METAL CARBIDES

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I. Introduction

Over eighty of the elements in the Periodic Table are metals, most of these chemically combining with carbon to form carbides. Elements definitely not metals, and therefore excluded from this article, are the six noble gases: helium, neon, argon, krypton, xenon, and radon, and the halogens: fluorine, chlorine, bromine, iodine, and astatine. The elements oxygen, nitrogen, and hydrogen form important compounds with carbon, but these elements are not metals and the compounds they form are not carbides. Phosphorus and sulfur are excluded for the same reasons. On the other hand, the metalloid silicon forms silicon carbide, SiC, a carbide with important industrial and practical uses, both as an abrasive and as a refractory.

The major applications of metallic carbides are as cutting materials (abrasives) or for resistance to high temperatures (refractories); however, a number of metals form compounds with carbon having simple formulas such as CaC_2 and are metallic carbides. Becuase they yield acetylene, C_2H_2, on contact with water, such substances are usually termed acetylides. The acetylides are included in this review. Although ternary and more complex carbides are known, most of the available and reliable information is on binary carbides, chemical combinations between one metal and carbon. Many of the carbides in steels and ferrous alloys contain three or more elements, and these carbides have been extracted and studied in detail.

HISTORY

1. Prior to Moissan

The existence of metal carbides was mentioned by Berthollet and others as early as 1786, in connection with the changes produced in iron by small amounts of carbon (*34*). Ten years later A. F. de Fourcroy, one of the authors in de Morveau's Encyclopedia (*233*), proposed the term "carbide" in analogy to the similar terms sulfide and phosphide. In 1820 Berzelius (*35*) thought he had produced a definite series of carbides by heating the cyanides of some of the metals with ferrocyanides. Later work showed that what was actually obtained was a mixture of carbides of iron and the other metal. Berthelot (*33*) in 1866 described sodium and potassium carbides and showed how these two substances were related to acetylene, which is produced by these two carbides on treatment with water. The explosive carbides of copper, silver, and gold were also prepared, and descriptions of some of their properties appeared in the literature soon afterward. Other isolated investigations of carbides were published between 1820 and 1890, but systematic investigation of metallic carbides was due mainly to the work of H. Moissan, beginning about 1890 and covering a period of some 15 years after this date.

2. *Work of Moissan*

a. Preparation Methods. Moissan used most of the methods of carbide preparation known at the present time. He made extensive use of arc and tube electric furnaces, publishing one of the first books about them in 1897 (*209*). Three common methods for producing carbides are electric arc fusion of the metal or its oxide, passing carbonaceous gases over the heated metallic or oxide powder, and vapor phase deposition upon a hot filament. These will be discussed in more detail later.

Moissan was a pioneer in the use of all types of electric furnace then known for chemical applications, particularly in the preparation of carbides. Apparently he did not use the induction furnace, which was a somewhat later development. For example, in 1892, prior to the granting of a United States patent on a similar process the next year, he published a comprehensive account of the production of calcium carbide, CaC_2 (*214*). This was accomplished by using the electric arc to fuse calcium oxide with carbon. In his account, Moissan observed that, if the lime was impure and contained magnesia, fusion of the charge was delayed due to the higher melting point of MgO. Working with A. Etard (*226*), Moissan produced one of the rare earth carbides, yttrium carbide, YC_2, by heating the proper proportions of the metallic oxide and sugar charcoal in a carbon tube electric furnace. Reaction occurred upon fusion of the oxide. In his book on the electrical furnace, Moissan described the production of one of the two beryllium carbides by heating, in an ordinary electrically heated tube furnace, beryllium oxide and carbon mixed with a small quantity of oil. Reaction took place after 10–15 minutes at a high temperature.

As an example of the carburization method, Moissan (*215*) produced an impure magnesium carbide by passing acetylene over heated magnesium powder. The product so obtained had considerable quantities of free carbon as a contaminant. The vapor phase method, now widely used, involves deposition of the carbide or other product on a hot filament, the metallic portion of the compound formed being obtained by the decomposition of the metallic halide vapor. This process was developed by Van Arkel and others some 20 years after Moissan completed his work on carbides. However, one of the methods used by Moissan in the production of SiC involved vapor phase deposition (*217*).

Although the very high vacuum equipment now in use was not available 60 years ago, he did make use of reduced pressures. After preparing an acetylide of sodium, Moissan prepared sodium carbide by warming the acetylide under vacuum. Although he did not originate the common methods of producing acetylides, Moissan used and developed them.

These preparation methods include passing gaseous acetylene into aqueous metallic solutions made ammoniacal, passing acetylene into liquid ammonia solutions containing the dissolved metal, and heating the metal or oxide with carbon. The last of these three processes was used by Moissan in the production of diberyllium carbide (Be_2C), as was mentioned above (*215*). Techniques involving the use of gaseous acetylene to produce the acetylide followed by decomposition of the acetylide to form a carbide, as in the decomposition of $K_2C_2 \cdot C_2H_2$ to give K_2C_2, were used by Moissan to produce acetylides and carbides of the metals Li, K, Na, Rb, and Cs (*229*).

b. Carbides Produced by Moissan. At the time of his death in 1907, the Periodic Table ended with uranium, atomic number 92. If we exclude the noble gases including radon, the halogens including astatine, carbon itself, hydrogen, nitrogen, oxygen, phosphorus, and sulfur as nonmetals, we have a total of seventeen such elements. This leaves us with seventy-five metals including the metalloid, silicon, a very important carbide former. Six metallic elements, technetium, promethium, hafnium, rhenium, francium, and protactinium, were not discovered and isolated until long after the death of Moissan. Moissan prepared and published carbide preparations of thirty-one of the remaining sixty-nine metallic elements. Only the more important references will be given, as these elements are listed below in this section. Other references to the work of Moissan on these carbides will be cited as the elements are discussed individually.

At first glance, production of carbides for less than half the metals does not seem to be an imposing achievement but actually the reverse is true, as this section and the one immediately following will show. The work of Moissan on binary carbides was complete with analyses, reactions, and descriptive chemistry when published, and has remained largely, although not entirely, unchanged to the present day.

Moissan prepared both acetylides and carbides of the alkali metals lithium, sodium, potassium, rubidium, and cesium (*229*). In the family of alkaline earths, he made carbides of magnesium, calcium, strontium, and barium. He also made boron carbide and one of the beryllium carbides (Be_2C) (*215, 218*). In addition to producing silicon carbide or carborundum by more than one method, Moissan was one of the first to produce aluminum carbide, Al_4C_3 (*223*). Other elements between calcium, atomic number 20, and lanthanum, atomic number 57, from which Moissan made carbides and which have not been listed up to this point include titanium, vanadium, chromium, manganese, iron, yttrium, zirconium, niobium, molybdenum, and lanthanum itself (*210*). For the lanthanide series with atomic numbers between lanthanum and lutetium, atomic number 71, working either by himself or with others, he produced carbides of cerium, praseodymium, neodymium, and samarium (*210*). The last four elements for which Moissan produced binary carbides were tantalum, for which a carbide had been previously produced by Joly in 1876, tungsten, thorium, and uranium (*163*, *210*).

c. *Elements without Carbides Studied by Moissan.* Two of these elements were cobalt and nickel. For both of these metals, Moissan reported small solubility of carbon in the molten metal and separation of carbon as graphite with no carbide formation upon solidification (*204*). However, the carbides of nickel and cobalt were prepared at a much later time (*147*, *206*). In two separate investigations, one in 1896 and another in 1906, Moissan reported that ruthenium, rhodium, palladium, iridium, and platinum also dissolved measurable amounts of carbon when molten, with all of this carbon precipitating as graphite without any chemical combination after freezing of the melt took place (*225*). These same five binary metal-carbon systems were studied again as recently as 1960 by Nadler and Kempter (*236*). Their findings were essentially the same as those of Moissan. The other four metals which Moissan reported as forming no carbides were tin, lead, bismuth, and thallium (*219*, *227*).

The eleven metals for which Moissan reported no carbide formation, together with the thirty-one chemical elements for which he made binary carbides, give a total of forty-two. What about the other twenty-seven metallic elements known at the time of the death of Moissan in 1907? Four of these—copper, silver, gold, and mercury—had known and published carbides or acetylides when Moissan began his carbide studies about 1892 (*33*, *264*). Due perhaps in part to experimental difficulties connected with their radioactivity, no carbides of polonium, radium, or actinium have been made. There are also no known binary carbides of osmium, indium, antimony, or tellurium. Among the six metals discovered after the death of Moissan, no carbides have been reported for promethium, rhenium, and francium.

A carbide of lutetium has now been thoroughly investigated and established, but preparation of carbides of the lanthanide metals, gadolinium, terbium, dysprosium, europium, erbium, and thulium, as well as of scandium (which is not a lanthanide), was not completed until after the close of World War II. The remaining six metallic elements, zinc, gallium, germanium, arsenic, selenium, and cadmium, have been reported as forming carbides usually by only one or two investigators, and therefore the existence of such carbides is doubtful. For example, in 1923 Durand (*82*) reported the formation of a lead carbide, PbC_2, by adding calcium carbide to neutral lead acetate, but this has not been subsequently confirmed. This result is, of course, in contradiction to the findings of Moissan on the lack of formation of any lead carbide upon the freezing of a mixture of carbon and molten lead.

II. General Methods of Carbide Preparation

A. BINARY CARBIDES

1. Arc Fusion

This was probably the first method of carbide preparation which differed considerably from previously used chemical methods. It is often called the "Moissan fusion method," as the high temperature of the electric arc causes chemical combination and carbide formation directly between the metal and carbon. This was the first method of preparation of carbides of tungsten, molybdenum, titanium, and zirconium. Commercial tungsten carbide, W_2C, is still prepared on a large scale by this method, particularly when cast shapes which can be poured from the carbide melt are desired (*299*). Due to inability to control the arc temperature closely, and to unwanted decomposition of many carbides under the arc, other electrical heating methods have been used, such as direct resistance heating of the oxide and carbon mixture or use of carbon tube or other type of electrical furnace used solely as a source of heat and a high temperature. Moissan used other electrical methods such as those just mentioned, and they are still in use.

2. Carburization

In order to have lower temperatures which can be more accurately measured and more closely controlled than those obtained in the arc method, the metallic powder or the powder of its oxide is reacted with carbon. The source of carbon may be finely divided sugar carbon or carbon black, which is mixed with the oxide and heated either in air or in a suitable protective atmosphere. Sometimes carbon is supplied in both solid and gaseous forms and, in other cases, the metal or metal oxide powder is carburized entirely by a gaseous mixture, usually of hydrocarbons.

Since most metals or their oxides react with carbon at temperatures far below their melting points, a temperature range of 1200°–2000°C is sufficient for forming many carbides. As the reactants are solids, they can be intimately mixed by milling. This often results in the formation of oxide films, and this, together with loss of carbon to some types of protective atmosphere, makes it necessary in some preparations to use an excess of 5–10 % of solid carbon over stoichiometric proportions. Due to closer temperature control and lower temperatures involved, this method is widely used. It is used for the commercial production of carbides of molybdenum, tungsten, and tantalum (*292*).

Gaseous phase carburization, the carbon source being vaporized hydrocarbons, methane, carbon monoxide, or mixtures of these, has been used mainly on wires of metals such as tungsten (*314*) and tantalum (*30*). It is not a commercial method. However, the carburization of tungsten powder, using carbon monoxide and methane separately, has been reported (*144*), and seems to have large-scale carbide production possibilities.

3. *Vapor Phase Deposition*

The principal difference between this method and the gaseous phase carburization just described is in the use of metallic halide vapors. This method, by which metallic halide vapors and gaseous hydrocarbons react and deposit their carbide product on a heated filament, was first used by Van Arkel (*10*) in 1923. Using this procedure, he prepared carbides of tantalum and zirconium of high purity. The method produces not only carbides, but metals such as titanium and zirconium essentially free of metallic contamination, except for the slight amount that might come from the filament on which the element or compound is deposited. As a result of this wide and continued use, the variables involved in the method have been extensively studied.

4. *Other Carbide Preparation Methods*

The extraction of carbides by strictly chemical means such as acids, or by the use of electrolysis of steels and ferrous alloys, was used at least as long ago as 1887. In that year, Shimer (*312*) prepared TiC by treating a titanium-bearing cast iron with hydrochloric acid. Many of the known mixed carbides have been extracted from alloy steels by this method. It does have large-scale applications for the production of tantalum carbide (*197*). A carbide which is a solid solution of tungsten and titanium for the metallic portion has been made in this way, and a patent granted (*196*). The variation from a conventional electrolytic extraction consists of introducing the carbides into superheated molten nickel for formation of the solid solution. After cooling, the nickel is extracted by acid, leaving the solid solution carbide. Some advantages are claimed for such carbides as cutting tools over single carbides produced by carburizing. The methods outlined so far are used especially in the production of the carbides of vanadium, chromium, titanium, tantalum, tungsten, and molybdenum, the carbides used for machine tools. There are other carbide production methods, some of which can be used for making carbides of several elements, while others are isolated instances in the literature in which a single carbide has been reported without subsequent confirmation. No claim is made that this section covers all methods for the production of binary carbides.

One of the methods in rather wide use is the double decomposition method of Moissan. The metallic oxide and calcium carbide are heated to a temperature high enough to cause reaction. The products are the carbide of the metal and calcium oxide. The carbides of aluminum, chromium, molybdenum, and tungsten were prepared thus by Moissan (*227*). All four of these elements had been previously made by him by the arc fusion method. Another method that has been studied considerably is fused salt electrolysis of carbonates under such conditions that free carbon and metal are formed, which then unite and form a carbide (*8*). Tungsten and molybdenum carbides have been made by this method, but not on a commercial scale. Some of the difficulties encountered in the fused salt electrolysis method include high temperatures with accompanying instability of the carbonates and amounts of carbon set free by the various reactions involved, which are too small and too variable for carbide formation.

The mass spectrometer method has been widely used for preparation and identification of minute amounts of many substances, as well as in the separation of complex mixtures. A single report of the production of gallium carbide, GaC_2, by use of the mass spectrometer, was found (*66*). Within the evacuated spectrometer system, a graphite crucible and lid fitted with an effusion window were placed. The gallium contained in the crucible was melted by electron bombardment from a tungsten filament. The temperature was then raised by this means until enough gallium carbide vapors were produced to allow escape through the effusion window to the other portions of the mass spectrometer, where the carbide was identified. A report of a binary germanium carbide was also found. This element forms ternary carbides, which have been prepared repeatedly, but no confirmation of GeC has been found to date. In a French patent to Hamlet, granted in 1959 (*130*), a three-layer electroluminescent cell was described. One of the layers was stated to be GeC, with a thickness of 5–10 microns. It could not be determined from the patent abstract whether this carbide had been formed in the cell or otherwise prepared.

B. ACETYLIDES

1. Preparation from Metallic Ammonia Solutions and Gaseous Acetylene

The preparation of acetylides goes back at least a century to the work of Berthelot (*32*) and others. The first acetylides were prepared by passing gaseous acetylene C_2H_2 into aqueous solutions of the metallic ions, which had been made ammoniacal. The explosive acetylides of copper, silver, and gold were among the first to be made by this procedure. Somewhat later, the metal for which an acetylide was desired was dissolved in liquid ammonia and acetylene gas was passed into the solution. Among the acetylides thus produced, those of sodium and potassium will be discussed briefly. The acetylide of sodium, $NaHC_2$, is used in some organic syntheses, and its formation and decomposition to Na_2C_2 have been studied over the temperature range 100°–183°C, and an equation for the dissociation pressure of the "hydroacetylide" $NaHC_2$ has been obtained (*118*). The behavior of potassium is, as usual, similar, forming KHC_2 in liquid ammonia, which then decomposes to the "normal" carbide K_2C_2 upon careful heating. Other typical acetylides prepared by the liquid ammonia method include those of rubidium and cesium (*229*).

2. *Preparation from the Oxide Heated with Carbon*

Typical of this method are the electric furnace formation of calcium carbide from calcium oxide and carbon, and the similar formation of diberyllium carbide, Be_2C, by heating the oxide beryl and carbon to 1300°C. Both of these substances have previously been discussed.

Different authors are not consistent in their use of the term "acetylide." The term originated in part from the fact that the three alkaline earths form CaC_2, BaC_2, and SrC_2, which yield pure acetylene on contact with water (*213*). However, Mellor (*203*) refers to "carbide or acetylide." The preparation of substances, definite in composition by weight and in crystal structure, by use of the gaseous C_2H_2 seems to be logical justification for the term "acetylide"; so does the use of the term "hydroacetylide" for compounds such as $NaHC_2$. Not all carbides yield pure or nearly pure acetylene when placed in contact with water. Aluminum carbide, Al_4C_3, yields practically pure methane under such conditions. Moissan (*216*) found that the carbides CeC_2, LaC_2, ThC_2, and YC_2 give mixtures of methane and acetylene.

The behavior of the uranium carbide to which Moissan assigned the formula U_2C_3 is still more complex. Upon contact with water, this carbide produced a gaseous mixture consisting chiefly of methane, but also containing ethylene and hydrogen. In addition to gases, solid and liquid hydrocarbons are obtained when this carbide decomposes in cold water.

C. TERNARY OR HIGHER CARBIDES

1. *Ferrous Alloy Carbides*

For research purposes, these carbides are usually prepared by preparing a steel melt and adding the proper alloys to make the desired carbides (*183*). Vacuum induction melting is usually followed where highest purity is desired. If the carbides are to be extracted from larger melts of steel, where results representative of commercial materials are desired, more conventional methods are used, such as induction or arc melting (*37*). The carbides of high-speed steels have been studied by metallographic and X-ray means for many years (*12*, *360*). So have the carbides of other alloy steels. In addition to these two very common techniques, electron microscopy and lineal analysis—counting of particles of carbides along a number of lines of known length—have been used to a lesser extent and more recently (*153*, *195*).

In some investigations, X-ray diffraction patterns have been made on suitably ground and prepared steel specimens, and the carbides found on the patterns were then identified by comparison with knowns or by other standard diffraction methods (*68*). However, in most investigations the carbides have been extracted from the steel matrix and the extract studied. One of the reagents that has been used for carbide extraction is a dilute solution of HCl (5–10 % by volume). Dissolution of the steel by this reagent and analysis of the resulting carbide powder are at least as old as the work of Arnold (*11*) in 1914. The same reagent is still used, although at present electrolytic, rather than purely chemical, solution of the iron phase of the sample is usually employed (*37*). One of the advantages of the electrolytic technique over the use of only the acid is that the more rapid solution occurring, when the specimen is an electrolytic anode, reduces the danger of reaction of the reagent used to dissolve the iron with carbide phases present. Other difficulties that arise are formation of finely divided carbon as a soot, and flaking or peeling of the specimen, so that carbides are mechanically lost. A number of devices and a variety of apparatus and reagents have been used to overcome and reduce some of these difficulties. These include the construction of somewhat elaborate two-compartment electrolytic cells, use of a magnet to remove large flakes of the specimen from the carbide powder, and use of vacuum desiccators for drying, with admission of a limited and controlled amount of air to give slight surface oxidation for better storage. Two other reagents that have been used quite widely for electrolytic extraction of carbides from alloy steels are based, respectively, on citrate solutions and cadmium iodide. Investigations into the factors controlling electrolytic carbide extraction have been made by Blickwede and Cohen (*36*), and more recently by Gurry and others (*126*). Gurry and his co-workers made a quantitative study of practically all the reagents previously suggested for this purpose. They also used absolute methyl alcohol to prevent hydroxide formation, and a two-compartment cell. Cadmium iodide solution was found to be the most suitable electrolyte, and a hammer actuated by a cam, with the cam driven by a motor, was used to give constant removal of carbide from the specimen. This prevented reaction between the carbides and the reagent, as well as accumulation of a carbide layer on the specimen anode, thus allowing faster solution of the specimen. With more widespread use of the electron microscope, particularly since commercial high-resolution instruments have become available, papers describing special techniques for extraction of the small amounts of carbides needed for electron microscope study have been published (*80*, *357*). Objections to previously used methods include lengthy and uncertain procedures, and the use of a carbon support film 100 Å thick, which caused scatter and reduced resolution in electron microscopes, having a resolving power of 10 Å or less. Another fault of older electron microscopy replica methods was failure to remove very small carbide particles from the specimen.

2. *Carbides of Indium, Germanium, and Tin*

Ternary carbides of indium and germanium with the transition group metals nickel, cobalt, iron, and manganese have been prepared (*231*). A ternary carbide, having tin as the second element and manganese as the transition group metal, has been prepared and studied. The method used by Morgan to prepare these ternary carbides was to use an arc furnace under an inert atmosphere. The transition group metal and carbon were first melted and the third metal (indium, germanium, or tin) was then added. The argon atmosphere prevented volatilization first of the transition group metal, especially in the case of manganese, and then of the third metal of lower melting point which was also added last to prevent loss. Hutter and Stadelmaier made ternary carbides of indium and germanium with the same transition group elements that Morgan used, but using a high-frequency induction furnace and a graphite container for their charges (*157*).

III. Simple Carbides with Important Applications

A. Abrasive or Refractory Carbides

1. Boron

The first preparation of a boron carbide in an amount large enough for extensive study was by Moissan (*218*) in 1893. This was by an arc method. Between 1894 and 1905, several electric furnace methods for preparing boron carbide were devised. These are described by Hebert (*137*). In many instances the charge was contained in a carbon crucible. If extra carbon was needed, sugar carbon was usually used. The source of boron was either boric acid or amorphous boron prepared by use of magnesium (*220*). The arc method is still used for large-scale production. Scott (*305*), in a patent granted in 1964, describes a presently used electric furnace. The outer walls are formed by a steel cylinder cooled by a water spray.

The charge consists of B_2O_3 and coke, together with partially converted material from a previous run. Two electrodes are placed in the charge and a U-shaped current path is arranged so that, as the electrodes are raised, the boron carbide forms as two ingots, one beneath each electrode. The design is such that more material can be charged during the run. Initial current is 4000 amp at 120 V, increasing to about 6700 amp during most of the operation.

A higher purity boron carbide is produced by vapor phase deposition. Mierzejewska and Niemyski (*207*) produced pure crystalline boron carbide by thermal decomposition of BCl_3 and CCl_4 vapors on the surface of a heated graphite rod. A hydrogen carrier was used to regulate flow rate, and to help formation of boron carbide by removal of HCl from the reaction zone. Crystals 3–4 mm long were obtained under optimum growth conditions, which were stated to depend on flow rate and amount of hydrogen present with a temperature range of 1550°–1650°C. A British patent (*143*) describes production of boron carbide by treating BCl_3 vapor with methane at 1700°–2000°C and a pressure of about 5 mm Hg. Another report describes the production of boron carbide whiskers up to 1 cm in length by evaporation of boron carbide into vapor, which is carried by an appropriate gas flow over a heated substrate. The whiskers thus formed on the substrate were stated to support stresses up to 965,000 psi in tension, with an indicated modulus value of approximately 65×10^6 psi. These boron carbide whiskers were produced in connection with a study of the deposition of boron carbide as a strengthening material for an epoxy-based structural composite (*106*).

As a refractory, boron carbide has low thermal shock resistance and only fair resistance to oxidation at high temperatures. In a study of the use of boron carbides in cermets, it was found by Hamjian and Lidman (*129*) that, by milling commercial boron carbide powder of good purity with steel balls and allowing an intentional iron pickup, thermal shock resistance and oxidation behavior were both considerably improved. The iron-containing boron carbide powder after sintering withstood up to 25 cycles of thermal shock at 1800°F, compared to 3 and 9 cycles for two similar specimens without an iron addition. Oxidation behavior measured by unit weight loss at 1600°F was about two-thirds that of iron-free boron carbide.

A recent British patent (*109*) has been granted on the use of a mixture of boron carbide and boron nitride or diamonds as an abrasive. In this connection it is interesting to note that, in his discussion of boron carbide as known in 1905, Hebert (*137*) mentions that Moissan, during his researches on diamonds, found that boron carbide was hard enough to very slowly cut facets on diamonds.

The boron carbide produced in large quantity is usually given the formula B_4C. However, in a publication appearing in 1966, Lipp (*189*) states that the unit cell of boron carbide contains three B_4C molecules and therefore should be assigned the formula $B_{12}C_3$. Study of the bond lengths showed that boron carbide is predominantly covalent, and that one of the three carbon atoms can be replaced by another metallic element such as silicon or aluminum. This led to the discovery of a new class of compounds, $B_{12}C_{3-n}M_n$, in which M represents a substituted metal atom. In collaboration with Roder (*190*), Lipp published two subsequent papers on these compounds. The first describes the compound obtained when the substituted atom is aluminum, the second the result of making the M atom silicon. In a mass spectrographic study of the boron-carbon system, Verhaegen and his co-workers (*353*) identified as gaseous species the molecules BC_2 and B_2C. In addition to identifying these other two boron carbides in a gaseous state, they also measured their respective atomization energies.

