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LA-2942

LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS NEW MEXICO

A CRITICAL REVIEW OF REFRACTORIES

Printed in USA. Price $ 3.50. Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

LA-2942
UC-25, METALS, CERAMICS,
AND MATERIALS
TID-4500 (31st Ed.)

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REPORT WRITTEN: March 1964

REPORT DISTRIBUTED: August 13, 1964

A CRITICAL REVIEW OF REFRACTORIES*

by

Edmund K. Storms

*This report supersedes LAMS-2674, Parts I and II.

Contract W-7405-ENG. 36 with the U. S. Atomic Energy Commission

ABSTRACT

The literature concerning the Group-4a, -5a and -6a carbides and nitrides, and the carbides and nitrides of Th, U and Pu has been reviewed critically. The following properties have been discussed: preparation, phase relationship, lattice parameter and structure, appearance, chemical stability, hardness, resistivity, superconductivity, thermodynamic properties and vaporization. When possible, each property has been considered in light of the wide homogeneity range exhibited by these compounds.

Particular attention has been paid to methods by which the materials can be made oxygen- and nitrogen-free.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to various members of Group CMB-3 for sharing their broad experience with refractories. Discussions with and critical comments by Drs. M. G. Bowman and D. T. Vier have led to a clearer understanding of these systems and an improved presentation. In addition, the author is most grateful to Dr. W. G. Witteman for sharing his knowledge of the uranium-carbon system and for several encouraging discussions.

This literature review was made at the suggestion of Professor J. L. Margrave, Rice University, Houston, Texas, and will appear in the book, Chemistry of Nonoxide Refractories.

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GENERAL INTRODUCTION

This report is a revision of LAMS-2674, Parts I and II, to which a discussion of the nitrides and carbides of U, Th and Pu has been added. In general the literature covered extends from about 1930, depending on the system and the quality of the work, to March 1964. Although an effort has been made to present as complete a description of each system as possible, only that work which, in the author's opinion, would lead to a clearer understanding has been discussed in any detail. Most early work and some recent measurements have been largely ignored except to show the effect of oxygen content or to give an approximate measured value when no other exists. Many of the references cited, as well as several books, contain complete bibliographies of the early literature and may be consulted when necessary.

The carbides and nitrides discussed in this report suffer from two properties that have led to a considerable accumulation of questionable data. First, they are commonly single phase over a wide range of composition, and, second, they will form a solid solution with each other and with their respective oxide. Both of these factors will affect the properties of these materials, sometimes in a very striking manner. Without the use of care in preparing the compounds and the application of proper analytical techniques, an investigation may offer little meaningful information.

Because of these difficulties, it is essential that the composition of the material be indicated. If a chemical analysis is not practical, often the purity or stoichiometry can be estimated from the lattice parameter. The assumption that the difference between 100% and the sum of metal and C or N is due to oxygen has been used, but this will give only approximate answers at best. Even the direct analysis for oxygen is open to question, especially in the case of the Group-4a compounds. An excellent summary of analytical techniques has been published by Kriege (LA-2306, 1959).

In writing about the phase systems, certain conventions have been followed. The use of Greek letters has been avoided when the integral stoichiometry of the phase is known. When referring to a phase irrespective of composition, the integral metal/nonmetal mole ratio is used. When a particular composition is meant, the nonmetal/metal mole ratio is used. For example, Nb_2C refers to the entire hexagonal phase and $NbC_{0.5}$ indicates a particular composition. Neither designation suggests that the material of interest contains only one phase. $NbC_{0.6}$, according to the phase diagram, would contain both Nb_2C and NbC: a Nb_2C-phase with a composition of $NbC_{0.5}$ and a NbC-phase with a composition of $NbC_{0.71}$. Greek letters are applied to phases for which the integral composition is not known or to allotropic modifications. Thus, β-$TiC_{0.05}$ designates the β form of titanium containing dissolved carbon.

All lattice parameters are reported in angstrom units. Early values have been converted from kx units by the factor 1.00202. In some cases, when the unit is in doubt, the unit which would give the best agreement with later data has been used. In all cases, the original paper has been consulted for a clarification of this vexing point.

PART I

GROUP-4a, -5a AND -6a CARBIDES

INTRODUCTION TO THE GROUP-4a, -5a AND -6a CARBIDE SYSTEMS

These carbides share several very unique properties; they contain some of the highest melting substances presently known, and most of the compounds are hard and chemically inert. Such properties are very attractive to the hard metal industry as well as to the relatively new field of high temperature chemistry.

These same properties, however, make a study of these materials somewhat difficult. This difficulty is compounded by the ease with which these refractories can be contaminated by oxygen, either dissolved in the starting materials or from the surrounding atmosphere. Also, because of the high melting points, the temperature needed to reach equilibrium in a reasonable time is correspondingly higher than that encountered in normal chemistry. Because insufficient attention has been paid to these difficulties in the past, most observations are mainly qualitative in nature.

Several interesting generalities occur in this group of nine elements. The highest carbide phase, the one which is in equilibrium with graphite, is either fcc or will convert to this form before melting. Cr_3C_2 is apparently the only exception. In all cases, the composition of this phase lies at or below $MC_{1.0}$. If another compound forms, it does so near the composition $MC_{0.5}$ and has a structure which is almost hcp, if only the metal lattice is considered. Again the only exception is in the chromium system. The composition range of the "hexagonal" structure is relatively narrow, although the cubic form can exist over an amazingly wide range. This phenomenon is caused by vacant positions in the carbon lattice and not by interstitial solution of the metal or a lower carbide. For this reason, these materials are called defect compounds.

The highest melting point within a Group occurs at the sixth period and, within a period, the Group-5a carbides generally have the highest melting point. Thus, TaC apparently is the highest melting carbide, with a value in excess of 4000° C.

All of the carbides begin to rapidly evaporate both metal and carbon atoms near their melting temperature. This leads to a congruent vaporizing composition which changes in a regular way within the group. The Group-4a carbides vaporize congruently near $MC_{1.0}$. Within Group-5a, VC loses metal, NbC goes to $NbC_{\sim 0.73}$, and TaC goes to Ta_2C. Within Group-6a, Cr_3C_2 loses metal, Mo_3C_2 goes to Mo_2C, and WC will eventually revert to the metal.

The highest heats of formation are found in Group-4a, with a steady decrease as one moves to the other Groups.

Superconductivity is absent in Group-4a, but occurs at a relatively high temperature in Group-5a if the composition of the cubic phase is near $MC_{1.0}$. The temperature in Group-6a is intermediate in value.

Trends in hardness and electrical conductivity are less clear because of the difficulties associated with these measurements. Apparently VC, TiC and, perhaps, W_2C are the hardest carbides. The stoichiometric carbides are only slightly more resistive than the pure metals, and, it is interesting to note, the resistivity increases as carbon is removed from the lattice.

The Group-5a carbides show a characteristic color change from the usual gray cast when the composition is near $MC_{1.0}$. Unfortunately this phenomenon has not yet been explored.

These trends are fairly well established and have been used to some degree in evaluating the data presented in the following discussion.

Chapter I. 1

The Group-4a Carbides

Elements of Group-4a form only one carbide. This carbide has a simple NaCl-type structure, and the lattice is preserved throughout an amazingly wide range of composition, even to about $MC_{0.50}$. Although the same crystal structure is maintained, most of the physical properties change drastically. For example, when the maximum amount of carbon has been removed, the lattice contracts by about 0.01 A, the melting point drops by over 1400°, and the hardness is almost halved. Although few properties have been measured as a function of composition, it is expected that each will show a similar, pronounced variation. The great stability of these carbides produces, in the case of HfC, one of the highest melting materials, and gives TiC the highest hardness measured for a pure metal carbide.

The composition range of ZrC does not extend to the integral stoichiometry, but that of TiC and HfC apparently does. ZrC and TiC both show a maximum in the melting point which is not at the integral stoichiometry, and HfC is assumed to behave in the same way. The MC compound forms eutectics with both the metal and carbon. This simple relationship is complicated somewhat by an allotropic transformation exhibited by each metal which is raised by the dissolution of carbon, forming a peritectoid.

Even though these carbides can be prepared from the oxides, the last trace of dissolved oxygen is very difficult to remove. Its effect on the lattice parameter and hardness has been demonstrated, and one would expect the other properties to be affected as well.

Both ZrC and HfC exhibit congruent vaporization near the upper phase boundary, and TiC loses Ti preferentially at low temperatures but may become congruent near its melting point.

and Rudy, 1960; Farr, 1962), it is more reasonable to expect eutectic rather than peritectic melting in the TiC system. The peritectoid reaction, however, seems well established with the earlier work of Jaffee, Ogden and Maykuth (1950).

TiC has a particularly wide homogeneity range. Cadoff and Nielsen (1953) place the lower limit at $TiC_{0.49}$. This is too high according to Ehrlich (1949), Rengstorff (1947), and Ragone (1951), who give a limit at $TiC_{0.28}$. The presence of oxygen, however, will shift the phase boundary in this direction. The upper limit of TiC is difficult to obtain because of the very slow equilibrium with graphite and because oxygen can fill the lattice sites instead of carbon. Storms (1963[a]) places the limit at $TiC_{1.0}$ after cooling from the melt. Norton and Lewis (1963) give $TiC_{0.95}$.

It should be realized when evaluating the results above, that oxygen and nitrogen in small quantities cause an increase in the melting point at low carbon contents. In addition, the solubility of carbon in the metal is increased by the presence of these impurities (Stone and Margolin, 1953). Thus, these authors suggest that the material used by Ehrlich (1949) suffered from the presence of 3-4 wt % oxygen and nitrogen. Also the peritectic at 1700° reported by Kurnakov and Troneva (1962) can be explained in this way.

No additional phases other than those mentioned above have been confirmed.

Reported melting temperatures for TiC fall in the range between 2940° (Engelke, Halden and Farley, 1960) and 3250° (Schwarzkopf and Kieffer, 1953). The general lack of analytical data, for both carbon and oxygen in the melted material, makes a choice based on the present literature highly arbitrary.

A value of 3080°C for the TiC-C eutectic temperature (Portnoĭ, Levinshiĭ and Fadeeva, 1961) was not supported by a more recent measurement by Storms (1963[a]) who observed melting at 2780 ± 25°C.

A phase diagram, shown in Figure I. 1. 1, is based on what seems to be the most reliable information. The melting point of Ti (1660°) was taken from work of Schofield and Bacon (1953).

Lattice Parameters and Structure

The lattice parameters for TiC and Ti are shown in Table I. 1. 1. The parameters for TiC are given for the quenched-in phase boundary composition at room temperature. The cubic β-Ti cannot be retained upon cooling.

Lattice parameter measurements as a function of composition are shown in Figure I. 1. 2. Recent work by Norton and Lewis (1963) has revealed a maximum in the curve similar to that found in the ZrC system. Several measurements by Storms (1963[a]) support this observation as shown in the figure. Ehrlich's values, although they agree with early determinations, are too low because of the presence of oxygen and nitrogen, as described previously. Thus, it would appear that oxygen lowers the parameter, makes the curve more gradual and extends the range of homogeneity. Based on the upper curve in Figure I. 1. 2, the density decreases from 4.91 g/cm^3 at $TiC_{1.0}$ to 4.57 g/cm^3 at $TiC_{0.6}$. Neutron diffraction studies have shown that the carbon atoms are statistically distributed in the octahedral voids, and all the metal positions are filled by Ti atoms (Gorbunov et al., 1961).

