}_7\text{C}_3$ ) <sup>7</sup>		..
Chromium	$\text{Cr}_{23}\text{C}_6$	1550	6.97	..	Cubic (complex)	$\left. \begin{aligned} a &= 10.638 \\ a &= 13.98 \\ c &= 4.523 \\ a &= 2.821 \\ b &= 5.52 \\ c &= 11.46 \\ a &= 4.30^{24} \\ \text{or } a &= 4.152^{23} \\ a &= 4.3189^{25} \\ \text{or } a &= 4.3251^{25} \end{aligned} \right\}$	..
	$\text{Cr}_7\text{C}_3$	1665	6.92	..	Hexagonal		..
	$\text{Cr}_3\text{C}_2$	1890	6.68	..	Orthorhombic		..
Vanadium	$\text{V}_4\text{C}_3$ } VC	2830	5.36	9-10 Moh's scale	Cubic c.p.	$\left. \begin{aligned} a &= 4.3189^{25} \\ \text{or } a &= 4.3251^{25} \end{aligned} \right\}$	..
Titanium	TiC	3140 ± 90	4.25	8-9	Cubic c.p.		- 114 ± 2
Molybdenum	$\text{Mo}_6\text{C}$	2687 ± 50	8.9	7-9	Hexagonal c.p.	$\left. \begin{aligned} a &= 2.99 \\ c/a &= 1.58 \\ a &= 4.88 \\ c/a &= 1.34 \\ a &= 4.4404 \end{aligned} \right\}$	..
	$\text{MoC}$	2692 ± 50	8.58	7-8	Hexagonal c.p.		..
Niobium	NbC ( $\text{Nb}_4\text{C}_3$ )	3500 ± 125	7.82	..	Cubic c.p.	$\left. \begin{aligned} a &= 4.687 \\ a &= 2.99 \\ c/a &= 1.575 \\ a &= 2.894 \\ c/a &= 0.973 \\ a &= 3.091 \\ c/a &= 1.595 \\ a &= 4.445 \end{aligned} \right\}$	- 45 ± 2
Zirconium	ZrC	3550	6.90	8-9	Cubic c.p.		..
Tungsten	$\alpha$ - $\text{W}_2\text{C}^\dagger$	2857 ± 50	17.20	9-10	Hexagonal c.p.	$\left. \begin{aligned} a &= 4.687 \\ a &= 2.99 \\ c/a &= 1.575 \\ a &= 2.894 \\ c/a &= 0.973 \\ a &= 3.091 \\ c/a &= 1.595 \\ a &= 4.445 \end{aligned} \right\}$	..
	WC	2867 ± 50	15.50	9	Hexagonal c.p.		..
Tantalum	$\text{Ta}_3\text{C}$	..	..	..	Hexagonal c.p.	..	
Hafnium	TaC	3875 ± 150	14.48	9	Cubic c.p.	$\left. \begin{aligned} a &= 4.687 \\ a &= 2.99 \\ c/a &= 1.575 \\ a &= 2.894 \\ c/a &= 0.973 \\ a &= 3.091 \\ c/a &= 1.595 \\ a &= 4.445 \end{aligned} \right\}$	..
	HfC	3887 ± 150	12.20	..	Cubic c.p. (probably)		..

\* Unstable, but retainable: persistent in melt † Transformation  $\alpha$ - $\text{W}_2\text{C}$  to  $\beta$ - $\text{W}_2\text{C}$  above 2400° C. ‡ Various reported between - 20 and + 8

with chromium, but the formation of this carbide is sluggish and can be suppressed by rapid cooling. In that case the metastable system Cr-Cr<sub>7</sub>C<sub>3</sub> prevails. Figure 1 (f) shows the diagram according to Friemann and Sauerwald,<sup>30</sup> including the metastable system.

The crystal structures have been determined mainly by Westgren's school, and are as follows:

Cr<sub>23</sub>C<sub>6</sub><sup>31</sup> (referred to earlier as Cr<sub>7</sub>C, but the modified formula should be accepted) = complex face-centred cube with 116 atoms per unit cell (92 chromium, 24 carbon).

Edge of unit cube = 10.638 kX.

Cr<sub>7</sub>C<sub>3</sub> = hexagonal<sup>32</sup> with 80 atoms (56 chromium, 24 carbon) per unit cell;  $a = 13.98$  kX,  $c/a = 0.324$  kX.

Cr<sub>3</sub>C<sub>2</sub> = orthorhombic<sup>33</sup> with 20 atoms (12 chromium, 8 carbon) per unit cell;  $a = 2.821$  kX,  $b = 5.52$  kX,  $c = 11.46$  kX.

The solid solubility of carbon in chromium is practically nil. (The chromium carbides will be considered in more detail below.)

#### Vanadium-Carbon (Fig. 1 (g))

The stable vanadium carbide has the cubic NaCl type of structure. Its composition has been reported as either VC or V<sub>4</sub>C<sub>3</sub>, but both may exist independently. The lattice parameter has been reported as  $a_0 = 4.30$  kX,<sup>34</sup> while Maurer, Döring, and Pulewka<sup>35</sup> determined the identical spacing  $a_0 = 4.152 \pm 0.05$  kX for what they presume to be two different compounds VC and V<sub>4</sub>C<sub>3</sub>. It is probable that a solid solution VC-V<sub>4</sub>C<sub>3</sub> exists (defect lattice, carbon atoms being omitted from the ideal NaCl cell), and that the values 4.30 and 4.13 kX (Osawa and Oya<sup>36</sup>) apply to approximately the two ends of the range. In steels the carbide V<sub>4</sub>C<sub>3</sub> is liable to appear. Desch,<sup>37</sup> in an account on iron-carbon-vanadium alloys, reaffirms this composition, which Wever, Rose, and Eggers<sup>38</sup> include in their ternary diagram as the only one.\* A carbide V<sub>2</sub>C has been noted by Osawa and Oya of hexagonal close-packed structure which, however, remains very doubtful, and may have been produced by impurities (nitrogen) present (Hansen<sup>40</sup>).

Figure 1 (g) gives the vanadium-carbon diagram based on the work of Ruff and Martin<sup>41</sup>; V<sub>4</sub>C<sub>3</sub> has also been tentatively inserted.

#### Titanium-Carbon (Fig. 1 (h))

The very stable titanium carbide TiC is of the NaCl type of structure<sup>34</sup> ( $a_0 = 4.3189$  kX, according to Metcalfe's<sup>42</sup> recent paper on the WC-TiC system). A compound Ti<sub>2</sub>C, analogous to V<sub>2</sub>C, has also been

\* The following observation may be mentioned here in evidence. An annealed high-speed steel sample rich in vanadium showed, on X-ray examination, besides ferrite and the normal carbide Fe<sub>4</sub>W<sub>2</sub>C, a cubic carbide of NaCl type of structure, which would agree with vanadium carbide, lattice parameter  $a_0 = 4.17$  kX. This would indicate a composition deficient in carbon (vacant metalloid sites in VC). A solid solubility of vanadium in VC has been presumed by Hägg<sup>39</sup> to extend from VC to V<sub>2</sub>C, and for a composition 14.1 wt.-% of carbon the spacing 4.13 kX has been reported by Osawa and Oya.<sup>36</sup> Assuming this value to be correct and Vegard's law to apply up to VC (19.1 wt.-% of carbon), the present composition follows to be 15.3 wt.-% of carbon = 43 at.-%, i.e., of a formula very near Desch's V<sub>4</sub>C<sub>3</sub> (= 42.86 at.-% of carbon).

suspected to exist of a hexagonal close-packed structure (Jacobson and Westgren<sup>7</sup>), but this is uncertain. Hume-Rothery's<sup>43</sup> work on TiC and on its solubility with TiN (and that of other workers) showed that in titanium-bearing steels carbon is tied to form TiC up to the limit of available titanium. In the presence of stronger carbide-formers (e.g., tungsten, niobium, tantalum) TiC tends to be at least partially intersoluble with the additional carbide; in conjunction with WC, TiC plays an important part in hard-metal metallurgy, which will be referred to later.

Figure 1 (h) indicates the titanium-carbon system, though this, as are some of the subsequent systems, is mainly tentative.

#### Molybdenum-Carbon (Fig. 1 (i))

The stable molybdenum carbides Mo<sub>2</sub>C and MoC are known. In both, the metal atoms are arranged in a hexagonal close-packed lattice with interstitial hexagonal sheets of carbon atoms (Westgren and Phragmen<sup>44</sup>). These authors, however, consider Mo<sub>2</sub>C to be a solid solution of carbon in metallic molybdenum, while Hoyt<sup>45</sup> and most other observers adhere to the existence of the independent compound. Complete intersolubility between the body-centred cubic molybdenum and hexagonal Mo<sub>2</sub>C is, of course, not possible. Sykes, van Horn, and Tucker<sup>46</sup> found that Mo<sub>2</sub>C forms a eutectic with molybdenum at 1.8% of carbon and 2200°C. Mo<sub>2</sub>C is formed by peritectic reaction between 5.5 and 10% at 2400°C. The solubility of carbon in solid molybdenum is very small, becoming 0.09% at 1500-2000°C.

The molybdenum-carbon diagram is represented in Fig. 1 (i).