2. *Silicon*

Space limitations do not permit a detailed review of the very large number of papers on silicon carbide, SiC, also commonly called carborundum. The original process, which Acheson (*3*) first patented in 1893, is still used for large-scale production. A coke core is placed between two graphite electrodes to give a conducting layer, which is then covered with sand to a height of about 8 feet in the center of the pile. At the start of the run, a current of about 1700 amp at 165 V is used. After some 90 minutes, the current is increased to 6700 amp. Both amorphous and crystalline silicon carbides are obtained as products.

The fact that the vapor phase method was used by Moissan in addition to the arc method for making SiC was mentioned previously. Commenting on the Acheson process in his book, Moissan (*211*) states that, in the Acheson method, there are a large number of small arcs of varying intensity along the length of the charge when the current is first established, rather than a single arc as is usual in other types of electric arc furnace. He further states that the current does not attain a steady value until some 5 hours after the beginning of the run. The Acheson process for producing SiC was in commercial operation at the time that Moissan began his study of the electric furnace and compounds such as carbides and nitrides in 1892.

A typical method for preparation of high-purity SiC is that of Merz and Adamsky (*205*). By the thermal decomposition of CH_3SiCl_3 in hydrogen at 1500° ± 50°C, a high-purity silicon carbide of wurtzite structure was obtained. The present status of silicon carbide as an abrasive and refractory has been reviewed by Parche (*251*).

The number of different structural forms, or polytypes, of SiC is so large that two different notations, one due to Ramsdell (*265*) and one due to Zhdanov (*374*, *375*), are in use to designate them. According to Verma (*354*), over forty different polytypes have been described, and no one theory is able to provide a completely satisfactory explanation for the growth of all the structural types. Certain features of some of these structurally different forms fit a screw dislocation growth theory, but many other growth features do not (*313*, *355*).

3. *Titanium*

The binary carbides of the Group IV metals—titanium, zirconium, and hafnium, the Group V metals—vanadium, niobium (columbium), and tantalum, and those of Group VI—chromium, molybdenum, and tungsten—have been critically reviewed with respect to their high-temperature use by Storms (*323*). His survey covers the literature on the carbides of these nine transition metals as well as the carbides of uranium, thorium, and plutonium. Much of the earlier work on the high-melting transition metal carbides, especially where property measurements are concerned, is stated by Storms to have little value due to varying oxygen content in the carbides made by these earlier investigators.

Titanium, zirconium, and hafnium all form only one carbide having a simple NaCl-type structure. This structure is maintained over a wide composition range which, according to Storms (*325*), extends to $TiC_{1.0}$ and $HfC_{1.0}$, respectively, but ZrC apparently is not found as a single phase at $ZrC_{1.0}$. The separation of a titanium carbide from cast iron by Shimer in 1887 (*312*) was mentioned earlier. Commercially, most TiC is still prepared by arc reduction of TiO_2 with carbon, the method described and published by Moissan (*224*) in 1895. This method yields a titanium carbide satisfactory for hard metal use, but the product thus obtained has a variable amount of oxygen, and drastic modification of the arc method or use of different methods is necessary for preparing a pure oxygen-free TiC.

Three methods that produce titanium carbide of high purity are the vapor deposition method, use of calcium carbide, and special arc melting methods. Vapor deposition from $TiCl_4$, hydrogen, and hydrocarbon vapor, with the formation of the titanium carbide on a tungsten wire, was developed by Campbell and others (*61*) in 1949. If calcium carbide free of hydroxide and oxide is used, the reaction between CaC_2, $TiCl_4$, and H_2 at 800°C yields a pure TiC, calcium chloride, and gaseous HCl as products. The carbide can be washed free of calcium chloride and calcium carbide with water. This method was published by Imai and others (*158*) in 1957. In principle it follows the old double decomposition method of Moissan, but varies from the original method in the use of gaseous reactants. Cadoff and Nielsen (*60*) prepared a pure TiC by the arc method. They used iodide titanium and spectroscopic grade carbon as the starting materials. Oxygen and nitrogen contamination were prevented by first evacuation to a low pressure, argon flushing, and melting under a partial pressure of specially purified argon. The leak rate of the furnace was also held to a low and controlled value.

The sodium chloride structure extends from $TiC_{1.0}$ or very nearly integral stoichiometry down to $TiC_{0.49}$. As an example of the drastic changes of properties when enough carbon is removed to leave the TiC single-phase field (below $TiC_{0.49}$), Storms (*324*) states that the hardness is halved, although the contraction in lattice parameter is only 0.01 Å. In spite of this, titanium carbide of high purity is certainly one of the three hardest carbides formed by any of these nine metals, and may have the highest penetration hardness. The oxygen present in commercial material does not cause appreciable hardness loss for refractory or cutting tool applications, but causes so much variation in quantitative values that measurements without an accompanying statement of the oxygen content of the TiC tested are of no significance. The other pure monocarbide that may equal or exceed TiC in hardness is VC.

4. *Zirconium*

A zirconium carbide mixed with graphite made by use of the electric arc was prepared by Troost (*346*) a century ago in 1865. Until the separation of hafnium from zirconium in 1923, all zirconium carbides contained hafnium as an impurity. In addition, for the same reasons discussed for the preparation of titanium carbide, oxygen and nitrogen may be present even when zirconia or zirconium metal free of hafnium is used as a starting material. The reduction of ZrO_2 with carbon takes place in three steps with formation of Zr_2O_3, then ZrO, and finally ZrC. Long heating under a partial vacuum reduces the oxygen content of zirconium carbide thus prepared to a low value, but Storms (*326*) states that there is no reliable analytical method for oxygen under these particular conditions.

In order to obtain a carbide with low oxygen content, carbon is reacted with zirconium metal or zirconium hydride. Another similarity between preparation of zirconium and titanium carbides is that diffusion and reaction between carbon and the metal are slow even when the temperature is high enough so that liquid is present. Vapor phase deposition from a mixture of $ZrCl_4$, hydrogen, and gaseous hydrocarbons produces a pure crystalline ZrC. The reaction temperature range is 1730°–2430°C. Both ZrC and TiC prepared in this way were reported in the same 1949 publication by Campbell and his associates. In the investigation of the zirconium-carbon system published by Sara in 1965, the starting materials were zirconium hydride and spectrographic grade graphite powders. Impurities in the graphite were stated to be under 0.5 ppm; the zirconium hydride contained hafnium 94 ppm, nitrogen 80 ppm, and hydrogen 2.12%. The powders were mixed, presintered under vacuum at 800°C, and then heated to desired temperature-reaction ranges in vacuum resistance furnaces up to a temperature level of 2850°C. Above this temperature, a special flux concentrator was employed in which either vacuum or gaseous atmosphere could be used.

Sara (*286*) used metallographic techniques, differential thermal analysis, and X-ray diffraction methods in addition to melting point determinations and chemical analysis in his investigation. He reported the maximum on the liquidus for single-phase ZrC of NaCl-type structure at 3420°C and approximately 46 atomic % carbon. At 1800–3200°C Sara reported the lower composition limit of the ZrC phase field as 38.5 atomic % carbon. In agreement with the work of Farr as quoted by Storms (*99*), Sara found the carbon-rich side of the ZrC field at 49.4 atomic % carbon at 2400°C, and at 49.1 atomic % at a eutectic temperature of 2850°C. On the basis of his own work, Sara reported a limit for the ZrC field at 3200°C at 48.9 atomic % carbon. Hence, as was mentioned above, zirconium monocarbide ZrC apparently does not extend to integral stoichiometry. Both Storms and Sara also found that the lattice parameter of ZrC has a maximum. Sara reports this maximum at 48.5 atomic % carbon. Compositions richer in carbon but still in the single-phase field show lower lattice parameters. This behavior is unusual.

The chief technical use of zirconium carbide is as a component of cemented hard metal cutting tools. Cobalt is often used as a metallic binder. Due to a comparatively low price for zirconium oxide of high purity as a starting material, as well as the ability of ZrC to form solid solutions with other carbides, attractive practical possibilities exist (*300*). Applications of zirconium carbide for limited use and of small practical importance include using the substance as an electrode material, for refractory crucibles, or as incandescent filaments. Due to the low neutron capture cross section of zirconium, there are nuclear applications of both the metal and the carbide. Zirconium carbide has been used as a coating 1–2 mm thick to delay release of fission products from uranium carbide fuel elements (*28*). Measurements of properties of fuel elements in the form of rods of $U_{0.5}Zr_{0.5}C$ have been reported (*122*). Thermal emission and electrical conductivity were among the properties studied.

5. *Hafnium*

The same preparation methods discussed for the carbides of titanium and zirconium are used in making HfC. At temperatures of 1800°–2000°C, reduction of HfO_2 with carbon yields hafnium carbide. Long heating under vacuum is necessary to remove small amounts of oxygen so that $HfC_{1.0}$ is closely approached. Vapor deposition of HfC on a tungsten filament from a mixture of $HfCl_4$, hydrogen, and methane produces high-purity material. This type of preparation of HfC was also reported in the work of Campbell and others in 1949 (*61*). The vapor phase technique was apparently first applied to the production of hafnium carbide by Moers (*208*) in 1931. In 1959 Nowotny and his associates produced oxygen-free hafnium carbide by the reaction of hafnium hydride (HfH) and carbon (*245*).

The hafnium-carbon system shows a single carbide of NaCl-type structure existing over a wide composition range, which apparently extends to $HfC_{1.0}$. Choice of the best value of lattice parameter is complicated by the presence of zirconium, oxygen, and nitrogen, as well as by carbon deficiency and the fact that, as $HfC_{1.0}$ is approached, the lattice parameter becomes almost independent of composition. Based in part on his own work, Storms (*327*) quotes a value of 4.639 Å for oxygen-free $HfC_{1.0}$ containing no zirconium. He also states that, in view of the maximum in lattice parameter with variation in carbon content known to exist in the zirconium-carbon system, the possibility of a similar occurrence for HfC cannot be excluded. The lower limit of the single-phase HfC at 1550°C was placed, by Benesovsky and Rudy in 1960, at 37 atomic % carbon (*31*). Apparently the only fairly recent phase diagram for the system hafnium-carbon also appeared in this same 1960 paper. It was reprinted with very little change by Kieffer and Benesovsky in their review of transition metal carbides, which appeared in 1964 (*174*).

In 1930 Agte and Alterthum (*6*) published melting point values for a number of the carbides of these same nine transition group metals. Among their melting point values were: HfC 4160° ± 150°K (3887°C), and TaC 4150° ± 150°K (3877°C). The value for hafnium carbide has been quoted widely in the literature since then, accompanied in many cases by statements that HfC was the highest melting or one of the highest melting carbides. These melting points were determined by use of a calibrated optical pyrometer by the method of Pirani and Alterthum (*260*), in which a rod-shaped specimen is heated by passing a strong direct current through it. A small hole is drilled obliquely to the axis of the rod to provide a black body for temperature determination. For metals, liquid will flow out of the hole when fusion occurs; with carbides, the melting point is taken as the temperature at which liquid appears at the bottom of the black body hole. It is interesting to note that, in their original determinations, Agte and Alterthum gave the melting points of tantalum carbide and hafnium carbide as being only 10 degrees apart. Later publications tended to show hafnium carbide melting at least 100 degrees above tantalum carbide. In 1962 Russian workers (*20*) published a melting point for $HfC_{0.91}$ of only 3520°C. This material was contaminated with oxygen. However, in 1963 Adams and Beall (*4*), working with hafnium carbide that contained 2 % by weight zirconium, oxygen, and nitrogen averaging 260–420 ppm and 70–110 ppm, respectively, found substantially the same melting point for hafnium carbide as that of Agte and Alterthum. Stoichiometric HfC contains 6.3 % by weight carbon; the zirconium content of the material used by Beall and Adams raised theoretical total carbon content to 6.42 %. Using a specially built melting point apparatus after the design of Agte and Alterthum, and a calibrated optical pyrometer, they found the following melting points: carbon 5.29 %, 3880°C; carbon 5.81 %, 3795°C; carbon 6.22 %, 3895°C; carbon 6.59 %, 3870°C. The melting point uncertainty is stated as ±150°C. Rudy and Benesovsky also used a value of 3900°C for the melting point of stoichiometric HfC in the phase diagram of the Hf-C system published in 1960. Beall and Adams found their maximum melting point lying at a composition to the left of $HfC_{1.0}$. On the other hand, Storms (*330*) gives the melting point of TaC as 4000°C at a composition of $TaC_{0.8}$ in his phase diagram of the Ta-C system published in 1964.

Due in part to scarcity and higher cost, hafnium carbide has found limited use in hard metal cutting tools. Recent lowering in the price of hafnium-containing starting materials may change this. The high melting point of hafnium carbide makes it useful for applications such as nuclear rocket nozzles and other such rocket parts (*69*). A French patent has recently been granted on the plasma flame spraying of hafnium, titanium, and zirconium carbides (*76*).

6. *Vanadium*

Methods of preparation of vanadium carbides closely follow those previously discussed for hafnium, titanium, and zirconium carbides. Moissan's preparation of a carbide having a formula close to $VC_{1.0}$ was mentioned previously. Starting with coal ashes having a vanadium content, he prepared V_2O_5. Mixing this with sugar carbon, he heated the mixture electrically in a carbon tube to obtain the carbide in a crystalline form. Commercial production of vanadium carbide is from graphite mixed by ball milling with ammonium vanadate, vanadium pentoxide, or vanadium sesquioxide as the source of vanadium. In a few cases vanadium metal powder is used (*293*). After pressing into compacts the material is carburized under hydrogen at 1800°C. The product of this first carburization ranges from 15.8 to 16.9% by weight combined carbon. The theoretical carbon content for vanadium monocarbide $VC_{1.0}$ is 19.08% by weight. A second carburization of commercially produced crude carbide under vacuum at 1600°–1700°C raises the combined carbon content to as much as 18.5% by weight. Free graphite is found in almost all commercial products. Some of the difficulty in attaining a carbide that is truly $VC_{1.0}$ is due to the formation of isomorphous vanadium nitride and vanadium monoxide. Another method of obtaining vanadium carbides is from vanadium-containing alloy steels by dissolving away the iron matrix in suitable solvents.

Vapor phase deposition of vanadium monocarbide on a tungsten wire was reported by Moers (*208*) in 1931, and by Campbell and others (*61*) in 1949. The gaseous materials used were VCl_4, hydrogen, and a hydrocarbon. The temperature range of carbide formation is 1500°–2000°C. Difficulty due to formation of vanadium metal, which then alloys with the tungsten deposition wire so that separation is not possible at high filament temperatures, is encountered. To overcome this, the temperature is first held at about 1430°C until a layer of vanadium carbide of sufficient thickness is formed to cover the filament and enable a clean separation of the deposited material. The temperature can then be raised to 1500°–2000°C for more rapid carbide formation and deposition. According to Storms (*328*), another objection to the vapor deposition method is that a product of varying composition is obtained. However, single crystals of vanadium carbide can be produced by the vapor deposition method.

Freedom from nitrogen, carbon monoxide, and especially oxygen is also necessary to produce a vanadium carbide of uniform composition and high combined carbon content. With pure starting materials, a carbide free of impurities can be produced by careful arc melting. Upon powdering the arc melted button, or by slow reaction upon exposure to air, recontamination will take place. Storms recommends using powdered vanadium metal or vanadium hydride with carbon as starting materials, and melting in a good vacuum (under 10^{-5} torr). By using a graphite crucible and holding somewhat below the melting point, volatile metallic impurities will also be removed. In contrast to TiC and HfC, vanadium monocarbide does not reach $VC_{1.0}$. The phase diagram of Storms and McNeal (*337*) published in 1962 shows the single-phase VC field extending to $VC_{0.88}$ at 1000°C, and having a slightly lower carbon content at the temperature of peritectic decomposition near 2650°C. The lower limit of the monocarbide field is from $VC_{0.60}$ at 2165°C to $VC_{0.72}$ at the base temperature of the diagram, 1000°C.

The vanadium-carbon equilibrium diagram also illustrates another feature common to the carbide systems of the three metals of this group—vanadium, niobium, and tantalum. This is the confirmed existence of a second carbide usually represented as V_2C, Nb_2C, or Ta_2C. All three of these compounds show structures belonging to the hexagonal system. Another feature common to all three of these metal-carbon systems is the existence of one or more rather unstable carbides of unknown crystal structure, which are often approximated as M_3C_2 ($M = V$, Nb, or Ta). The V_2C phase forms peritectically at 2165°C having a composition at this temperature of $VC_{0.56}$; the composition at the eutectic temperature (1630°C) is $VC_{0.33}$. At the base temperature of 1000°C, the V_2C field extends from $VC_{0.47}$ to $VC_{0.50}$. The eutectic horizontal extends from $VC_{0.09}$ to $VC_{0.33}$. The solubility of carbon in solid vanadium is reported as less than $VC_{0.01}$ at 1000°C (*125*). Therefore hexagonal V_2C extends practically to pure vanadium at temperatures lower than about 1100°C. As would be expected from periodic relationships, the systems niobium-carbon and tantalum-carbon also show a eutectic as carbon is added to the liquid metal, with formation of an M_2C carbide by a peritectic reaction at higher carbon content and at a higher temperature.

The principal use of the carbides of vanadium is in alloy steels. They have been used to a limited extent in solid solution with other carbides for hard metal cutting tools. Although vanadium carbide is easily produced and relatively inexpensive for a hard metal carbide, it has found little use thus far because commercial vanadium carbide is thought to be of insufficient cutting hardness. According to Storms (*329*) and Gurevich and Ormont (*125*), this is not true of a vanadium carbide uniform in composition and high in carbon content, such as $VC_{0.88}$. Material of this kind and composition will show a penetration hardness reading exceeded only by TiC.

7. *Niobium*

This chemical element is often referred to in the United States as columbium. In this review, it will be designated as niobium. The monocarbide can be formed by the Van Arkel vapor deposition method, as is true for the other Group IV and V metals reviewed. The first niobium carbide was produced by the reduction of $K_2O \cdot 3Nb_2O_5$ with carbon at a temperature of about 1500°C by Joly (*164*) in 1877. Large-scale production of niobium carbide uses Nb_2O_3, Nb_2O_5, or niobium metal powder. This is heated with carbon black to 1300–1400°C in a carbon tube furnace. Freedom from oxygen for technical purposes is stated to present no special difficulties (*294*). A niobium carbide of higher purity can be prepared by careful reduction of Nb_2O_5 or by heating elemental niobium and carbon powders properly mixed, provided a sufficiently high temperature is reached. Storms and Krikorian (*336*) found that heating in vacuum for 30 minutes at 1900°C eliminated 0.28 % by weight oxygen and 0.66 % nitrogen in a commercial NbC sample. However, to react all the carbon in this type of material required much longer times. At 1800°C elimination of free carbon required about 38 hours. Use of a hydrogen atmosphere or a higher temperature shortens the carbon elimination time considerably.

Among the differences between the phase diagrams for the vanadium-carbon and niobium-carbon systems are the higher temperature ranges for Nb-C. Storms shows a maximum melting point for the NbC phase field of near 3500°C at a composition $NbC_{0.86}$. At the base temperature of 1500°C the NbC field extends very nearly to $NbC_{1.0}$. The composition and temperature of maximum melting were given by Engelke and others (*95*) in 1960 as 3420°C for a composition $NbC_{0.92}$, estimated from the lattice parameter. In 1958, using the same arc melting method, Brownlee (*55*) obtained 3485°C for $NbC_{0.95}$. In his diagram of the Nb-C system published in 1964, Storms shows a horizontal line extending to the right from the high-carbon boundary of the NbC field at a temperature of about 3300°C. There is evidence that this is a eutectic horizontal. Storms states that this illustrates the fallacy of expecting the maximum melting point to appear at the stoichiometric ratio, as $NbC_{1.0}$ melts some 200°C below the maximum melting point attained at a composition containing slightly less carbon. Formation of hexagonal Nb_2C is by a peritectic reaction analogous to the peritectic formation of hexagonal V_2C. Storms shows this peritectic temperature as 3090°C, while the peritectic temperature in the V-C system is only 2165°C. The extent of the Nb_2C field at the base temperature of the diagram is very narrow and not fully confirmed. It apparently extends to $NbC_{0.5}$ and is shown by Storms as bounded at this value. The corresponding region of the V_2C phase field is appreciably wider. Another difference between the two systems is the existence of small but measurable solid solubility of carbon in niobium metal. The body-centered cubic terminal solid solution (designated "alpha" by Storms) extends from a maximum of $NbC_{0.08}$ at the eutectic temperature (2335°C) to only 100 ppm at 1500°C.

Niobium carbide used alone has not found cutting tool applications. As is also the case for the vanadium carbides, solid solution carbides containing fairly large amounts of NbC have found limited use. For special applications, where a material free of tungsten carbide is desirable and where high wear resistance is not required, NbC-cobalt, VC-NbC, and NbC-TaC mixtures have been used (*302*). Niobium carbide has also been used to improve the stability of uranium monocarbide (UC) fuel elements (*368*). Using powder metallurgy methods, UC-NbC and UC-ZrC solid solution carbide pellets were formed for possible use in high-temperature gas-cooled reactors. Some of the advantages found included increased resistance to water corrosion, prevention of undesirable lattice transformations in UC with accompanying dimensional changes, increased compatibility with graphite to 2000°C, and increased resistance to atmospheric oxidation. The extension of compatibility with graphite to 2000°C required that the NbC content be above 63 mole %.

8. Tantalum

Tantalum carbide was made by Joly (*163*) in 1876, a year before his production of niobium carbide. The method used was heating Ta_2O_5 or tantalites with sodium carbonate and carbon at about 1500°C. Other preparation methods are very similar to those used for obtaining niobium or vanadium carbides. Tantalum carbide can be made by the vapor deposition method with suitable modifications in technique to prevent deposition of tantalum metal on the tungsten wire. The menstruum method with aluminum as menstruum has also been used. Arc melting may be employed; however, it tends to produce a carbon-deficient TaC. Commercial TaC can be made by carburizing an intimate mixture of Ta_2O_5 and carbon black at either 1700°C under purified hydrogen or at 1600°C in vacuum (*295*). This carbide can also be made cheaply by melting a ferrotantalum alloy high in tantalum (60–70 %) in an induction furnace and adding enough carbon to make the melt viscous. After cooling, the brittle melt is crushed and the tantalum carbide extracted by treatment with HCl. The carbon-deficient material thus obtained is mixed with carbon and carburized under hydrogen at 1600°–1700°C.

Preparation of high-purity tantalum carbide usually begins with carefully outgassed elemental powders. The procedure adopted by Lesser and Brauer (*188*) was to heat the powdered mixture in a graphite crucible under vacuum at 1000°C until reaction began with gas and heat evolution. After cessation of gas evolution, the temperature was raised to about 2000°C and held 15 minutes. After cooling, the product was powdered to aid diffusion of carbon. The powder thus obtained was then reheated, and this heating and powdering cycle was continued until a pure product was obtained. High temperature and a hydrogen atmosphere aid in the formation of pure tantalum carbide in a shorter time. In general, oxygen and nitrogen are more difficult to remove from tantalum carbide than from niobium carbides containing the same amounts of these two gaseous impurities.

The phase diagram for the tantalum-carbon system is similar, in most respects, to that of niobium-carbon. Terminal solid solubility exists at the tantalum end; there is a eutectic between the terminal solid solution and hexagonal Ta_2C, which in turn is formed by a peritectic reaction from TaC and liquid at a higher temperature. TaC has a wide range of temperature and composition existence. In composition, the monocarbide phase field extends to or attains the stoichiometric ratio $TaC_{1.0}$. Eberle and others (*83*), in a 1966 publication, state that at a temperature of 2000°C the monocarbide extends from $TaC_{0.8}$ to $TaC_{1.0}$. The diagram of Sara and Lowell (*285*) in 1964 places the carbon-rich TaC boundary at 49.5 atomic % carbon at 2250°C, with the low-carbon boundary for this same temperature at 41.7 atomic % carbon. TaC, in a manner similar to NbC, also melts at a very high maximum temperature and an accompanying carbon content less than stoichiometric.

The other principal feature of the Ta-C system is the proven existence of a TaC-C eutectic. All of the above features appeared on the first complete diagram of the tantalum-carbon system, published by Ellinger in 1943 (*85*). This carbon-rich TaC-C eutectic is placed, by Sara and Lowell, at 61.2 atomic % carbon at a temperature of 3375°C. They also place the temperature of peritectic formation of Ta_2C at 3240°C, with no change from stoichiometric Ta_2C below this temperature. The low-carbon boundary at the eutectic temperature of 2825°C is at 26.5 atomic % carbon. Above the eutectic temperature, the Ta_2C/Ta_2C + liquid boundary was found at 29 atomic % carbon. Below the eutectic Ta_2C again becomes richer in carbon by a slight amount. The peritectic formation and the limits of the Ta_2C phase field are not completely confirmed.