Appearance

TiC has a shiny, metallic gray color.

Chemical Stability

Like the other refractory carbides, TiC is very inert to acids, although it will dissolve in a mixture of HNO_3 + HF. The stability of the carbides to attack by acid increases in the following order:
Mo_2C-HfC-ZrC-TiC-WC-W_2C-NbC-TaC (Kopyleva, 1961).

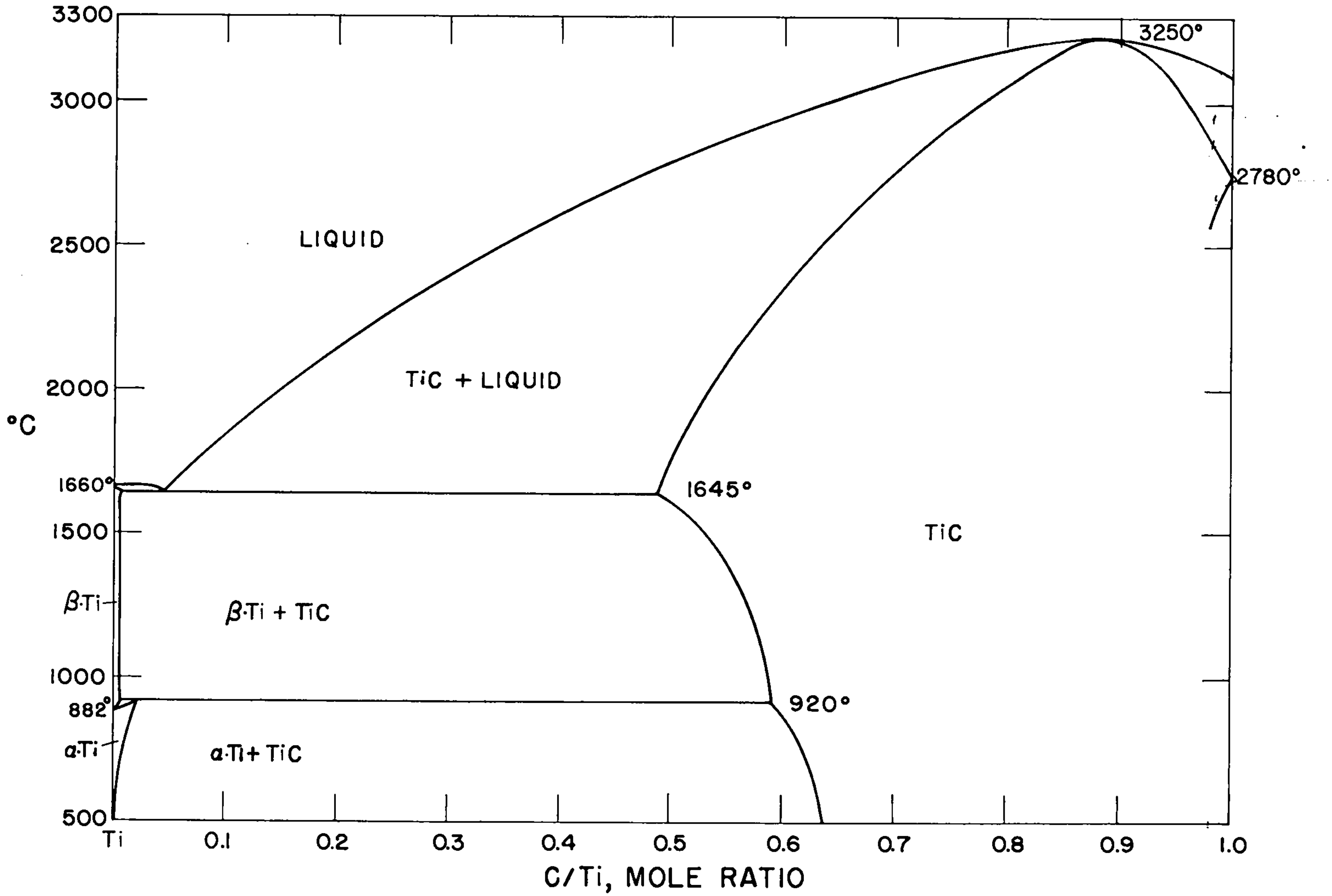

Figure I. 1. 1 Phase Diagram of the Ti-TiC System

TABLE I.1.1

Structure and Lattice Parameter of Ti and TiC

Phases in Equilibrium	Composition of First Phase	Structure	Lattice Parameter, A	Investigator
α-Ti	pure	hcp	a = 2.95111 ± 0.00006 c = 4.68433 ± 0.00010	Wood (1962)
β-Ti	pure	bcc	a = 3.280 ± 0.003	Rare Metals Handbook (1961)
α-Ti + TiC	α-$TiC_{0.016}$	hcp	a = 2.9550 c = 4.7025	Cadoff and Nielsen (1953)
TiC + Ti	$TiC_{0.61}$(cooled from the melt)	fcc	a = 4.3127	Cadoff, Nielsen and Miller (1955)
TiC	$TiC_{0.85}$(maximum)	fcc	a = 4.3305	Norton and Lewis (1963)
TiC + C	$TiC_{1.0}$	fcc	a = 4.3280	Storms (1963[a])

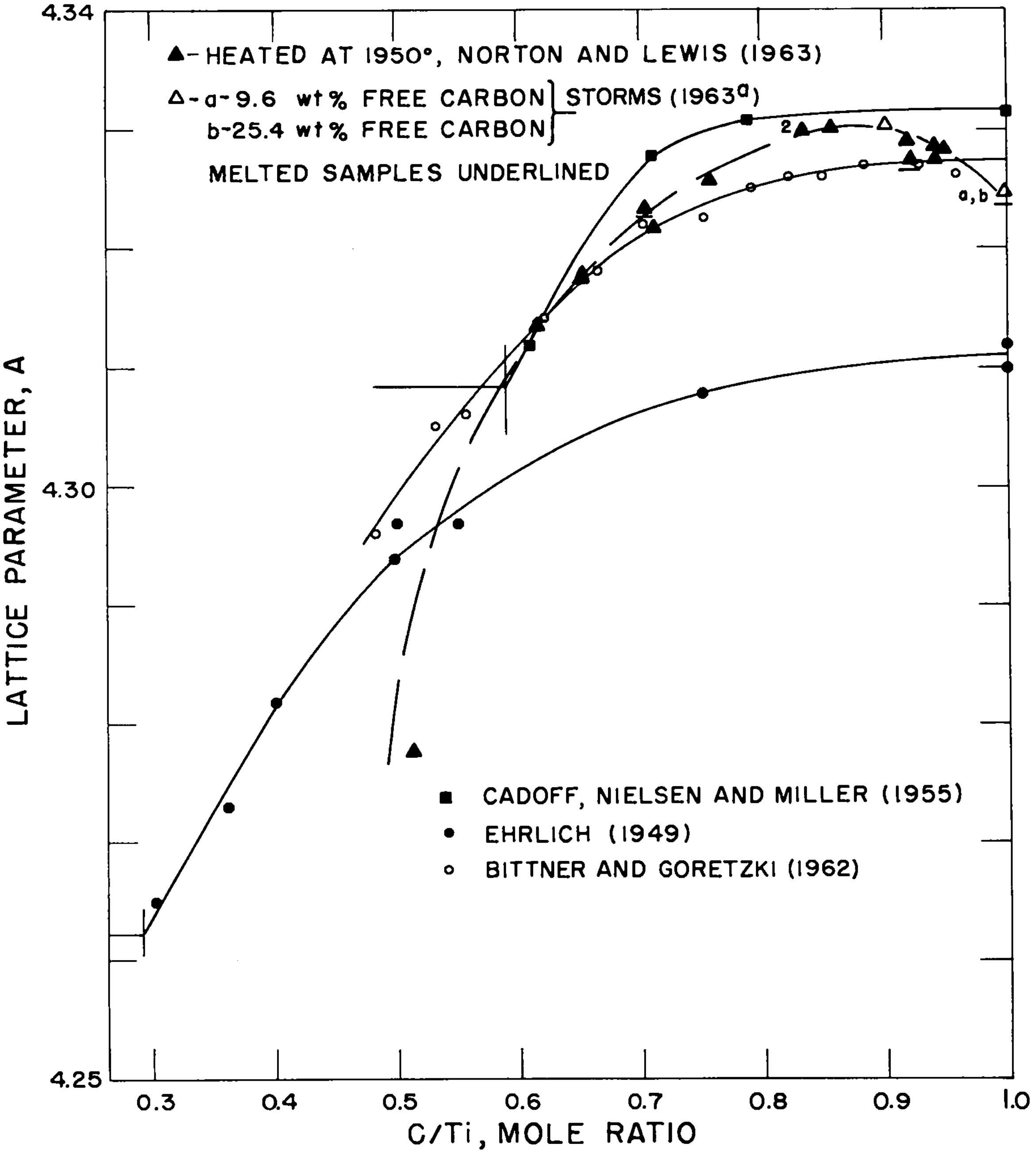

Figure I. 1. 2 Lattice Parameter of the TiC Phase as a Function of Composition

TiC is oxidized rapidly by oxygen, N_2O, or CO_2 at 1200°C (brightness temperature), but does not react with N_2, H_2, or CO at this temperature (Pollard and Woodward, 1950). On the other hand, Zelikman and Govorits (1950), after a detailed study of the reaction between TiC and N_2, conclude that the amount of nitrogen in TiC should not exceed a few tenths of 1% at 1800-2000° under a N_2 pressure of about 0.01 atm, with a trend to a lower solubility at higher temperatures. Above 1500°, a pressure in excess of 1 atm is necessary to cause complete nitriding.

Hydrogen at a pressure of 10^{-3} atm does not react with TiC between 298° and 2000°K (Philipp, 1961; Ohlinger, 1959[a]). However, May and Hoekstra (1961) find that TiC is attacked at higher pressures.

Hardness

Cadoff, Nielsen and Miller (1955) obtained, with a 300 g load, a Vickers hardness with values between 1600 and 2800 and an S-shaped variation with composition. The presence of oxygen raised the hardness and caused brittleness. On the other hand, Koval'skii and Makarenko (1953) found a linear variation which extrapolated to 2900 kg/mm^2 at $TiC_{1.0}$. Jones (1956) reported 3100 DPH when graphite was present (Table I.3.4). Meerson and Umanskii (1953) cite a value of 2850 kg/mm^2 without giving a composition. Gilman and Roberts (1961) give 3200 kg/mm^2, which agrees with the value found by Kieffer and Kölbl (1949). Williams (1961) obtained 2300 kg/mm^2 from a large single crystal of TiC containing graphite precipitated along the 111 phases. TiC appears to be one of the hardest pure carbides known, and for this reason it is used extensively in the hard metal industry.

Electrical Resistivity

Recent determinations of the electrical resistivity give the following room temperature values: 52.5 μohm-cm (L'vov, Nemchenko and Samsonov, 1960), 68 μohm-cm (Rudy and Benesovsky, 1960), 59.5 μohm-cm with +1.52%/deg (0.90 μohm-cm/deg) temperature coefficient (Samsonov, 1956^b) and 72 μohm-cm (Glaser and Ivanick, 1952). The composition and purity of the samples used were not stated. Since the resistivity changes rapidly with composition, these values have very little significance except to show that the measurements were made on material which was close to the stoichiometric composition. Older values are consistently much higher. Kolomoets and co-workers (1958) obtained a value of 50 μohm-cm for a pressed sample of $TiC_{1.0}$ + 0.14 wt % free C.