#### Niobium-Carbon (Fig. 1 (j))

The niobium carbide NbC is stable and of the NaCl type of structure<sup>34</sup> (Friederich and Sittig<sup>47</sup>; the spacing observed by the author is  $a_0 = 4.4404$  kX). McKenna<sup>48</sup> observed  $a_0 = 4.4578$  kX for NbC. No further carbide is formed by niobium. However, Eggers and Peter,<sup>49</sup> in investigating the iron-niobium-carbon system, found the formula Nb<sub>4</sub>C<sub>3</sub> more nearly correct than NbC (Agte and Altherthum<sup>50</sup>). Their observed lattice parameter is  $a_0 = 4.46$  kX, i.e., larger than that given by Friederich and Sittig<sup>47</sup> and the present value. The formula Nb<sub>4</sub>C<sub>3</sub> has not been verified, and some indirect but questionable support may be derived from V<sub>4</sub>C<sub>3</sub>, vanadium being of the same valency as niobium. A homogeneity range NbC/Nb<sub>4</sub>C<sub>3</sub>, similar to the suggested VC/V<sub>4</sub>C<sub>3</sub>, possibly exists.

#### Zirconium-Carbon (Fig. 1 (k))

The stable ZrC<sup>34</sup> has the NaCl type of structure ( $a_0 = 4.687$  kX<sup>51</sup>). A second zirconium carbide ZrC<sub>2</sub> has been suspected by Ruff and Wallstein,<sup>52</sup> but this was probably a mixture of ZrC + C.<sup>40</sup>

#### Tungsten-Carbon (Fig. 1 (l))

The carbide WC, which forms the basis of sintered hard-metals, has been investigated by numerous workers; its structure is hexagonal close-packed, isomorphous with MoC (Westgren and Phragmen<sup>44</sup>).

The second carbide  $W_2C$ ,\* isomorphous with  $Mo_2C$ , also has hexagonal symmetry, but Westgren considers this as a solid solution of carbon in metallic tungsten, the metal being supposed to possess a hexagonal form. The existence of  $W_2C$  as an independent compound has, however, been confirmed by Sykes<sup>53</sup> (among others). There is also a conflict as to whether WC and  $W_2C$  are largely or even completely intersoluble, or are two separate compounds. Certain research has supported the solid-solution-range theory, *i.e.*,  $W_2C$  would be in effect WC with a deficiency of carbon atoms. WC and  $W_2C$  show structural relationships (to be discussed in a later section) which make such an intersolubility of particular interest. W.P. Sykes,<sup>53</sup> Adelskjöld, Sundelin, and Westgren,<sup>54</sup> and Becker<sup>55</sup> established the existence of the two independent

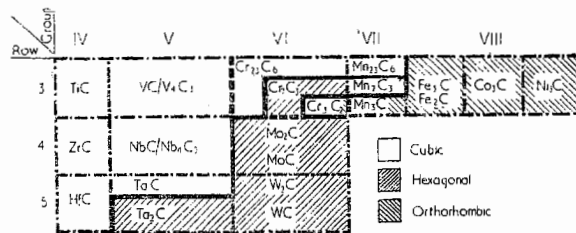


Fig. 2—Relationship between carbide structure and the position of the metal in the periodic table

carbides. K. Becker<sup>55-57</sup> found  $W_2C$  to exist in two modifications ( $\alpha$ - and  $\beta$ - $W_2C$ ). The  $\alpha$ - $\beta$  transformation occurs at 2400° C., but by rapid cooling  $\beta$ - $W_2C$  can be partially preserved; it transforms into the  $\alpha$  form by mechanical work. The structure of  $\beta$ - $W_2C$  is not known, but, according to Becker, the pattern produced by the phase almost agrees with that of  $\alpha$ - $W_2C$ , though indicating a higher symmetry, the transformation being similar to the relation of  $\alpha$  and  $\beta$  quartz.

Sykes' tungsten-carbon diagram is shown in Fig. 1 (*b*). It gives the main phase-equilibria with fair certainty, but the  $\alpha$ - $\beta$  forms of  $W_2C$  are omitted.

A recent paper by Horsting<sup>58</sup> confirms that  $W_2C$  is capable at high temperatures of dissolving limited amounts of tungsten as well as carbon. Reference should also be made to two recent papers on the powder metallurgy of tungsten carbide by Brownlee, Geach, and Raine,<sup>59</sup> and by Sandford and Trent.<sup>60</sup> The solid solubility of carbon in tungsten is negligible.

#### Tantalum-Carbon (Fig. 1 (*m*))

The very stable tantalum carbide TaC has the NaCl type of structure<sup>34</sup> ( $a = 4.445$  kX).<sup>51</sup> According to Burgers and Basart<sup>51</sup> the carbide  $Ta_2C$  also exists and possesses the hexagonal close-packed structure and probably two allotropic forms similar to  $W_2C$ . McKenna<sup>48</sup> re-determined the lattice dimensions of TaC, agreeing with Burgers and Basart.

#### Hafnium-Carbon (Fig. 1 (*n*))

Hafnium carbide HfC,<sup>34</sup> which possesses the highest melting point among all simple carbides, probably has the NaCl type of structure; the only evidence for this is that Agte and Alterthum<sup>50</sup> reported a continuous series of solid solutions TaC-HfC.

\* Cf. Table I for lattice dimensions.

## STRUCTURE RELATIONS AMONG CARBIDES

Classified by their structure symmetry, the binary carbides reviewed above possess one of three types of structures:

- Class 1, cubic (NaCl type): TiC,  $V_4C_3$ , ZrC, NbC, TaC
- Class 2, hexagonal close-packed:  $Mo_2C$ , MoC,  $W_2C$ , WC,  $Ta_2C$
- Class 3, orthorhombic:  $Fe_3C$ ,  $Fe_2C$ ,  $Mn_3C$ , and (probably)  $Co_3C$  and  $Ni_3C$

There is a simple relationship between carbide structure and the position of the metal in the periodic system, which may be represented as shown in Fig. 2.

Chromium (and to a less definite extent manganese) occupies a singular position, in that each of its three carbides has a structure of the same symmetry as, though not identical with, one of the three types:  $Cr_{23}C_6$  is cubic (complex face-centred cube with 116 atoms per unit cell),  $Cr_7C_3$  hexagonal, and  $Cr_3C_2$  orthorhombic; *i.e.*, the metal-richest carbide of chromium simulates class 1, the intermediate one class 2, and the carbon-richest one class 3. This transitional position of chromium is reflected in the part it plays as an alloying element in steels, where the metal is liable to be partitioned between a ferrite (or austenite) solid solution, cementite,  $Cr_{23}C_6$ , or  $Cr_7C_3$ , in a manner dependent on heat-treatment, and composition to a more sensitive degree than the other metals, *i.e.*, it is controllable more readily than is the case with either the stronger carbide-formers (*e.g.*, titanium, vanadium, niobium, molybdenum, tungsten), which always tend towards a definite binary or ternary carbide, or with the weaker ones (manganese, iron, cobalt), tending towards matrix solid solutions or cementite formation. This comparative lability of chromium will form an important part in considering the iron-chromium-tungsten (molybdenum)-carbon system below.

The transitional character of chromium already reveals itself to some extent in its two adjacent elements, vanadium and manganese, both of which show ambiguity in their carbide-forming tendencies. As mentioned before, the vanadium carbide has been variously reported as VC,  $V_4C_3$ , or  $V_2C$ , and the NaCl type of structure holds true for either VC or  $V_4C_3$  as the actual composition. Assuming, with Desch,  $V_4C_3$  to be correct, this means the progressive fall in carbon/metal in the following order:

Titanium: TiC, 1 carbon to 1 metal atom in NaCl type of carbide.

Vanadium:  $V_4C_3$ , 1 carbon to  $1\frac{1}{3}$  metal atoms in NaCl type of carbide, with vacant lattice sites.

Chromium:  $Cr_{23}C_6$ , 1 carbon to approximately 4 metal atoms in complex face-centred cube.

Manganese has been conflictingly reported to form either  $Mn_3C$  of cementite structure or  $Mn_{23}C_6$  and  $Mn_7C_3$  of the same structure as their chromium analogues. In fact, both views might be correct, dependent on whether impurities or heat-treatment in the observers' experiments caused a predisposition towards an iron carbide or a chromium carbide formation.

The reason for the above relation of carbide structure with the periodic system must be sought in Hägg's laws connecting the interstitial structures of hydrides, borides, carbides, and nitrides,<sup>61</sup> with

the radius ratio of the non-metal/metal atom. If this ratio does not exceed a certain value, approximately 0.59, the lattices of metal atoms are simple, *i.e.*, cubic or hexagonal close-packed, both with co-ordination number 12; if it exceeds this value, complex structures arise. In the cubic close-packed structures the carbon atoms can occupy either the tetrahedral or the octahedral positions between the metal atoms to conform with either the NaCl or the ZnS type of structure. The lattice is, however, stable even with only partial occupation, so that solid solutions are liable to occur. In both the hexagonal and the cubic close-packed (metal) structures, carbon atoms can be introduced to have the maximum co-ordination number, *viz.*, into those positions in which they occupy the largest space possible, concomitant with the condition that there must be contact between the non-metal and the surrounding metal atoms. The co-ordination number of non-metal atoms in normal interstitial structures is either six or four, depending on the type of position occupied.

The atomic radius  $r_M$  of the relevant elements and the radius ratios for the carbides are shown in Table II. The value for the carbon atom may be taken either as that in the diamond,  $r_C = 0.77$  kX, or, as in the case of the sodium chloride type of structures, the difference  $\frac{1}{2}a_0 - r_M$ , assuming that the carbon atoms truly occupy the octahedral and no other positions. The latter value would, by definition of the atomic radius, be the sounder one, but in general the location of the carbon atoms in the heavy metal lattice cannot be taken as sufficiently certain from the prevalent structure determinations, as the line intensities depend almost entirely on the metal lattice, and the carbon positions have mainly been deduced from their indirect effect on the metal configuration. For the compounds of the NaCl type of structure it was of interest to compare the observed cube-edges, using the best available data, with those calculated as the sum of Goldschmidt's atomic diameters, and  $r_C = 0.77$  kX (diamond). Table II shows that the divergence is quite appreciable, the observed value being the smaller throughout. This discrepancy may have several explanations:

(1) Some carbon positions are left vacant, the formula MC not being strictly correct.