The chief point of interest for the Ta-C system is the maximum melting temperature and accompanying composition of the monocarbide TaC. The melting points of TaC at 3877°C and of HfC at 3887°C, made by Agte and Alterthum in 1930, were mentioned in connection with the Hafnium-carbon system. A melting point for $TaC_{0.8}$ of 4000°C, given by Storms in his 1964 phase diagram for Ta-C, is based on drawing the solidus in this region to match the general shape of the similar Nb-C diagram (*330*). On the basis of extensive experiments by different methods, Sara and Lowell (*285*) place the maximum melting point of TaC at 3825°C (+100°, −0°) and at a composition of about 48.5 atomic % carbon. Sara (*287*), in a paper published late in 1965, using the same techniques employed for determining the melting point of TaC, gives a maximum melting value for HfC of 3830°C at a composition containing 47.5 atomic % carbon. This value was based on melting values obtained from some fifty hafnium carbide samples. The composition range of this maximum melting region was found to be only about 2 atomic % carbon wide, dropping almost vertically to 3150°C on the high-carbon side. On the hafnium-rich side, the decrease in temperature of the solidus was more gradual, but the formation of liquid in large amounts prevented unimpaired recovery of the samples for chemical analysis. Thus, after some 35 years, the melting points of these two refractory carbides seem to remain within the uncertainty range originally given by Agte and Alterthum.

Primary interest in tantalum carbide has been in its use as a refractory during the last decade. Although TaC does not have the extreme hardness of TiC or VC, it is important in carbide cutting tools because of its tendency to reduce the welding tendencies of the steel chips removed by the cutting tool. In solid solution mixtures with other carbides, TaC has been used to obtain tungsten-free cutting tools for use during time of war when countries, such as Germany during World War II, were cut off from supplies of tungsten (*301*).

9. *Chromium*

The phase diagram for the chromium-carbon system, published by Bloom and Grant (*38*) in 1950 and republished by Schwarzkopf and Kieffer, unchanged, in 1964, shows three chromium carbides. Cr_3C_2 decomposes peritectically slightly above 1900°C; Cr_7C_3, also peritectically, at 1782°C. The third carbide of chromium to which Bloom and Grant assigned the formula Cr_4C, but which is now most often referred to as $Cr_{23}C_6$, forms by a third peritectic reaction at 1518°C. The respective crystal structures are: Cr_3C_2, orthorhombic with 20 atoms per unit cell; Cr_7C_3, hexagonal with 80 atoms per unit cell; and $Cr_{23}C_6$ complex face-centered cubic with 116 atoms per unit cell. Other carbides have been reported, particularly CrC, which Bloom and Grant made repeated unsuccessful attempts to produce. Hansen and Anderko (*132*), in their review of this binary carbide system and accompanying diagram published in 1958, also found insufficient evidence for the inclusion of CrC. In his critical review of refractories published in 1964, Storms (*331*), states that the work done on the chromium-carbon system does not furnish sufficient information to warrant the construction of a valid phase diagram. The only one of three chromium carbides with a melting point high enough to be of refractory or cutting tool interest is Cr_3C_2. The melting point of this compound at about 1900°C is almost the same as that of the metal chromium at 1875°C. In explanation of the fact that the metals of Group VI (Cr, Mo, and W) have higher melting points, although their carbides have lower melting points, Storms suggests that the strong metal-to-metal bonds, which are broken by dissolved carbon, are not replaced by stronger metal-carbon bonds in the carbide. This formation of stronger metal-carbon bonds, especially in the formation of hafnium and tantalum carbides, is borne out by the heats of formation. In Group VI, the carbide heats of formation are much lower and the carbides are much less stable than those of Group IV (Ti, Zr, Hf) and Group V (V, Nb, Ta).

Historically, the first production of a chromium carbide was by Moissan (*212*) in 1893. Using an inclined carbon tube electrically heated, he produced 20 kg chromium metal by reducing Cr_2O_3 with carbon. By the use of a large excess of carbon, masses of crystals of Cr_3C_2 were obtained. The carbide to which Moissan assigned the formula Cr_4C was found in the form of short reddish brown needles on the chromium ingots he prepared. Technical preparation of Cr_4C_2 is still by reduction of Cr_2O_3 (*296*). Powder compacts containing 3 parts Cr_2O_3 and 1 part carbon black, intimately mixed and pressed, are heated to 1600°C in a carbon tube furnace under hydrogen. For best results, this temperature must be maintained fairly closely, as the lower carbides form under the same conditions at lower temperatures. Below 1300°C, the major product is Cr_7C_3. Due to the importance of chromium in alloy steels, many of the studies on chromium carbides have been made on material isolated from these steels. Iron is also a major impurity in chromium metal. For these reasons, much of the published work is on Fe-Cr-C rather than the binary chromium-carbon system. Thermal decomposition of chromium carbonyl (*250*) produces a layered mixture of Cr and Cr_3C_2. Chromium carbides can also be produced by arc heating of the elemental powders but, due to the high vapor pressure of chromium at its melting point, metal losses by vaporization are considerable.

Cr_3C_2 has been used with limited success in carbide cutting tools low in tungsten or tungsten-free. In this case, it is used in small amounts in conjunction with other carbides. Large amounts (60–85% Cr_3C_2) of this chromium carbide, used with a nickel or copper-nickel binder free of cobalt, form a material that is acid-resistant and wear-resistant of special use for valve parts in the chemical industry (*174*). A cermet containing about 35% Cr_3C_2, together with TiC, and nickel as an infiltrating agent, has been prepared and used with some success by Kaizo and Suto (*168*). In such applications, the chromium content gives a marked increase in resistance to atmospheric oxidation.

10. Molybdenum

There is general agreement that slight but measurable terminal solid solubility of carbon in molybdenum exists, and that the eutectic between the molybdenum-rich alpha solid solution and the Mo_2C phase is at about 2200°C (*83*). Mo_2C is the only carbide of molybdenum stable thermodynamically below 1000°C. The width of this phase field is placed, by Storms (*332*), at $MoC_{0.44}$ to $MoC_{0.50}$ from a base temperature of 1000°C to the eutectic temperature at 2200°C. The formation of Mo_2C takes place by a peritectic reaction at a temperature of about 2400°C. This is the only molybdenum carbide having any practical use. The crystal structure of

Mo_2C was formerly believed to be hexagonal but, since the neutron diffraction determination of Parthe and Sadagopan (*252*) in 1963, an orthorhombic Mo_2C seems to be quite firmly established.

The diagram published in 1966 by Eberle and others (*83*), as well as the Mo-C diagram of Kieffer and Benesovsky (*174*) 2 years earlier, shows MoC as melting congruently with the maximum on the liquidus at slightly above 2500°C. The 1964 diagram also shows the MoC (or gamma) phase participating in a eutectic with carbon at 2470°C. Eberle states that at 2000°C the homogeneity ranges in the entire Mo-C system are not worth mentioning. There has been considerable disagreement in the literature over the formulas and crystal structures of reported molybdenum carbides, richer in carbon than Mo_2C. Elliott (*87*) lists ten "MoC" phases with hexagonal close-packed, hexagonal, face-centered cubic, and WC-type structures. In the earlier literature, this carbide was often termed Mo_3C_2. The summary given by Rudy and others (*275*) in 1963 is consistent and in accord with most of the recent experimental results. At about 2700°C a carbide, Mo_3C_2, crystallizes from the melt. The stacking sequence of the layers of metal atoms is face-centered cubic (ABCABCA · · ·). Between 2000 and 2200°C, the face-centered cubic structure changes with great velocity into a hexagonal type (eta "MoC"), in which the metal atoms are characterized by the vertical layer sequence ABCACBABCA. Below 1800°C the hexagonal structure decomposes, but at a much slower rate, into Mo_2C and carbon. By the use of high pressures (*67*) or by very rapid quenching of the melt (*274*), it is possible to obtain the cubic form at room temperature. Most of these observations made by Rudy in 1963 were confirmed in 1965 by the work of Heetderks and others (*138*). Using differential thermal analysis methods, the temperature of decomposition of the hexagonal (eta) MoC_{1-x} into Mo_2C and carbon was found to be 1665°C; the decomposition temperature of cubic (alpha) MoC_{1-x} into the hexagonal eta phase is listed as 1960°C.

Priority in the preparation of molybdenum carbides belongs to Moissan. He first prepared Mo_2C in 1893 by reducing molybdenum oxide with carbon in the electric arc (*222*). Working with Hoffmann (*230*) in 1904, a carbide approximating MoC was obtained by fusing molybdenum and aluminum in the presence of coke, and treating the solidified mass with NaOH or sodium carbonate to isolate the carbide. The carbide Mo_2C can be prepared by a number of methods. These include reduction of MoO_3 with carbon, carburizing molybdenum metal powder with graphite in a carbon tube vacuum furnace, reaction of molybdenum metal with CO or CH_4, decomposition of molybdenum carbonyl vapor on an electrically heated carbon rod above 1300°C under vacuum, and fused salt electrolysis of MoO_3 with sodium borate, sodium carbonate, and lithium fluoride. Technical production of molybdenum carbides begins with reduction of pure MoO_3 to the metal with hydrogen at about 900°C. The molybdenum powder is then intimately mixed with carbon black and carburized under hydrogen in a carbon. tube furnace at 1400°–1500°C (*297*).

Technical Mo_2C is too soft to be used alone in cutting tools. It is used in solid solution with other carbides, particularly where tungsten-free mixtures are desired. Some Mo_2C crucibles and coatings have been employed in the preparation of aluminum from aluminum oxide by processes involving aluminum carbide or aluminum nitride as an intermediate step. Cermets for reactor fuel elements have been made by coating Al_2O_3 granules with a mixture of molybdenum and molybdenum carbide, obtained by the thermal decomposition of molybdenum carbonyl vapor (*364*).

11. Tungsten

Historically, the first production of tungsten carbide was by Moissan (*222, 227*), using the carbon arc furnace for fusion, as was previously mentioned. Moissan produced W_2C either by recombining molten tungsten metal with carbon or by reduction of WO_3 with either carbon or calcium carbide in the carbon arc. Technically, the fusion process permits practical production of W_2C and W_2C-WC eutectic mixtures, which can be cast into desired shapes or used in the manufacture of tungsten carbide base hard facing materials.

The monocarbide (WC) is technically produced for large-scale use in cemented hard metals by carburizing tungsten metal powder with carbon black in carbon tube or, sometimes, in open high-frequency furnaces under hydrogen. Other methods of producing tungsten carbides include isolation from tungsten-bearing steels and iron, carburization of metallic tungsten or WO_3, carburization of tungsten wires using carbon monoxide or naphthalene vapors, and fused salt electrolysis in a manner similar to that used in the preparation of molybdenum carbides. Due to the importance of both tungsten metal and tungsten carbides, many different production methods that can be used for making tungsten carbides are known. Some of these, such as production of ammonium paratungstate from tungsten carbide scrap, are of practical importance in special cases. A number of others are mainly of academic interest. Schwarzkopf and Kieffer have given a lengthy review of carbide production methods for tungsten in 1953 (*298*) and again in 1960 (*303*).

In his extensive study of the tungsten-carbon system, published in 1965, Sara (*286*) used tungsten powder, Acheson graphite powder, and tungsten monocarbide (WC). The monocarbide analyzed 6.15% carbon, 0.11 % oxygen, and 93.72 % by weight tungsten. The tungsten analyzed 99.14 % W, 0.05 % C, and 0.90 % by weight oxygen. The graphite showed 99.99 % by weight carbon. After blending, the samples were prepared by hot- and cold-pressing. The hot-pressing was carried out in carbon molds at 1800°C under an argon atmosphere. Use of inert atmosphere enabled composition changes during processing to be held to within ±0.5 %. The cold-pressed samples were sintered in vacuum at 1100°C before being used at higher temperatures.

The two principal methods of study were differential thermal analysis and quenching studies. Phase analysis was by chemical, metallographic, and X-ray diffraction techniques. Temperatures were measured by means of a calibrated optical pyrometer. Metallographic and X-ray methods correlated directly in all cases. Due to precipitation taking place in most samples, lattice parameter measurements could not be used to establish solid solution ranges. This fact casts doubt on previously reported work for this system in which solid solubility was established by the lattice parameter method. Due to the extremely high temperatures involved and the problem of containing the melts, no attempt was made to establish liquidus relations for any region of the system.

The equilibrium relations of the system based in large part on one hundred and twenty-five quenching samples are shown as data points on the published diagram. Beginning at the tungsten side, the diagram shows a eutectic between W and W_2C occurring at a temperature of 2710°C. The eutectic liquid contains 25 atomic % carbon. No investigation has been made of the solubility of tungsten in carbon. The solubility of carbon in tungsten was reported by Goldschmidt and Brand (*116*) to be 0.3 atomic % carbon at the eutectic temperature, decreasing to about 0.05 atomic % near 2000°C and to trace amounts at lower temperatures. Goldschmidt and Brand used lattice parameter measurements and metallographic examination. No attempt was made by Sara to determine the solid solubility of carbon in tungsten. The extent of the W_2C solid solution field (simple hexagonal) was found, by Sara, to be much wider than was previously believed. At a temperature of 2795°C and a composition of 30 atomic % carbon ($W_{2.35}C$), Sara found a maximum on the solidus. This is in good accord with the classic work of Sykes (*340*), who gave the temperature of the W_2C maximum as between 2650 and 2750°C. No evidence was found by Sara with any of the methods he used—metallographic examination, differential thermal analysis, or X-ray diffractometry—of the existence of a high-temperature modification of W_2C, previously reported by several investigators including Goldschmidt and Brand in 1963. On the low-carbon side, the phase relations of W_2C are fairly simple. At the eutectic temperature (2710°C), the composition is about 26 atomic % tungsten ($W_{2.84}C$). With decreasing temperature, there is a slight increase in solid solubility of carbon to 28 atomic % at the lowest measured temperature (2460°C) for $W_{2.57}C$. The corresponding high-carbon limit at 2460°C for the W_2C solid solution field is $W_{2.00}C$. However, relations for the high-carbon side of this single-phase solid solution field are more complex. At a temperature of 2525°C, Sara found decomposition of a high-temperature form of WC (cubic beta WC) by a eutectoid reaction into alpha WC (simple hexagonal) of stoichiometric composition and into W_2C. Metallographic examination showed that at the eutectoid temperature W_2C could take carbon into solution. No attempt was made by Sara to find the maximum carbon solubility in W_2C at this temperature. The eutectoid composition is given as approximately 37.5 atomic % carbon. With increasing temperature, W_2C returns to the stoichiometric $W_{2.00}C$ at 2670°C and remains at this value to 2760°C, where it participates in another eutectic for which the eutectic liquid contains 36 atomic % carbon. The other solid freezing from this second eutectic is the high-temperature form of WC.

All samples containing over 38 atomic % carbon melted at temperatures above 2785°C. Differential thermal analysis showed that melting temperatures were virtually isothermal at approximately 2770°C, between W_2C and carbon. On the basis of metallographic examination of quenched samples containing 38, 40, and 45 atomic % carbon, it was concluded that the high-temperature cubic (beta) WC formed by a peritectic reaction at 2785°C from elemental carbon and a liquid containing about 40 atomic % carbon. Based upon metallography and differential thermal analysis, beta WC was found to decompose by a peritectoid reaction at 2755°C with carbon into alpha WC (hexagonal), which remained at nearly stoichiometric composition to the lowest temperature measured (2460°C).

The eutectoid decomposition of beta WC has been described. This reaction was first detected by a heat effect, observed on cooling for all compositions richer in carbon than W_2C, by differential thermal analysis methods. It was fully confirmed by metallographic examination, which showed typical eutectoid microstructures. Further metallographic studies on quenched samples, with compositions between 37.5 % and 50 atomic % carbon, showed that the solvus for the beta WC field extended over to alpha WC. Subsolidus quenching experiments, conducted on the tungsten-rich side of the field W_2C and beta WC at temperatures from 2550°C up to the solidus, showed coexistence of beta WC and W_2C up to the beginning of melting. On the basis of these findings, Sara concludes that the cubic high-temperature phase is the monocarbide and not W_2C as previously postulated by others. X-ray studies by microfocus methods on retained beta WC showed a face-centered cubic pattern with a lattice parameter of 4.215 Å. This was for a composition $WC_{0.82}$. No attempt was made to obtain a range of compositions and a correlation between cell constant and carbon content. Sara states that, from the metallographic evidence, beta WC may be thought of as having approximate limits of $0 \leqslant x \leqslant 0.41$ in WC_{1-x} at the solidus line. These limits change with decreasing temperature until the eutectoid temperature is reached at 2525°C and $x = 0.40$. No mention of the work of Orton (*249*) was made by Sara. According to Elliott (*88*), Orton found by thermodynamic calculations and reaction studies that W_2C decomposed by a eutectoid reaction at 1215°C into W and WC. Orton also found a peritectoid decomposition of WC into W_2C and carbon at 1315°C. These temperatures and reactions are very much different from those found by Sara. The experimental difficulties in detecting such heat effects by differential thermal analysis methods in this temperature range, well over 1000 degrees below the corresponding reactions studied by Sara, should have been very much less and therefore more easily detectable.

Cutting tools based on tungsten carbides were the first of this type of material to be introduced during World War I. Compositions based upon tungsten carbides continue to dominate the cutting tool field to the present time. The two most widely used types are WC plus WC-Mo_2C-TiC solid solutions and WC-TiC-TaC alloys. Although WC apparently does not have as great penetration hardness as TiC, the wear resistance and cutting action of WC-cobalt mixtures on short chip materials, such as cast iron, glass, and porcelain, lead to almost exclusive use of WC-Co in such applications. Due to the high density of tungsten and its carbides, they are generally used as an insert or refractory facing in applications where saving weight is of primary importance. As an example of such carbide coatings for tools and dies, Fellom (*102*) has described a spark discharge method by which a very thin WC coating is placed on the base metal, good shock resistance being obtained. A German patent granted to Frehn (*103*) describes the use of a small boron addition to tungsten carbide cobalt alloys that are to be used for plasma flame spraying. The boron aids by giving better and faster bonding to the base metal, and also suppresses undesirable decomposition of WC into carbon and W_2C.

B. ACETYLIDES

1. Calcium

Both $Ca(HC_2)_2$ and CaC_2 will be discussed in this section. The first of these substances was prepared by Moissan (*229*) in 1898 by the action of acetylene on calcium dissolved in liquid ammonia. More recent studies, particularly of stability of $Ca(HC_2)_2$, were made by Vaughn (*352*) in 1937 and by Corbellini and Turner (*70*) in 1960. The same method of preparation was used in these subsequent studies of the compound.

The second compound, CaC_2, has wide and important industrial and practical applications. The preparation, use, and chemical future of calcium carbide, as well as a full account of initial production of the substance, have been thoroughly covered by Scobie (*304*). In this article, the four long-recognized polymorphs of CaC_2 are listed as follows: CaC_2 "IV," cubic, stable above 447°C; CaC_2 "III" is known only as a metastable phase; below 25°C the form CaC_2 "II" is found; and tetragonal CaC_2 "I"—stable between 447 and 25°C—is the one most common in commercial calcium carbide. These polymorphic relations are in agreement with those published by Bredig (*48*) in 1942. In 1959 Borchert and Roder (*43*) published work based on Weissenberg and rotation X-ray diffractometry, indicating that the polymorphs II and III of the above scheme belonged to the tetragonal system, having very large unit cells ($a_0 = 23.40$ Å). The high-temperature polymorph IV, in agreement with previous work, was reported to be cubic. These two workers also expressed the view that the polymorph stable below about 435°C was III, and that I and II were metastable phases produced by "application of pressure." In his comments on the work of Borchert and Roder published in 1961, Bredig (*51*) states that the structure of the polymorphs II and III cannot be considered to be established, and that the tetragonal symmetry found by Borchert and Roder was in disagreement with earlier work indicating lower symmetry, perhaps triclinic for II. He strongly disagrees with the pressure relations of Borchert and Roder, and sets forth his views that the common tetragonal form I is stable from room temperature to around 450°C, and that the polymorph stable below room temperature, designated by Bredig as II, is one of lower symmetry.

2. *Sodium*

Both the carbides of sodium ($NaHC_2$, the hydroacetylide, and Na_2C_2, the dicarbide) were prepared and described by Berthelot (*33*) in 1866. The dicarbide, Na_2C_2, is a brown substance, usually prepared by carefully heating $NaHC_2$. The dicarbide has very little, if any, practical use. The hydroacetylide, $NaHC_2$, finds considerable use in organic syntheses such as the preparation of acetylenic carbinols and glycols. Preparation of $NaHC_2$ is usually by passing gaseous acetylene into liquid ammonia in which metallic sodium has been dissolved. Recently Ashby and Foster (*13*) used sodium hydroacetylide in the preparation of boranes.

C. REACTOR USE

1. *Uranium*

Uranium has three binary carbides, UC, U_2C_3, and UC_2. Obtaining the carbides of uranium, especially the monocarbide UC, in a condition in which there is freedom from dissolved oxygen or nitrogen is a difficult and not completely solved problem. The literature concerning the preparation and properties of the purest known uranium carbides has been critically reviewed through 1963 by Storms (*333*). Although a large amount of work has been done on the system uranium-carbon, the diagram is not yet completely established, particularly in composition ranges richer in carbon than the sesquicarbide, U_2C_3.

On the basis of extensive experience at Los Alamos, Storms states that UC and UC_2 can be prepared with a high degree of purity by arc melting uranium and carbon in an inert atmosphere, preferably one of helium. Carbon is used in the form of spectroscopic graphite, uranium as freshly cleaned metal. The ingredients are placed in a shallow depression on the copper furnace hearth. Air is evacuated, after which the system is filled with either argon or helium. For greater purity, the arc is struck with a carbon electrode rather than with tungsten; use of helium shortens the melting time and reduces carbon pickup. A zirconium button is usually melted first to further purify the inert gas. After this, the arc is transferred to the uranium carbon mixture. The button is usually turned on edge and remelted several times to ensure homogeneity. Mixtures of UC and UC_2 can be produced by reacting uranium with methane or propane. Using methane, the product below 650°C is mainly UC; above 900°C mostly UC_2 is obtained. Kalish and Litton (*169*) prepared a uranium carbide UC (4.4% by weight carbon) by carburizing uranium hydride with methane or propane. This product was suitable for use as a reactor fuel element. Preparation of uranium carbides from carbon and oxides of uranium is attractive from a cost standpoint, but the product thus obtained is impure and must be purified by arc melting or lengthy high-vacuum purification. Mallett (*201*) and others prepared master alloys containing up to 12% by weight carbon by heating UO_2 with monatomic carbon (Norblack) at temperatures of 1700–1900°C, using induction heating and a graphite container for the charge. These master alloys were mixed with uranium chips and then subjected to repeated arc melting for homogeneity and purity.

The monocarbide UC is face-centered cubic; UC_2 is cubic at high temperatures and tetragonal at low temperatures; the sesquicarbide U_2C_3, which seems to be a nearly stoichiometric compound, is body-centered cubic. Identification of the structure type by X-ray diffraction has been carried out by many investigators. In addition, the carbon positions in all three of the uranium carbides have been determined by neutron diffraction by both Austin (*19*) and Atoji and Medrud (*14*); the results are in good agreement and substantiate the X-ray difffraction results.

Preparation of U_2C_3 in a nearly pure form has presented difficulties. The compound is not usually found in material quenched from above 1800°C. By heating UC and UC_2 mixtures in the temperature range 1250–1800°C, and mechanically stressing the solid mixture, Mallett (*200*) showed that larger and larger amounts of U_2C_3 were produced as the theoretical composition (7.03% by weight carbon) was approached. The fact that mechanical stressing was essential in the production of U_2C_3 was also noted by later workers, but other factors are involved in its formation and retention. Henney *et al.* (*139*) suggested that ease of formation of U_2C_3 was a function of the nitrogen and oxygen content. The sesquicarbide apparently forms sluggishly after an incubation period by a process of nucleation and growth. This was the conclusion of Norreys (*243*), who followed the formation of U_2C_3 by the electrical resistivity method. Witteman and Bowman (*366*) also found that U_2C_3 formation was by nucleation and growth. The method used by Witteman and Bowman to follow the formation of U_2C_3 was a refined thermal analysis method, in which the negative of the slope of the first derivative of the cooling curve was simultaneously displayed on the oscilloscope screen with the cooling curve itself. This greatly increased the ability to detect solid state changes. On the other hand, Gillam (*110*) suggested that U_2C_3 may form from UC_2 by a slight shift in the position of the uranium atoms and that, although the transformation is sluggish, it is of a diffusionless shear or martensitic type.

Many of the features of the uranium carbon phase diagram are still in dispute, but the tentative diagrams of Storms (*334*) and Bowman (*46*) are recent, and seem to be accepted. The following list of the principal features of the U-C system is based upon the discussion of Storms:

(a) Uranium metal melts at 1132°C. The solidified metal has three crystal forms, the transition from alpha (orthorhombic) to beta (tetragonal) taking place at 667°C. The second transition from beta to gamma (body-centered cubic) is at 775°C. Addition of carbon lowers the transitions to eutectoids at 665.9 and 771.8°C, respectively. The solubility of carbon in uranium is very slight, not over 185 ppm at the eutectic temperature 1117°C. The values quoted are based on the careful and accurate work of Blumenthal (*40*) and his associates.