In a recent paper by Vainshtein and co-workers (1961), measurements of the conductivity as a function of composition, obtained by L'vov, Nemchenko, Verkhoglyadova and Samsonov, were cited. Their work shows a linear variation between 52 μohm-cm at $TiC_{1.0}$ and 180 μohm-cm at $TiC_{0.59}$. Using single crystals, Williams and co-workers (1964) found a variation that deviated somewhat from a straight line.

Superconductivity

Titanium metal becomes superconducting at about 0.40°K (Steele and Hein, 1953; Smith, Gager and Daunt, 1953). Hardy and Hulm (1954) could find no evidence for superconductivity in TiC above 1.2°K but, according to Meissner and Franz (1930), the carbide does become superconducting at about 1.1°K.

Thermodynamic Properties

A determination of ΔH_{298} by combustion calorimetry gave -43.9 ± 0.4 kcal/mole for a composition near $TiC_{1.0}$ (Humphrey, 1951). The carbide was $TiC_{0.996}$ (total carbon) with 0.60% impurities and was the same material used by Naylor (1946) for his heat capacity measurement. Recently Vidale (1961), employing optical absorption to measure the concentration of metal in the vapor over the metal and carbide, obtained -35.5 ± 0.5 kcal/mole for ΔF_f° (2220°K) and calculated, using Naylor's data, a value of -42.7 ± 0.5 kcal/mole for ΔH_{298}°. These values apply to a composition of TiC which is in equilibrium with carbon at 2220°K. Kibler and co-workers (1963) calculated -42.8 ± 1.2 kcal/mole from a Langmuir study of $TiC_{0.96}$.

The first determination of the high temperature heat content was made by Naylor (1946) on a possibly inhomogeneous sample. His measurements were expressed by the following equation:

$$H_T - H_{298.16} = 11.83T + 4.0 \times 10^{-4}T^2 + 3.58 \times 10^5/T - 4765 \text{ cal/mole}$$
$$(298\text{-}1800°K; \pm 0.5\%).$$

Recently workers at the Southern Research Institute (1963) have reported heat content values in Btu/lb from which the following equation was recalculated:

$$H_T - H_{298.16} = 10.63T + 11.32 \times 10^{-4}T^2 + 1.7 \times 10^4/T - 3470 \text{ cal/mole}$$
$$(533\text{-}2900°K).$$

Low temperature heat capacities and entropy were reported by Kelley (1944) for $TiC_{0.96}$ containing about 0.75% oxygen. A value of 5.8 ± 0.1 e.u. was given for S_{298}°, and C_p at 294.9°K was found to be 7.987 cal/mole-deg.

No variation of the above properties with composition has been made.

Vaporization

Chupka and co-workers (1958) were unable to obtain mass spectrometric evidence for the molecular species, TiC. In spite of this, Bolgar, Verkhoglyadova and Samsonov (1961) have concluded from Langmuir experiments that there is a molecular species which decomposes just after leaving the surface. Their values for the evaporation rate are so inconsistent with previous measurements, and their conclusion (see Nb-NbC system) is so unlikely that their results should be viewed with doubt until further work is done. Fujishiro and Gokcen (1961[a]) measured the pressure of Ti over TiC, using Knudsen effusion, but obtained a pressure 12 times higher than would be predicted from measured thermodynamic functions. This discrepancy was pointed out, but no reason was suggested. Vidale (1961) reports that the pressure of Ti over the metal at 1666° (the melting point) is equal to the metal pressure over $TiC_{(s)} + C_{(s)}$ at 2220° according to measurements by resonance line absorption. Langmuir experiments done at General Electric Company have been summarized in a report by Kibler and co-workers (1963). In this work the weight lost by $TiC_{0.96}$ was measured between 2109° and 2540° K with values of 2.42×10^{-8} g/cm^2-sec and 1.14×10^{-5} g/cm^2-sec at the respective limits. They also presented thermodynamic arguments which suggest that the Ti-C system vaporizes congruently only above 2800° K. Although it is clear that vaporization from $TiC_{0.96}$ is nearly congruent, there is insufficient data to show how TiC actually behaves in this regard.

I.1.2 The Zirconium-Zirconium Carbide System

Preparation

As early as 1865, ZrC was prepared from zirconia and carbon by Troost. Somewhat later, Moissan (1893^a) prepared the carbide by the same reaction in the electric arc. Almost all early measurements were based on material made by heating ZrO_2 and graphite, usually in an evacuated furnace.

The reduction of ZrO_2 proceeds in three steps with the formation of Zr_2O_3, then ZrO, and finally the carbide. The Zr_2O_3 begins to form at 940-960°, and ZrO is produced above 1240° (Meerson and Samsonov, 1952). If the heating is continued in a partial vacuum (1-1.5 torr) to a temperature of 2300° and held for about 6 hours, according to Zhelankin and co-workers (1958), the oxygen content can be reduced to below 0.01 mole ratio (O/Zr). Unfortunately there is still no method which gives a reliable oxygen analysis, and reported oxygen values are open to some doubt.

When a low oxygen content is desired, the product is best produced by reacting Zr or ZrH with carbon. As with titanium, the reaction between the elements is slow even when a liquid phase is formed (Anderson and co-workers, 1950). After the carbide has been produced, a long heating in high vacuum is necessary to remove the last trace of oxygen. The McKenna process using a cobalt melt also appears to reduce the oxygen level (Farr, 1962).

Pure crystalline deposits of ZrC can be formed from the gas phase containing $ZrCl_4 + H_2$ and a hydrocarbon vapor. The reaction goes between 1730° and 2430° (Campbell and co-workers, 1949).

Finely powdered zirconium and, to a lesser extent, the carbide are pyrophoric and should be handled accordingly.

Phase Relationships

One carbide having an integral stoichiometry of ZrC and two crystal modifications of the zirconium-carbon solid solution occur in this system.

A variety of values for the range of the ZrC phase and melting temperatures have been reported (Koval'skii and Makarenko, 1951; Samsonov and Rozinova, 1956; Agte and Alterthum, 1930; Brownlee, 1958; Agte and Moers, 1931; Friederich and Sittig, 1925; Schwarzkopf and Kieffer, 1953). From the techniques used and the reported lattice parameters, it can be inferred that the materials studied by these workers contained a significant amount of oxygen and/or nitrogen.

Recent work by Farr (1962) and Sara and co-workers (1963) has been done under conditions which would prevent this contamination. Farr (1962) observed Zr-ZrC eutectic melting at 1810°, a melting point maximum of 3400 ± 50° at $ZrC_{0.82\pm0.02}$, and melting of the ZrC-C eutectic at 2850 ± 50° with $ZrC_{0.965}$ in equilibrium with graphite. Sara and co-workers (1963) could find no significant decrease in the Zr melting point when carbon was present. However, they found that the ZrC melting point maximizes at 3420° and $ZrC_{0.85}$, and that the ZrC-C eutectic melts at 2850°, thus confirming the work of Farr (1962). This eutectic temperature also compares well with a value of 2800° measured at the U. S. Bureau of Mines (Anderson and co-workers, 1950). Benesovsky and Rudy (1960) obtained 1830° for the Zr-ZrC eutectic temperature.

Eutectic compositions of $ZrC_{<0.02}$ (Sara and co-workers, 1963) and $ZrC_{0.05}$ (Benesovsky and Rudy, 1960) have been reported for the Zr-ZrC region, and of $ZrC_{1.86}$ (Sara and co-workers, 1963) and $ZrC_{1.80}$ (Anderson and co-workers, 1950) in the region between ZrC and C.

This is another example of a system in which the maximum melting temperature does not lie at the 1:1 metal-carbon ratio and, in fact, the integral composition is not even formed at high temperatures. Although no complete study was made, Farr did find that, by dropping to 2400°, the carbon content could be raised to at least $ZrC_{0.98}$. The low carbon boundary apparently lies between $ZrC_{0.62}$ (Sara and co-workers, 1963) and $ZrC_{0.55}$ (Farr, 1962),depending on the cooling rate or temperature.

Zirconium metal has two allotropic modifications, a hexagonal form below 865° (Duwez, 1951) which converts to the cubic form above this temperature. If the element can be compared to titanium, the transformation temperature will be raised by the presence of carbon to give a peritectoid reaction. Preliminary work by Sara and Dolloff (1962) indicates that this temperature is raised to about 885°.

The melting point of Zr metal is 1855 ± 15°, measured by Deardorff and Hayes (1956).

Lattice Parameter and Structure

ZrC has a NaCl-type crystal structure and, like the other carbides, forms a subtraction type lattice between about $ZrC_{0.54}$ and $ZrC_{0.98}$. No other carbide phases have been confirmed (Table I. 1. 2).

Because of the difficulty in maintaining the material free from oxygen and nitrogen, both of which lower the lattice parameter, most determinations have given values below 4. 69 A. Recent measurements by Sara and co-workers (1963), using very pure preparations, have revealed a maximum in the lattice parameter variation. Their values are shown in Figure I. 1. 3. This very unique observation has been confirmed subsequently by Storms (1963[a]) as indicated in the figure.

The density based on the curve in Figure I. 1. 3 increases from 6. 294 g/cm^3 at $ZrC_{0.55}$ to 6. 572 g/cm^3 at $ZrC_{0.98}$.

TABLE I.1.2

Structure and Lattice Parameter of Zr and ZrC

Phases in Equilibrium	Composition of First Phase	Structure	Lattice Parameter, A	Investigator
α-Zr	pure	hcp	a = 3.2323 c = 5.1477	Holmberg and Dagerhamn (1961)
β-Zr	pure at 980°	bcc	a = 3.616	Skinner and Johnston (1951)
ZrC + Zr	$ZrC_{0.55}$	fcc	a = 4.691 ± 0.001	Farr (1962)
ZrC	$ZrC_{0.82}$	(maximum)	a = 4.7017 ± 0.0005	Figure I.1.3
ZrC + C	$ZrC_{0.95}$	fcc	a = 4.6983 ± 0.0003	Sara and co-workers (1963)