(2) Partial ionization exists, implying that the bonding, *e.g.*, in TiC, is not simply a metallic one with interstitial metalloids, but that it tends towards an ionic compound.

(3) The carbon positions are not necessarily the octahedral ones, but are displaced, *e.g.*, in a tendency to produce the ZnS rather than the NaCl type of structure.

Explanation (1) appears to be the most probable, in view also of the observed differences in composition of the compounds (atomic metal/carbon ratio  $> 50\%$ ). The correctness of Hägg's rule is, however, clearly shown in Table II, *i.e.*, for the close-packed cubic and hexagonal carbides of titanium, zirconium, vanadium, niobium, tantalum, molybdenum, and tungsten, the radius ratios fall below 0.59, for the more complex ones of chromium, manganese, and iron, above 0.59. The relationship between structure of carbides and the periodic table is therefore linked with the variation of atomic size as a function of atomic number, though other factors enter as well.

#### Interrelation of Carbides

Referring again to Fig. 2, the carbide structures of lowest symmetry (orthorhombic) are the least stable. Iron can, however, form an integral part of ternary, more stable carbides. On reviewing the available data (given in a later section on ternary systems), the following rules apply:

(1) In conjunction with metals belonging to class 1 (*i.e.*, those which form cubic carbides), iron forms no ternary carbides nor solid solutions; the available carbon is tied up by these metals.

(2) In conjunction with metals belonging to class 2 (*i.e.*, those which form hexagonal carbides), iron does form ternary carbides which themselves are cubic, and have a limited solubility for iron (*viz.*,  $\text{Fe}_3\text{W}_3\text{C}/\text{Fe}_4\text{W}_2\text{C}$ ,  $\text{Fe}_3\text{Mo}_3\text{C}/\text{Fe}_2\text{Mo}_2\text{C}$ ).

(3) In conjunction with the metal-forming transitional carbides (chromium), no ternary carbides are formed, but the primary carbides of both iron and chromium possess considerable mutual solubility.

Table II  
ATOMIC RADIUS RATIOS IN CARBIDES

Metal	Atomic Radius $r_M$ for 12 Co-ordination*	Lattice Dimensions ( $a_0$ ) for Unit Cube			$r_C/r_M$ , Assuming $r_C$ :	
		Observed	Theoretical†	Divergence, %	= 0.77 (Diamond)	= $\frac{1}{2}a_0 - r_M$
Cubic carbide: Titanium	1.46	4.3251 <sup>43</sup>	4.46	+ 3	0.53	0.48
Zirconium	1.60	4.687 <sup>51</sup>	4.74	+ 1	0.48	0.46
Hafnium	...	...	...	...	...	...
Vanadium	1.35	4.152 <sup>35</sup>	4.24	+ 2	0.57	0.54
Niobium	1.47	4.440 <sup>†</sup>	4.48	+ 1	0.52	0.51
Tantalum	1.47	4.445 <sup>51</sup>	4.48	+ 1	0.52	0.51
Transition carbide: Chromium	1.28	...	...	...	0.60	...
Hexagonal carbide: Molybdenum	1.40	...	...	...	0.55	...
Tungsten	1.41	...	...	...	0.55	...
Orthorhombic carbide: Manganese	1.29	...	...	...	0.60	...
Iron	(in $\gamma$ -Mn) 1.26 (in $\gamma$ -Fe)	...	...	...	0.61	...

\* V. M. Goldschmidt's values † Observed by the author ‡ As  $a_0 = 2(r_M + 0.77)$

(4) In conjunction with the metals belonging to class 3 (*i.e.*, those which form the orthorhombic carbides  $Mn_3C$ ,  $Co_3C$ ,  $Ni_3C$ ), iron forms its own carbide (cementite), which is isomorphous and completely intersoluble with the latter. (Manganese is liable, however, to play a double rôle and to simulate a transitional carbide-former, in which case a ternary carbide may occur.)

These rules are of direct application to the understanding of the iron-chromium-tungsten (molybdenum)-carbon system, to be dealt with later. In a generalized form (and applied with due caution) they may help to predict compound formation in other steel systems, *e.g.*, those involving titanium and niobium. Too few experimental data are, however, available to permit such generalization at present.

Carbides within each structure class are liable to show complete or partial intersolubility, depending largely on whether the atomic size factor is favourable or not. For instance, the systems TaC-NbC and TiC-TaC show continuous solid solutions at all temperatures, while others do so only at high temperatures, segregation taking place on cooling (*e.g.*,  $W_2C$ -TaC<sup>34</sup>). The same is true for the system tungsten-carbide/titanium-carbide, recently examined by Metcalfe<sup>42</sup> as the basis of hard-metals. It has been shown by Brownlee and co-workers<sup>59</sup> that at 2000° C. TiC dissolves up to 75% of WC, at 1500° C. 45% of WC, while for lower temperatures a rapid fall of solubility occurs. On the other hand, no intersolubility occurs, *e.g.*, in the system  $W_2C$ -ZrC.<sup>62</sup> These observational facts can, in many cases, be related to the atomic sizes shown in Table II, *e.g.* :

	Difference in Size of Metal Atom, %	Solubility
TaC-NbC	0	Continuous
TiC-TaC	1	Continuous
$W_2C$ -TaC	4	Continuous at high temp., partial at low temp.
TiC-WC	3.5	Partial
$W_2C$ -ZrC	13	Nil

There are, however, certain solubility data available, *e.g.*, those of Molkov and Vicker,<sup>63</sup> which show that the atomic size factor is by no means the only governing one, and that valency and other factors enter as well. According to Agte and Altherthum<sup>50</sup> TaC-ZrC and TaC-HfC also form continuous series of solid solutions, though the zirconium atom is exceptionally large. (No information is available regarding hafnium.) The stoichiometric ratio of carbon/metal in the carbide end members naturally has a considerable influence, and the mutual replaceabilities of metal atoms in a given structure depend on whether the distribution of interstitial carbon atoms prevailing in the first compound leaves sufficient space for the foreign metal atoms to be accommodated. There are cases, of which the system  $Fe_3C$ - $Cr_{23}C_8$  is an example (*cf.* later), in which a different type of carbon bonding is favoured by the solute atom, even though substitution still takes place (*e.g.*, to favour a tetrahedral rather than an octahedral carbon configuration), so that in effect the stoichiometric ratio is bound to alter even within an apparent isomorphous series of solid solutions; the series is strictly not isomorphous as far as the carbon distribution is concerned, though it would appear so from the X-ray pattern.

Nitrides, borides, hydrides, and some oxides should also be referred to in this connection, because of their isomorphy and solubility relations with the carbides; *e.g.*, the system TaC-TaN forms a complete series of solid solutions,<sup>64</sup> and so does TiC-TiN (Hume-Rothery<sup>43</sup>). A practical example of the application of these principles may here be mentioned.

X-ray analysis of the electrolytic carbide extract from a titanium-bearing austenitic steel showed two phases, each of the NaCl type of structure. They corresponded to a nitrogen solid solution in TiC and a carbon solid solution in TiN; from the parameters the amounts of mutual replacement were estimated as follows :

Compound	Amount, %	Lattice Parameter, kX Hume-Rothery	Present Author	Solid Solution*
TiC, pure	...	4.325	...	...
Ti(C,N)	70	...	4.3245	0.65% N in TiC
Ti(N,C)	30	...	4.2419	9.6% C in TiN
TiN, pure	...	4.2330	...	...

\* Assuming the validity of Vegard's law.

Small white flakes in the extracted powder were found to contain segregates of nitride, *viz.*, 65% Ti(N,C) 35% Ti(C,N), around silica particles. Evidently melting and cooling conditions had not permitted equilibrium to be reached, otherwise a single, not two-phase, solid solution would have appeared. The compound referred to by metallurgists as "cyanonitride" is thus not a real compound, but consists of primary solid solutions. Figure 3 shows photometer records illustrating variations in amounts.

A point shown by this example well illustrates the structure rules of carbides in steels formulated above. The steel can be obtained in either an austenitic or a ferritic condition, and on X-ray analysis the carbide extracts showed the following constituents :

Ferritic	Austenitic
Ti(C,N)	Ti(C,N)
Ti(N,C)	Ti(N,C)
(Cr,Fe) <sub>23</sub> C <sub>8</sub>	No further phase

Thus the only compounds associated with the austenitic condition are the cubic close-packed ones

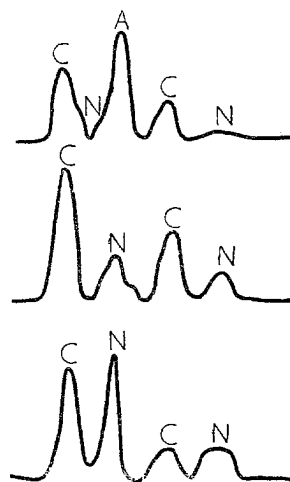


Fig. 3—Photometer records illustrating variations in amount of austenite (A), carbide TiC (C), and nitride TiN (N) in residues from titanium-bearing steel

(class 1) of titanium ; any carbon in excess of the amount which can be tied up by the available titanium appears in austenitic solution. In the ferritic condition, on the other hand, with its low matrix solubility for carbon, the extra carbon which has now been freed, and no longer finding any class 1 element available, forms the complex cubic chromium carbide as structurally the nearest approach to class 1.