(b) From the eutectic point, which is placed by Blumenthal at 500 ppm by weight carbon (0.98 atomic % carbon), the liquidus rises sharply to a maximum at about 2550°C near stoichiometric UC. This portion of the liquidus was redetermined by Blum (*39*) in 1965. Based on experimental points to 2400°C, Blum extrapolates to a maximum for stoichiometric UC at about 2550°C. Storms shows a maximum at 2560°C for $UC_{1.0}$.

(c) There is retrograde solubility along the portion of the solidus between the UC maximum and the eutectic at 1116.6°C. Blum places the minimum at 4.36% by weight carbon ($UC_{0.94}$) and at a temperature of about 2150°C. Below 1500°C, the solidus rejoins the composition vertical for UC (stoichiometric) down to the eutectic temperature. This last statement varies slightly from the diagram of Storms, who shows a dashed and therefore uncertain region of "cubic solid solution" that does not rejoin the $UC_{1.0}$ vertical until the eutectoid at 665.9°C is reached upon cooling.

(d) There are three compounds, UC, U_2C_3, and UC_2, in the uranium carbon system. UC is face-centered cubic and stable (although it may contain oxygen and nitrogen and be either hypostoichiometric or hyperstoichiometric as well) from room temperature to its melting point, the value of this maximum melting having been discussed under (b). The sesquicarbide U_2C_3 is body-centered cubic and decomposes without melting at about 1800°C. The dicarbide UC_2 is stable from about 1500°C to its melting range, which is placed by Storms above 2450°C. There is also a crystal structure change in UC_2 from tetragonal (below) to cubic (above) near 1785°C. The portion of the diagram in which this takes place is uncertain and therefore left blank by Storms and Bowman. Elliott (*89*), from the literature published through 1961, gives the transition temperature of UC_2 as 1820°C and shows a eutectoid at 61.6 atomic % carbon occurring at 1800°C. The "cubic solid solution" of Storms [mentioned under (b)] decomposes at this eutectoid point to UC and tetragonal UC_2 according to the diagram proposed by Elliott. Elliott's diagram also agrees very closely with the U-C phase diagram of Chubb and Dickerson (*64*), published in 1963.

(e) Between the stoichiometric compositions of UC and UC_2, there is a minimum melting solid solution. The temperature of the minimum is placed by Storms at near 2450°C with a composition approximately $UC_{1.5}$. Elliott places this minimum at 57.5 atomic % carbon and at a temperature of 2350°C.

(f) The sesquicarbide U_2C_3 apparently decomposes by a peritectoid reaction at a temperature slightly below 1800°C. Storms shows the vertical as a solid line, indicating that the peritectoid decomposition is fairly certain, but does not indicate the temperature of the peritectoid horizontal. This value is given by Elliott as 1775°C; Elliott shows the U_2C_3 vertical dashed and therefore uncertain above 1400°C.

(g) Above 1800°C, there is a "hat-shaped" solid region containing UC and beta (cubic) UC_2. This miscibility gap rises to a maximum. The temperature of the maximum and the composition limits of this two-phase solid region constitute one of the greater uncertainties of the U-C system. Storms places the maximum at 2050°C and at $UC_{1.35 \pm 0.05}$ with the lower boundary at 1800°C extending from $UC_{1.06}$ to about $UC_{1.6}$. Later work by Sears (*306*) and others places the maximum above 2090°C, the decomposition horizontal at 1820°C, and the miscibility gap limits between $UC_{1.1}$ and $UC_{1.2}$ on the uranium-rich side, and at about $UC_{1.65}$ on the carbon-rich side.

The retrogression of the solidus along the carbon-rich boundary of the liquid plus UC phase field may be influenced by the presence of dissolved oxygen, particularly if any free uranium is present that could increase the ease with which oxygen will dissolve. The resulting U(C, O) solution, if heated in a vacuum in the absence of any free UO_2, could form free uranium with evolution of CO. This retrograde behavior was first suggested by Buckley (*56*) in 1961, from examination of quenched alloys in the UC composition range that contained various impurities, as well as free uranium. Buckley also found that rapidly quenched UC was a defect structure. From the behavior of the lattice parameter, he suspected a retrograde behavior of this portion of the solidus. The retrogression was found, experimentally, by Magnier and Accary (*198*) in 1963. They ascribed this behavior to formation of an unidentified compound by a peritectic reaction. No experimental support for such behavior has been found, according to Storms.

Two other points in connection with the presence of oxygen in the U-C system will be briefly mentioned. The first is the maximum in the lattice parameter of UC. This was first reported by Accary (*2*) in 1963. He found that the lattice parameter rose from 4.9598 Å for his purest sample to 4.9613 Å for UC containing 1800 ppm by weight of oxygen. This behavior has been found by several other investigators, including Anselin and his co-workers (*9*). After the maximum is passed, the lattice parameter rapidly decreases to a saturation value, reported by Stoops and Hamme (*322*) in 1964 to be 4.9519 Å.

The second point is the presence of dissolved "UO" in compositions near $UC_{1.0}$. Uranium monoxide of stoichiometric composition is not known as an isolated stable phase. In what is properly the ternary system U-C-O, the limits found for a single U(C, O) phase in equilibrium with UO_2 and U below 1400°C range from compositions as low as $UC_{0.75}O_{0.25}$, as reported by Stoops and Hamme, to as high as $UC_{0.2}O_{0.8}$, reported by Sano (*284*) in 1963. On the other hand, Anselin states that UC in equilibrium with U_2C_3 and UO_2 can dissolve no more than about 5 atomic %

oxygen, while UC_2 and U_2C_3 dissolve essentially no oxygen. Other factors discussed by Storms, which affect solubility and ease of solution of oxygen, include stoichiometry of the UC, annealing temperature, and CO pressure. The difficulty of excluding all oxygen affects both the high- and low-carbon UC phase boundaries as well as the lattice parameter.

Nitrogen is essentially insoluble in UC_2 and U_2C_3. The effect of nitrogen on the lattice parameter of UC above 1200°C is one of contraction, the opposite of the effect of oxygen. In fact, all or any part of the carbon atoms in UC can be replaced by nitrogen. It was found by Rough and Chubb (*273*) that nitrogen reacts with the molten carbide to displace carbon from the monocarbide and produce some UC_2. If such behavior of nitrogen is not known and taken into account, a low and incorrect value would thus be obtained in attempting to locate the high-carbon UC phase boundary.

In conclusion, two recent applications and nonresearch aspects of uranium carbides will be reviewed. The first of these is pilot production of slightly hypostoichiometric UC by a fluidized bed technique (*257*). Finely divided uranium metal particles were reacted in a stainless steel vessel, using hydrogen propane atmospheres and pressures of 1, 10, and 20 atmospheres. Temperatures used were 600, 700, and 750°C with times ranging from 3 to 20 hours. Stoichiometric UC could be obtained and was produced. The advantage for reactor fuel elements of a uranium monocarbide slightly less than $UC_{1.0}$ is that there is greater compatibility with the stainless steel cladding, as well as less carbon present that might diffuse to the cladding wall and cause detrimental grain boundary corrosion of the stainless steel. The low-melting uranium metal resulting from such monocarbide decomposition would also tend to cause premature failure of the reactor fuel elements.

Uranium carbide in combination with zirconium carbide (UC-ZrC) has also been studied with regard to fabrication, cladding, diffusion, and fission product release both as a fuel and in connection with thermionic emission for space power applications (*369*). Many of the problems encountered in using uranium carbides and those of other metals in reactors are discussed in the two-volume work edited by Russell (*281*).

D. First Transition Group Metals

1. *Manganese*

The carbides of manganese in isolated form have practically no use. They are important in steels and other ferrous alloys, either as compounds of manganese and carbon, or in more complex metallic alloys in which manganese is one of the metallic elements of the carbide. In analogy to cementite (Fe_3C), the manganese carbide known and studied for the longest period of time has often been assigned the formula Mn_3C. However, there is not general agreement on the number of carbides in the system Mn-C, their formulas, and crystal structures. The early studies of manganese carbides were upon material obtained by acid or electrolytic isolation from steels and cast irons. Most of the work published during the past 15 years has been on carbides prepared from distilled manganese and graphite or sugar charcoal. The volatility of manganese, attack upon the refractories, and affinity of manganese for oxygen and nitrogen have complicated the problem of obtaining the manganese carbides as pure substances of definite composition.

The diagram of the manganese-carbon system shown by Hansen (*133*) is based on the work of Isobe (*159*) and Kuo and Persson (*184*). Older diagrams did not show the four polymorphic forms of manganese. Considerable efforts have been made, with varying degrees of success, to show that carbides of manganese are isomorphous with carbides, nitrides, and other compounds of other elements, particularly those of iron and chromium, which are the horizontal nearest neighbors of manganese in the periodic table.

The table of Kuo and Persson, published in 1954 and reproduced by Hansen, shows five manganese carbides. In order of increasing carbon content, these are: $Mn_{23}C_6$ of cubic structure, presumably isomorphous with $Cr_{23}C_6$; a carbide of unknown crystal structure, stable at 850–1000°C, to which Kuo assigned the formula Mn_7C_2 (22.22 atomic % carbon); Mn_3C orthorhombic and isomorphous with Fe_3C; Mn_5C_2 monoclinic and stable up to 1050°C; and, finally, Mn_7C_3 trigonal and isomorphous with Cr_7C_3.

In 1957 Picon and Flahaut (*259*) published the results of a study of the carbides of manganese in which analytical and X-ray diffraction methods were used. They were unable to index the carbide that was richest in manganese as cubic with formula $Mn_{23}C_6$, finding that their diffraction patterns were consistent with a tetragonal structure to which they assigned the formula Mn_4C. Two carbides having the formula Mn_6C_2 were obtained. One of these was orthorhombic, having lattice parameters in good agreement with those published by Kuo. Picon and Flahaut indexed the other carbide of formula Mn_6C_2 as belonging to the hexagonal system. Three other carbides of formula Mn_8C_3, with structures in order of increasing carbon content triclinic, hexagonal, and cubic, respectively, were also found by these two investigators, making a total of six different carbides in the system Mn-C. In commenting on this work, Elliott (*90*) stated that it was not definitive enough to warrant changes in the equilibrium diagram proposed by Hansen.

The agreement in the case of Mn_3C shown between the results of Picon and Flahaut and of Kuo does not seem to be disputed by later researchers. Investigations by Senateur and others (*309*) in 1962, as well as by Jack (*160*) and Duggin and Hofer (*78*) in 1966, confirm the existence of monoclinic Mn_5C_2 as suggested by Kuo. The carbide of unknown structure to which Kuo and Persson tentatively assigned the formula Mn_7C_2 was prepared and studied by Bouchard and Fruchart (*44*) in 1964. From the results of Seeman-Bohlin powder patterns (iron K alpha radiation) and from chemical analysis and density determinations, a formula $Mn_{15}C_4$ with a hexagonal unit cell ($a_0 = 7.492$ Å, $c_0 = 12.070$ Å) was found to fit their results.

Bouchard and Fruchart (*45*) also re-examined the region of the Mn-C system in which Picon and Flahaut found three manganese carbides having the formula Mn_8C_3. The results of these two studies were not in agreement, for the portion of the system where manganese was present associated with quantities of carbon greater than or equal to the concentration of Mn_7C_3. From temperatures averaging 850°C, Bouchard and Fruchart found a trigonal carbide Mn_7C_3 in agreement with the work of Kuo and Persson. If the same manganese carbon mixtures were heated above 900°C and cooled slowly, only one phase was again obtained and not a mixture of three phases. However, this last carbide gave a Seeman-Bohlin powder pattern in which intensities did not vary with the manganese : carbon ratio, but the pattern was more complex than that of the 850°C product. This slowly cooled phase was determined by Bouchard and Fruchart to have an orthorhombic pseudohexagonal structure. They also pointed out that the structure thus assigned to Mn_7C_3 was very similar to the structures assigned to Ru_7B_3 and Cr_7C_3. The work of Fruchart and his collaborators also agrees with that of Kuo in the existence of $Mn_{23}C_6$ isomorphous with $Cr_{23}C_6$.

In summary, the bulk of the evidence at the present time seems to indicate the existence of five carbides of manganese: $Mn_{23}C_6$ cubic, Mn_3C orthorhombic, Mn_5C_2 monoclinic, Mn_7C_3 orthorhombic pseudohexagonal, and $Mn_{15}C_4$ of hexagonal symmetry corresponding to the Mn_7C_2 of unknown crystal structure reported by Kuo and Persson.

2. *Iron*

The enormous literature on the carbides of iron contains numerous fragmentary references to carbides with various suggested formulas not subsequently confirmed. The review on the nature of iron carbides published by Hofer (*149*) in 1966 after 20 years of work in the field obviates the necessity of discussing various unconfirmed iron carbides. The only carbide of iron that forms from ordinary atmospheric cooling of liquid iron-carbon melts is cementite, Fe_3C, now called theta iron carbide. The "iron-carbon" diagram is usually terminated for this reason at the carbon content corresponding to Fe_3C (6.7 % by weight carbon). There is also no point in discussing here the iron-carbon diagram. The reviews given by Hansen (*134*) and Elliott (*91*) selectively summarize the many noteworthy papers concerning the metastable iron-iron carbide and the stable iron-graphite systems. The crystal structure of cementite is orthorhombic and the analysis of its structure published by Lipson and Petch in 1940 (*191*) is still accepted.

Hofer discusses five iron carbides, cementite (theta), hexagonal close-packed iron carbide (epsilon), Hagg carbide (chi), Eckstrom and Adcock carbide (FeC), and Pomey carbide (hexagonal). Except for cementite, these carbides mainly find uses as catalysts in syntheses, such as the Fischer-Tropsch, which produce higher hydrocarbons and waxes from hydrogen and carbon monoxide. In fact, the Eckstrom and Adcock carbide has been found only in the catalysts of synthetic liquid fuel installations and had not been separately synthesized in the laboratory by 1965. Epsilon iron carbide is also formed during the tempering of hardened martensitic steels, and a large number of papers concerning the relations of epsilon iron carbide in the tempering processes have appeared during the last 20 years. Greek letter distinction of the iron carbides has been suggested to reduce some of the confusion in the literature, and to designate the three most common carbides. As was previously mentioned, both Pomey carbide and epsilon carbide are characterized as belonging to the hexagonal system.

Epsilon iron carbide is quantitatively formed by the reaction of the carbon in carbon monoxide with finely divided alpha iron at temperatures near 170°C. The composition of the product thus formed is within 2 atomic % carbon of Fe_2C. The structure is quite simple and analysis of the powder X-ray diffraction pattern gives an unambiguous determination of a close-packed hexagonal structure. The carbide formed during the tempering of steels seems to be lower in carbon content, one suggested formula being $Fe_{2.4}C$. The variation in carbon content can be explained by analogy with the iron-nitrogen system, if epsilon carbide is assumed to be a nonstoichiometric compound in which there is variation, from nearly three iron atoms per carbon atom to two iron atoms per carbon atom at the other end of the range. Since decomposition occurs near the Curie temperature of epsilon carbide, this cannot be precisely determined, but is not more than 20 degrees above 380°C.

Chi iron carbide can be obtained in a condition free of detectable traces of epsilon iron carbide by allowing carbon monoxide to react with finely divided alpha iron at a temperature near 230°C. This carbide can also be produced by isothermal vacuum decomposition of epsilon carbide at temperatures above 230°C. Above about 420°C, the chi iron carbide formed by such a process decomposes, in turn, to theta iron carbide. The powder diffraction pattern of chi iron carbide (formula assigned Fe_2C without insistence upon stoichiometry) has been indexed as belonging to the orthorhombic system, but the lattice parameters thus obtained are rather large. According to Hofer, the indexing, crystal class, and lattice parameters of chi iron carbide are questionable. However, the Curie temperature is known accurately as 247°C, which compares with 210°C for cementite and near 380°C for epsilon carbide. However, a number of techniques, such as X-ray diffraction, gravimetric carbiding studies, thermomagnetic measurements, studies on oxides and nitrides, and information obtained from the tempering of steels, must also be taken into account in distinguishing and characterizing the carbides of iron.

The Pomey (*262*) carbide has been known only since 1954, and was found in connection with the study of bainitic transformations in steels. Extensive studies of this carbide (which is also assigned the formula Fe_2C) have not been made. Determinations of the Curie point as 380°C and of a hexagonal structure from a powder X-ray diffraction pattern are based upon material electrolytically extracted from heat-treated steel (*263*).

The Eckstrom and Adcock (*84*) carbide seems to have a composition near FeC and a Curie point of about 250°C. According to Hofer, attempts to synthesize this carbide in an isolated form in the laboratory have so far been unsuccessful.

3. *Cobalt*

Probably the most important use of cobalt carbides is as part of mixed carbides such as Co_3W_3C in tool steels and high-speed steels. The isolated carbides of cobalt have been studied mainly in connection with the Fischer-Tropsch process. Catalysts based upon cobalt were standard for this synthesis in Germany from about 1938 to 1944, but have been superseded since that time both in Germany and elsewhere by catalysts based upon iron, which are cheaper in first cost and more flexible. The carbon-cobalt phase diagram has been reviewed by Hansen (*135*) and supplemented through 1961 by Elliott (*92*). There is evidence of terminal solid solubility of carbon in cobalt and of a eutectic of cobalt with graphite. Hansen places this eutectic at 1309°C and at a composition of 10.8 atomic % carbon in his partial carbon-cobalt diagram.

The preparation of a cobalt carbide Co_2C was reported by Bahr and Jessen (*25*) in 1930. By allowing carbon monoxide to react with finely divided cobalt below 225°C, a product containing 9.25% by weight carbon (which is the amount for the formula Co_2C) was obtained after some 400 hours. No further gain in weight was experienced in this temperature range for times nearly double 400 hours. The work of Bahr and Jessen was repeated by Hofer and Peebles (*145*) in 1947. From X-ray diffraction patterns of their Co_2C, Hofer and Peebles concluded that the structure was orthorhombic with a narrow composition range. This carbide preparation was repeated by several other sets of research workers between 1947 and 1952. Considering the catalytic nature of the carbide formation, good agreement was obtained for the orthorhombic lattice parameters. In addition, Drain and Michel (*77*) determined that the structure of Co_2C was isotypic with Co_2N, whose structure had been established by Juza and Sachse (*166*) in 1945.

In 1937 Meyer (*206*) reported a carbide Co_3C prepared by carburizing cobalt with illuminating gas at temperatures of 450°–600°C. The identification of the carbide as Co_3C was based on an X-ray diffraction pattern nearly identical with cementite Fe_3C. In commenting on the work of Meyer, Hofer states (*147*) that, in performing similar experiments, he and his associates never found such a cementite-like carbide. In 1961 Nagakura (*238*) carburized thin evaporated films of cobalt with illuminating gas for several hours at temperatures below 550°C. He found two orthorhombic carbides, identified by electron diffraction, having formulas of Co_2C and Co_3C. Nagakura's values for Co_3C showed reasonably good agreement with those of Meyer, and for Co_2C with those tabulated by Hofer.

4. *Nickel*

There is agreement on the existence of a single carbide of nickel having a hexagonal structure and the formula Ni_3C. Hofer (*148*) mentions other reported but unconfirmed carbides such as Ni_6C. Attempts to establish the structure of Ni_3C as orthorhombic rather than hexagonal, partially by analogy with cementite (Fe_3C), have failed. Some question has also been raised as to the stability of nickel carbide. This is answered, to some extent, by the results of Nagakura (*237*). In 1957 he published results of formation of Ni_3C by carburizing thin nickel films below 450°C. He found that the lattice parameters of the Ni_3C prepared in this way were those of a hexagonal structure, and that they remained unchanged after 1 year.

One of the first reported preparations of nickel carbide was by Bahr and Bahr (*24*) in 1928. The preparation was similar to that of cobalt carbide. Finely divided nickel was treated with carbon monoxide at 250 or 270°C. The curve of % carbon absorbed against time became horizontal at the composition Ni_3C. A limited use of nickel as a catalyst in early developments of the Fischer-Tropsch process led to other studies involving nickel carbide. After 1945, the development of the cheaper and more flexible iron catalysts made the study of nickel catalysts and nickel carbide of only academic interest. The reaction between nickel and carbon monoxide has recently been studied by Escoubes (*97*) and his associates. Temperatures below 330°C and pure finely divided nickel were found essential to formation of Ni_3C.

In an initial report on high-pressure synthesis of diamond, Strong (*338*) mentions the formation of nickel carbide in some instances. There is also evidence that nickel-carbon melts, especially under high pressure, act in a manner similar to iron and carbon, forming two eutectics, one with graphite and another with nickel carbide.

IV. Binary Carbides of the Other Metals

A. Elements with Established Carbides without Use

1. *The Alkali Metals*

Except for the use of $NaHC_2$ in organic syntheses, the carbides of the other alkali metals—lithium, potassium, rubidium, and cesium—seem to be without application. It seems pertinent to mention the "interstitials" or "insertion compounds" of these metals. These substances are excluded from this review as being chemically different from the carbides of alkali and other metals, which show nearly stoichiometric compositions involving small numbers of metal and carbon atoms. The "interstitial" compounds, also sometimes called "graphites," are assigned formulas such as KC_8, CsC_{16}, and RbC_{16}. They have been reviewed at length by Hennig (*142*). Other insertion products of lithium, sodium, and potassium with graphite have recently been found by Stein (*321*).

a. Lithium. The acetylide of lithium was prepared by Moissan (*229*) by passing acetylene into liquid ammonia containing dissolved lithium. The product was obtained in the form of transparent crystals, which Moissan analyzed. He also prepared the carbide Li_2C_2 by heating lithium carbonate and carbon in an electric furnace, using a carbon tube closed at one end as a container. The results of two recent preparations and structure determinations of Li_2C_2 are in disagreement. In 1962 Secrist (*307*) prepared single crystals of the carbide by heating lithium and graphite in an argon atmosphere at 700°C, using an iron capsule as a container. From Weissenberg photographs the structure of Li_2C_2 was found to be monoclinic. However, in 1965 Juza and Volker (*167*) made a structure determination of Li_2C_2, which they reported as of 98.8–99.2% purity.

They obtained good agreement between measured and calculated densities for an orthorhombic structure. The lattice parameters obtained showed large differences from the parameters of Li_2C_2 published by Secrist.

b. Potassium. The acetylide of potassium KHC_2 is prepared by reaction of acetylene with potassium dissolved in liquid ammonia. The dicarbide K_2C_2 is obtained by careful heating of potassium acetylide. The acetylide has been determined to be face-centered tetragonal; one of the first determinations of this structure was by von Stackelberg (*318*) in 1930.

c, d. Rubidium and Cesium. Moissan (*229*) prepared $RbHC_2$, Rb_2C_2, $CsHC_2$, and CsC_2 by the same methods as for potassium acetylide and carbide. In 1960 these four substances were prepared by Corbellini and Turner (*70*), using the Moissan techniques. A study of the stability of the hydroacetylides (MHC_2) of the alkali metals at 20°C showed KHC_2 to be the most stable, $NaHC_2$ the least stable, with the rubidium and cesium acetylides occupying intermediate positions.

2. *Alkaline Earths; Beryllium and Aluminum*

a. Beryllium. Most of the published work is for diberyllium carbide, Be_2C. The reduction of BeO with carbon yielding Be_2C was thermodynamically studied by Motzfeldt (*234*) in 1964 over the temperature range 1500°–2050°C. The melting point of this carbide was reported by Hansen (*136*) to be near 2400°C. Reduction of beryllia with carbon was used by Lebeau (*187*) in 1895 and by Moissan (*215*) to produce a beryllium carbide to which they assigned the formula Be_4C_3. Moissan used two electrical furnace methods, heating the mineral beryl in a carbon tube and mixing beryl and calcium carbide, then heating the mixture electrically. Recently a patent was granted to Schwartz (*290*) covering the use of Be_2C as part of a reactor core material used with a ceramic coating to prevent oxidation. Preparation of beryllium dicarbide (BeC_2) by passing acetylene over beryllium powder heated to 450°–600°C was reported by Durand (*81*) in 1924.

b. Magnesium. An impure magnesium carbide prepared by passing acetylene gas over magnesium powder was reported by Berthelot (*33*) in 1866. Moissan (*228*) also prepared magnesium carbide by this method in 1898. Two magnesium carbides, MgC_2 and Mg_2C_3, were established by the work of Novak (*244*) in 1910. Both of these carbides were also prepared and studied by Bredig (*49*) in 1943 and Schneider and Cordes (*288*) in 1955. The tetragonal MgC_2 can be prepared by heating a ternary mixture of $MgCl_2$, calcium carbide, and NaCl above the ternary eutectic at 425°C, or by passing pentane vapors over molten magnesium at a temperature of 700°C, In 1964 Jonich and Reu (*165*) reported preparation of Mg_2C_3 by dipping graphite yarn in a magnesium solution and then exploding the "wire" of graphite by charged capacitors. Bredig prepared Mg_2C_3 by passing acetylene over magnesium shavings held at 500°C.

c. Strontium. Preparation of $Sr(HC_2)_2$, by passing acetylene into a liquid ammonia solution containing strontium and subsequent decomposition of the acetylide into SrC_2, was also investigated by Corbellini and Turner in 1960. The acetylides of the alkaline earths were found to be less stable than those of the alkali metals. At 20°C, a reduced pressure (0.5 mm Hg) was found to be favorable for decomposition of strontium acetylide. About 20 hours were necessary for complete formation of SrC_2. At present there seems to be little interest in the carbides of strontium, which have been known since the time of Moissan.