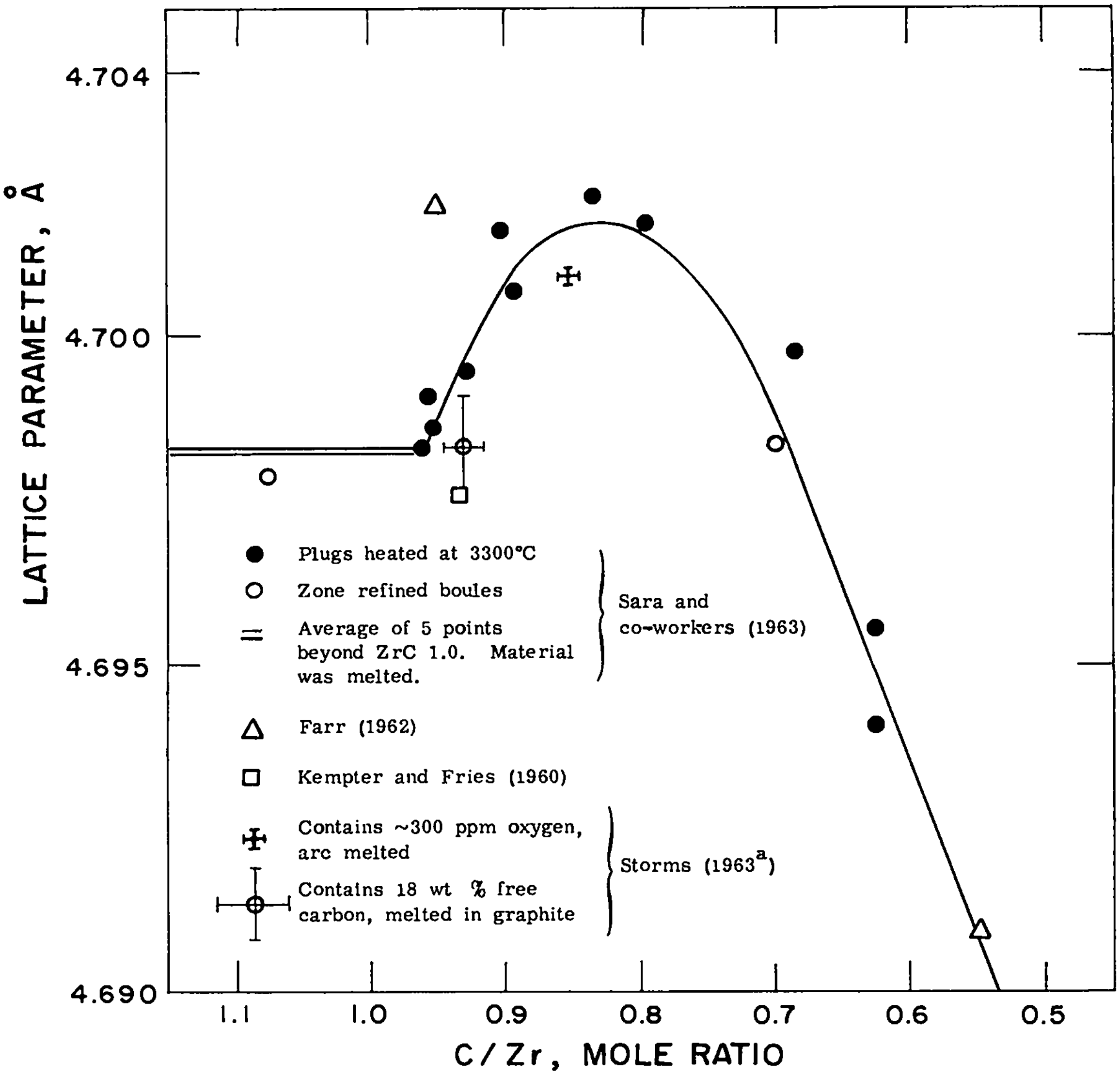

Figure I.1.3 Lattice Parameter of ZrC as a Function of Composition

Chemical Stability

ZrC, depending on physical form or fineness, is readily attacked by oxygen above about 500°. Above 1500° it reacts with nitrogen to form the nitride. Attack by the halogens leads to the formation of the tetrahalide.

Nonoxidizing acids have no effect, but the carbide will dissolve in HNO_3 + HF or in H_2SO_4.

Hardness

The hardness of ZrC is in some doubt. Meerson and Umanskii (1953) cite a value of 2836 kg/mm^2 obtained by Soviet investigators, Kieffer and Kölbl (1949) give 2600 kg/mm^2, Jones (1956) obtained 2200 DPH (Table I. 3. 4).* The variation of hardness with composition was found by Koval'skii and Makarenko (1951) to be linear. Their curve extrapolates to 2700 kg/mm^2 at $ZrC_{1.0}$, while at $ZrC_{0.52}$ 1850 kg/mm^2 was measured. A similar result by Samsonov and Rozinova (1956) leads to 2900 kg/mm^2 and 2000 kg/mm^2 as the limits. However, because of the very low lattice parameters (4.582-4.683 A) and the wide homogeneity range ($ZrC_{0.27}$-$ZrC_{1.0}$) reported by the latter workers, the presence of considerable oxygen and/or nitrogen can be inferred.

Electrical Resistivity

Recent room temperature values for the electrical resistivity are 42 μohm-cm (Rudy and Benesovsky, 1960), 56.6 μohm-cm with a temperature coefficient of +0.596%/deg (Samsonov, 1956[b]), 50.0 μohm-cm (L'vov, Nemchenko and Samsonov, 1960), 65 μohm-cm with a 0.074 μohm-cm/deg temperature coefficient (Taylor, 1962), and 67 μohm-cm (Kolomoets et al., 1958). The latter value was measured on material having 88.19% Zr, 11.53% bound carbon, 0.12% free carbon and 6.4% residual porosity. The value is corrected for the porosity.

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*See page 89

Preliminary work (Taylor and Kakata, 1962) shows that $ZrC_{0.93}$ has a resistivity of 127 μohm-cm at 800° and 223 μohm-cm at 2200° with a slight positive deviation from a straight line between these extremes.

Superconductivity

ZrC was found to be a normal conductor down to 1.2°K (Hardy and Hulm, 1954). The pure metal becomes superconducting at about 0.6° (Smith and Daunt, 1952; Matthias and Corenzwit, 1955).

Thermodynamic Properties

A value of -44.1 ± 1.5 kcal/mole was obtained for $\Delta H^\circ_{f\,298}$ from combustion calorimetry (Mah and Boyle, 1955). This value is compromised somewhat by the presence of 0.78% total of oxygen and nitrogen for which a unique correction could not be made. From vaporization studies, Pollock (1961) calculated a value of -47.7 ± 5 kcal/mole for $\Delta H^\circ_{f\,298}$ and -38.9 ± 1.5 kcal/mole for $\Delta F^\circ_{f\,2675^\circ K}$. This applies to ZrC in equilibrium with graphite. Using optical absorption to determine the amount of Zr in the vapor over ZrC + C, Vidale (1961) obtained $\Delta F^\circ_{f\,2740^\circ K} = -38.8 \pm 1.0$ kcal/mole, from which a value of $\Delta H^\circ_{f\,298} = -47.6 \pm 3$ kcal/mole was calculated using the heat capacity estimates of O. H. Krikorian (1955). Kibler and co-workers (1963) calculated $\Delta F^\circ_{f2740} = -39.2$ kcal/mole from their Langmuir studies.

Low temperature heat capacity measurements have been reported recently by Westrum and Feick (1963). A recalculation on the basis $ZrC_{0.95}$, the analyzed composition, gives the following values at 298.15°: $C_p = 9.00$ cal/mole-°K, $S^\circ = 7.92$ e.u., and $H^\circ - H^\circ_0 = 1392$ cal/mole. The high temperature heat content has been measured between 260° and 2600° with an ice drop calorimeter by Neel and co-workers (1960). Their values are in essential agreement with the estimation of Krikorian (1955) which is given by the equation

$$H_T - H_{298} = 11.06T + 7.6 \times 10^{-4}T^2 + 2.43 \times 10^{-5}/T - 4179 \text{ cal/mole.}$$

Vaporization

Pollock (1961) has studied the evaporization process by both Knudsen and Langmuir techniques. At 2673°K, the Langmuir method gave an evaporation rate of 2.04×10^{-6} g/cm^2-sec. The general consistency between the two methods led Pollock to conclude that the evaporation coefficient is unity and that there is essentially no ZrC in the vapor. Coffman and co-workers (1960[a]), using the Langmuir technique and the same assumptions, gave the following pressures over congruent ZrC; $\log P_C = 7.2877 - 3.8586 \times 10^4/T$ and $\log P_{Zr} = 7.7282 - 3.8586 \times 10^4/T$. These equations are in agreement with the results of Pollock. Bolgar, Verkhoglyadova and Samsonov (1961) also studied this system by the Langmuir method and reported pressures that are about 10^3 higher than those cited above.

Farr (1962) observed that even the presence of an inert atmosphere could not prevent the rapid loss of Zr when Zr-rich ZrC was heated near its melting point. Heating in vacuum above 3300°C will eventually lead to a composition of $ZrC_{0.82}$ (Farr, 1962). Conclusions that the congruent composition lies near $ZrC_{1.0}$ must be re-examined in light of the recently observed maximum in the ZrC lattice parameter curve. Pollock (1961) observed a surface lattice parameter which was higher than that of the bulk material. Instead of having a higher composition than the bulk, as he assumed, the surface actually was at $ZrC_{\sim 0.9}$, i.e., near the congruent composition. The lattice parameter increase observed by Coffman and co-workers (1960[a]) also suggests that the initial high stoichiometry was being lowered by evaporation to a value near $ZrC_{0.92}$. If ZrC is similar to NbC, the congruent composition should go to a lower value as the temperature is raised; thus Farr's value is not inconsistent.

I. 1. 3 The Hafnium-Hafnium Carbide System

Preparation

As with the other carbides, HfC is often prepared from the reduction of the oxide by graphite. The reaction

$HfO_2 + (x - y + 2)\,C = HfC_xO_y + (2 - y)CO + Q_p$

has been studied between 1743° and 2003°K by Zhelankin and co-workers (1959), for which they obtain a Q_p of -132 ± 3 kcal/mole. Samsonov and Paderno (1961) reported that at 1000-1200°C this reduction proceeded through Hf_2O_3; at 1300-1800° the HfC-HfO solid solution formed; and, finally, between 1800° and 2000° HfC formed with a carbon-deficient lattice. Repeated 1 hour heatings at 1900° resulted in a product near $HfC_{1.0}$. The final removal of oxygen requires a long heating in high vacuum ($< 1 \times 10^{-5}$ torr)

Moers (1931[a])pioneered the technique whereby HfC is produced from the reaction $HfCl_4 + CH_4 + (H_2) = HfC + 4HCl + (H_2)$. Campbell and co-workers (1949) have extended this reaction to produce a coating of HfC on a heated tungsten filament.

The purest HfC can be produced by reacting the elemental powders either by arc melting or by powder metallurgy. Like the other elements in this group, Hf does not react quickly with carbon. Therefore, some patience is needed to obtain a uniform product when starting with the elements. The reaction between HfH and C goes much more quickly and also produces an oxygen-free product (Nowotny and co-workers, 1959).

Phase Relationship

The phase relationships have been summarized by Benesovsky and Rudy (1960) in a tentative phase diagram based partly on their work. In this diagram, eutectic melting between Hf and HfC occurs at about 2000°, a maximum melting temperature of 3900° is shown at $HfC_{1.0}$ and the HfC-C eutectic is estimated to melt at 3000°. The only melting point determination for $HfC_{1.0}$, which has been quoted extensively, was reported in 1930 by Agte and Alterthum as 3887°.

Recently, Avarbe et al. (1962), while measuring the melting point of various compositions, obtained 3520°C for $HfC_{0.91}$. Their lattice parameter values suggest a severe oxygen contamination which would cause an increased uncertainty in the melting temperature at lower carbon contents. Four values have been reported for the HfC-C eutectic temperature; namely, about 2800° (Cotter and Kohn, 1954), 3260° (Portnoi et al. 1961), 3276° (average) (Adams and Beall, 1963), and 3150° (Dolloff, 1963).

According to Benesovsky and Rudy (1960), the lower limit of the HfC phase lies somewhere between $HfC_{0.54}$ and $HfC_{0.59}$ at 1550°. The general form of the phase diagram is expected to be similar to those of the Ti-C and Zr-C systems. The metal transforms from hexagonal to body-centered cubic at 1760° (0.2 wt % Zr) (Krikorian and Wallace, 1964) and melts at 2222°C (Deardorff and Hayes, 1956).