**THE STRUCTURES OF  $Cr_{23}C_6$ ,  $Fe_4W_2C$ , AND  $Fe_3C$**

The structures of the three carbides  $Cr_{23}C_6$ ,  $Fe_4W_2C$ , and  $Fe_3C$ , are of special relevance in considering the iron-chromium-tungsten (molybdenum)-carbon alloys, and will here be briefly compared.

The unit cell of  $Cr_{23}C_6$  is shown in Fig. 4, of  $Fe_4W_2C$  in Fig. 5, and of cementite in Fig. 6. Table III summarizes the chief data on atomic distribution and distances ;  $Cr_7C_3$  and the two tungsten carbides are also included.

**$Cr_{23}C_6$  and  $Fe_4W_2C$**

Westgren and his collaborators have determined the structures of  $Cr_{23}C_6$  and  $Fe_4W_2C$ .<sup>31, 65</sup>

The two cubic unit cells have the cube edge 10.64 and 11.04 kX for  $Cr_{23}C_6$  and  $Fe_4W_2C$  respectively ; there are 92 and 96 atoms per unit cell. Subdividing each into eight cubes, the corners of these are alternately surrounded in  $Cr_{23}C_6$  (Fig. 4) by cubo-octahedra and cubes, and in  $Fe_4W_2C$  (Fig. 5) by octahedral units and tetrahedral ones. The octahedra are randomly occupied by tungsten and iron, the tetrahedra by iron. In  $Cr_{23}C_6$  a further metal atom is placed at the centre of each eighth cube (c positions) ; these are significant as being those occupied by any tungsten in solution. A limit to the capacity of this carbide to dissolve tungsten is thus set, because any tungsten in excess of 8 out of 92 would find no room in the structure ; the phase-change  $(Fe,W,Cr)_{23}C_6 \rightarrow Fe_4W_2C$  is then brought about, consisting of the rearrangement of the cubo-octahedral and cubic units to form the plain octahedral and tetrahedral ones of  $Fe_4W_2C$ . (N.B.—It would be mistaken to attribute to these units anything but geometrical meaning ;

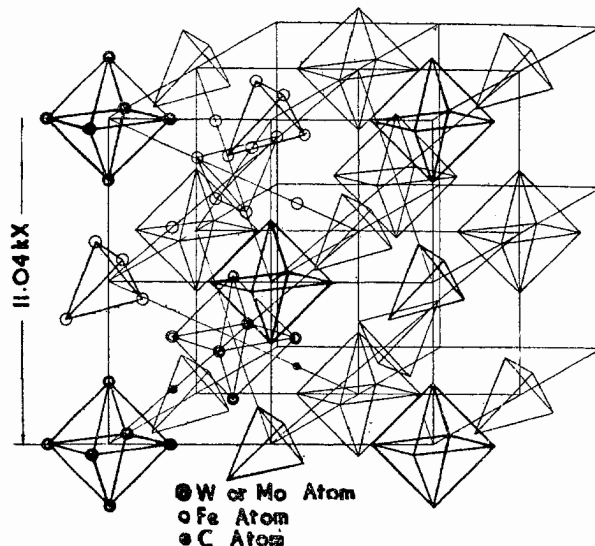


Fig. 5—Unit cell of carbide  $Fe_4(W,Mo)_2C$ ;  $Fe_3(W,Mo)_3C$

they are not molecular “clusters” in the physical sense, but are convenient to describe the structure.) In  $Cr_{23}C_6$  the chromium can be replaced by iron up to approximately 30%, whence onwards the presence of some tungsten is necessary in the lattice in order to enable it to dissolve more iron ; without this tungsten the  $(Cr,Fe)_{23}C_6$  structure becomes unstable and cementite would be formed instead. This can be explained on the grounds that the substitution of chromium by iron in  $Cr_{23}C_6$  is not entirely random, but that the cubic (f) positions are occupied preferentially by iron atoms. Since the iron atom is of smaller size than chromium (diameter 2.52 as against 2.57 kX), too much space becomes available at the (c) positions for them to continue taking either iron

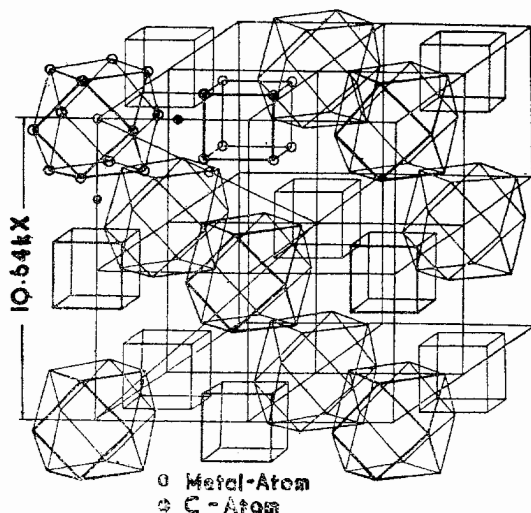


Fig. 4—Unit cell of carbide  $(Cr,Fe,W,Mo)_{23}C_6$

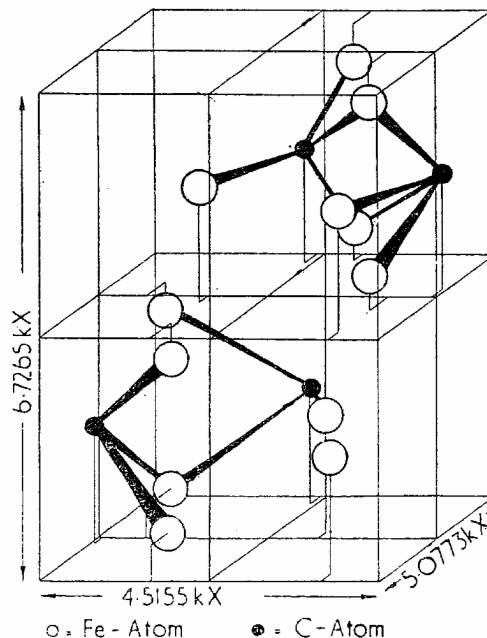


Fig. 6—Unit cell of cementite  $Fe_3C$

Table III  
COMPARISON OF STRUCTURES OF Fe<sub>3</sub>C, Cr<sub>23</sub>C<sub>6</sub>, Fe<sub>4</sub>W<sub>2</sub>C, Cr<sub>7</sub>C<sub>3</sub>, AND WC/W<sub>2</sub>C (SALIENT FEATURES)

	Cementite, Fe <sub>3</sub> C	Cr <sub>23</sub> C <sub>6</sub> -Fe <sub>11</sub> W <sub>2</sub> C	Fe <sub>4</sub> W <sub>2</sub> C	Cr <sub>7</sub> C <sub>3</sub>	WC	W <sub>2</sub> C
Symmetry	Orthorhombic	Cubic	Cubic	Hexagonal (trigonal)	Hexagonal	Hexagonal
Space Group	Fbmm	Fm 3 m	Fd 3 m	C <sub>6h</sub>		
Unit Cell Dimensions	$a = 4.5144, b = 5.0787,$ $c = 6.7297$ kX	$a_0 = 10.638 - 10.51$ kX	11.04 kX	$a = 13.98, c = 4.523$ kX	$a = 2.94,$ $c = 2.86$	$a = 2.99,$ $c = 4.72$ kX
Volume of Unit Cell	154 kX <sup>3</sup>	1204 - 1160 kX <sup>3</sup>	1340 kX <sup>3</sup>	489 kX <sup>3</sup>	approx. 64.2 kX <sup>3</sup>	105 kX <sup>3</sup>
Number of Atoms per Unit Cell	16 = 12 Fe, 4 C	116 = 92 metal, 24 C	112 = 96 metal, 16 C	80 = 56 metal, 24 C	12 = 6 W, 6 C	9 = 6 W, 3 C
Atomic Parameters	8 Fe at $x = 0.333, y = 0.183,$ $z = 0.065$ (a positions) 4 Fe at $u = 0.167, v = 0.040$ (b positions) 4 C at $u_1 = 0.47, v_1 = 0.14$ (c positions)	4 Cr at 000 (a positions) 32 Cr at $uuu, \bar{u}\bar{u}\bar{u}, u\bar{u}\bar{u}, \bar{u}u\bar{u}, u\bar{u}u, \bar{u}u\bar{u}$ (f positions) 8 Cr at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (c positions) 48 Cr at $000, 000, 000, 000, 000, 000, 000, 000$ (b positions) 24 C at $w00, w00, w00, w00, 00w, 00w, 00w, 00w$ (e positions)	16 Fe at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (d positions) 32 Fe at $uuu, \bar{u}\bar{u}\bar{u}, u\bar{u}\bar{u}, \bar{u}u\bar{u}, u\bar{u}u, \bar{u}u\bar{u}$ (f positions) 16 W at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (c positions) 16 C at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (c positions)	2 Cr at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ 54 Cr + 24 C at 13 positions: $rst; s = r, \bar{r}, t; \bar{s}, r - s, \bar{t}; s, r, \bar{t} + \bar{s}; r, s - r, \bar{t} + \bar{s}; r - s, s, \bar{t} + \bar{s}$ Parameters not finally determined	W at 000 C at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	W at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ C at 00
Environment: Number and Distances (kX) of Neighbouring Atoms	8 Fe at (a): 11 neighbours: 1 at 2.49, 2 at 2.51, 1 at 2.52, 1 at 2.54, 1 at 2.55, 2 at 2.62, 1 at 2.67, 4 at 2.68 4 Fe at (b): 12 neighbours: 2 at 2.52, 2 at 2.54, 2 at 2.65, 2 at 2.67, 4 at 2.68 4 C at (c): 6 neighbours: 1 at 1.85, 1 at 1.89, 2 at 2.06, 2 at 2.5 kX	4 Cr at (a): 12 neighbours: at 2.49, 8 Cr at (c): 4 at 2.49, 12 at 2.95 32 Cr at (f): 1 Cr at 2.49, 3 Cr at 2.45, 6 Cr at 2.74, 3 C at 2.10 48 Cr at (h): 1 Cr at 2.49, 4 Cr at 2.51, 6 Cr at 2.74, 8 Cr at 2.95, 2 C at 2.10 24 C at (e): 8 Cr at 2.10	16 Fe at (d): 6 Fe at 2.34, 6 W (Fe) at 2.79, 32 Fe at (e): 6 Fe at 2.34, 6 W at 2.74, 3 W at 2.79 32 W and Fe at (f): 4 Fe at 2.74, 2 Fe at 2.79, 2 W at 2.92, 4 W at 3.05, 2 C at 2.10 16 C at (c): 6 W (Fe) at 2.10	Each W: 9 W at 2.78 3 C at 2.15 Each C: 6 W at 2.15 6 C at 2.99	Each W: 6 W at 2.94 6 C at 2.22 Each C: 6 W at 2.22 6 C at 2.86	Each W: 9 W at 2.78 3 C at 2.15 Each C: 6 W at 2.15 6 C at 2.99
Shortest Distances, kX	Fe-Fe = 2.49; Fe-C = 1.85	Cr-Cr = 2.49; Cr-C = 2.10	Fe-Fe = 2.34; Fe-W = 2.74; W(Fe)-C = 2.10	W-W = 2.94 W-C = 2.22 C-C = 2.86	W-W = 2.78 W-C = 2.15 C-C = 2.99	
Atomic Substitution	Fe probably randomly replaceable by Cr	In Fe <sub>2</sub> W <sub>2</sub> C, W occupies the 8 (c) positions, Fe the 84 (a, f, and h) positions	Fe-W randomly replaceable in 48 (f) positions between Fe <sub>4</sub> W <sub>2</sub> C and Fe <sub>3</sub> W <sub>3</sub> C			