Bredig (*48*) included a tabulation of the different crystalline forms of strontium and barium carbides in his study of the polymorphs of calcium carbide. For strontium these were: SrC_2 face-centered cubic, stable above 370°C and unstable below this temperature; SrC_2(I), face-centered tetragonal, metastable below –30°C, stable from –30 to 370°C, and unstable above 370°C; SrC_2(II) of unknown crystal structure, stable below –30°C, metastable from –30°C to an unknown upper limit, completely unstable above 370°C. Small amounts of impurities cause marked changes in stability ranges.

d. Barium. As would be expected, there are marked similarities between strontium and barium carbides. The same methods of preparation produce barium acetylide $Ba(HC_2)$ and the carbide BaC_2. The stability of barium acetylide is very small. Vaughn (*352*) found that $Ba(HC_2)_2$ decomposed at ambient temperature under an atmosphere of ammonia in a few minutes. By comparison, the corresponding sodium acetylide $NaHC_2$ remained white and undecomposed for 10 hours in dry air at room temperature. Bredig reported two polymorphs of BaC_2, a face centered cubic form stable above 150°C (±50°C), unstable below this range on slow cooling, and metastable on quenching in the same temperature interval. The other form, BaC_2(I), was found to be face-centered tetragonal, unstable above 150°C (±50°C) and stable below this range. In 1964 Nelson and others (*240*) used BaC_2 containing radioactive carbon-14 in a study of the permeation of polymer films. Hydrolysis of the barium carbide yielded acetylene containing tagged carbon atoms and barium hydroxide.

e. Aluminum. In 1924 Durand (*81*) reported preparation of an aluminum acetylide $Al_2(C_2)_3$ by passing acetylene over finely divided aluminum at a temperature of 450°–500°C. Most of the work on aluminum carbide has been done on Al_4C_3, which was prepared by Moissan (*223*) in 1894 by heating aluminum and carbon in the electric furnace. Many later workers have also used this method. A different and somewhat novel method for making hexagonal Al_4C_3 was reported by Horiguchi (*152*) in 1966. The carbide was prepared by causing reaction between aluminum powder and acetylene black by means of an explosive charge. The hexagonal crystal structure of Al_4C_3 was determined by von Stackelberg (*319*) in 1934 and has been confirmed by the results of many subsequent investigations, including that of Cox and Pidgeon (*71*) in 1963.

3. *Lanthanides; Scandium and Yttrium*

Scandium and yttrium, together with lanthanum, which are vertically above each other in the Periodic Table, are included here with the fourteen rare earth elements from cerium through lutetium. The only element for which a monocarbide is generally agreed upon is ScC for scandium. No mention of any carbides of promethium was found in the literature, so this element is excluded from this section of the review. A dicarbide of europium EuC_2 has recently been prepared and similar dicarbides, such as YC_2, LaC_2, and GdC_2, are known for all of these elements except scandium and promethium. Most of these dicarbides are tetragonal in crystal structure, having a structure type similar to calcium chloride. Cubic sesquicarbides, such as Pr_2C_3 (isotypic with Pu_2C_3), have been shown to exist for lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, and dysprosium. Holmium carbide was found by Spedding and others (*316*) to be dimorphic, showing both a cubic structure of plutonium sesquicarbide type and a structure similar to Y_2C_3. The structure of Y_2C_3 is also shown by the sesquicarbides of erbium, thulium, and lutetium. The symmetry of these sesquicarbides is lower than tetragonal or hexagonal, and has not been determined. Tri-rare earth carbides such as Sm_3C were prepared by Spedding and others (*316*) for all of the elements from samarium, atomic number 62, through lutetium, atomic number 71, with the exception of europium. The structure of these tri-rare earth carbides was of an iron nitride (Fe_4N) type belonging to the cubic system. Many of these metal-rich carbides show a considerable range of carbon solubility with M_3C (M = metal) usually being found near the center of the range of composition.

In 1964 Dean and others (*74*) published the results of X-ray studies of the carbides of gadolinium, dysprosium, holmium, erbium, and yttrium, showing the existence of rhombohedral Gd_2C, Dy_2C, Ho_2C, Er_2C, and Y_2C. In addition to information from X-ray diffraction studies, some of the dicarbides (e.g., CeC_2) and sesquicarbides (e.g., Tb_2C_3) have been studied by neutron diffraction methods. This will be noted below for the carbides for which such neutron diffraction studies have been published.

Most of the dicarbides, sesquicarbides, and tri-rare earth carbides

(Y_3C) were prepared by compressing filings of the purified metal with carbon and arc melting the resulting compact. The precautions taken with these reactive rare earth metals and other details of carbide preparation are given by Spedding and his associates (*316*). Arc melting was done under a helium or argon atmosphere, and glove boxes with positive pressure and an inert atmosphere were also necessary. In order to avoid repetition, carbides that can be prepared by arc melting of the metal (or, in some cases, the oxide) with carbon will not be described for each element. Special preparation methods (such as the tantalum bomb method for carbides of samarium, thulium, europium, and ytterbium) will be outlined.

a. Scandium. The carbide of formula Sc_4C_3 reported in 1925 by Friederich and Sittig (*104*) was not subsequently confirmed. Preparation of ScC by heating Sc_2O_3 and carbon above 1500°C was accomplished by Vickery and his co-workers (*356*) in 1959. A similar preparation was made by Nowotny and Auer-Welsbach (*18*) in 1961. In this last investigation, a carbide that reached stoichiometric ScC was not obtained, and it was suggested that a formula such as Sc(C, O) or ScC_{1-x} might be in better accord with the experimental results. Vickery reported ScC as hexagonal, Nowotny cubic scandium monocarbide. Another preparation of ScC made by Samsonov and others (*283*) was reported to produce a cubic product. All of these structures were based upon powder X-ray diffraction patterns and, as Vickery pointed out, an unambiguous determination of crystal structure would require single crystals of scandium monocarbide. Such a determination apparently has not been made and published.

b. Yttrium. The dicarbide of yttrium YC_2 has been known since its preparation by Moissan and Etard in 1896 (*226*). The determination of the crystal structure as body-centered tetragonal, of calcium chloride type, is based upon X-ray diffraction work by several investigators including Gschneidner (*316*) and confirmed by the neutron diffraction determination made by Atoji (*15*). The existence of yttrium sesquicarbide Y_2C_3 is not questioned. As reported by Gschneidner (*124*), the symmetry is lower than tetragonal or hexagonal, similar to the sesquicarbides of erbium, thulium, and lutetium and not fully worked out or determined.

Samsonov and others (*179*, *283*) have published two reports of the preparations of a monocarbide YC. In the first, published in 1962, YC was prepared by heating Y_2O_3 with carbon *in vacuo*. The formation temperature of YC thus prepared was reported as 1800°–1900°C. The melting point of yttrium monocarbide was stated to be $1900° \pm 50°C$. In the second report published in 1964, Y_2O_3 was reduced with CO *in vacuo*. At a temperature of approximately 1700°C an oxycarbide, to which the formula Y_2C_2O was assigned, apparently formed, which decomposed at approximately 1900°C to YC and CO. Support for the existence of such an oxycarbide came from room temperature oxidation studies. When YC was oxidized there was an initial increase in weight, indicating oxycarbide formation; on the other hand, when YC_2 was similarly oxidized there was a continuous loss of weight.

As a result of microscope studies of some low yttrium-carbon alloys, a face-centered cubic carbide covering a range from $YC_{0.25}$ to $YC_{0.40}$ (Y_4C to Y_5C_2) was found by Spedding and others (*316*). Since the composition Y_3C is approximately midway between these solubility limits, this carbide was termed "triyttrium carbide." No evidence of any ordered structure was found in the powder X-ray diffraction patterns of this carbide of yttrium or for the similar tri-rare earth carbides of samarium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Spedding and his associates suggested that the atoms of lanthanum, cerium, praseodymium, and neodymium were too large to permit formation of tri-rare earth carbides.

In the 1964 study of the yttrium carbon system by Dean and his coworkers (*74*), the interval $YC_{0.30}$ to $YC_{0.65}$ was re-examined. The published work also covered a similar composition range for the systems of gadolinium, dysprosium, holmium, and erbium with carbon. It was found that, as carbon was increased from metal-$C_{0.3}$, the face-centered cubic structure in which the carbon atoms were randomly arranged changed, particularly in the vicinity of metal-$C_{0.5}$ (e.g., Y_2C), to a distorted rhombohedral structure. This change was explained as being due to an ordering of the carbon atoms. Samples prepared at low temperatures (800°–1300°C) were found to be M_2C to the exclusion of MC. The rhombohedral phase was found to disappear at about metal-$C_{0.6}$. High temperatures and compositions far from $MC_{0.5}$ tended to prevent the formation of the rhombohedral phase. However, for some compositions in the vicinity of $MC_{0.5}$, the rhombohedral structure was found to persist even after arc melting and subsequent solidification. The rhombohedral determination was based upon the appearance of single, double, and triple diffraction lines, which indexed much better for a rhombohedral than for a face-centered cubic unit cell.

c. Lanthanum. Lanthanum has two carbides, the dicarbide LaC_2, body-centered tetragonal of calcium chloride type, and a sesquicarbide La_2C_3, cubic and of Pu_2C_3 structural type. Neutron diffraction studies by Atoji (*17*) confirm the structures determined by X-ray diffraction. A phase diagram for the lanthanum-carbon system has been published by Spedding and others (*317*), covering the lanthanum-rich part of the diagram which includes both carbides. At a temperature of 0°C, both La_2C_3 and LaC_2 exist over composition ranges of 1–2 weight % carbon.

La_2C_3 decomposes peritectically at 1415°C into liquid and LaC_2, which at that temperature contains 12.8 % carbon. Up to a temperature of about 1200°C, LaC_2 shows a constant composition, 14.4 % by weight carbon. At 1800°C, tetragonal alpha LaC_2 changes to cubic beta LaC_2, remaining cubic to a congruent melting point at about 2355°C. This polymorphic change in lanthanum dicarbide is in agreement with the work of Bredig (*50*).

d. Cerium. Tetragonal CeC_2, the dicarbide, and cubic Ce_2C_3, the sesquicarbide, of cerium are both prepared by conventional arc melting techniques. Neutron diffraction investigations confirming X-ray diffraction results as to crystal structure and carbon atom positions have been made by Atoji (*17*), for both of the cerium carbides. The existence of a cubic or hexagonal monocarbide CeC, as suggested by Brewer and Krikorian (*52*) and Vickery (*356*), was not confirmed by the later work of Spedding and others (*316*) or by Warf and Palenik (*358*). Spedding suggested that the CeC reported by Brewer and Krikorian was probably a solid solution of carbon in cerium. A tricarbide CeC_3, suggested by Vickery, was not found by either Spedding or Warf and Palenik. At the composition for CeC_3 given by Vickery, Spedding and his associates found, from the results of microscopic examination, chemical analysis, and X-ray diffraction, only mixtures of free carbon and CeC_2. The same results were obtained whether such alloys were quenched or slow-cooled from the liquid state.

e. Praseodymium. There is agreement that this element has two carbides, the dicarbide PrC_2, tetragonal and isotypic with calcium chloride, and a cubic sesquicarbide Pr_2C_3. A neutron diffraction determination of structure and carbon atom positions has been carried out by Atoji and Williams (*16*) for the sesquicarbide.

f. Neodymium. Neodymium likewise has two carbides, Nd_2C_3 body-centered cubic, showing a structure like that of U_2C_3, and NdC_2 tetragonal with calcium chloride structure type.

g. Samarium. Since the boiling point of samarium is below 2000°C, arc melting could not be used for preparation of samarium carbides. Weighed amounts of the metal and carbon were therefore heated in a tantalum bomb for periods of 2–24 hours at appropriate temperatures in the range 1200°–2000°C (*316*). Samarium is one of the metals for which a cubic carbide of iron nitride (Fe_4N) type, having the formula Sm_3C with some range of carbon solubility, was prepared by Spedding, Gschneidner, and others (*316*). As is true of the other rare earths except promethium, which apparently has no known carbides, there is a tetragonal dicarbide of samarium SmC_2, and the usual cubic sesquicarbide Sm_2C_3.

h. Gadolinium. In addition to cubic Gd_2C_3 and tetragonal GdC_2 as listed by Gschneidner (*124*), Dean and his associates (*74*) in 1964 found a rhombohedral Gd_2C similar to Y_2C, which has already been discussed. It is also of interest to note that, due to the large neutron capture cross section of gadolinium, it is one of the metals mentioned in a patent for preparing carbide spheres as reactor fuels or poisons, which was granted to Goeddel (*113*) in 1965. The other cubic carbide is Gd_3C.

i. Terbium. No carbide Tb_2C was reported by Dean and others. The three carbides TbC_2, Tb_2C_3, and Tb_3C have the same crystal structures as the corresponding gadolinium carbides. Atoji (*17*) made neutron diffraction studies of both TbC_2 and Tb_2C_3.

j. Dysprosium. A rhombohedral Dy_2C was reported by Dean and his co-workers (*74*). Apparently no neutron diffraction determinations have been made of the other three carbides—cubic Dy_3C, tetragonal DyC_2, and cubic Dy_2C_3.

k. Holmium. Preparation of a holmium carbide was reported by Petterson in 1895 (*258*). The method of Moissan was followed, reduction of oxide mixed with carbon by means of an electric arc. The rhombohedral carbide Ho_2C, found by Dean and his associates in 1964, was subjected to neutron diffraction analysis by Bacchella and others (*22*), confirming the rhombohedral structure and establishing numerical values for C-Ho and Ho-Ho interatomic distances. Holmium sesquicarbide was found by Gschneidner (*124*) to have two crystal forms, one of lower symmetry, similar to Y_2C_3, the other form being body-centered cubic of Pu_2C_3 structure type. The tri-rare earth carbide Ho_3C is cubic (Fe_4N type); the dicarbide HoC_2 is tetragonal, as are the other rare earth dicarbides.

l. Erbium. Dean, Lallement, and others (*74*) also reported rhombohedral Er_2C. The other three erbium carbides, Er_3C, ErC_2, and Er_2C_3, are the same in structure as the corresponding dysprosium carbides.

m. Thulium. Carbides of thulium, as is also true for those of samarium, are prepared in a tantalum bomb rather than by arc melting. As is also true of the other rare earth elements from samarium to lutetium, a tri-rare earth carbide Tm_3C is formed. Thulium sesquicarbide Tm_2C_3 is of Y_2C_3 type of lower symmetry and unknown crystal structure. The other carbide TmC_2 fits into the series of the other rare earth dicarbides belonging to the tetragonal system.

n. Ytterbium. The three carbides YbC_2, Yb_2C_3, and Yb_3C are prepared by the tantalum bomb method. The tetragonal dicarbide YbC_2 has been studied by Atoji (*15*) by neutron diffraction methods. Knowledge of the structure of the sesquicarbide is incomplete but, according to Spedding, Gschneidner, and others (*316*), Yb_2C_3 does not seem to belong to either the Pu_2C_3 or Y_2C_3 structure types. The other carbide is cubic Yb_3C.

o. Lutetium. The three carbides of lutetium can be prepared by arc melting. Following the usual rules, LuC_2 is tetragonal, Lu_3C is cubic, and the sesquicarbide Lu_2C_3 is of symmetry lower than tetragonal or hexagonal and seems to be of Y_2C_3 type.

p. Europium. Preparation of europium dicarbide, EuC_2, was reported by Gebelt and Eick (*107*) in 1964. Two methods of preparation were used. Europium sesquioxide (Eu_2O_3) was mixed with spectroscopic graphite, and heated by induction in a graphite crucible with a lid of graphite having an orifice allowing effusion under a vacuum better than 10^{-5} mm Hg at 1450°C. The dicarbide was also prepared by heating europium metal mixed with graphite in a stainless steel bomb under a helium atmosphere for 12 hours at 1050°C. Gebelt and Eick suggested that previous failures to prepare EuC_2 by the induction heating method were probably due to vaporization of EuC_2 from the crucible, or disproportionation and loss of europium as the metallic vapor. X-ray diffraction powder photographs showed agreement between the structure of EuC_2 and the other rare earth dicarbides. The unit cell was body-centered tetragonal. A French patent granted in 1966 to Holtzberg and others (*151*) described preparation of EuC_2, Eu_2C_3, and a tri-rare earth type carbide Eu_3C. Preparation was by heating stoichiometric amounts of europium metal and graphite under vacuum. The charge was contained in a refractory metal crucible, and heating was by induction to 1500°C with rapid cooling. In agreement with the work of Gebelt and Eick, EuC_2 was body-centered tetragonal of calcium chloride type. The Curie temperature of the dicarbide was found to be 40°K. The sesquicarbide Eu_2C_3 was reported to be body-centered cubic of Pu_2C_3 structure type. In agreement with the similar rare earth carbides from samarium through lutetium, Eu_3C had a body-centered cubic defect lattice of Fe_4N type. The vaporization of EuC_2 has also been studied by Gebelt and Eick (*108*), the temperature dependence of the vapor pressure of europium in equilibrium with solid EuC_2 being measured over the temperature range 1130°–1600°K.

4. The Actinides

a. Thorium. Two carbides of thorium approximating, if not including, the stoichiometric compositions ThC and ThC_2 have been studied extensively. The two preparation methods most widely used are arc melting of thorium metal and carbon, and heating compressed powder mixtures of the metal and carbon below the melting point. Questions of purity arise in the discussions of lattice parameter and other properties of thorium carbides, because of the reactivity of the metal with nitrogen and especially with oxygen. Generally speaking, higher purities are obtained by arc melting.

The monocarbide ThC is face-centered cubic, of NaCl type with defect structure. Recent work by Takeuchi, Honma, and others (*343*) places the maximum carbon content for ThC at 49 atomic % carbon from 1350°C to room temperature with no composition change. The melting point of the monocarbide is near 2600°C. The value published by Wilhelm and Chiotti (*363*) in 1950 is in agreement with the results of Henney and Jones (*140*) published in 1966. The recent investigations by Henney and Jones, covering the composition range from ThC to ThC_2, and by Takeuchi and his associates, from thorium metal to ThC, supplement each other without overlap. However, considering the many changes found in the Th-C system since Wilhelm and Chiotti published a Th-C phase diagram in 1950, these two recent publications cannot be considered to completely and finally establish the phase relations for this system.

The chief features of the thorium-rich portion of the phase diagram are (1) a eutectic at about 1650°C, the horizontal extending from beta thorium (0.5 at. % C) to alpha thorium (6.5 at. % C) with the eutectic composition 4.5 atomic % carbon, and (2) a peritectic reaction at about 1875°C. The peritectic horizontal extends from about 5 atomic % carbon at the liquid end to ThC with a composition at this temperature of 33 atomic % carbon. The peritectic point is at 16 atomic % carbon, and the peritectic product is alpha thorium. According to the diagram of Takeuchi and others, the alpha field widens rapidly below the peritectic temperature, extending from thorium to about 8 atomic % carbon at the base temperature (about 1000°C). Although they did not determine the melting point of ThC, it is stated that the boundary, between the two-phase field liquid plus ThC and the single-phase field for solid ThC, shifts toward the high-carbon side and reaches the melting point of thorium monocarbide.

Thorium dicarbide is monoclinic at temperatures below 1400°C, at least on the thorium-rich side. This structure has been accepted since publication of single crystal determinations, including neutron diffraction results, by Hunt and Rundle (*156*) in 1951. In 1962 Kempter and Krikorian (*172*) indexed the low-temperature form of thorium dicarbide as pseudo-orthorhombic. In 1965 Gantzel, Langer, and others (*105*), using standard thermal analysis, differential thermal analysis, and high-temperature X-ray diffraction, found thorium dicarbide remaining monoclinic to 1427°C, then changing to tetragonal. The tetragonal structure persisted to 1481°C, changing to cubic above this temperature and remaining cubic to a high melting temperature near 2600°C. Similar results were obtained by Henney and Jones in their work on the portion of the Th-C system from ThC to ThC_2, as was previously noted. Henney and Jones also made metallographic studies of thorium carbon alloys in addition to using the techniques employed by Gantzel, Langer, and their co-workers. Henney and Jones placed the monoclinic-tetragonal change of ThC_2 at 1410°C, and the tetragonal-cubic transformation at about 1500°C. For the region between ThC and ThC_2, these transformations occurred at about 1290°C and 1490°C, respectively. They also found that, above about 2100°C, a solid solution between cubic ThC_2 and ThC existed. The high-temperature forms (cubic and tetragonal) of the dicarbide could not be retained to room or other low temperature by rapid cooling or quenching. These high-temperature forms were identified by high-temperature X-ray diffraction supplemented by differential thermal analysis.

In order to try to resolve the question as to whether ThC and ThC_2 can be prepared with stoichiometric compositions, an investigation was carried out by Bradley and Kegley (*47*) in 1964. Chemical analyses were supplemented by X-ray diffraction and metallographic examination. It was found that thorium monocarbide existed over a composition range from $ThC_{0.94}$ (4.6 wt. % C) to at least $ThC_{0.81}$ (4.0 wt. % C) and probably lower. The high-carbon limit for the single-phase dicarbide field was found to be $ThC_{1.95}$ (9.2 wt. % C), not attaining the theoretical composition $ThC_{2.0}$. Specimens having thorium-carbon ratios $ThC_{0.99}$ to $ThC_{1.88}$ (4.9–8.9 wt. % C) were found to be two-phase mixtures of mono- and dicarbides. This range of composition for the ThC-ThC_2 phase field is in agreement with the phase diagram for the portion of the Th-C system from 4 to 11 weight % carbon, published in 1966 by Henney and Jones.

By analogy with the uranium-carbon system, a sesquicarbide Th_2C_3 might be expected. Electrical resistivity measurements for the Th-C system, made in 1964 by Korbitz (*178*), gave some indication of the existence of a thorium sesquicarbide. However, Henney and Jones found no indication of such a sesquicarbide either in their high-temperature X-ray diffraction investigations of the binary Th-C system in the region where Th_2C_3 should be found, or in their subsequent investigation (*141*) of the thorium-uranium-carbon system. No mention of Th_2C_3 was made by Gantzel and others in their work on the Th-C system by the methods (except metallographic examination) used by Henney and Jones.

It is not completely accurate to say that thorium carbides are without practical use, as both thorium carbides and thorium-uranium carbides are used in nuclear reactors. Typical of such applications is the patent granted in 1963 to Goeddel and Simnad (*112*). The patent describes production of reactor fuel bodies by mixing finely divided graphite and silicides of thorium and uranium in the desired proportions, and adding a small amount (3–4 wt. %) of a diffusion bonding agent, such as finely divided zirconium, molybdenum, titanium, or other suitable elemental powder; the mixture is then heated to 1500°–1800°F under mechanical pressure (above 3000 psi) and slowly cooled.

b. Protactinium. Two references to carbides of this element were found. In 1954 Sellers and his co-workers (*308*) reported preparation of PaC by reduction of PaF_4 with barium in a carbon crucible at 1400°C. Due to health hazards and small amounts of available material, only minute amounts (50–100 micrograms) were prepared. The report of the compound as PaC was based on an X-ray diffraction pattern, but the data thus obtained would not differentiate protactinium monocarbide from the monoxide of the element. No lattice constant was reported. In 1962 Lonsdale and Graves (*192*) used the Knudsen effusion technique to measure the vapor pressure of PaC_2 over a dilute solid solution of PaC_2 in ThC_2. The temperature range covered was 2000°–2900°K.

c. Neptunium. Three carbides of neptunium have been prepared. The crystal systems and structure types for each carbide have been established by X-ray diffraction methods. As in the case of protactinium, small amounts (microscale) were made. The preparation of NpC, Np_2C_3, and NpC_2 was published by Sheft and Fried (*311*) in 1953. The X-ray diffraction analyses and structure determinations were carried out by Zachariasen and Flettinger (*373*). In the preparation of all three carbides, the carbon source was a graphite crucible containing the neptunium compound. The crucible was placed within a vacuum system in which a small partial pressure of hydrogen was maintained. The dicarbide NpC_2 was prepared from neptunium oxide at a temperature, obtained by induction heating, of 2660°–2800°C. For preparation of the other two carbides, neptunium trifluoride (NpF_3) was reduced with lithium vapor at about 1200°C in a tantalum wound resistance furnace. Analyses of the reduction products by X-ray diffraction showed about 5 parts Np_2C_3 to 1 part NpC. The sesquicarbide Np_2C_3 was found to be cubic, isotypic with Pu_2C_3. The monocarbide NpC was found to belong to the cubic system. The dicarbide NpC_2 was very similar to ThC_2, monoclinic, but also indexing very well with a pseudotetragonal unit cell. The thermionic emission of Np_2C_3 was determined by Cranston and Barger (*72*), as part of an investigation of the thermionic emission constants of actinide carbides and oxides.

d. Plutonium. Due to uses of plutonium carbides in reactors, a considerable and increasing amount of literature exists pertaining to these carbides. This is true in spite of the high health hazards encountered in laboratory or large-scale work on plutonium and its compounds. Phase relationships in the system plutonium-carbon are complicated by the fact that the metal plutonium has six polymorphic forms. Four carbides are known and generally agreed upon. PuC, cubic with a carbon-deficient

NaCl-type structure, is formed peritectically at about 1650°C. This carbide is the most important in applications of plutonium carbides. The single-phase composition range at about 590°C is placed by Storms (*335*) between $PuC_{0.77}$ and $PuC_{0.9}$, narrowing at lower temperatures. Pu_3C_2, of unknown crystal structure, is apparently a line compound rather than an intermediate phase having a composition range. Each of the six polymorphic forms of the metal plutonium transforms in contact with Pu_3C_2 which, in turn decomposes into epsilon Pu and the monocarbide PuC at 575°C. The sesquicarbide Pu_2C_3 is cubic, having a structure type similar to that of many other carbides, particularly the rare earth sesquicarbides. It was identified and characterized by Zachariasen (*372*) in 1952. It forms peritectically at about 2050°C with nearly stoichiometric composition. The remaining carbide PuC_2, of unknown crystal structure, forms above 1750°C and is shown on the Pu-C phase diagram, given by Mulford and his associates (*235*), as the product of another high-temperature peritectic reaction at about 2250°C. There are a number of uncertainties in the phase diagram of the plutonium-carbon system, particularly in the high-carbon region from 60 atomic % carbon (Pu_2C_3) to 100 atomic % carbon. However, most of the features of the Pu-C system diagram published by Mulford and others in 1960 have subsequently been confirmed in the diagrams of Burnham and others (*59*) and by Storms.