Lattice Parameters and Structure

HfC has a face-centered cubic (NaCl-type) structure. Reported lattice parameters have varied from 4.46 A (Becker and Ebert, 1925) to 4.646 A (Curtis, Doney and Johnson, 1954) for $HfC_{1.0}$. The choice of the best value is complicated because the presence of Zr (a common impurity) raises the parameter, but oxygen and nitrogen, as well as a carbon-deficient structure, cause a lowering. Probably the best parameter for oxygen-free $HfC_{1.0}$ containing no Zr is 4.6390 ± 0.0005 (Dolloff, 1963; Storms, 1963^{b}). This leads to an x-ray density of 12.67 g/cm^3. At the lower phase limit, the lattice parameter is about 4.61 A (Benesovsky and Rudy, 1960). As with the other Group-4 carbides, the lattice parameter becomes almost independent of composition as the 1:1 ratio is approached. In view of the maximum found recently for the ZrC and TiC phases, such behavior cannot be ruled out in this system.

Hardness

The following hardness values have been reported: 2600 kg/mm^2 (100 g Knoop) for HfC + C (Cotter and Kohn, 1954), 2913 ± 300 (Vickers) (Curtis, Doney and Johnson, 1954), 1675 DPH for $HfC_{0.95}$ (Table I.3.4) (Jones, 1956), and the formula $H = 2000 + 52C$, where C is at. % carbon and H is kg/mm^2 (Avarbe et al., 1962). The material used by the latter workers probably contained considerable dissolved oxygen. Using a 100 g load, Adams and Beall (1963) found that the Knoop hardness varied from 1815 kg/mm^2 at $HfC_{0.42}$ to 2276 kg/mm^2 at $HfC_{1.00}$.

Electrical Resistivity

Rudy and Benesovsky (1960) recently have reported a value of 37 μohm-cm for the resistivity of HfC. The only other value appears to be 109 μohm-cm determined by Moers in 1931[b].

Superconductivity

HfC is not a superconductor above 1.23°K (Meissner, Franz and Westerhoff, 1932). The metal is normal down to 0.08°K (Hein, 1956).

Thermodynamic Properties

Combustion measurements by Zhelankin and Kutsev (1964) have given ΔH°_{298} as a function of composition, with values falling on a nearly straight line from -54.2 ± 0.3 kcal/mole at $HfC_{0.99}$ to -51.7 ± 0.4 at $HfC_{0.67}$.

The equation $H_T - H_{298} = 12.70T + 2.20 \times 10^{-4}T^2 + 5.4 \times 10^5/T - 5616$ cal/mole (440°-3016°K) has been calculated by Kibler et al. (1963) to fit their heat content measurements and those of Neel et al. (1960). Levinson (1964), using $HfC_{0.98}$ with <400 ppm Zr, obtained $H_T - H_{310} = -20.79 + 5.817 \times 10^{-2}T + 3.314 \times 10^{-6}T^2$ cal/g (1286°-2805°K, ±1.8%), which agrees with the above work within the stated error.

Vaporization

Kibler et al. (1963) measured the evaporation rate of HfC from 2310° to 3145°K, with values of 3.04×10^{-9} and 8.74×10^{-5} g/cm^2-sec at the respective limits. They concluded that $HfC_{\sim 1.0}$ vaporizes congruently.

Chapter I.2

The Group-5a Carbides

As one examines the carbides of each successive Group, one finds that the phase relationships and crystal structures become more complex. Thus, the Group-5a carbides are found to form "hexagonal"* M_2C and cubic MC, as well as a rather unstable M_3C_2 structure. The crystal structure of the latter compound has not yet been determined.

The M_2C phase forms a eutectic with the metal, and melts peritectically by decomposing into the MC phase. Below the eutectic temperature, its homogeneity range is very narrow. In general, the properties of this phase are not well known.

Characteristically, the MC phase has a wide composition range which extends down to about $MC_{0.71}$. Over this range, the lattice parameter changes by about 0.04 A and the melting point has extremes which are about 500° apart. The integral stoichiometry is never formed, and, in fact, the VC phase terminates at about $VC_{0.88}$.

Unique to this Group is a color change that occurs near the high carbon phase boundary. TaC becomes a golden yellow color, and NbC

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* Recent observations have raised a doubt whether hcp is the correct structure designation for many of the M_2C compounds. Where this doubt exists the usual hexagonal designation will be contained in quotes.

develops a lavender tint from the normally gray color. On the other hand, VC shows no marked color change, probably because of the low carbon content at the high carbon boundary.

Recent superconductivity measurements show that the high transition temperature of NbC and TaC decreases rapidly as carbon is removed from the lattice. Below about $MC_{0.83}$ there is no evidence for superconductive behavior down to 2° K. In addition, the M_2C structure, which was thought to be superconducting, is now known to be normal above 2° K.

I. 2. 1 The Vanadium-Vanadium Carbide System

Preparation

Vanadium carbide was first prepared by Moissan in 1893[b] during his comprehensive studies with the electric arc furnace. By heating a mixture of V_2O_5 and sugar charcoal in the absence of air, a carbide near $VC_{1.0}$ was obtained. Since that time, most work has been based on a carbide prepared in essentially the same manner, from the reaction of carbon with V_2O_5 or V_2O_3. These results are highly compromised because there is always doubt that all of the oxygen has been removed. This is especially true when low temperatures and short heating times are employed, as was generally the case. Meerson and Krein (1960) studied the reduction of V_2O_3 with carbon to determine conditions which would produce oxygen-free VC. They found it necessary to heat for more than 2 hours between 1700° and 1800° in a CO pressure of 1-10 torr to reduce the oxygen content to below the limit of detection. Because they did not analyze for oxygen directly, but relied on the relationship $100 - (V + C_{total}) = $ wt % oxygen, the limit of detection was about 0.8%. Zhelankin, Kutsev and Ormont (1958), while observing the same reaction, found that a temperature of 2300°C held for about 2 hours with a pressure of 1-1.5 torr would reduce the oxygen content below 0.2 wt %. In this case, the oxygen was determined directly by activation analysis using the reaction $O^{16}(\gamma, n)O^{15}$. The lowest temperature at which V_2O_5 will react with carbon is 435°C (Elyutin, Merkulova and Pavlov, 1958).

The stoichiometry of the carbide also determines the ease with which oxygen can be eliminated. This can be inferred from the data of Krainer and Konopicky (1947) which was obtained by heating V_2O_5 with various amounts of carbon at 1500° in a hydrogen atmosphere. Their results show that the higher the carbon content, the smaller the oxygen content of the product. The results reported by Gurevich and Ormont (1957) also show this effect (Figure I. 2. 2), although the indicated oxygen contents should not be taken too seriously, because they did not analyze for oxygen directly. The amount of deviation to the right of the curve is a better indication of the impurity content.

Vanadium carbide has been obtained from alloy steel after a suitable solvent for the iron has been applied. On the basis of this method the discredited phases V_5C (Ôsawa and Ôya, 1930), V_4C_3 (Arnold and Read, 1912) and V_2C_3 (Pütz, 1906) were reported. It is now clear that the V_5C phase is actually the hexagonal V_2C, as first suggested by Westgren (1930), and the V_4C_3 phase is cubic VC with a composition near the low carbon phase boundary. According to many authors, this is the usual composition occurring in vanadium-alloy steels.

Moers (1931[a]) found that the carbide would deposit on a tungsten wire when the wire was heated at 1500-2000° in an atmosphere of VCl_4, H_2 and a hydrocarbon. Campbell and co-workers (1949) also investigated this reaction. Although the method might be used to obtain single crystals, it does not give a product of uniform and predictable chemical composition.

Pure carbide of uniform composition can be obtained conveniently by starting with powdered vanadium metal or hydride, and carbon. Because the carbide will react avidly with oxygen and less rapidly with N_2 and CO at high temperatures, it is necessary, when seeking the purest carbide, to heat in a good vacuum (better than 10^{-5} torr). If a graphite crucible is used and the temperature is held somewhat below the melting point, volatile metal impurities will also be removed. If care is taken, pure materials can also be prepared by arc melting. However, subsequent powdering of the hard button can recontaminate the sample. Also, the powdered carbide will react slowly with air.

Phase Relationship

In 1930 Ôsawa and Ôya presented a phase diagram which contained the phases V_5C and V_4C_3. Later Goldschmidt (1948) combined his data with the melting point determinations of Ruff and Martin (1912) and proposed a diagram showing eutectic melting between vanadium and V_4C_3. Finally, with the confirmation of the hexagonal V_2C phase by Hardy and Hulm (1954), Schönberg (1954) and Rostoker and Yamamoto (1954), Hansen and Anderko (1958) drew a partial diagram from the latter's data, showing eutectic melting at 1650° between V and V_2C and peritectic melting of the V_2C phase. The first complete phase diagram was reported by Storms and McNeal (1962), Figure I. 2. 1. They show a solidus which drops from 1888°C at the pure metal to eutectic melting at 1630° between $VC_{0.09}$ and $VC_{0.33}$; peritectic melting of the V_2C phase at 2165° according to the reaction $VC_{0.56} \rightleftharpoons VC_{0.60}$ + liquid; and peritectic melting of the VC phase beginning at $VC_{0.85}$ and extending beyond $VC_{1.0}$ at a temperature of 2650°. The melting point of VC is lower than the value of 2830° reported by Friederich and Sittig (1925), 2750° reported by Ruff and Martin (1912) and the recent value of 2780° by Engelke, Halden and Farley (1960). It is suggested that impurities in the material used in the first two studies and the failure to make emissivity corrections in the last work are the cause for this discrepancy.