or chromium, and from one critical composition onwards the larger tungsten or molybdenum atom\* is required to fill them (atomic diameter 2.82 and 2.80 kX). It is observed in practice that the "detachment" in the iron-chromium-tungsten-carbon system of the  $\text{Cr}_{23}\text{C}_6$  single-phase field from the ternary side iron-chromium-carbon occurs at approximately 30 at.-% of iron, which is the same proportion as available (f) sites, viz., 32 out of 92 = 35% of iron. The agreement is within the error of known data, but is not bound to be exact, since some replacement by tungsten might be expected to begin already before all cubic positions are filled by iron. Similarly, as Westgren has pointed out, with adequate tungsten supply, chromium can be entirely replaced by iron in  $\text{Cr}_{23}\text{C}_6$ , and the proportion of tungsten to achieve this is defined by the proportion of available (c) positions, i.e., 8 out of 92, which gives rise to the formula  $\text{Fe}_{21}\text{W}_2\text{C}_6$ .

### Carbon Environment

In  $(\text{Cr,Fe,W})_{23}\text{C}_6$  the carbon atoms occupy positions on the cube edges between the cubo-octahedra and cubes, each carbon having eight metal neighbours. In  $\text{Fe}_4\text{W}_2\text{C}$ , on the other hand, they lie between the two tungsten octahedra, on the cube diagonal, each carbon atom being itself surrounded by the slightly distorted octahedron bounded by two faces of the regular tungsten octahedra (cf. Fig. 5). There are thus six neighbours to each carbon. It is interesting to note that this carbon environment in  $\text{Fe}_4\text{W}_2\text{C}$  is already identical with that in tungsten carbide  $\text{W}_2\text{C}$ ; in both cases the surrounding tungsten configuration is that of two isosceles triangles inverted. The fact that in the  $\text{Fe}_4\text{W}_2\text{C}$  structure the carbon atoms should choose to surround themselves entirely with tungsten, not iron, atoms is noteworthy as indicating a stage preliminary to the formation of tungsten carbide. In cementite the metal environment of carbon is also six-fold, but it consists of two congruent, not inverted, triangles (prism, as shown in Fig. 7 (a)) (Lipson<sup>21</sup>). These two types of six-fold co-ordination (viz., A that of congruent, and B that of inverted triangles) are of considerable interest because this difference recurs in the plain tungsten carbides. The two carbides  $\text{W}_2\text{C}$  and WC, which are both of hexagonal structure, differ in so far as in WC the tungsten and the carbon atoms each form a set of interpenetrating

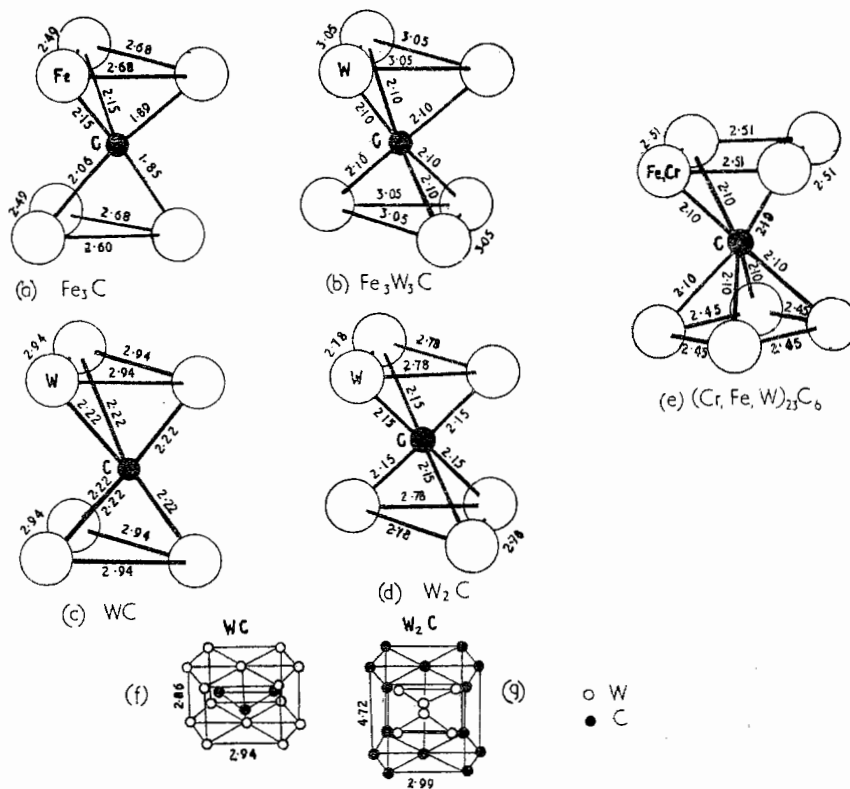


Fig. 7—(a)–(e) Carbon environment in carbides of iron, chromium, and tungsten; (f) and (g) unit cells of WC and  $\text{W}_2\text{C}$

simple hexagonal lattices, whereas in  $\text{W}_2\text{C}$  the tungsten atoms form an almost *close-packed* lattice, the carbon atoms a *simple* hexagonal lattice (see Figs. 7 (f) and 7 (g)). Thus the repeat of close-packed atomic sheets in the *c* direction is :

In WC : W — C — W — C — W, etc.

In  $\text{W}_2\text{C}$  : W — W' — C — W — W' — C, etc.

(where W and W' signify layers of tungsten atoms rotated through 30° to arrive at close-packing†).

The carbon environment of the two tungsten carbides is thus also that of a 6-co-ordination, the metal neighbours being related to the carbon atom in the two distinct manners (types A and B above) found in cementite and  $\text{Fe}_4\text{W}_2\text{C}$  respectively. The following is a summary of the environments :

Carbide	Co-ordination	Environment of C-atom Configuration
Cementite $\text{Fe}_3\text{C}$	6	Type A (congruent triangles)
$(\text{Cr,Fe,W})_{23}\text{C}_6$	8	Transition type (squares on either side of carbon)
$\text{Fe}_4\text{W}_2\text{C}$	6	Type B (inverted triangles)
WC	6	Type A
$\text{W}_2\text{C}$	6	Type B

Thus in the iron-chromium-tungsten-carbon system (and this principle may extend to others) the metal environment to the carbon atom in the carbides occurring is repeated for entirely different carbide compositions, but changes from the congruent type A to the inverted type B with increasing metal/carbon ratio. The carbide  $(\text{Cr,Fe,W})_{23}\text{C}_6$  is abnormal in

\* Molybdenum throughout the present argument may replace tungsten.

† For further comment, see later section (p. 357).



showing 8- instead of a 6-co-ordination and, being intermediate in composition to  $\text{Fe}_3\text{C}$  and  $\text{Fe}_4\text{W}_2\text{C}$ , appears to have adopted this 8-fold environment as a compromise between the two 6-fold types, but it is queried whether in Westgren's structure (Fig. 5) the carbon positions shown should be finally accepted. Their re-examination by accurate photometry is suggested.

The reason why the carbon content decreases in the carbides  $\text{Fe}_3\text{C}-(\text{Cr,Fe,W})_{23}\text{C}_6-\text{Fe}_4\text{W}_2\text{C}$  (in this order), also follows from an examination of the structures (Figs. 4-6), since the number of equivalent lattice points available for carbon becomes progressively less.