Plutonium carbides of high purity are prepared by arc melting either the metal or PuO_2 with carbon, or by powder metallurgy methods. According to Storms, if the starting materials are pure and the arc melted button is remelted at least 6 times, homogeneous products are obtained. Arc methods fail for Pu_2C_3 and compositions in this range, due to extreme sensitivity of this carbide to thermal shock, making it necessary to use compressed powder techniques. When this is done, the powders used as starting materials are generally the element plutonium, PuO_2, or $PuH_{2.8}$ mixed with carbon.

Technical methods for producing plutonium and plutonium-uranium carbides include carbothermic reduction of the oxide or oxides, reaction of the metal with elemental carbon, or reactions with gaseous hydrocarbons. Riley (*271*) outlines a representative preparation of plutonium carbide on a scale larger than that intended solely for laboratory use such as X-ray diffraction samples. Batches (400 gm) of PuO_2 or PuO_2 and UO_2 were mixed with the desired amount of carbon by ball milling (under CCl_4) for 12 hours. A portion of the mixture was then wrapped in tungsten foil and hot-pressed at temperatures of 1000°–2000°C under pressures up to 3 tons psi. By use of two hot-pressing stages, densities greater than 90 % of theoretical were achieved.

5. *Unstable Carbides and Acetylides*

The compounds of the metals gold, silver, copper, and mercury formed by the action of acetylene have been known for many years. In the case of copper, acetylides have been known since the work of Quet (*264*) in 1858. All of the acetylides are unstable and some are violently explosive. Recent interest in these compounds has centered around their use, particularly silver acetylide nitrates ($Ag_2C_2 \cdot AgNO_3$), as detonators and for explosive forming at low temperatures.

a. Copper. If acetylene is passed into an ammoniacal solution of cuprous chloride, a precipitate of Cu_2C_2 is formed. If cupric chloride is used, a red precipitate of CuC_2 is obtained, which is very unstable and cannot be dried without decomposition. In fact both copper acetylides explode upon drying, which has been known since the work of Quet in 1858 and Berthelot (*32*) in 1860. Powder X-ray diffraction patterns of copper acetylides, silver acetylides, and $AgC_2 \cdot AgNO_3$ have been published by Tanaka and Mizushima (*344*).

b. Silver. Moissan (*221*) found no evidence of the formation of any carbide upon solidification of molten silver containing carbon. The silver acetylides were prepared by Quet in 1858 and Berthelot in 1860 by passing acetylene into ammoniacal silver nitrate. Thermal and photodecomposition of silver acetylide (Ag_2C_2) has been studied by McCowan (*194*). The decomposition produced hexagonal silver and carbon as an amorphous residue. Use of silver acetylides in slurry form as an explosive-forming technique was reported by Baker and Hoese (*26*) in 1965.

c. Gold. One method of preparing Au_2C_2 is by passing acetylene into aqueous aurous thiosulfate, $Au_2S_2O_3$. Gold acetylides were prepared by Berthelot (*33*) in 1866. Other gold acetylides obtained by mixing AuI in liquid ammonia with $KC{:}CH$ yielded first Au_2C_2, then $K_2(HC{:}CAuC{:}CH)$ as well as $Au_2C_2 \cdot NH_3$, according to Nast and Kirner (*239*). The colorless complexes are strong electrolytes, nonexplosive but sensitive to light and moisture. The brown $Au_2C_2 \cdot NH_3$ was found to be highly explosive.

d. Mercury. The mercurous compound $Hg_2C_2 \cdot H_2O$ can be formed by passing acetylene, for a period of 30 hours, into an aqueous suspension of mercurous acetate kept in the dark. The mercurous acetylide is obtained as a white precipitate. Attempts to eliminate the water in $Hg_2C_2 \cdot H_2O$ by drying at 100°C result in decomposition. Early work on preparation of mercurous acetylides was by Plimpton (*261*) and by Burkard and Travers (*58*) in 1902. Mercuric acetylide HgC_2 was obtained by Keiser (*170*) in 1893 from the action of purified gaseous acetylene on a solution of mercuric and potassium iodides containing a little potassium hydroxide. This compound darkens upon slow and gradual heating to 100°C. Rapid heating causes violent explosive decomposition to carbon and finely divided mercury. In 1952 Babko and Grebel'skaya (*21*) reported the preparation of HgC_2 by passing acetylene into 0.1 *N* $K_2Hg(CN)_4$ solution that contained 0.1 *N* KOH. Solubility products for $Hg(C_2H_2)_2$ have recently been calculated by Tur'yan (*349*).

B. METALS WITHOUT REPORTED BINARY CARBIDES

1. *The Transuranium Elements* (*atomic numbers 95 through 103*)

This group includes the elements americium, curium, berkelium, californium, einsteinium, fermium, mendelevium, nobelium, and lawrencium. Beyond einsteinium, it is doubtful if isotopes are known having long enough half-lives for carbides to be prepared. All of these elements except americium are available in only very small quantities. Since americium is similar in chemical behavior to europium, it seems to be a reasonable although admittedly speculative assumption that, in addition to experimental difficulties resulting from the radioactivity of americium, there are other difficulties similar to those only recently overcome in the preparation of a carbide of europium. No mention of carbides was found for any element beyond plutonium, atomic number 94.

2. *Members of the Second and Third Transition Groups*

a. Ruthenium. A hexagonal carbide RuC similar to WC was reported by Kempter and Nadler (*171*) in 1960. The carbide was found as a minor phase in compressed ruthenium carbon pellets inductively heated to high temperatures in a helium atmosphere. The largest amount of the minor RuC phase was obtained by heating pellets compressed from a mixture of 1 part metal to 10 parts graphite for 4 hours at 2600°C. X-ray powder diffraction data were obtained in an 114.59-mm diameter Debye camera, using iron radiation filtered with cobalt. This was supplemented by back-reflection examination. Hexagonal lattice constants were reported as $a = 2.90775$ and $c = 2.82176 \pm 0.00001$ Å for RuC. An attempt to duplicate the work of Kempter and Hadler was made by Jeantet and Knapton (*161*) without success. In addition to using ruthenium-graphite mixtures, they added tantalum in an effort to stabilize RuC. In their X-ray diffraction work they used a 90-mm diameter Debye camera and filtered copper radiation. They remarked that the agreement between hexagonal WC and the hexagonal RuC found by Kempter and Nadler was very good.

Kempter discussed the work of Knapton in a later paper published in 1964 (*173*). The previous work of Kempter and Nadler was repeated and RuC was again found to be present. An extensive spectroscopic examination of samples having RuC lines showed the absence of W or Ta, as well as other elements that might have formed or stabilized carbides.

b. Rhodium. In 1960 Nadler and Kempter (*236*) reported a eutectic temperature in the rhodium-carbon system of 1694 ± 17°C. No attempt was made to determine the eutectic composition. Preparation of rhodium carbide by heating rhodium metal with graphite in a high-temperature spectrographic furnace was reported by Lagerqvist and Scullman (*186*) in 1966. The band spectra were examined and determined, using a high-pressure xenon lamp as light source. An optical pyrometer was not available that would measure the temperatures reached, which were stated to be sufficient to melt metallic tungsten. No investigation was made of the low temperature stability of RhC.

c. Palladium. No report of simple palladium carbides was found in the literature. Nadler and Kempter (*236*) in 1960 found a eutectic temperature in the palladium-carbon system of 1504 ± 16°C for palladium with maximum impurities of 7 ppm by weight. The graphite used was of spectrographic grade. Complex organic acetylenides of palladium were prepared by Greaves and Maitlis (*117*) in 1966.

d. Rhenium. Modern work on the rhenium-carbon system begins with that of Hughes (*154*) in 1959. He reviewed the previous contradictory literature and conducted extensive investigations, which were negative as to the formation of a rhenium carbide. Hughes found a eutectic temperature on the rhenium-rich side of the system at 2480°C and 16.9 atomic % carbon. This was in good agreement with the 1960 determination of this eutectic by Nadler and Kempter (*236*), who reported a value of 2486 ± 18°C. For alloys above the eutectic composition, carbon separated as flake graphite. The results published in 1963 by Evstyukhin and others (*98*) confirm the work of Hughes as to the Re-C eutectic temperature and composition. From X-ray diffraction patterns of quenched Re-C alloys, the existence of a dicarbide or monocarbide of rhenium is suggested. As many as five additional diffraction lines above those for graphite and rhenium metal were found in some diffraction patterns.

e. Osmium. In the same papers mentioned above for the ruthenium-carbon system, the osmium-carbon system was also examined. The same preparation techniques and methods of identification were used. Kempter and Nadler (*171*) in 1960 and again in 1964 (*173*) reported preparation of OsC having a hexagonal WC-type structure. Lattice constants were reported as $a = 2.90572 \pm 0.00007$ and $c = 2.82166 \pm 0.00019$ Å. Jeantet and Knapton (*161*) also failed in attempts to produce OsC as well as RuC.

f. Iridium. No report of a simple binary approximately stoichiometric carbide of iridium was found in the literature. The eutectic temperature for the iridium-rich side of the iridium-carbon system was found by Nadler and Kempter (*236*) to be 2296°C for spectroscopic grade graphite and iridium having total impurities of 430 ppm by weight.

g. Platinum. Using the high-temperature spectrographic methods discussed above for rhodium, Neuhaus and others (*242*) recently reported band spectra for PtC. Nadler and Kempter (*236*) found a Pt-C eutectic at 1736° ± 13°C from work on platinum wires in contact with spectrographic graphite.

3. Lanthanides

a. Promethium. This element is now the only rare earth metal for which no published report of a carbide was found. This may be due partly to the fact that promethium has been isolated for only some 20 years and that only small quantities are available. Preparation of a number of promethium compounds including the oxide, oxalate, phosphate, fluoride, and chloride was recently reported by Weigel (*359*).

4. The Radium Metals

a. Francium. Due to the short life of the isotopes of francium and to the minute quantities available, the chemistry of francium can be studied only on the tracer level. This makes the preparation of a carbide very difficult and unlikely. From a direct search for francium carbides, no published report of such compounds was found.

b. Radium. Again, no published report of the preparation of radium carbide was found. This may be due to experimental difficulties connected with the radioactivity of the element and to lack of interest. From its position in the Periodic Table just below barium, an acetylide and a carbide probably having the formula RaC_2 would be expected.

c. Actinium. Lack of published information on a carbide of actinium is apparently for the reasons just given for radium. Since one of the isotopes of actinium has a half-life of 22 years and there are reports of commercial production of the metal, it is available in amounts large enough for laboratory carbide production. Carbides of other elements in the actinide series—thorium, protactinium, uranium, neptunium, and plutonium—are known, and have been discussed.

5. Other Metals without Binary Carbides

Some of the elements in this and the next section, for which no binary carbides are reported or for which the evidence of such compounds is somewhat scanty, have ternary carbides to be mentioned later.

a. Indium. No published information on binary carbides was found. Ternary carbides containing indium are known.

b. Tin. The work of Moissan, repeated by Ruff and Bergdahl (*279*) in 1919, showed that only traces of carbon dissolved in molten tin, precipitating as graphite on freezing. Ternary metallic carbides containing tin are known.

c. Antimony. Ruff and Bergdahl (*279*) found that boiling antimony dissolves a maximum of 0.094% by weight carbon, which precipitates as graphite on freezing. No published information on either binary or ternary carbides of antimony was found.

d. Tellurium. No binary carbides are reported in the literature.

e. Germanium. A French patent granted to Hamlet (*130*) in 1959 reported preparation of a layer of germanium carbide (GeC) 5–10 microns thick as one of the three layers of an electroluminescent cell. In 1966 Sharanina and others (*310*) reported preparation of $Cl_3GeC\vdots C(CH_3)$ from germanium tetrachloride and trialkylstannylacetylene.

f. Bismuth. Ruff and Bergdahl (*279*) found the solubility of carbon in boiling bismuth to be 0.023% by weight carbon, which completely separated as graphite on freezing. The solubility of carbon in liquid bismuth at lower temperatures (750°–300°C) was investigated by Griffith and Mallett (*121*) in 1953. Again, all carbon separated as graphite on completion of freezing, and no evidence of formation of any carbide of bismuth was reported. The solubility of carbon in liquid bismuth was very slight, varying from 0.0003% by weight carbon at 750°C to 0.00016% by weight carbon at 300°C.

g. Polonium. According to Bagnall (*23*), reaction between milligram amounts of polonium and carbon monoxide does not occur. Polonium has high volatility. It is suggested that, if polonium metal is deposited on silver, a polonium carbonyl may be formed, the silver acting as a catalyst when the deposit is exposed to carbon monoxide. Direct search of the literature gave no evidence of polonium carbide.

C. Binary Carbides Reported but not Confirmed

1. Gallium

The gaseous species Ga_2C_2 was identified in 1958 by Chupka and his associates (*66*), using mass spectrometric methods. The compound was prepared by placing gallium metal in a graphite crucible with a graphite lid. The lid contained an effusion window allowing escape of the Ga_2C_2 vapor. The crucible was heated by electron bombardment from a tungsten filament surrounding the graphite effusion cell. Ternary metallic carbides containing gallium are known.

2. *Technetium*

In 1962 Trzebiatowski and Rudzinski (*348*) reported preparation of a technetium carbide, which X-ray diffraction studies indicated to be a face-centered cubic phase TcC. The diffraction lines of TcC were found for technetium-carbon compositions between 1.5 and 11.5 weight % carbon. The carbide was prepared by carburizing technetium metal with hydrogen-benzene mixtures or by heating the metal with a large excess of graphite at temperatures of 700°–1100°C. Giorgi and Szklarz (*111*) in 1966 reported preparation of technetium carbide of unspecified composition by vacuum inductive heating of technetium metal contained by a graphite crucible to its melting point. The technetium metal was specially purified, spectrographic analysis showing 10 ppm of iron as the only detectable impurity. Magnetic susceptibility studies showed that the technetium carbide thus prepared became superconducting at 3.85°K.

3. *Selenium*

In 1955 a patent was granted to Morningstar (*232*) for carbon diselenide prepared from carbon tetrachloride and hydrogen selenide. The compound was stated to be insoluble in water, with a boiling point of 124°C and a melting point of –45°C. In 1939 Barrow (*27*) reported the emission spectrum of CSe in the vapor of selenium heated with carbon, but this has not been confirmed by isolation of the solid compound.

4. *Zinc*

Durand (*81*) in 1924 reported preparation of zinc carbide (ZnC_2) by two methods. The first method was passing acetylene over pure zinc dust, temperature reported as 450°C; the second was passing acetylene through a solution of zinc-ethyl, $Zn(C_2H_5)_2$, in ligroin (b.p. 129°–130°C). Reiffenstein and others (*269*) in 1965 reported preparation of ternary carbides (of eta type) containing zinc. In these ternary carbides, niobium or tantalum was about 44 atomic %, carbon about 14 atomic %, and the remaining 42 atomic % was mainly aluminum with intentional replacement of part of the aluminum by zinc in some of the carbides prepared.

5. *Arsenic*

The preparation of arsenic tricarbide (AsC_3 or As_2C_6) from $AsCl_3$ and $Mg_2C_2I_2$ was reported by de Mahler (*199*) in 1921. In 1966 Kuz'min and Pavlova (*185*) published preparations for acetylene derivatives of arsenic, in which the atomic refraction of arsenic was significantly different from that in ordinary arsines. The simplest of these compounds was $Pr_2AsC{\vdots}CAsPr_2$ ($Pr = CH_3CH_2CH_2$). By passing acetylene into ethylmagnesium bromide dissolved in diethyl ether, a bifunctional Grignard reagent was formed as a dark oil; Pr_2AsI was added and, after refluxing an hour and allowing the mixture to stand overnight, the arsine formed upon treatment with acidified NH_4Cl.

6. *Thallium*

Schwarz (*291*) reported a superconducting thallium carbide in 1932. The carbide was said to be superconducting up to 9.2°K. No method of preparation or formula was given; also no subsequent confirmation was found in the literature. Ternary carbides of perovskite type such as Dy_3TlC were prepared by Haaschke and others (*127*) in 1966.

7. *Lead*

In 1923 Durand (*82*) reported the preparation of a lead carbide of formula PbC_2 by adding calcium carbide to an aqueous solution of neutral lead acetate. Durand stated that this was the first compound known in which bivalent lead was combined directly with carbon. No published report of successful repetition of this work was found. Masson and Cadiot (*202*) in 1965 reported preparation of acetylene derivatives of lead. The method used was similar to that used in preparing simple acetylides of other metals. One of the simplest of these lead derivatives of acetylene was $(Et)_3PbC{\vdots}CCH_3$. Suitable sodium alkynides were dissolved in liquid ammonia or hydrocarbons, and triethyl- or triphenyllead halides were added to the dissolved sodium alkynides. In addition to determining melting points and boiling points, infrared and ultraviolet spectra were measured and for some substances nuclear magnetic resonance.

8. *Cadmium*

Durand (*81*) also reported preparation of cadmium carbide, CdC_2, by passing acetylene over fine cadmium shavings at an elevated temperature. As is also true of the carbides of lead and zinc that Durand reported, subsequent published confirmation was not found.

V. Carbides Containing Three or More Elements

A. COMPLEX CARBIDES IN FERROUS ALLOYS

As was previously stated, this article is mainly a review of binary carbides. No extensive or complete coverage of ternary and more complex carbides will be attempted. A number of elements having no known or well-established binary carbides have fairly well-confirmed ternary carbides. Many ternary carbides are members of the same class or group such as the perovskite-type carbides, while other complex carbides do not fit known structure types. Only recent and representative carbides and publications will be discussed.

Two of the carbides found widely in alloy steels may be quite simply represented by type formulas M_6C and $M_{23}C_6$ (in which M = metal atoms, and C = carbon). Substitution of two or more metals causes formation of ternary or more complex carbides. Formulas vary quite widely from author to author; generally such substitutions of metal atoms do not change the crystal structure class of the resulting carbide, so Greek letter designations are used. This letter notation is fairly uniform although some exceptions are found. Some of these classes, such as those of the eta (η) carbide type, are also found in other ternary or complex carbides not based upon iron.

Historically, the first investigation of ternary carbides using X-ray diffraction methods, in addition to the techniques of metallography, heat treatment, and older metallurgical methods, was published by Westgren and Phragmen (*360*) in 1928. From Laue and rotation photographs of ferro-tungsten crystals and from synthetic melts, these workers assigned the most probable formula Fe_4W_2C to a face-centered cubic structure having a unit cell containing a large number of atoms. A similar ternary carbide Fe_4Mo_2C was also found. The possibility that Fe_3W_3C might be more correct was mentioned. It can be seen that these formulas all conform to M_6C. The 1928 publication was stated to be a preliminary report. This carbide type is generally referred to as an eta (η) carbide, and there are also variations to be mentioned later in this section. For carbides of this type, as found in high-speed steels, which were first extensively investigated as to their ternary carbides, the range of solid solubility is from Fe_3W_3C to Fe_4Mo_2C in tungsten-based steels, and from Fe_3Mo_3C to Fe_4Mo_2C in molybdenum-based alloys. The unit cell contains 112 atoms (96 metal and 16 carbon atoms) and the lattice parameter is $a = 11.06$ Å. These results were obtained for such carbides by Westgren (*361*) in 1933 on what he termed "the double carbide of high-speed steel," which is now by general agreement called the eta carbide type. In this paper, Westgren gave the space group and atomic positions, assigning Fe_3W_3C as the most probable formula. In the same year he also published a structure determination of $Cr_{23}C_6$, which with substitution gives rise to another widely found type of complex carbides (*362*). For $Cr_{23}C_6$, his published structure determination showed that the carbide was face-centered cubic with 116 atoms per unit cell (92 chromium and 24 carbon); the space group is O_h^5, and the positions and coordinates of all the carbon and chromium atoms are given. Westgren also pointed out that this $M_{23}C_6$ type of carbide was widely distributed in stainless steels and in low-alloy steels containing tungsten and molybdenum. The heavier metal atoms were found to preferentially occupy one set of atomic positions, not being randomly or statistically distributed. Two such substituted carbides mentioned in this paper are $Fe_{21}W_2C_6$ and $Fe_{21}Mo_2C_6$.

In 1954 Carroll, Darken, and others (*63*) found a similar iron borocarbide of formula $Fe_{23}(C,B)_6$, in which part of the carbon atoms had been replaced by boron. This compound was found in steels having intentional boron additions. The numerical and structural results were very close to those of Westgren obtained 20 years earlier. This $Cr_{23}C_6$ "type" of structure also occurs widely in ternary carbides, not exclusively in ferrous alloys. Goldschmidt (*114*) termed these carbides, which he represented by $(Cr, Fe, Mo, W)_{23}C_6$, kappa (κ) carbides, and others have followed this notation.

The paper in which Goldschmidt proposed this kappa notation was published in 1948, and was the first part of an investigation of the structure of carbides in alloy steels. It was an extensive review of binary and ternary carbides in ferrous alloys, and is still a valuable source. In Part Two of this investigation, published by Goldschmidt (*115*) in 1952, the experimental results of an investigation of the quaternary iron-chromium-tungsten-carbon system and of work on various commercial-type high-speed steel alloys were set forth. Compositions and carbides in the high-speed steel portion of the quaternary were the chief object of the investigation. The original composition of high-speed steel found by Taylor and White was (by weight) 18W-4Cr-1V, carbon 0.70%, sulfur and phosphorus each below 0.05, manganese 0.25, silicon 0.25, and the balance iron. The major change since the adoption of this "original" high-speed steel in the decade 1900–1910 has been partial replacement of tungsten by molybdenum. As can be seen from Westgren's results for eta carbides, such a partial molybdenum replacement is of little importance as far as the carbides of high-speed and other alloy steels are concerned. In addition to eta and kappa carbides, Goldschmidt found two other carbides in variously heat-treated high-speed steels. One of these two carbides was V_4C_3 of rock salt structure. This was found only in compositions with excess vanadium; lesser amounts of vanadium occurred as a substituent in eta and kappa carbides. Finally, Goldschmidt also found that with certain heat treatments a new cubic carbide, which he designated as η^* (eta star), was formed with simultaneous liberation of tungsten. The cube edge of this new eta carbide was much shorter (10.96 *kx*) than that of normal eta carbide (11.07 *kx*). With respect to the carbides of high-speed steels, the work of Goldschmidt seems to be still substantially correct.