Below the solidus, the phase relationship is similar to the other Group-5 carbides. Carbon is essentially insoluble in the metal, being less than $VC_{0.01}$ at about 1000° (Gurevich and Ormont, 1957). V_2C is found between $VC_{0.47}$ and $VC_{0.50}$, giving it a somewhat wider homogeneity range than Nb_2C. The VC phase starts near $VC_{0.72}$ and, it is interesting to note, does not extend to the composition $VC_{1.0}$. Although this is not unique among the Group-5 carbides, the extent to which the VC-C phase boundary deviates from the 1:1 ratio is rather unusual. Early workers placed the upper limit near $VC_{0.75}$, i. e., V_4C_3 (Osawa and Oya, 1930; Morette, 1938), but later work has demonstrated that the limit is much higher. Schönberg (1954) observed that compositions above $VC_{\sim 0.8}$ could not be produced without the presence of free carbon, but he assumed this was due to a slow reaction rate. Meerson and Krein (1960) also could not produce VC with a composition higher than $VC_{0.92}$. Schnell (1960), working with pure materials, placed the boundary

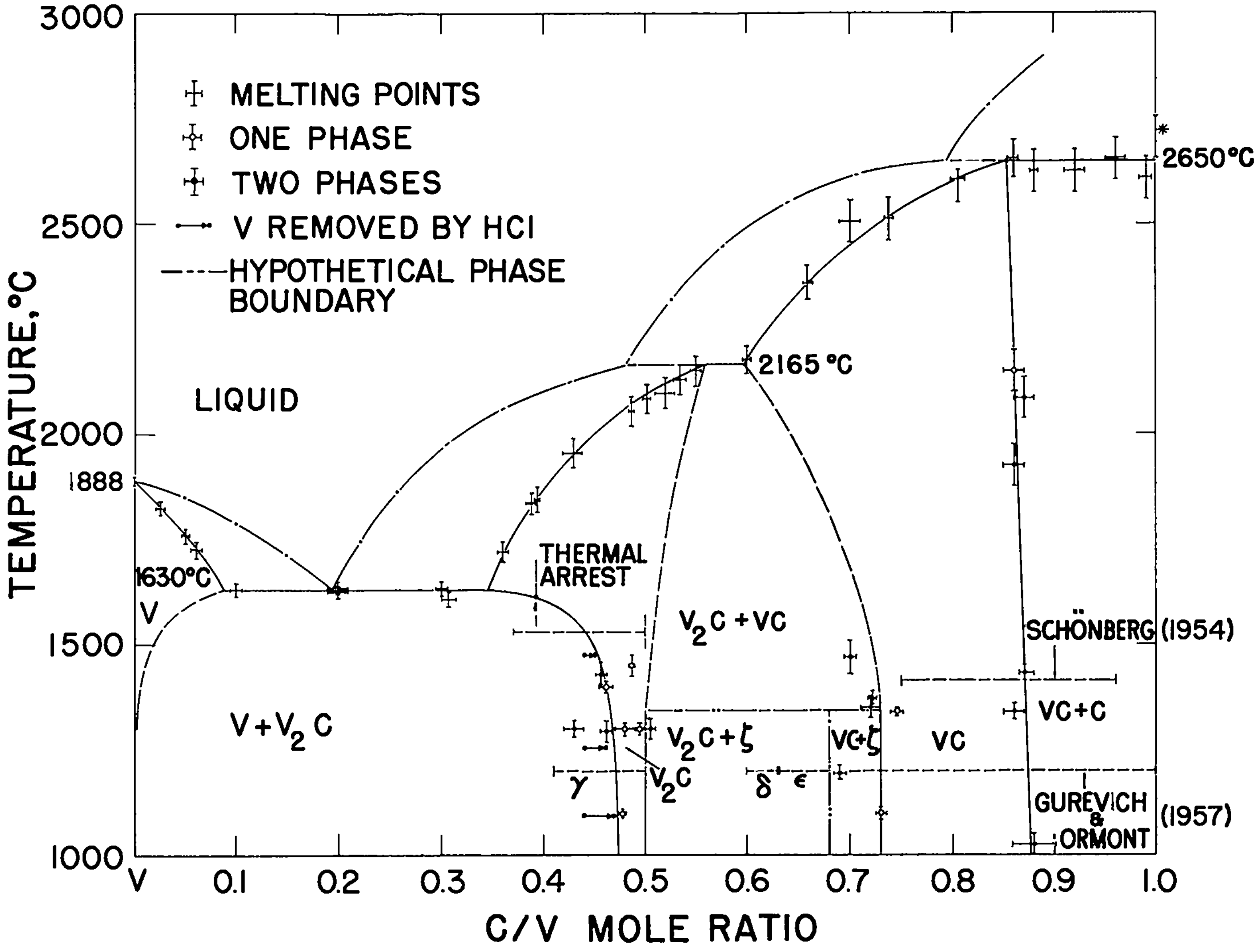

Figure I.2.1 Phase Diagram of the V-VC System (Storms and McNeal, 1962) below $VC_{0.92}$. Rudy and co-workers (1962[b]) found that most of their samples contained free carbon at $VC_{0.85}$. Storms and McNeal (1962), as can be seen from Figure I. 2. 1 give $VC_{0.88}$ as the limit at 1000° with a trend to lower carbon contents at higher temperatures. Most other authors either mention that all of the free carbon had not quite reacted or assumed that they were working with single-phase $VC_{1.0}$.

Two other phases have been reported in this system, a cubic δ phase by Gurevich and Ormont (1957) and a ζ phase by Storms and McNeal (1962). The δ phase was not seen by the latter authors, probably because their material was more homogeneous. Insufficient work has been done to confirm the existence of the zeta phase. It is, however, very similar to the zeta phase found in the TaC system by Lesser and Brauer (1958). This phase is indicated on the phase diagram (Figure I. 2. 1), but, because of its hypothetical nature, no effort has been made to modify the phase boundaries in its region.

Lattice Parameters and Structure

The structure and lattice parameters for the established phases V, V_2C and VC are shown in Table I. 2. 1. Because the V_2C and VC phases have fairly wide homogeneity ranges, the lattice parameters are given for compositions at the phase boundaries at 1300°. Between these extremes, the lattice parameters will change with composition as is shown for the VC phase in Figure I. 2. 2. As shown in the figure, the lattice parameter at the VC-V_2C phase boundary is strongly influenced by the heating temperature between 1348° and 1430°. Quenching in vacuum from above 1430° produces a composition of $VC_{0.73}$ with a lattice parameter of 4. 125 A. Below 1344° the composition and lattice parameter are $VC_{0.738}$ and 4. 131 A, independent of temperature. This, according to Storms and McNeal (1962), might be due to the appearance of the ζ phase. In the same manner, $VC_{0.48}$ is the lowest V_2C compo-

TABLE I. 2. 1

Structure and Lattice Parameter of V, V_2C and VC

Phases in Equilibrium	Composition of First Phase	Structure	Lattice Parameter, A	Investigator
V	pure	bcc	a = 3.0240 ± 0.0003	James and Straumanis (1961)
$V_2C + V$	$VC_{0.47}$	hcp	a = 2.8855 ± 0.0005 c = 4.5705 ± 0.0005	Storms and McNeal (1962)
$V_2C + VC$	$VC_{0.50}$	hcp	a = 2.9020 ± 0.0005 c = 4.577 ± 0.001	Storms and McNeal (1962)
$VC + V_2C$	$VC_{0.73}$	fcc	a = 4.1310 ± 0.0005	Storms and McNeal (1962)
VC+ C	$VC_{0.87}$	fcc	a = 4.1655 ± 0.0003	Storms and McNeal (1962)

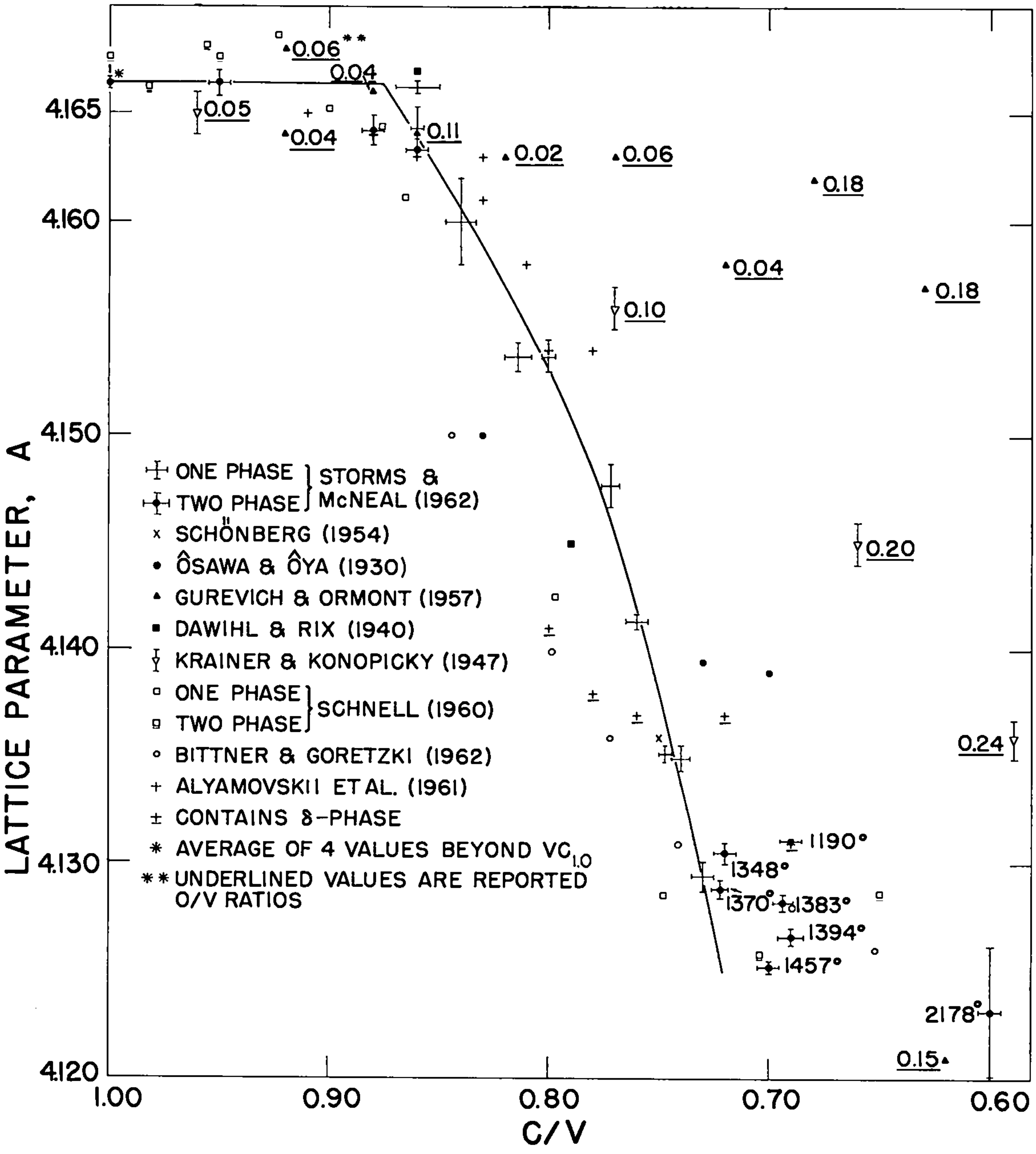

Figure I. 2. 2 Lattice Parameter of the VC Phase as a Function of Composition

sition that can be quenched in by radiant cooling in vacuum.

The x-ray density of the VC phase, calculated from the values in Figure I.2.2, is 5.649 g/cm^3 at both phase boundaries with a minimum of 5.607 g/cm^3 at $VC_{0.78}$. NbC shows a minimum at this same composition (Kempter, Storms and Fries, 1960). V_2C has an x-ray density of 5.665 g/cm^3 at $VC_{0.50}$.

Chemical Stability

V_2C is dissolved slowly by hot 1:1 HCl, leaving a carbon residue. VC is inert under these conditions (Storms and McNeal, 1962). Both carbides are attacked by concentrated HNO_3, H_2SO_4 and $HClO_4$, slowly at room temperature and vigorously when heated. Hot NaOH has no effect. Powdered V_2C reacts slowly with air at room temperature.

VC will react with dry HCl gas at 750° to produce CH_4, H_2, VCl_2 and some VCl_3 (Oldham and Fishel, 1932). It has a high rate of oxidation in air at 800° (Cockett and Watt, 1950) and will burn in oxygen to produce V_2O_5. VC, when heated in nitrogen, will gradually convert to the nitride, but it is considered structurally stable up to 2400° (Bradshaw and Matthews, 1959).