#### Cementite and $(\text{Cr,Fe,W})_{23}\text{C}_6$

The structure of cementite, shown in Fig. 6 (*cf.* also Table III), consists of a complex network of slightly distorted triangular prisms of iron atoms, with the carbon atoms placed approximately centrally so as to possess six iron neighbours. It has been discussed by Lipson and Petch<sup>21</sup> (who re-determined it), Hume-Rothery,<sup>22</sup> and Petch,<sup>23</sup> *e.g.*, to discover its relation to austenite and ferrite. These papers may be referred to for details. In practice it is found that with only slight differences in heat-treatment and composition of low chromium, tungsten, and molybdenum steels, it is possible to produce  $(\text{Cr,Fe,W,Mo})_{23}\text{C}_6$  instead of cementite.

Experiments show that for a given steel (6% of chromium and 1.1% of carbon) cementite can be produced by quenching from the austenitic region, while  $(\text{Cr,Fe})_{23}\text{C}_6$ , cementite, or  $(\text{Cr,Fe})_7\text{C}_3$  can be precipitated on annealing at a subcritical temperature, depending on the high-temperature history previous to the anneal; it is therefore considered worth while to search for any structure relationship. Hume-Rothery has shown that by a comparatively simple shear mechanism it is possible to obtain the cementite lattice from that of martensite, and thus claims a closer relationship of cementite to the body-centred than to the face-centred cubic lattice. (Actually the argument has become affected by Lipson and Parker's subsequent structure determination of martensite, showing the carbon positions to lie on the tetragonal *c* edges, and on two basal planes of the tetragonal unit cell, not at the face-centres as assumed by Hume-Rothery; but, being based on displacements of the metal, not the carbon atoms, it still remains essentially valid.) On the other hand, as the co-ordination of each iron atom in cementite is approximately 12, with the structure is nearly close-packed in common with austenite.

The carbide  $(\text{Cr,Fe})_{23}\text{C}_6$  is related to austenite and martensite in a remarkable manner. The cubo-octahedra (Fig. 4) (Westgren's *h* positions) which form an integral unit of repeat in this carbide, are, in fact, the simplest possible compromise between a face-centred and a body-centred cube. They may be considered as a face-centred cube in which the atoms *F* at the face-centre have been "forced outward" by the insertion of an atom *B* at the body-centre, so as to render all atoms equidistant from the latter. The body-centred cube is already present as part of the cubo-octahedron, as is apparent from Fig. 4. By the

insertion or removal of one atom *B*, a ferrite-like or austenite-like unit can thus be arbitrarily produced, which is the one occurring in this carbide. It involves the majority (52 out of 92) of its metal atoms, the simple cubic units (*f* positions) alternating with the cubo-octahedra and the 8 (*c*) atoms; it may be noted that by the simple device of placing the (*c*) atoms inside the *f* cubes, instead of outside, a body-centred cube is obviously produced, similar to that already existing in the cubo-octahedra. The total number of available *f* and *c* atoms (32 and 8) is just the correct one for this operation and accounts for all remaining metal atoms.

Expressed briefly, the carbide structure (metal atoms) is composed as follows:

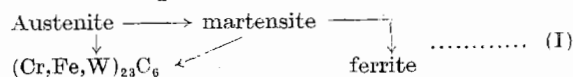
Unit	Atoms Involved (number and position)	Operation Producing this Unit
Cubo-octahedra ("Hybrid" between body-centred and face-centred cube)	48 ( <i>h</i> ) and 4 ( <i>a</i> )	Insert one atom into face-centred cube
Simple cube	32 ( <i>f</i> )	Remove one atom from body-centred cube
Single atom ( <i>c</i> )	8 ( <i>c</i> )	
	(Total 92)	

(These "operations" are not, of course, real ones occurring during the formation of the carbides, but are hypothetical and are intended to bring out the relationship with austenite and ferrite.)

It is significant that the 8 (*c*) positions are those filled by the larger tungsten or molybdenum atoms, when present, which would find no room inside the cube, but do so outside.

The carbon atoms in  $(\text{Cr,Fe,W})_{23}\text{C}_6$  are placed interstitially between the cubo-octahedra and the simple cubes, as against their known positions in austenite at the centre of the face-centred cube. The insertion of the extra metal atom (*a*) into the face-centred cube (to form the cubo-octahedra) has clearly made it impossible for it to retain a position corresponding to austenite, so that it has become "displaced" outside this unit, giving the carbide its characteristic structure.

It is considered on the above grounds that the structure relation between this carbide and both austenite and ferrite is sufficiently close for visualizing that the carbide lattice is formed as a stable alternative to martensite during the decomposition of austenite. It is characteristic that, *e.g.*, in certain austenitic and semi-austenitic heat-resisting steels, the carbide  $(\text{Cr,Fe,W})_{23}\text{C}_6$  is the one coexisting with and precipitating from austenite at high temperatures, while at lower temperatures the following transformation takes place:

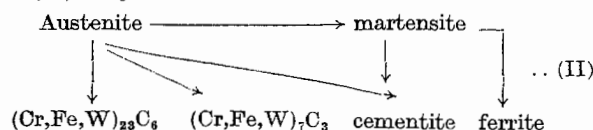


Both martensite and  $(\text{Cr,Fe,W})_{23}\text{C}_6$  are able to form from austenite by a spontaneous transformation of the lattice, not involving atomic diffusion and therefore proceeding instantaneously. The partition of atoms between the metastable martensite and the stable carbide at any one stage of heat-treatment must be decided by free-energy considerations; it seems probable that a saturation solid solution of carbon in parent austenite will favour a collapse into

the carbide, a lower carbon content one into martensite.

Considering the formation of cementite in ferritic low-chromium steels as an observed alternative to  $(\text{Cr,Fe,W})_{23}\text{C}_6$ , it follows that the atomic rearrangement in the form of the cementite tetrahedral units offers itself as a third possibility. Since cementite occurs in the quenched state together with martensite,  $(\text{Cr,Fe,W})_{23}\text{C}_6$  in the annealed state together with ferrite, it appears that the latter carbide is the truly stable one (for the given composition), but that it is easier spontaneously to produce the cementite and martensite lattices as metastable intermediate stages.  $(\text{Cr,Fe,W})_7\text{C}_3$  is found, for the same composition, to be a fourth possible structure formed by low-temperature heat-treatment, probably as a metastable product.

The previous set of reactions (I) or the following set (II) may therefore occur :



The existence in the quaternary phase diagram of the tongue-shaped  $(\text{Cr,Fe,W})_{23}\text{C}_6$  field detaching itself from the ternary iron-chromium-carbon side at approximately 30% of iron and joining to  $\text{Fe}_{21}\text{W}_2\text{C}_6$ , shows that set (I) is favoured for high-chromium contents, but also for lower ones, provided that sufficient tungsten is present, while set (II) is favoured by low-alloy steels, though, to form  $(\text{Cr,Fe,W})_7\text{C}_3$ , sufficient chromium will have to be present.

An examination of the structures of cementite and  $(\text{Cr,Fe,W})_{23}\text{C}_6$  does not reveal any simple relationship, and it is probably not advisable to attempt deriving one directly from the other, but to relate each to either austenite or martensite, or both, and to consider them as independent and alternative arrangements. The same applies to  $(\text{Cr,Fe,W})_7\text{C}_3$ .

#### Equivalent Unit Cells

It may, however, be of interest to point out one relation between the carbide structures based on volume considerations.

If 8 orthorhombic unit cells of cementite, each containing 16 atoms, are stacked together, this enlarged volume of  $(2 \times 4.51) \times (2 \times 5.08) \times (2 \times 6.73) = 1234 \text{ kX}^3$  forms an aggregate directly comparable with and equivalent to one unit cell of  $(\text{Cr,Fe,W})_{23}\text{C}_6$  and of  $\text{Fe}_4\text{W}_2\text{C}$ . The formulæ of the three carbides thus are :

	Equivalent Volume, $\text{kX}^3$
$\text{M}_{96}\text{C}_{22}$ (= cementite)	1234
$\text{M}_{22}\text{C}_{21}$ (= $(\text{Cr,Fe,W})_{23}\text{C}_6$ )	1204 to 1160 (for $\text{Cr}_{23}\text{C}_6$ and $\text{Fe}_{21}\text{W}_2\text{C}_6$ )
$\text{M}_{96}\text{C}_{16}$ (= $\text{Fe}_4\text{W}_2\text{C}$ )	1346

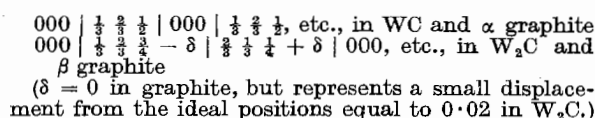
In each carbide 96 metal atoms (except for four missing in one) fill, with their carbons, an integral number of cells with a volume of the same order of magnitude; these form "elementary bricks" on which a study of carbide relations in steels may usefully be based. The fact that the number of carbon atoms associated with these 96 (92) metal atoms decreases as 32/24/16 with increasing  $W : (\text{Fe} + \text{Cr})$

ratio follows naturally from the places they occupy and space considerations in each lattice (*cf.* above) and strongly suggests that the series of compounds

$\text{Fe}_{96}\text{C}_{32} - (\text{Fe,W})_{92}\text{C}_{24} - \text{Fe}_{48}\text{W}_{48}\text{C}_{16} - \text{tungsten metal}$  (with some latitude for solid solutions) forms a pseudo-binary system, in which the formation of further stable structures with intermediate carbon contents is quite possible (*e.g.*, a hypothetical tungsten-rich carbide  $(\text{Fe,W})_{96}\text{C}_8$ ). This pseudo-binary character of the series falls into line with experimental results given later.