A third important type of ternary carbide found in ferrous alloys is formed by substitution of part of the iron atoms in orthorhombic cementite, Fe_3C, by other elements without change in the crystal structure. Such elements are manganese or chromium and, in smaller amounts, tungsten, molybdenum, or vanadium. Such substitution produces carbides that are written as $(Fe,Mn)_3C$ or $(Fe,W)_3C$ and similarly for other elements that partially replace the iron atoms in cementite. A recent study of such a carbide, synthesized from the elements iron, manganese, and carbon and to which the formula $(Fe_{1.8}Mn_{1.2})C$ was assigned, has been carried out by Duggin and others (*79*). The experimental techniques used included chemical analysis, electron microprobe analysis, X-ray diffraction, and neutron diffraction. The results obtained showed that the iron and manganese atoms were randomly distributed, the deviation from a statistically random distribution being about 5%. Comparison of results for $(Fe_{1.8}Mn_{1.2})C$ was made with those obtained by Fasiska and Jeffrey (*101*) in 1965 for $(Fe_{2.7}Mn_{0.3})C$. The atomic coordinates of the carbon atoms in both of these carbides were found to agree very closely. The importance of the investigation by Fasiska and Jeffrey was that it was perhaps the first single crystal investigation of the cementite structure. In order to obtain single crystals, it was necessary to introduce manganese, hence the formula $(Fe_{2.7}Mn_{0.3})C$. The refinements (including use of computer programs) that Fasiska and Jeffrey were able to make enabled determination of the position of iron atoms to a standard deviation of 0.001 Å, and of carbon atoms to a standard deviation of 0.01 Å. However, these final positions were within 0.12 Å for carbon atoms and within 0.03 Å for iron atoms of those obtained for Fe_3C by Lipson and Petch (*191*) in 1940, which have since been generally accepted.

B. OTHER COMPLEX CARBIDES

Mention has been made of the eta and kappa types of ternary or more complex carbides, and of differences in the use of Greek letter designations. The difference in the use of "kappa" illustrates this. As proposed by Goldschmidt, kappa carbides were those of $Cr_{23}C_6$ type with substitutions, face-centered cubic with 116 atoms per unit cell. On the other hand, Rautala and Norton (*268*) used the term "kappa" for a carbide in the hexagonal system found in the ternary Co-W-C having a proposed formula $Co_3W_{10}C_4$ with a range of homogeneity of less than 1%. The next year (1953) Kuo (*182*), in a discussion of the work of Rautala and Norton, agreed with this designation of a hexagonal kappa carbide, listing two other similar such carbides he had found in the systems Ni-W-C and Mn-W-C. Kuo proposed no specific formulas for his two kappa carbides. For all three of these hexagonal kappa carbides, the *a* and *c* parameters had identical values. This use of "kappa" to designate a hexagonal structure in carbide and other phases has been followed by Nowotny and his associates. In a paper on "New Kappa Phases" by Reiffenstein, Nowotny, and others (*270*) published in 1966, fifteen such phases are tabulated. All the *c*/*a* axial ratios are close to unity, ranging from 1.048 for Mn_3Al_{10} to 0.986 for a kappa phase in the quaternary system W-Mn-Al-C. Formulas were allocated to only a few of these kappa phases, such as $Mo_{12}Cu_3Al_{11}C_6$. Other quaternary systems, such as W-Fe-Al-C and Mo-Co-Al-C, showed hexagonal kappa phases. Thus, the Greek letter designation is not always consistent for kappa phases.

More consistency is found for the eta or M_6C carbides, which apparently are always cubic with the unit cell containing 112 atoms as first described by Westgren (*361*). The division into two types—η_1 (eta sub-one), for which V_3Cr_3C is a typical formula, and η_2 (eta sub-two), which includes the "double carbide" Co_2Mo_4C and $Ni_2(Ta,Ti)_4C$—was proposed by Kuo (*181*) in 1953. The cube edge for the η_2 carbides was longer than for η_1. A publication by Reiffenstein and others in 1965 (*269*) follows the proposals of Kuo and Westgren, and describes a number of new eta carbides. The alloys investigated contained: Nb or Ta about 44 atomic %, carbon about 14 atomic %, and the remaining 42 atomic % was Al + (V, Cr, Mn, Fe, Co, Ni, Cu, or Zn). The usual atomic % values for Al were 6, 14, 20, or 30 atomic %, various quaternary combinations being obtained to make up the balance of the desired quaternary alloy from one of the metals within the parentheses. The eta carbides thus prepared were identified by powder X-ray diffraction patterns. A wide range of homogeneity was found in several of these quaternary systems, and it was tentatively concluded that aluminum was important for the formation of these eta carbides. A comparison of calculated and observed intensities for Ta_3CrAl_2C showed good agreement for a structure of eta carbide type.

It was previously mentioned that a number of metals, without binary carbides or with doubtful binary carbides, have ternary or more complex carbides that are fairly well confirmed. A single such ternary carbide for these metals, when known, will now be listed, although gallium, indium and germanium, which seem to be without binary carbides, are found in many ternary carbides of different structure types. Many of the known ternary carbides can be placed in a few structure types, although information on the ternary system as a whole may be incomplete and sketchy.

Probably the structure type with the largest number of known examples is that of the perovskite carbides. These carbides have face-centered cubic structures with atoms of a lower melting metal at the cube corners, atoms of a transition metal at the six face centers forming an octahedron around a carbon atom at the interior (or body) center of the cube. All of the following carbides have this perovskite structure, and are taken from the tables of Nowotny and others (*247*) published in 1964: palladium—Pd_3InC, platinum—Pt_3InC, indium—Fe_3InC, tin—Mn_3SnC, germanium—Co_3GeC, gallium—Mn_3GaC, zinc—Ni_3ZnC, thallium—Ti_3TlC, and lead—Pd_3PbC.

Cadmium (*247*) and arsenic (*42*) have ternary hexagonal carbides, which have been termed "H" phases by Nowotny and his associates. Part of the carbon atoms are at the center of an octahedron formed by six transition metal atoms. The vertical stacking sequence for this hexagonal type of structure is: A (low melting metal, arsenic or cadmium in this particular instance); B (transition metal); A (transition metal); B (low melting metal). Carbon atoms are at the centers of the octahedra formed by two successive transition metal layers. For cadmium, such an H phase has the assigned formula Ti_2CdC; for arsenic, the H phase V_2AsC is found in the V-As-C ternary system.

In 1967 Holleck and Thummler (*150*) found, in the system Zr-Os-C, a cubic carbide with lattice parameter 12.4 Å, of partially filled Ti_2Ni structure to which the formula Zr_4Os_2C was assigned. Carbides of rhenium and iridium were not reported in this paper, but an eta nitride phase Zr_4Ir_2N, cubic with edge length 12.35 Å, was found; a complex oxide of rhenium (also having the same partially filled Ti_2Ni structure), Zr_4Re_2O (a = 12.35 Å), was also prepared.

The other carbide structure types (for ternary and more complex carbides, nitrides, oxides, and intermetallic compounds) included in the 1964 classification by Nowotny and others (*247*) are:

(a) T_3M_2X phases with a filled beta-manganese type cubic structure such as Mo_3Al_2C and Nb_3Al_2N. In this notation, T denotes a transition group metal, M is a metametal or lower melting point metal from Groups IIB through VB of the Periodic Table excluding silicon and germanium, and X is a metalloid, usually carbon or nitrogen, but occasionally boron or oxygen.

(b) Phases with partially filled Mn_5Si_3 structure. This structure type is hexagonal, space group $D8_8$. The type formula is $T_5M_3X_{(1-x)}$, the metalloid varying in composition as the subscript $(1 - x)$ indicates. A phase of this type has been found in the ternary system Zr-Si-C (no specific formula assigned); other examples include $Mo_5Ge_3(C)$, $Nb_5Si_3(X)$, and binary compounds such as Mg_5Hg_3, Y_5Si_3, and Mo_5Si_3.

These structure types—eta, kappa, H phases, perovskite, T_3M_2X, and $T_5M_3X_{(1-x)}$—classify over two hundred substances, chiefly ternary carbides and nitrides. Over eighty of the listed phases are ternary carbides. However, new structure types are also found as more research on ternary and complex carbides is completed and published. An example of such a new carbide structure type is contained in a 1967 paper by Jeitschko and Nowotny (*162*) on the crystal structure of Ti_3SiC_2. From a single crystal X-ray investigation, this carbide was found to belong to the hexagonal crystal system, $a = 3.068$, $c = 17.669$ Å; $c/a = 5.759$, with space group D_{6h}^4—$P6_3/mmc$.

No consideration of the methods of producing these complex carbides has been made up to this point. One of the first preparations of one of these ternary carbides was by Morgan (*231*) in 1954. One of his formulas was $Mn_{65}In_{15}C_{10}$. An arc furnace was used with an argon atmosphere instead of vacuum to avoid volatilization of manganese. Many of the perovskite carbides have been prepared by Stadelmaier and his coworkers. In 1959 Hutter and Stadelmaier (*157*) described an induction furnace method by which they prepared perovskite-type carbides. The transition metal was manganese, iron, cobalt, or nickel, and the second metal was indium or germanium. In order to obtain alloys of high carbon content, the transition metal was melted with carbon and the charge in many cases was placed in a graphite container. After melting the transition metal, the lower melting point metal such as indium or germanium was then added to minimize loss.

The other principal method of producing these complex carbides is by the techniques of powder metallurgy. Among other advantages, some of the problems associated with the high vapor pressures of metals, such as zinc and cadmium, at the temperatures of molten transition metals, such as iron and nickel, are avoided. In commenting on the production of these carbides, Nowotny, Jeitschko, and others (*247*) state that many of them can be produced by hot-pressing. Times up to 1500 hours at temperatures of 700°–900°C may be necessary. The transition metal employed is usually of very fine particle size (10 microns or smaller); the lower melting metal is used as larger particles (up to 0.5-mm diameter) in order to avoid loss, and the pressing is carried out under pressures of several atmospheres. In some cases, better results were obtained if the two metal powders were cold-pressed with graphite so that they were embedded in a graphite matrix, before hot-pressing. For carbides containing zinc, cadmium, or gallium, the hot-pressing method could not be used. Closed quartz tubes were used to contain the powders, and extremely long sintering times were necessary to obtain reaction and carbide formation. A week at 900°C for Mo-Ga-C gave no sign of reaction. Other papers mention heating times as long as 1500–2000 hours to obtain measurable carbide formation in some systems.

VI. Properties of Carbides

A. CRYSTALLOGRAPHIC PROPERTIES

Extensive numerical property tables for carbides seem unnecessary. Large collections and tables including the crystallographic information about most carbides are already available. For X-ray crystallographic information, the largest single source is probably the ASTM Powder Data File (*367*). Another large collection of similar information is Pearson's (*254*) book *Handbook of Lattice Spacings and Structures of Metals and Alloys*. The extensive (15 volumes to date) *Structure Reports*, published by the International Union of Crystallography (*255*), contain many carbide structure determinations. A similar set of such tables, containing 60 pages of carbide, boride, hydride, nitride, and oxide structures, is the volume by Taylor and Kagle (*345*) published in 1963.

TABLE I

CRYSTALLOGRAPHIC DATA FOR SELECTED CARBIDES

Nominal formula	Crystal system	Ref.	Lattice constants (in Å)		
			a	*b*	*c*
EuC_2	Tetragonal	(*107*)	4.045		6.645
V_2C	Orthorhombic	(*370*)	4.577	5.742	5.037
V_2C	Hexagonal	(*370*)	2.885		4.560
Nb_2C	Hexagonal	(*371*)	5.407		4.960
Nb_2C	Orthorhombic	(*371*)	10.920	4.974	3.090
Ti_3SiC_2	Hexagonal	(*162*)	3.068		17.669
Zr_3Fe_3C	Cubic	(*150*)	11.80		
Zr_4Os_2C	Cubic	(*150*)	12.41		
Nb_4Co_2C	Cubic	(*150*)	11.63		
Nb_4Ni_2C	Cubic	(*150*)	11.64		
Ta_4Co_2C	Cubic	(*150*)	11.59		
Ta_4Ni_2C	Cubic	(*150*)	11.61		

Another considerable problem is the variation of lattice parameter with purity and composition, including a large number of carbides that apparently are never stoichiometric, but have defect or excess structures. For the carbides of the important refractory metals, such as titanium, zirconium, hafnium, tantalum, niobium, chromium, molybdenum, vanadium, and tungsten, the values available have been critically reviewed (up to 1964) and discussed at length by Storms (*323*). A similar review of crystallographic and other properties of the carbides of iron was published by Hofer (*149*) in 1966. Much of the recent work (especially for 1962–1967) on ternary and complex carbides by Nowotny, Benesovsky, and their associates and students has been published in the journal *Monatshefte für Chemie*. For these reasons, the short Table I is limited to values for a few carbides such as europium dicarbide which is comparatively new, to carbides such as V_2C and Nb_2C where recent redeterminations have been made, and to a small number of ternary carbides. Some (but not all) of these results have previously been given in the text of this review.

B. DENSITIES, MELTING POINTS, AND TEMPERATURE-STABILITY RANGES

Again, repetition of a large amount of data from other sources seems needless. Densities are almost always listed with X-ray diffraction data; the temperature-stability ranges of carbide polymorphs are dependent upon purity, as is also true for lattice parameters. The work of Bredig (*48*) on the polymorphic carbides of calcium, strontium, and barium has been discussed. The formation and rapid decomposition of molybdenum monocarbide MoC have been mentioned, showing the effect of small amounts of other elements in stabilizing a carbide. Nowotny (*246*) states that small additions of other elements, such as $(Mo_{0.95}Hf_{0.05})C_{1-x}$ or nonmetals such as $MoC_{1-x}B_{0.03}$, will stabilize the MoC phase. Stability of the important refractory carbides (of Groups IVA, VA, and VIA of the Periodic Table) with respect to chemical and temperature stability has been discussed by Storms (*323*).

The melting temperatures of tantalum and hafnium carbides were discussed previously. A very recent publication by Rudy and Progulski (*278*) presents in detail the results of 2 years of investigation into the melting points of carbides, refractory metals, high-temperature eutectic and peritectic isotherms in carbide and boride systems, and boride melting points. A modified and refined Pirani-type furnace was employed. In the Pirani method, the specimen is of bar type, having a black body hole drilled in it for temperature determination, the specimen being supported by two water-cooled electrodes and heated by electrical means. An optical pyrometer sighted on the black body hole allows reading of the temperature as liquid appears. The paper contains a long discussion of methods for reducing and compensating for temperature errors in the use of the optical pyrometer and in calibrating the instrument to a high limit of about 4000°C. The question of maintaining specimen purity is also discussed. The chief improvement over previous Pirani-type furnaces was the use of a fast-response power-feedback circuit to eliminate runaway problems, as well as incorporation of suitable preheating techniques to overcome poor electrical conductance of some materials at low temperature. (The original paper should be referred to for experimental details.)

The values published by Rudy and Progulski were stated to be based upon material of high purity, analytically defined. Each numerical value was the average of a large number of measurements, since the melting points obtained were part of a 2-year investigation into the phase diagrams of refractory metal systems for carbides and borides. As a matter of interest, the melting points of six of the highest melting monocarbides, as stated by Rudy and Progulski, are compared in Table II with those given previously in this review. According to this latest work, TaC is the highest congruent melting carbide with a melting point exceeding that of HfC by about 60°C. Rudy and Progulski mention in their paper that the data of Agte and Alterthum (*6*) obtained by the Pirani method must still be considered of high precision, although their results were published over 30 years ago.

TABLE II

CONGRUENT MELTING POINTS OF CUBIC (NaCl) CARBIDES

			Rudy and Progulski		
Carbide	M.P.	Reference	T_f[a]	Composition (at.% C)	Average reproducibility
TiC	(none)		3067° ± 25°	44 ± 1	±15°
ZrC	3420°	Sara (*286*)	3440° ± 25°	45 ± 1	±10°
HfC	3895°	Beall (*4*)	3928° ± 40°	48.5 ± 0.3	±20°
VC	(none)		2648° ± 12°	43 ± 0.5	±8°
NbC	3485°	Brownlee (*55*)	3613° ± 26°	44 ± 1	±8°
TaC	3825°	Sara (*285*)	3983° ± 40°	47 ± 0.5	±15°

[a] Mean value and estimated overall temperature uncertainty. All temperatures in centigrade degrees.

VII. Available Phase Diagrams

A. BINARY CARBIDES

If a single reliable source had to be chosen for phase diagrams for binary metal carbides, the volume *Constitution of Binary Alloys* by Hansen and Anderko (*131*), in conjunction with the supplement by Elliott (*86*), would serve the purpose. The literature is reviewed through 1961 in these two volumes. The binary metal-carbide systems of industrial and refractory importance (titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, and tungsten) are shown in later phase diagrams (1964 in both cases) in the review by Storms (*323*) and in the article by Kieffer and Benesovsky (*174*) in the Kirk-Othmer *Encyclopedia of Chemical Technology* (*177*). A later article covering most of these transition-metal carbide systems is that by Eberle and others (*83*) in 1966. Hansen's work covers all known binary metal-carbon systems. Where more detail is necessary, the literature must be consulted.

B. TERNARY AND HIGHER CARBIDES

1. *Ferrous Alloys*

Although the binary metal-carbon systems are reliably evaluated by Hansen, no comparable collection seems to be available for any of the ternary or quaternary systems whether ferrous or nonferrous. To say that any ternary metal-carbon diagram is completely known would probably be a misleading and inaccurate statement. The great number of possible combinations in comparison to binary diagrams, and the need in ternary diagrams for a considerable number of vertical and horizontal sections, increase the work required to put a ternary diagram into final form beyond the present state of knowledge. The available information ranges from studies made over 40–50 years for such ferrous alloy systems as Fe-Cr-C in stainless steels and Fe-W-C in high-speed and other alloy steels to fragmentary reports of a single carbide, such as Zr_4Os_2C recently reported by Holleck and Thummler (*150*) in the system Zr-Os-C. Three areas in which considerable work has been done on ternary and more complex carbide systems are ferrous alloy systems, refractory transition metal-carbon systems, and those based mainly upon uranium, of interest primarily in nuclear reactors. Sufficient interest due to financial and other reasons exists to maintain continuing investigations in these fields. For other ternary or more complex metal-carbon systems, investigations are sporadic and uneven in nature and content.

In order to give an idea of work on important ferrous ternary alloy carbide systems, Fe-Cr-C and Fe-W-C will be used. The system Fe-Cr-C occurs in stainless, high-speed, and many other alloy steels. The system Fe-W-C contains the carbides that allow a cutting edge to be maintained at a dull red heat, which is the origin of the designation 'high-speed steel."

A ternary diagram for a portion of the system Fe-Cr-C, based partly upon their own work on austenitic stainless steels, was published by

Aborn and Bain (*1*) in 1930. In the same year and in the same journal, Krivobok and Grossmann (*180*) published another ternary diagram for this system. The literature to 1940 was collected and reviewed by Kinzel and Crafts (*176*, *176a*). The iron-carbon-chromium phase diagram up to 4% by weight carbon and to 38% chromium was reinvestigated by Bungardt *et al.* (*57*) in 1958. Metallographic, dilatometric, and X-ray diffraction methods were used. A still later investigation of alloys near 70% chromium was published by Pepperhoff and others (*256*) in 1962. Strauss (*339*) began his investigations into nonrusting steels as early as 1909, and in 1924 published a structural diagram for the iron-rich corner of the Fe-Cr-Ni-C alloy system. For the austenitic stainless steels, chromium contracts the austenite field while nickel expands the region of stable austenite. The base composition of these highly corrosion-resistant stainless steels was decided upon as a result of phase diagram studies (during the period 1920–1930), since 8% by weight of the more expensive element nickel is the minimum amount that will give a nearly stable austenite at room temperature with 18% by weight of the element chromium, so that the high intrinsic corrosion resistance of both these elements is also utilized. The "18-8" stainless steels can lose their corrosion resistance by grain boundary precipitation of $Cr_{23}C_6$. To overcome this, an addition of Ti or Nb is usually made, forming more stable TiC or NbC, so that no carbon remains for formation of the injurious chromium carbide at the grain boundary. As was previously mentioned, nickel forms no stable binary carbides from steel melts. In view of these facts, it is interesting that a recent (1966) investigation by Stadelmaier (*320*) reported unsuccessful attempts to form any ternary carbides in the nickel-rich corner of six ternary systems, which included Ni-Ti-C, Ni-Nb-C, and Ni-Ta-C. The corresponding cobalt-rich ternaries were also included. No ternary carbides were found in any of these twelve ternary combinations.

Although the high-speed steels were originally based upon the composition 18W-4Cr-1V-C–0.70 in % by weight, molybdenum has been so widely used, especially for the last 25 years, to replace part of the tungsten in such steels, that something about both Fe-W-C and Fe-Mo-C is necessary. In 1931 Grossmann and Bain (*123*) published a book *High Speed Steel*, which contained an admittedly tentative isothermal section and a "pseudobinary" section for Fe-W-C. However, 3 years later the monograph *Alloys of Iron and Tungsten* by Gregg (*120*) contained a 40-page chapter on the ternary Fe-W-C. This chapter was based largely on the work of Takeda (*341*); the chief criticism offered by Gregg was that Takeda's diagram was too theoretical with insufficient experimental support. The work of Westgren on Fe_4W_2C was also discussed by Gregg in this volume. The companion volume *Alloys of Iron and Molybdenum* by

Gregg (*119*), published in 1932, contained only a 5-page appendix for the ternary Fe-Mo-C, commenting on the work of Takei (*342*), also published in 1932. A later important review was published by Goldschmidt (*114*) in 1948, as was previously mentioned. Both binary and ternary carbides in alloy steels were reviewed, binary and ternary diagrams published, and a bibliography of ninety-three references was included. A description from the literature of the system Fe-V-C appeared, as well as schematic isothermal sections typifying Fe-W-C and Fe-Mo-C. The experimental results obtained by Goldschmidt (*115*), in the second part of his researches on the carbides of high-speed steels, have been discussed above. In this second paper, he included a perspective view of the quaternary Fe-Cr-W-C, showing the location and extent of the various binary and ternary carbide phases and the approximate location of the usual high-speed steel composition in the system. Vanadium and its carbides in high-speed steels were separately discussed.

The following year (1953) Kuo (*183*) published isothermal sections for both the stable (Fe-graphite-W) and metastable (Fe-W-Fe_3C) diagrams at 700°C. The carbides found in ternary space for the stable section were Fe_3C, WC, M_6C (composition limits Fe_3W_3C to Fe_4W_2C, structure face-centered cubic), and $M_{23}C$ (also face-centered cubic, ideal composition $Fe_{21}W_2C_6$). These carbides all had analogs in the Fe-Mo-C system, which also contained (according to Kuo) two hexagonal forms of a molybdenum monocarbide "MoC"; this last controversial monocarbide need not be further discussed here. Kuo did not include isothermal sections for Fe-Mo-C in his paper, but his text amply covered the binary and ternary carbides of molybdenum-containing steels (Fe-Mo-C). Finally, in 1960 Campbell, Reynolds, and others (*62*) published a considerably expanded study of the Fe-Mo-C system. In general their findings agreed with those of Kuo and Takei; but, in the Campbell paper, isothermal sections for Fe-Mo-C were at 700, 925, and 1200°C, and eight vertical sections, five of varying molybdenum content (0.40, 0.80, 1.50, 3.0, and 6.0 wt. % Mo) and three of different carbon contents (0.40, 0.80, and 1.10 wt. % C), were included. The carbide phases found included Fe_3C or $(Fe,Mo)_3C$; $(Fe,Mo)_{23}C_6$, designated kappa carbide following Goldschmidt's notation; $(Fe,Mo)_6C$, called omega carbide; and Mo_2C, called theta carbide. The methods chiefly used were metallography by conventional light microscopy and heat treatment; some electron microscopy was performed, and X-ray diffraction was used to confirm identification of carbide phases. The alloy range was 0.05–1.3 % by weight carbon, 0.03–6.0 % by weight molybdenum, and the balance iron.

The references cited should be enough to show that extensive work has been done on ternary carbon-containing systems of ferrous alloys.

Literally hundreds of papers on high-speed steels have been printed in the last 40 years. In view of these facts, it is somewhat surprising to find a statement such as that made by Rassaerts, Kieffer, and others (*266*) in 1965 that no reference to the ternary system V-Cr-C could be found in the literature. It is true that this is not an iron-based ternary, but vanadium, chromium, and carbon are all important elements in the high-speed steels. The much greater complexities present in ternary and more complex alloy systems as compared to binaries, and in addition the fact that since high-speed steels have important practical applications much of the research is of an applied character, probably explain the absence of any prior publication on V-Cr-C.

2. *Other Systems*

Two principal areas of interest are ternary diagrams, centering mainly around uranium or plutonium carbides, and recent reinvestigations of ternary carbide systems, such as Hf-Ta-C and the paper on V-Cr-C just mentioned.