Hardness

It is important to keep in mind that all of the physical properties of VC will be a function of composition. Furthermore, because $VC_{1.0}$ cannot be produced, measured properties should not be attributed to this composition. An example is represented by the range of hardness values that have been reported; from 2094 kg/mm^2 (Meerson and Umanskii, 1953) to about 3000 kg/mm^2 (Gaev, 1953; Kieffer and Kölbl, 1949). As Gurevich and Ormont (1957) point out, the hardness will change with composition. With this in mind, they obtained a hardness of 2140 kg/mm^2 for V_2C and values between 2850 and 3000 kg/mm^2 across the range of the VC phase. In addition they found the abrading ability of high carbon VC to equal that of SiC. Jones (1956), during a study of the Group-4a, -5a, and -6a carbides, found VC (containing free carbon) equal in hardness to WC (2250 DPH) and exceeded only by TiC (3100 DPH) (Table I. 3. 4). The work of Kieffer and Kölbl (1949) is also consistent with this observation. It would appear, contrary to popular belief, that VC ($VC_{0.88}$) is one of the hardest pure carbides known.

Electrical Resistivity

Rudy and Benesovsky (1960) have reported a specific resistance value of 60 μohm-cm at 20° C for VC in equilibrium with carbon. This can be compared to 156 μohm-cm obtained by Friederich and Sittig (1925) using material of dubious purity and composition.

The other mechanical and electrical properties are highly questionable because, if the overall composition is reported as $VC_{1.0}$, at least 2. 3 wt % graphite will be present to change the gross properties.

Superconductivity

Vanadium metal becomes superconductive at about 5. 1°K, (Corak et al., 1956; Hulm and Blaugher, 1961). V_2C and VC are not superconducting down to 1. 2°K (Hardy and Hulm, 1954; Giorgi et al., 1963).

Thermodynamic Properties

The heat capacity at low temperatures has been reported for VC by Shomate and Kelley (1949) and the heat content at high temperatures by King (1949), using the same material. The values are shown in Table I. 2. 2. Although they were unable to detect the presence of free carbon in a material analyzing $VC_{1.0}$, there must have been at least 2. 3 wt % carbon present. Therefore, a correction has been applied and the resulting values for $VC_{0.87}$ (the composition at the temperature of preparation) are listed. Workers at the Southern Research Institute (1963) measured the heat content above 533°K of $VC_{0.97}$. Their values are higher than King's even after a correction to the same carbon content has been made.

TABLE I.2.2

Thermodynamic Properties of VC Corrected to $VC_{0.87}$

King (1949)

$H_T - H_{298.16} = 8.65T + 1.58 \times 10^{-3}T^2 + 1.68 \times 10^5 T^{-1} - 3282$ cal/mole

$C_p = 8.65 + 3.16 \times 10^{-3}T + 1.68 \times 10^5 T^{-2}$ cal/mole-deg

(400-1611°K)

- - - - - - - - - - - - - - - - - - - -

Shomate and Kelley (1949)

$C_{p298.16} = 7.70$ cal/mole-deg

$S^\circ_{298.16} = 6.59$ e.u./mole

The heat of formation of VC has been measured recently by several techniques with good agreement. Mah (1963) obtained $\Delta H_{298} = -24.35 \pm 0.40$ kcal/mole by combustion calorimetry using material of uncertain purity and stoichiometry. Volkova and Geld (1963) measured several compositions of VC by the same technique. Although they give $\Delta H_{298} = -24.5 \pm 1.8$ kcal/mole as the average value, their data fall into two sets about 3 kcal/mole apart, both of which vary with composition as expected. Using the lower set of values, ΔH_{298} varies from -24.0 to -21.6 kcal/mole over the range between $VC_{0.882}$ and $VC_{0.724}$. By studying the variation of CO pressure with temperature over VC + V_2O_3 + C, Worrell and Chipman (1964) calculated $\Delta H_{298} = -24.1 \pm 0.7$ kcal/mole for $VC_{0.88}$ and estimated -22.2 ± 2.0 kcal/mole as the heat of formation of $VC_{0.73}$. Meerson and Umanskii (1953) cite a value of -27.5 kcal/mole for ΔF_{298} and Samsonov (1956^a) obtained $\Delta H = -30.2$ kcal/mole at 1550°C from a tensimetric method. A third law treatment of the vapor pressure data obtained by Fujishiro and Gokcen (1962) gives $\Delta H_{298} = -22.7 \pm 5.0$ kcal/mole.

Worrell and Chipman (1964) have estimated the heat of formation of V_2C as -35.2 ± 5 kcal/mole.

Vaporization

All compositions studied by Storms and McNeal (1962) were found to lose vanadium preferentially when heated in vacuum. Evaporation became noticeable above 1500°, and an inert atmosphere was needed to suppress the pronounced loss of vanadium above 1800°C.

Using Knudsen effusion techniques, Fujishiro and Gokcen (1962) have studied the vaporization process between 2482°K and 2513°K. In this interval the vapor pressure of vanadium can be represented by $\log P_{(atm)} = -30700/T + 7.63$. They concluded from weight loss experiments that atomic vanadium is the only vapor species.

I.2.2 The Niobium-Niobium Carbide System

Preparation

Niobium carbide with a composition near $NbC_{1.0}$ was first prepared by Joly (1877) from the reaction of $K_2O \cdot 3Nb_2O_5$ with carbon. Nb_2O_5 has been used as a starting material by most early workers and is presently used in the industrial preparation of the carbide.

The reaction between Nb_2O_5 and carbon begins at 675° (Elyutin, Merkulova and Pavlov, 1958). Below 1200°, NbO_2 and NbC_x are the main products, and these react between 1450° and 1500° to give a NbC_xO_y solid solution (Shveikin, 1958). Shveikin, in a series of papers, has studied this reaction in some detail. A continual rise in temperature at first favors formation of the carbide, but at higher temperatures and correct stoichiometry, Nb metal is formed. This reaction has also been used to produce ductile alloys of niobium and tantalum (Kolchin and Cheveluva, 1959; Downing and co-workers, 1961). The form of the carbon determines the ease with which the reduction will proceed (Shveikin and Gel'd, 1961).

Pure NbC can be easily obtained either from the above reaction or by heating the elemental powders together, provided that a sufficiently high final temperature is used. This is necessary to eliminate the oxygen and nitrogen, and to bring about a complete reaction with the carbon. Storms and Krikorian (1960) found that both oxygen and nitrogen could be essentially eliminated from a commercial sample of NbC containing 0.28 wt % oxygen and 0.66 wt % nitrogen if the material was heated in vacuum above 1900° for about 30 min. However, they found that considerably longer times are needed to react all of the carbon. The reaction rates are such that longer than 38 hr at 1800° would be necessary to bring equilibrium to a mixture of graphite and niobium powders starting at $NbC_{0.74}$. A H_2 atmosphere or a higher temperature can shorten this time considerably.

It is possible to deposit the carbide from the gas phase onto a hot object. Moers (1931[a]), by heating a tungsten wire to 900-1000° in a gas containing $NbCl_5$, H_2 and hydrocarbons, was able to deposit NbC containing some free metal. The metal can easily be converted to the carbide by heating it in a hydrocarbon + H_2 mixture as was demonstrated by Campbell and co-workers (1949). Protective coatings have been applied to graphite by exposing the surface to $NbCl_5$ vapor while at high temperature (Blocher and co-workers, 1958). In this process the formation of NbC is diffusion-controlled.

Phase Relationship

Three solid phases are known in the Nb-NbC system: the bcc solid solution of carbon in Nb metal, the "hcp" compound Nb_2C and the fcc compound NbC. Goldschmidt in 1948 and Pochon et al. in 1959 have given tentative phase diagrams, but the first complete study was reported in 1960 by Storms and Krikorian, and confirmed in its major respects by Kimura and Sasaki (1961). Their results along with the data of Brauer and Lesser (1959[a]) and Elliott (1961) are shown in Fig. I. 2. 3. Beginning at the pure metal, the solidus drops from 2467° (Schofield, 1957) to the eutectic temperature of 2335° between $NbC_{0.08}$ and $NbC_{0.39}$. There is very good agreement between other measurements of this temperature, namely, 2335° reported by Pochon et al. (1959), 2328° obtained by Nadler and Kempter (1960), and 2340 ± 20° measured by Kimura and Sasaki (1961). At $NbC_{0.39}$ the melting point rises to 3090°, whereupon Nb_2C decomposes according to the reaction $NbC_{0.52} = NbC_{0.56} +$ liquid. Nadler and Kempter (1960) and Kimura and Sasaki (1961) obtained 3080° ± 50° for the peritectic temperature. From the peritectic, the melting point rises

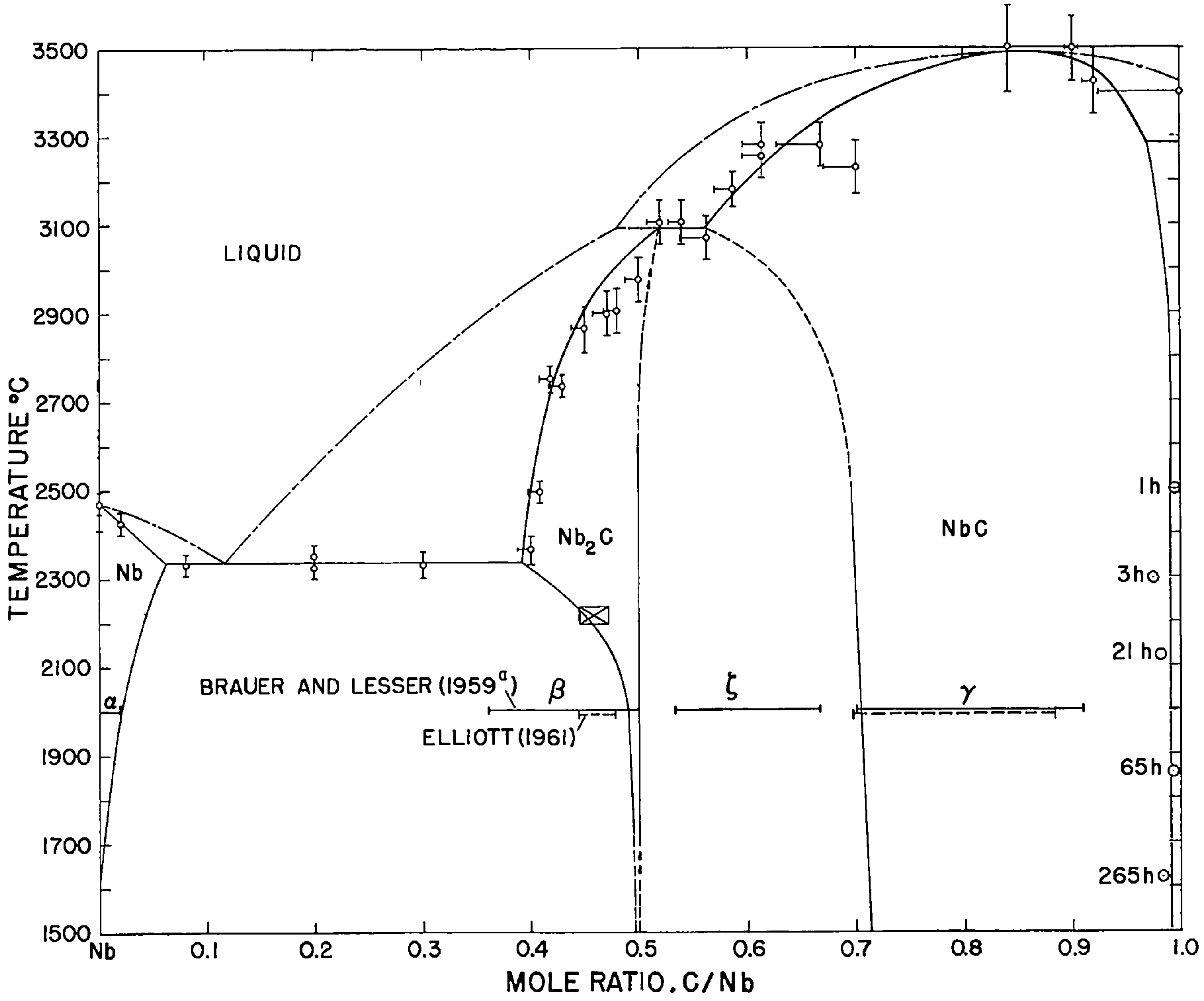

Figure I. 2. 3 Phase Diagram of the Nb-NbC System to a maximum of 3500° at about $NbC_{0.86}$ and drops to 3250° with eutectic melting between NbC and graphite. These temperatures are in good agreement with those of Nadler and Kempter who have reported 3480° as the maximum and 3220° for the NbC-C eutectic temperature and Kimura and Sasaki (1961) who reported 3500 ± 50° and 3300 ± 50° for the respective temperatures. Engelke et al. (1960) obtained 3420° by arc melting a material which, according to the lattice parameter, had a composition of $NbC_{0.92}$. Brownlee (1958), using the same technique, obtained 3485° for $NbC_{0.95}$. A recent paper by Portnoǐ et al. (1961) claims a eutectic temperature of 3150° for a material of unknown purity.