#### Possibility of Lattice-Fault Formation in Tungsten Carbides

A point arose out of the above discussion on tungsten carbide structures which requires some expansion. There is an analogy between  $\text{W}_2\text{C}$  and WC on the one hand, and the two crystalline forms of graphite, reported by Lipson and Stokes,<sup>66</sup> on the other. In ordinary graphite ( $\alpha$ ) the hexagonal close-packed sheets of carbon atoms repeat every alternate layer, and in the second type ( $\beta$ ), every third layer. In WC and  $\text{W}_2\text{C}$  the same difference applies, the repeat of close-packed tungsten and carbon layers being as follows :



In hexagonal cobalt Edwards and Lipson<sup>67</sup> have found the phenomenon of "fault formation," *i.e.*, the existence of imperfections in the stacking of lattice planes. This consists of irregularities in the period of repeat of the close-packed cobalt layers in which the sequence of packing is liable to change from the type  $ABABAB$ , etc., to  $BCBCBC$ , etc. (in the direction of the hexagonal axis). In the tungsten carbide structure conditions are favourable for similar "faults" to occur, and if it is true that WC and  $\text{W}_2\text{C}$  are partly intersoluble, such faults must necessarily occur during the transition  $\text{WC} \leftrightarrow \text{W}_2\text{C}$ . It appears probable that hardness and other properties of the tungsten carbides will be considerably affected by fault formation. If pure WC and pure  $\text{W}_2\text{C}$  have the ideal layer lattices, as in graphite, easy slip and therefore reduced hardness might be expected in the direction parallel to the hexagonal basal planes, but it would require only a small amount of excess tungsten in WC or of excess carbon in  $\text{W}_2\text{C}$  in order to destroy this anisotropy, by introducing sufficient imperfections in the manner of stacking.

This would have a considerable bearing on the properties of hard-metal tool materials, since cracking and weakness may well be caused by external contacts (*e.g.*, during pressing or under the influence of the material worked by the tool in operational practice). Remembering that cobalt metal is commonly used as the binder to tungsten carbide in tool tips, it may be relevant to note that both share the close-packed structure and the inherent liability to form Lipson-type faults, which, during the mixing and sintering process, may produce special conditions of diffusion and adhesion at the cobalt-carbide interface.

for alloys with more than 50% (approximately) of manganese (Öhman<sup>81</sup>). Schenck, Meyer, and Mayer<sup>82</sup> carburized iron-manganese alloys and suggested five undefined carbides ( $\mu$ ,  $\mu_a$ ,  $\mu'_a$ ,  $\mu'_b$ ,  $\mu'$ ) besides  $(Fe, Mn)_3C$ ; phase-fields described by these authors do not correlate with those given previously.

Öhman<sup>81</sup> reported a high-manganese double carbide, hitherto unconfirmed, occurring in an alloy with 68% of manganese, 25% of iron, 7% of carbon. (The approximate atomic formula works out as  $Fe_{19}Mn_{56}C_{25}$ , or  $(Fe, Mn)_3C$  with  $Mn : Fe = 3 : 1$ , but this is probably not the actual carbide composition.) The symmetry is monoclinic, with  $a = 5.05$ ,  $b = 4.56$ ,  $c = 11.61$  kX,  $\beta = 97.63^\circ$ , space group  $C_{2h}^6$ . Further details are unknown, and it is premature to speculate on its nature, considering the multiplicity of phases in the manganese corner, namely (a) metallic manganese with its three allotropic forms of anomalous structures, each possessing a different carbon solubility, (b) the  $\beta$  form of  $Mn_3C$  reported by Vogel and Döring (cf. Fig. 1 (e)), which, unlike  $\alpha$ - $Mn_3C$ , possesses a high solubility for manganese, and (c) the existence of  $Mn_7C_3$  and  $Mn_{23}C_8$  as alternatives to  $Mn_3C$ . Öhman's monoclinic carbide quite possibly corresponds to an intermediate form during transformations between iron solid solutions in any of these phases, and during the transition  $(Fe, Mn)_3C \leftrightarrow (Mn, Fe)_7C_3 + (Mn, Fe)_{23}C_8$  it may well mark the junction in the ternary diagram between carbide class 3 (orthorhombic) and classes 1 and 2 (cubic and hexagonal). The possibility of an analogue of it existing in the iron-chromium-carbon system cannot be ignored.

#### Iron-Vanadium-Carbon

*Phase-Fields:*  $\alpha$ ,  $\alpha + V_4C_3$ ,  $\alpha + V_4C_3 + Fe_3C$ ,  $\alpha + Fe_3C$ .

A diagram has been derived by Vogel and Martin<sup>83</sup> and by Wever, Rose, and Eggerts,<sup>88</sup> who give a space model. It has been reviewed by Desch.<sup>37</sup> A 4-phase reaction  $\gamma \rightarrow \alpha + V_4C_3 + Fe_3C$  takes place at  $690^\circ C$ . The two carbides do not form solutions. The compound  $FeV$  probably coexists with  $\alpha + V_4C_3$ , but this was not determined. Maurer, Döring, and Pulewka<sup>35</sup> discuss whether  $V_4C_3$  and  $VC$  exist in steel. No attempt has been made to incorporate  $VC$  (or a possible  $V_2C$ ) into the diagram.

#### Iron-Titanium-Carbon

*Phase-Fields:*  $\alpha$ ,  $\alpha + Fe_3Ti$ ,  $\alpha + Fe_3Ti + TiC$ ,  $\alpha + TiC$ ,  $\alpha + TiC + Fe_3C$ ,  $\alpha + Fe_3C$ .

A diagram has been derived by Tofaute and Büttinghaus.<sup>84</sup> A critical review of published systems has been given by Northcott.<sup>55</sup> The section  $\alpha$ - $Fe \rightarrow TiC$  is a pseudo-binary system, not  $Fe_3Ti \rightarrow Fe_3C$  as suggested by Vogel<sup>86</sup>; Fishel and Robertson<sup>87</sup> studied the distribution of carbon between iron and titanium carbides. (Cf. also earlier remarks on  $TiC$ .)

#### Iron-Niobium-Carbon

*Phase-Fields:*  $\alpha$ ,  $\alpha + Fe_3Nb_2$ ,  $\alpha + Nb_4C_3 + Fe_3Nb_2$ ,  $\alpha + Nb_4C_3$ ,  $\alpha + Fe_3C + Nb_4C_3$ ,  $\alpha + Fe_3C$ ,  $Fe_3C + Nb_4C_3$ ,  $Fe_3Nb_2 + Nb_4C_3$ .

A diagram has been derived by Eggers and Peter,<sup>49</sup> who also determined the binary system iron-niobium. A space model of the system is given. Decomposition  $\gamma \rightarrow \alpha + Nb_4C_3 + Fe_3C$  takes place at  $705^\circ C$ . In

their view, carbide  $NbC$  is superseded by  $Nb_4C_3$ .

#### Iron-Zirconium-Carbon

*Phase-Fields:*  $\alpha$ ,  $\alpha + Fe_3Zr_2$ ,  $\alpha + ZrC + Fe_3Zr_2$ ,  $\alpha + ZrC$ ,  $\alpha + ZrC + Fe_3C$ ,  $\alpha + Fe_3C$ ,  $Fe_3C + ZrC$ ,  $Fe_3Zr_2 + ZrC$ .

A diagram has been derived by Vogel and Löhberg.<sup>88</sup> The section  $\alpha$ - $Fe \rightarrow ZrC$  is a pseudo-binary system, which divides the system into two distinct regions. Decomposition  $\gamma \rightarrow \alpha + ZrC + Fe_3C$  takes place at  $780^\circ C$ .

#### Iron-Tantalum-Carbon

No information seems to have been published, but it is probable that the system will differ in important respects from the iron-niobium-carbon system, since two carbides,  $TaC$  and  $Ta_2C$ , exist. The existence of a ternary iron-tantalum-carbide (by analogy to the iron-tungsten-carbon) system is distinctly possible, though not reported.

The iron-chromium-carbon, iron-molybdenum-carbon, and iron-tungsten-carbon systems, omitted above, will be discussed in a later part.

#### Survey

One outstanding fact in surveying the systems (cf. Table IV) is the small number of genuine double carbides occurring. In most ternary systems the only carbides formed are solid solutions derived from the surrounding binary carbides; the chief ternary carbide established with an independent structure is Westgren's high-speed steel carbide  $Fe_4W_2C$ , with its isomorph  $Fe_4Mo_2C$ ; here iron can be substituted up to the compositions  $Fe_3W_3C$  and  $Fe_3Mo_3C$ . The compounds  $(Fe, W)_{23}C_8$  and  $(Fe, Mo)_{23}C_8$  listed in Table IV are also true ternary carbides as far as the system iron-tungsten (molybdenum)-carbon is concerned, but are isomorphous with the binary  $Cr_{23}C_8$ . The approximate compositions of these compounds are  $Fe_{21}W(Mo)_2C_6$ . This is of obvious importance in discussing the quaternary system iron-tungsten-chromium-carbon.

Although it is possible that the existence of some ternary carbides in any of the systems has not yet been discovered, it appears that the consistent failure of previous investigators to detect any but the binary carbides in ternary alloys is not accidental; many of the equilibrium diagrams derived are sufficiently well founded to leave no room for the insertion of a ternary compound (e.g., iron-nickel-carbon, iron-vanadium-carbon).