For nuclear fuels, the system U-Pu-C investigated by Dalton (*73*) is of considerable importance. Equilibrium phases between 50 and 60 atomic % carbon were studied by light microscopy and X-ray diffraction. Complete solid solubility of uranium sesquicarbide in plutonium sesquicarbide was observed. Another important and unsettled question is the effect of oxygen on uranium carbides, leading to a study of the system U-C-O. Two recent publications from the large number on this ternary system are one by Stoops and Hamme (*322*) and one by Anselin and others (*9*) on the system (U,Pu)(C,N,O) covering sintered carbides, carbonitrides, and oxycarbides. The constitution of the systems U-C-Mo, U-C-Re, U-C-W, U-C-Nb, and U-C-Y has been studied and reported by Chubb and Keller (*65*). Farr and Bowman (*100*) found a number of previously unreported ternary carbides of uranium in a partial phase diagram study. These carbides were of the type UMC_2 (where M is a metal atom). These included $UMoC_2$ (m.p. 2350° ± 30°C, orthorhombic) and UWC_2 (m.p. 2575°C, also orthorhombic). Lattice parameters for all the carbides they prepared were stated, as well as carbon-rich alloy eutectic temperatures for $UReC_2$ (2115 ± 30°C), $UCrC_x$ (1770 ± 30°C), and $UTcC_x$ (1865 ± 30°C). Only the lattice parameters that were stated to be of a preliminary nature will be given here. A second ternary technetium carbide $UTcC_2$ melted at approximately 1800°C; it was orthorhombic with $a = 5.4$, $b = 3.22$, and $c = 10.9$ Å. $UReC_2$ was orthorhombic with $a = 5.5489 \pm 0.0057$, $b = 3.2229 \pm 0.0004$, and $c = 10.7416 \pm 0.0086$ Å. This rhenium-containing carbide was also reported by Chubb and Keller. Tetragonal carbides containing iridium and rhodium were also reported by Farr and

Bowman. The formulas assigned were $UIrC_2$ and $URhC_2$. The manganese carbide of this formula type $UMnC_2$ was orthorhombic, $a = 5.04 \pm 0.01$, $b = 3.172 \pm 0.0002$, and $c = 10.74 \pm 0.02$ Å.

Included in the systems and phase diagrams investigated or reinvestigated by Rudy, Nowotny, Benesovsky, and their associates (mainly refractory carbide systems), we mention first the investigation of the system Hf-Ta-C by Rudy and Nowotny (*276*) in 1963. The form of the system at 1850°C was examined by use of samples prepared by pressing and vacuum sintering. Ta_2C was found to dissolve more than 10 mole % hafnium carbide. The phase Ta_3C_2 (zeta) has a narrow hafnium concentration range. Rudy and Chang (*277*) published isothermal sections at temperatures of 1300°–1900°C for the following ternary systems: V-W-C, Nb-W-C, Ta-W-C, Cr-W-C, V-Mo-C, Nb-Mo-C, Ta-Mo-C, and Cr-Mo-C. Some of the data were obtained from the literature, some from their own experiments. Not over two isothermal sections, some of which were thermodynamically calculated, were shown for any single system. Later work on the ternary V-Cr-C by Rassaerts and others (*267*) has also been published. The homogeneity range of V_2C (hexagonal) was found to extend into ternary space to about $(V_{0.9}Cr_{0.1})C$, and of the orthorhombic form of V_2C to approximately $(V_{0.45}Cr_{0.55})C$.

VIII. Property Correlations

A. WITH PERIODIC TABLE

The fact that HfC and TaC have melting points higher than any metals is a classic example of the elementary rule that, if two elements combine chemically, the further apart they are vertically in the Periodic Table the greater the heat of formation and the higher the melting point of the resulting compound. Many of the rules and generalities attempting to show relations between carbides and position in the Periodic Table are of less value because of the existence of several known exceptions to the proposed rule. This is also the case with many of the empirical theories concerning bonding and structure (both electronic structure and especially crystal structure) of the transition metal carbides.

Goldschmidt (*114*) has proposed rules of this kind for binary and some transition metal ternary carbides, which have been quite widely quoted. For binary carbides, class 1 structures (cubic NaCl type) are formed by all the elements of Group IVA (TiC, ZrC, and HfC) as well as part of the elements of Group VA (VC, V_4C_3, NbC, and TaC). However, in Group VIA and for some of the elements of Group VA, structures of class 2, hexagonal close-packed (Mo_2C, MoC, WC, and Ta_2C), are formed. Beyond

Group VIA the predominating structure type is orthorhombic (Fe_3C, Ni_3C, Co_3C). In Group VIA, chromium forms carbides of all three structures, $Cr_{23}C_6$ cubic, Cr_7C_3 hexagonal, and Cr_3C_2 orthorhombic. Goldschmidt classifies chromium as an intermediate or labile element. Manganese also forms Mn_3C orthorhombic, Mn_7C_3 hexagonal, and $Mn_{23}C_6$ cubic. All the structures listed here are those given by Goldschmidt in 1948. In explanation of this structure sequence, Goldschmidt cites Hagg's (*128*) radius ratio rules: if the ratio of the radius of the smaller nonmetal atom to the metal atom is below 0.59, cubic or hexagonal close-packed structures with coordination number 12 are to be expected. For radius ratios above 0.59, complex structures result. Extending these principles to iron-based ternary carbides, Goldschmidt proposes that elements (such as Fe-Co-Ni) forming orthorhombic carbides will be the least stable. Elements belonging to class 1 forming cubic carbides (such as TiC) will form no ternary carbides or solid solutions with iron. The greater chemical affinity or lower free energy of such carbides ties up all available carbon chemically combined with the element of Group IVA or VA. This is exactly what is done to prevent injurious grain boundary precipitation of $Cr_{23}C_6$ in austenitic stainless steels by formation of TiC.

If hexagonal carbides are formed (class 2), iron will form a cubic ternary carbide having limited solid solubility for iron (such as Fe_3Mo_3C to Fe_4Mo_2C). With chromium, no ternary carbides containing iron are formed, but the primary carbides of both iron and chromium have considerable mutual solid solubility. Finally, the orthorhombic iron carbide Fe_3C is isomorphous and completely intersoluble with orthorhombic Mn_3C, Co_3C, and Ni_3C. Andrews and Hughes (*7*) have attempted to extend Goldschmidt's observations to hexagonal carbide and nitride phases of type M_2X, such as W_2C, Fe_3N to Fe_2N, and $Ta_2(C,N)$. For twelve transition metals (Hf in Group IVA is omitted)—Ti, Zr (IVA); V, Nb, and Ta (VA); Cr, Mo, and W (VIA) plus Mn, Co, Fe, and Ni beyond Group VIA—Andrews and Hughes state that with the exception of cobalt: (a) elements forming a close-packed structure in the metallic state form only that interstitial phase (carbide or nitride) with the alternative close-packed arrangement of metal ions (i.e., face-centered cubic metal, hexagonal close-packed carbide), and (b) if the metal itself does not possess a close-packed modification (body-centered cubic Mo for example), both types of close-packed interstitial phase will occur (chromium is a possible but by no means certain exception). From a tabulation of twenty-three hexagonal carbide and nitride phases of "M_2X" type, hexagonal phases appear to be limited to appearing at or near such a composition ratio. If all the interstitial sites are not occupied, the hexagonal interstitial phase may extend to M_3X (25 at. % C or N). Thus, special importance attaches to ratios of metal to carbon or nitrogen of 2:1 or 3:1. It is evident that the numerous exceptions that must be made lessen considerably the validity of such relations between crystal structure and position in the Periodic Table.

B. STRUCTURE AND BONDING

Bonding is generally understood to denote forces between atoms and, although in some cases the terms metallic, covalent, and ionic bond types are concepts somewhat at variance with reality, these terms are in common use and retained in the literature. Structure, on the other hand, is used in connection with the arrangement and location of electrons in atoms or molecules (electronic structure), as well as the space arrangements of atoms or groups of atoms (crystal structure). The crystal chemistry and crystal structures of carbides are dominated by a comparatively few isostructural types under which large numbers of individual carbides can be classified. A number of such structural types and the carbides belonging to them have been discussed. No mention has been made of the important part that octahedral structural units (in which a carbon atom is at the center of six metal atoms) play in the building up of the unit cells of these carbide structure types. As for bonding and bonding forces in carbides, two important types of theory or approach to the problem exist. One of these is the electron band theory (the approach of mathematical physics), while the other theories of bonding are marked by use of empirical assumptions in varying degrees. Empirical theories also vary widely in the extent of their application and prediction. Some are concerned with both electronic structure and crystal structure, while others are limited to one of these fields. A selection will be made among the many empirical theories of carbide bonding that have appeared during the last 25 years. Some of these, such as the proposals made by Rundle (*280*) in 1948, are still widely quoted and referred to in the literature. Other theories, such as that of Ubbeholde (*350*) attempting to use facts known about the palladium-hydrogen system to explain carbide bonding, are now mainly of historical interest. From the electron band approach to the problems of carbide bonding, two band structures for TiC have recently been published (in 1965 and 1966). Since TiC is an important transition metal monocarbide, having practical applications and with a considerable amount of information available with regard to its hardness, electrical resistivity, thermal conductivity, and elastic moduli, band theory can be applied. Most of the discussion of bonding will be limited to the "cubic carbides" having NaCl structure, typified by TiC. The so-called "saltlike" carbides, such as Al_4C_3, are not of great interest at present, and can be largely explained by conventional chemical concepts.

For classification of binary carbides, we mention again Goldschmidt's (*114*) class 1 cubic (TiC), class 2 hexagonal close-packed (W_2C), and class 3 orthorhombic (Fe_3C). This scheme was also extended to iron-containing ternary carbides, such as the eta carbide series from Fe_3W_3C to Fe_4W_2C. The structure determination for Fe_3W_3C by Westgren (*5*) in 1933 was also mentioned previously. In 1965 Bojarski and Leciejewicz (*41*) published results of a neutron diffraction study of Fe_3W_3C. Their data confirm the earlier studies as to the position of the carbon atoms and the atomic parameters in the Fe-W-C system. The carbon atoms are in octahedral coordination with iron and tungsten.

Reference has also been made to the tabulation and classification of ternary carbides by Nowotny, Jeitschko, and others (*247*). In a somewhat more recent publication (*248*) the same authors extended their previous tables including over eighty ternary carbides to include newer members of each type. Crystal systems, type formulas, and typical examples for each class include: T_3MX (T = transition metal, X = carbon or nitrogen, M = lower melting metal or meta-metal), cubic perovskite carbides (Tb_3AlC), T_3M_2X phases with a filled and ordered beta-manganese type structure (Mo_3Al_2C), the H-phases of type formula T_2MX (Nb_2SnC) belonging to the hexagonal system, the kappa carbides (following the designation by Kuo) hexagonal but with c/a ratios close to unity ($W_{10}Co_3C_4$) (*270*), and the eta carbides of type T_4M_2X such as Zr_4Zn_2C. For the perovskite carbides, the carbon atom at the interior center of the face-centered cubic unit cell is octahedrally surrounded by six transition metal atoms at the face centers of the cube. This octahedral coordination is termed T_6X by Nowotny. For the beta-manganese type carbides, the T_6X octahedra are united at their corners. In the unit cells of the hexagonal H phases similar octahedra are joined by their edges, while in the eta carbides some of the T_6X octahedra are united by faces. For the perovskite carbides, which have a relatively simple face-centered cubic unit cell and structure, the Hagg radius ratio may have to have the upper limit extended from 0.59 to 0.65, more complex structures appearing above 0.65. The octahedra with carbon atoms at the center (T_6C) in both the perovskite and kappa carbide phases are united at their corners. Finally, as we move from T_4M_2X to T_2MX to T_3MX, increasing the ratio of the transition metal T to the low melting metal M, we are also increasing a general tendency toward a closer packing of the parent metallic lattice.

Two principles of significance long recognized for carbide crystal structures are the Hagg radius ratio principle and Hume-Rothery's size factor rule. Hume-Rothery's favorable size factor rule states that complete solid solubility may be expected if the diameters of the two atoms entering the solid solution are not over 15 % apart. Above this limit, solid solubility will be restricted. This principle applies to carbides, and the largest amount of information is available for the refractory monocarbides. For example, ZrC forms complete series of solid solutions with HfC, TiC, NbC, and TaC where size factors are favorable, but has only limited solid solubility with VC. In the application of these two rules, particularly the radius ratio rule, it is often difficult to determine or assign the proper atomic diameters, especially to the metal atom, as the observed interatomic distances in carbides and nitrides differ considerably from those in the metal. This problem of choice of proper atomic radii has been recognized for 35 years and is of considerable importance in theories of bonding.

At this point, we will briefly mention a number of empirical theories proposed to explain atomic and electronic bonding in carbides, but which need not be discussed at length. Umanski (*351*) assumed that the carbon of carbides was ionized. He ascribed the high hardness of such carbides as TiC and VC to a keying action on slip planes by the nonmetal atoms in a manner similar to early theories of precipitation hardening in alloys. According to Neshpor (*241*), the modern Russian ideas of Samsonov (*282*) are of the same general nature. Samsonov offers an explanation of carbide bonding in terms of the ionization potential I of the nonmetal atom, and the repulsive or acceptor ability of a transition metal atom with unfilled *d*- or *f*-electron shells. For this donor or acceptor ability, Samsonov uses an expression $1/Nn$ in which N is the principal quantum number of the unfilled *d*-electron level, and n is the number of electrons in this same unfilled electron level. In accord with predictions from this ratio, the superconductivity transition temperature of carbides of Group IVA (Ti, Zr, Hf) increases sharply as $1/Nn$ becomes smaller.

The proposals of Engel, originally published in Danish in 1949, were reviewed at length and summarized by Brewer (*54*) in 1963. Besides a short article, published in English by Engel (*93*) in 1954, two longer articles (*94*) outlining his theories were published bilingually in both English and German in the journal *Radex Rundschau* in 1956. Engel considered the very small atoms of the second period (e.g., carbon) as forming interstitial solid solutions and intermediate phases with the transition metal. In small amounts, the small interstitial atoms are just placed between the base metal atoms, without materially changing the bonding pattern or lattice of the transition metal. Electrons from the small atom left the outer levels and entered into the unfilled *d* levels of the transition metal. Thus, the small atoms were ionized and an ionic bond was created, in addition to what Engel terms "the electron field cancellation bond, generally called the covalent and metallic bond." Intermediate phases such as carbides will be harder, stronger, and more difficult to melt because *d*-electron bonding, outer electron bonding, and ionic bonding add up to the most powerful bonding combination known. Some of the ideas proposed by Trost (*347*) were similar to those of Engel. The theory of Trost, the spatial electron concentration proposal by Schubert (*289*), and most of the other pertinent bonding theory on carbides and nitrides up to 1963 have been reviewed by Nowotny (*246*) in his article in the book *Electronic Structure and Alloy Chemistry of the Transition Elements* (*29*). In 1963 Dempsey (*75*) published what is essentially an empirical band theory for bonding in the refractory hard metals. A point to be noted from most of the empirical theories mentioned is the transfer of charge and electrons from the nonmetal to the metal, giving a bond of ionic character. By analogy with typical ionic solids, the brittleness of the cubic transition metal monocarbides is due to the presence of some ionic bonding. Somewhat at variance with theories emphasizing ionic character were the views of Kiessling (*175*) and Robins (*272*), who emphasized strong M-M (metal-metal) interaction based in part on the idea that cubic carbides show a close-packed metallic parent lattice. In his review article, Kiessling based his idea of strong metallic bonding in monocarbides upon plots made by Brewer and Krikorian (*53*) of the bonding energies of nitrides and carbides (MeX compounds), which were compared to the heat of sublimation of the pure metals. From the similarity in values, strong metallic bonding in carbides was inferred by Kiessling. Robins placed considerable importance upon resonance as a contribution to bond strength and crystal structure. For transition metals toward the center of the Periodic Table, a large number of hybrid (*spd*) bonding orbitals with comparable energy will be present. In such cases, the strength of bonding will depend upon a relationship between the electron concentration (N) and the effective coordination of the metal atoms (C). The maximum stability due to resonance is obtained when the number of bonding electrons per atom is approximately equal to half the effective coordination number. Robins emphasized transfer of electrons from the carbon atom to the unfilled *d* orbitals of the transition metal atom leaving singly ionized carbon atoms present. Considering TiC as an example, at room temperature titanium (according to Robins) has a distorted hexagonal close-packed structure, the distortion being due to the metal atoms (four valency electrons) reducing their effective coordination number below 12. Upon adding carbon, carbon atoms donate electrons to metal atoms, increasing the effective metallic valency. Carbon has so much donating power that addition of only a small amount of carbon causes change to a face-centered cubic lattice and a metallic coordination number of 12. We now have a new metallic phase (TiC) stabilized by the presence of carbon and in which carbon has a wide range of solubility. Robins does not rule out the possibility of ionic type bonding due to electron transfer, but points out that resonance covalent and metallic type bonding is more important in the cubic (NaCl) carbides.

The explanation of carbide bonding advanced by Rundle (*280*), which is so widely referred to, was in turn based upon Pauling's metallic bond radii (*253*). Probably the most important idea of Rundle's theory, and one that constituted an extension of Pauling's concepts, was the idea of half-bonds. The conditions for forming half-bonds are stated by Rundle to be: (1) One element, A, must have more stable bond orbitals than valence electrons. Therefore A will generally be a metal. (2) Another element, B, must have relatively few bond orbitals. This will limit B to hydrogen and the first-row nonmetals, particularly carbon and nitrogen. (3) The electronegativities of A and B must not differ so much that the bond formed is essentially ionic. If the above conditions are met, compounds of A and B may be formed in which not all the bond orbitals of A are used for bond formation unless some orbital of B is used for more than one bond. Consequently, it will generally be better for B to form two half-bonds than one single bond. The requirement that the metal must have more stable bond orbitals than valence electrons limits the possible metals to transition metals (group A in the Periodic Table) with unfilled *d* shells. Furthermore, the alkalies and alkaline earths, although belonging to A groups in the Periodic Table, will be too electropositive in character. If the metal is beyond the fifth group of the Periodic Table, (MX) structures of NaCl type are not formed. Carbon has but four stable bond orbitals, but the octahedral configuration found in TiC, for example, requires six bonds. Pauling had explained this by supposing that four electron pairs resonated among the six bonds. According to Rundle, this was not sufficient to explain the brittleness of carbide structures or the preference of the light element for octahedral bonds. If the situation was formally stated in Rundle's terms, one orbital used with one electron pair formed two stable bonds, each of which was a half-bond or, in Pauling's terms, had bond number $\frac{1}{2}$. If *sp* orbitals were used, two of the six bonds formed by the light element would be ordinary electron pair bonds and resonance would make all six bonds equivalent. In contrast to the ideas of Hagg, Rundle believed that metal positions were appreciably changed from the metallic pattern in formation of carbides, and that radius ratio would not provide the necessary octahedral interstices for the carbon atoms in the rock salt type of carbide structure. From a table of the available structures of the transition metals themselves, and the structures of their carbides and nitrides, Rundle concluded that rearrangement of metal positions was necessary to provide octahedral interstices for the nonmetal. To explain the unusual combination of brittleness with electrical conductivity, Rundle suggested that directional properties in bonding together with free electrons, a combination such as is found in graphite, were needed. Stated in other terms, directed but not localized bonds were needed. Preference for NaCl structure, high melting point, and hardness required metal-to-nonmetal bonds of considerable strength. Forming bonds with octahedral configuration through the half-bond concept explained formation of NaCl structure. Strong metal-to-nonmetal bonds could be partially due to a considerable amount of ionic character in the covalent and half-bonds. Rundle was aware of the increased distances between metal atoms in carbides as compared to metals, and that this would tend to weaken metal-to-metal atom bonds. He used Pauling's formulas for bond number and for metallic valence as well as Pauling's single-bond metallic radii to show that the monocarbides and mononitrides of most of the transition metals in the entire Periodic Table, which met Rundle's three requirements, had probable bond numbers of $\frac{1}{2}$ or $\frac{2}{3}$. Either of these bond numbers could be easily explained by Rundle's proposals. If the carbide had one third electron pair bonds and two thirds half-bonds, the electron density in the bond would be two thirds that of an ordinary single bond. Stated in Pauling's terminology, this would be a bond number of two thirds.

Hume-Rothery (*155*) made a number of criticisms of the theory of Rundle. He objected to use of Pauling's bond number rule without correction, on the ground that a shortening of apparent atomic diameter with decreasing coordination number is to be expected from the energy standpoint alone, without any consideration of a resonating valence bond theory. With regard to Rundle's suggestion that hardness and brittleness implied directed bonds, Hume-Rothery suggested comparison with ruthenium. This metal has a melting point of about 2550°C; it is metallic in properties with high electrical conductivity, so that the bond type must be essentially metallic, but ruthenium is also brittle enough to be ground to powder in an ordinary percussion mortar at room temperature. Therefore, why should the carbides that melted at even higher temperature, and thus were still further below their melting point at room temperature, be brittle because of directed bonds? Since the hexagonal close-packed structure possessed by many of the transition metals, such as titanium, possessed one octahedral interstice per atom, why should it be necessary for the metal atoms to change to a face-centered cubic structure in the carbide only to provide octahedral interstices? On this point, Hume-Rothery's conclusion is that, although formation of octahedral holes may be one factor, the face-centered cubic arrangement is favored by the metallic atoms in the carbide structure because it provides them with mutually perpendicular bonds to six neighbors. If the octahedral interstices in a hexagonal close-packed system of spheres were filled, not all of the metal-to-nonmetal bonds would be perpendicular. The qualitative picture of carbide bonding for MX carbides of NaCl structure suggested by Hume-Rothery is that interatomic distances make it almost certain that covalent rather than ionic bonding is involved, as neither a C^{4+} or C^{4-} ion would fit and provide a stable structure. Each carbon atom tends to acquire a share in an octet of electrons. Since each carbon atom has four of its own electrons, it must obtain on the average two thirds of an electron from each of its six metallic neighbors, giving rise to resonating covalent bonds. This last suggestion is the same as that of Rundle. To explain conductivity in TiC, ZrC, and HfC having tetravalent metal atoms, which must use all four of the metallic electrons in forming the octet, Hume-Rothery suggests that conductivity arises from the fact that only some of the hybrid (*spd*) orbitals are filled.

Two recent calculations of the electronic band structure of TiC were mentioned previously. The first of these, by Ern and Switendick (*96*), was carried out by the augmented plane wave (APW) method and band structures for TiN and TiO were also calculated. Density of states, Fermi energy, and contours of constant energy were obtained for each of the three compounds. A charge distribution in the APW scheme was derived from the equivalent of thirty-two points in the Brillouin zone, and the admixture of bands was analyzed. The results were stated to be consistent with the experimental data.

A year later (1966) Lye and Logothetis (*193*) published the results of a study on optical properties and band structure of titanium carbide. Reflectivity measurements of TiC through the visible and vacuum ultraviolet gave additional data, which reduced the uncertainties connected with a calculation of the electronic band structure of TiC. The energy band calculation was carried out, using the tight binding approximation by the two-center method of Slater and Koster (*315*). The results of the two calculations for TiC differed widely. In addition to differences due to the method of calculation and to the use of optical data, Lye and Logothetis suggest other reasons that may account for the discrepancies, including (1) the core potentials, (2) the constant potential V_c between the APW spheres of Ern and Switendick, (3) the ionicity of each atom in the unit cell, and (4) the APW sphere radii (dependent upon the core potentials and the Madelung displacements). The differences between the two calculations may have been due to inapplicable assumptions with respect to one or more of the factors just listed. (Reference to the original papers should be made for further details.) Our purpose here is to discuss the deductions made from Lye's calculation with respect to carbide bonding.

The energy band structure obtained by Lye showed a band structure for TiC having a high and rapidly varying density of states of *d*-like character, similar to the *d* states in the transition metals themselves. In addition, some net transfer of charge takes place from carbon atoms to titanium atoms, so that part of the binding is ionic; covalent bonding occurs not only between carbon and titanium atoms, but also between titanium atoms and between carbon atoms. The type of covalent bonding existing between the metal atoms is similar in origin to the band bonding of transition metals; this effect appears to account for the relatively high melting points of the transition metals. The high density of unfilled *d* states in the free atoms constitutes a relatively low energy reservoir for valence electrons of higher energy when the solid is formed, thus lowering the total energy of the system.

In commenting on the work of Lye, Williams (*365*) remarks that it is important to make clear what is new in this work, especially since so much has been written about the nature of bonding in the cubic carbides. The idea that charge is transferred from the nonmetal to metal in the carbide has been advanced by Umanski, Kiessling, Robins, and Dempsey, as was previously discussed. The work of Lye puts these ideas on a firmer basis and adds theoretical support. The presence of covalent bonding was emphasized by these earlier workers, as well as by Rundle. The calculation by Lye gives greater precision to this view. The work of Lye also emphasizes the complex influence of charge transfer on binding, a point not brought forth strongly in earlier work. There is a considerable ionic character in TiC bonding due to the presence of relatively few conduction electrons to act as a screen for the ionic interaction. The covalent bonds could be expected to be of a directed nature, leading to a large stiffness with respect to elastic carbide behavior in accord with observations.Both elastic and plastic deformation are also resisted by the ionic bonding.

IX. Summary

The binary metallic carbides available from the literature have been described. Methods for their preparation have been indicated. The occurrence and preparation of some ternary carbides have also been considered. Metals with no reported binary or ternary carbides include promethium among the rare earths, the transuranium elements beyond atomic number 94, francium, radium, actinium, polonium, antimony, tellurium, and bismuth. The extensive pioneer work of Moissan must be included in any discussion of metallic carbides. Phase diagrams for a number of the important refractory metal-carbon systems have been discussed in some detail. A discussion of some of the problems of bonding in the cubic binary carbides of the transition metals is also included.

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