Among non-ferrous ternary carbide systems involving the present steel-alloying elements, Westgren and co-workers<sup>54</sup> have explored whether in the carbides  $Fe_3W_3C$  and  $Fe_3Mo_3C$ , iron is replaceable by chromium, manganese, cobalt, and nickel, with the result that the isomorphous carbides  $Co_3W_3C^*$  and  $Ni_3W_3C$  exist; but these two can be decomposed by heat-treatment, the stability decreasing in the order  $Fe_3W_3C \rightarrow Co_3W_3C \rightarrow Ni_3W_3C$ . Molybdenum analogues of the same structure, such as " $Co_3Mo_3C$ ," have not been found, but Westgren observes "a pattern not agreeing with that of any known phase" in a 0.43% molybdenum, 0.87% carbon, cobalt-

\* Westgren suggests the formula  $Co_4W_3C$  as more probably correct than  $Co_3W_3C$ .

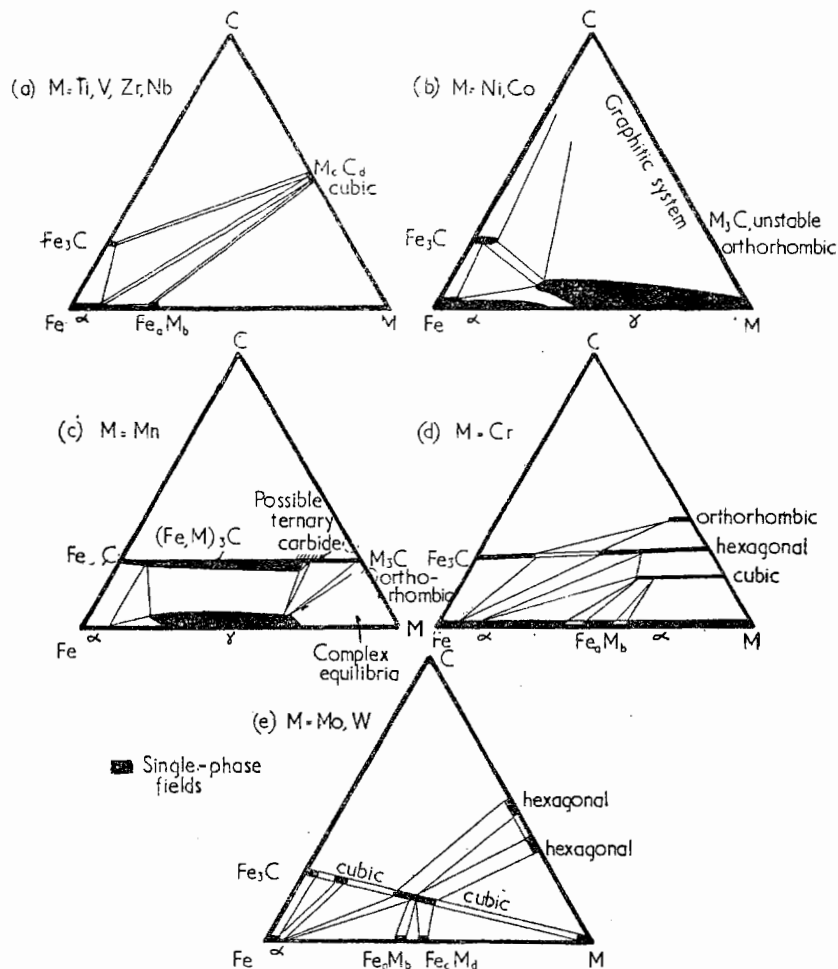
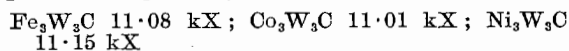


Fig. 8—Principal types of ternary carbide systems

molybdenum-carbon alloy. He also finds a "phase of unknown pattern" in the chromium-tungsten-carbon and in the manganese-tungsten-carbon systems, which may correspond to a double carbide of chromium-(manganese)-tungsten or a binary chromium-(manganese)-tungsten intermetallic compound. The lattice dimensions for the above three cubic compounds are given by Westgren as:



Among the present ternary systems five different types may be distinguished, represented diagrammatically in Fig. 8 (cf. also classes, p. 350). The types are directly related to the structure of the carbides and of the constituent metals:

*Type (1)—C.p. cubic carbide former (titanium, vanadium, zirconium, niobium, and possibly tantalum)*—Ferrite and the non-ferrous carbide form a pseudo-binary system. This divides the diagram into two fields, so that cementite cannot coexist with an intermetallic compound.

*Type (2)—Non-carbide former (nickel and cobalt)*—Ferrite, austenite, and cementite are the only stable phases (apart from graphite) and form a pseudo-ternary system.

*Type (3)—Orthorhombic (cementite-type) carbide former (manganese)*—A continuous series of solid solutions is formed between cementite and the non-ferrous carbide. In principle this is the same as type (2), since the  $\alpha$ - $\gamma$ -cementite pseudo-ternary system persists in the iron corner, modified only by the extension of the  $\text{Fe}_3\text{C}$  region. (This is consistent with the fact that if nickel and cobalt form their unstable carbides, these are also of  $\text{Fe}_3\text{C}$  structure.) A ternary carbide may occur under certain conditions, dependent on whether the solute remains a cementite-type of carbide former or simulates the transition type.

*Type (4)—Transition-type carbide former (chromium)*—Several non-ferrous carbides exist with a considerable solid solubility for iron. Equilibria occur as indicated in Fig. 8.

*Type (5)—Hexagonal carbide former (molybdenum and tungsten)*—Ternary carbides of cubic structure are formed in this type of diagram. Ferrite, cementite, and the non-ferrous metal itself form a pseudo-ternary system.

A detailed discussion of the connection between phase distribution and crystal structure

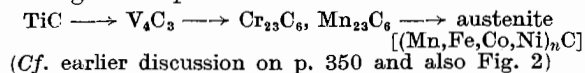
must be left over to a separate account,\* but one aspect is of special interest. Although types (1) and (2) represent opposite extremes in as far as in (1) the added metals are the strongest carbide formers (titanium, vanadium, zirconium, and niobium) and in (2) the weakest (nickel and cobalt), they nevertheless show an essential similarity if crystal structures are considered, as may be briefly shown in the following section.

#### Austenite and Carbide Structures

Petch<sup>91</sup> has shown that in austenite the carbon atoms occupy the octahedral positions of the face-centred cubic lattice, though, even for maximum saturation, only one among twelve of these sites is filled. Austenite may thus be regarded as isomorphous with the carbides of the NaCl type of structures, and structurally as a member of this group, but with most of the interstitial carbon positions vacated. The tendency for this defect lattice formation has already

\* Reference should be made to a paper by Shapiro and Strauss,<sup>89</sup> which deals with the position of the eutectoid in the iron-carbon system, as influenced by various elements, surveys the literature, and classifies the data. A valuable review on carbides has recently been carried out by Banyard.<sup>90</sup>

begun amongst the cubic carbides, when arranged according to the periodic table :



The character of austenite as "a carbide" of the cubic (class 1) type, in which no more than 12 carbon positions are occupied, is reflected in the ternary diagrams of types (1) and (2) above. They do not differ in principle, but only in so far as the  $\text{Fe}_3\text{C} +$  (e.g.)  $\text{TiC}$  duplex region in (1) is replaced by the  $\text{Fe}_3\text{C} +$  austenite region in (2), with a consequent shift of phase-fields into the iron corner.

In practice, the implication is that austenite and the cubic carbides should show a tendency to form,

at high temperatures, continuous or large series of solid solutions, provided that atomic sizes permit. This agrees with actual observation, e.g., in heat-resisting steels at high temperatures; the example of the titanium-bearing steel mentioned earlier (p. 352) is also a case in point. The mechanism of precipitation of the cubic carbide from austenite is then essentially one of carbon atoms segregating in certain lattice regions of the parent crystal, causing an expansion and eventual division into two related phases.

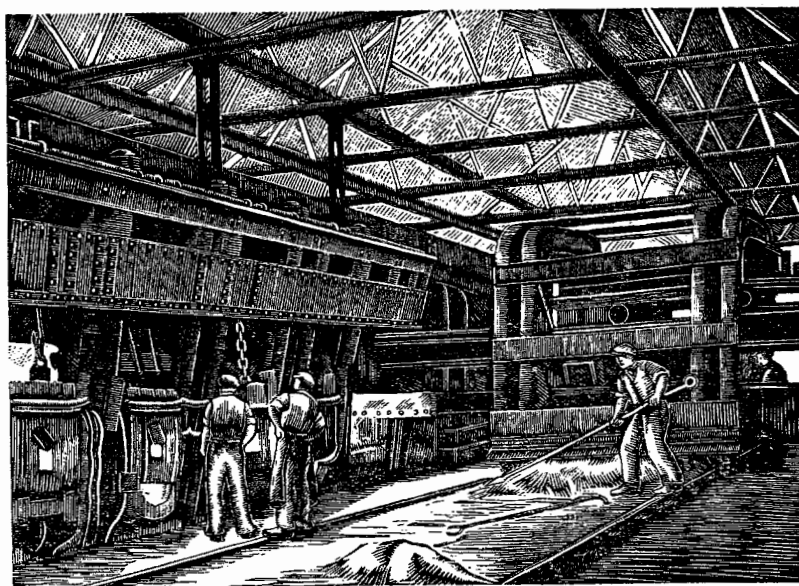
#### Acknowledgment

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Charging Steel Scrap into a Steel Furnace,  
from an original woodcut by Viva Talbot