The melting point range and the displaced maximum demonstrates again the fallacy of considering only the properties of the stoichiometric material. In this case, $NbC_{1.0}$ melts at the eutectic temperature which is almost 200° below the maximum. This same behavior is to be expected in most of the other systems, with the result that the spread in reported melting points is probably due to a variation in composition.

The solubility curve for niobium metal, according to Elliott (1961), shows that only 100 ppm carbon can dissolve at 1500° and, even at the eutectic temperature, $NbC_{0.08}$ (1 wt %) is the phase limit. Likewise, the Nb_2C phase has a rather narrow range of existence at low temperatures. There is, however, some disagreement over this observation, as can be seen in Figure I. 2. 3. Because of the techniques used, the work of Storms and Krikorian (1960) probably represents the most reliable relationship. The NbC phase exists from about $NbC_{0.70}$ to $NbC_{0.99}$. The disagreement in this region results from the increasingly slow reaction rates as the 1:1 ratio is approached. The times used to obtain the corresponding compositions, starting from $NbC_{0.99}$, are shown.

Recently, two other phases have been reported in this system. Pochon et al. (1959) found what they suggested was a tetragonally distorted form of NbC in arc-cast alloys containing about 0.066% carbon. This was designated as a delta phase. But, because it was converted to Nb_2C upon annealing at 1200°, it was dismissed as being metastable.

On the basis of one weak powder pattern line at $\theta = 19.70°$, Brauer and Lesser (1959[a]) suggested a zeta phase, the range of which is shown on Figure I.2.3. This is similar to their findings in the Ta-TaC system (Lesser and Brauer, 1958). Although neither Elliott (1961), Storms and Krikorian (1960), nor Kimura and Sasaki (1961) found evidence of this phase, subsequent work by Storms (1963[b]) has confirmed its existence, but at a lower temperature than that reported by Brauer. Recent evidence for a similar phase in the V-VC system gives additional support to Brauer's observation (Storms and McNeal, 1962).

Lattice Parameters and Structure

The structure and lattice parameters for the established phases Nb, Nb_2C and NbC are shown in Table I.2.3. Lattice parameters are given for the phase boundaries at 2000°. The lattice parameter of the NbC phase varies with composition according to the equation

$$a_o = 4.09847 + 0.71820\,(C/Nb) - 0.34570\,(C/Nb)^2,$$

where C/Nb is the mole ratio (Kempter, Storms and Fries, 1960). A refraction correction is included. As pointed out by Storms and Krikorian, the lattice parameter of alloys containing an appreciable quantity of oxygen and nitrogen will lie to the right of this curve. This is shown in Figure I.2.4, where the black circles represent material containing various amounts of these impurities. Thus, this equation can be used to verify the purity of a sample if the carbon and niobium

TABLE I. 2. 3

Structure and Lattice Parameter of Nb, Nb_2C and NbC

Phases in Equilibrium	Composition of First Phase	Structure	Lattice Parameter, A	Investigator
Nb	pure	bcc	a = 3.3000 ± 0.0003	Seybolt (1954)
Nb_2C + Nb	$NbC_{0.49}$	"hcp"	a = 3.127 ± 0.001 c = 4.965 ± 0.001	Storms and Krikorian (1960)
Nb_2C + NbC	$NbC_{0.50}$	"hcp"	a = 3.127 ± 0.001 c = 4.972 ± 0.001	Storms and Krikorian (1960)
NbC + Nb_2C	$NbC_{0.70}$	fcc	a = 4.4318 ± 0.0005*	Kempter, Storms, and Fries (1960)
NbC + C	$NbC_{0.99}$	fcc	a = 4.4707 ± 0.0003*	Kempter, Storms, and Fries (1960)

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* corrected for refraction

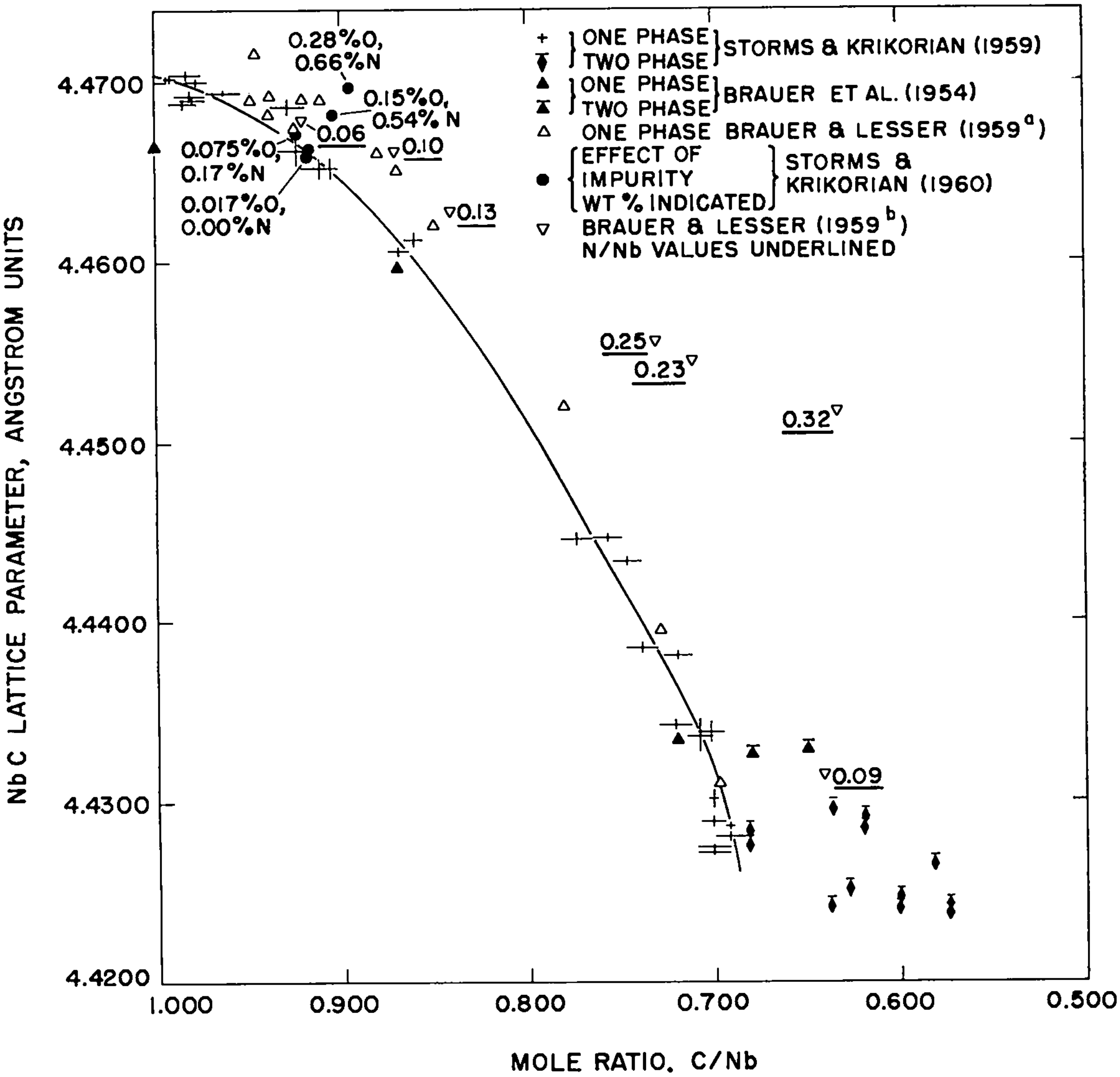

Figure I. 2. 4 Lattice Parameter of the NbC Phase as a Function of Composition contents are known or to obtain the C/Nb ratio if the sample is known to be pure.

An additional factor that will influence how data will fall with respect to the curve is the uniformity of composition throughout the material. Calculations of lattice parameters from powder patterns of single phase material generally produce values for the most abundant composition, whereas chemical analysis gives the average composition. Thus, when this information is plotted on Figure I. 2. 4, the points will fall to the left or right depending on whether the sample has been gaining or losing carbon during its previous treatment.

The density, based on the above equation, drops from 7.788 g/cm^3 at $NbC_{0.99}$ to a minimum of 7.716 g/cm^3 at $NbC_{0.785}$ and rises to 7.730 g/cm^3 at the NbC-Nb_2C phase boundary. The x-ray density of Nb_2C in equilibrium with NbC is 7.796 g/cm^3.

Appearance

Between the metal and about $NbC_{0.9}$, the powder has a gray metallic color. However, as more carbon is adsorbed, a subtle color change begins which develops into a lavender tint at $NbC_{0.99}$.

Chemical Stability

NbC is exceedingly unreactive; even boiling aqua regia will not attack the powder. A mixture of HNO_3 and HF is needed to cause dissolution.

When heated in oxygen, NbC will burn, and in air corrosion becomes severe above 1100°. By heating in nitrogen + H_2 or ammonia the carbide can be converted to the nitride.

There is apparently no reaction with H_2 (May and Hoekstra, 1961).

Hardness

The hardness of NbC, as well as the other physical properties, depends on the composition. Unfortunately, no study of hardness as a function of composition has appeared. Jones (1956) reported 1950 DPH for NbC + C (Table I. 3. 4), Foster and co-workers (1950) obtained 2470 kg/mm^2 for composition near to $NbC_{1.0}$, but which probably contained some tungsten. Meerson and Umanskii (1953) quote Soviet investigators as obtaining 2055 kg/mm^2, and Kieffer and Kölbl (1949) report 2400 kg/mm^2 for $NbC_{0.99}$. The hardness for Nb_2C has not been reported.

Electrical Resistivity

Rudy and Benesovsky (1960) claim a specific resistance of 35 μohm-cm at 20° for NbC in equilibrium with carbon. This contrasts sharply with the value of 60.2 μohm-cm reported by Samsonov (1956^b), 74 μohm-cm given in Schwarzkopf and Kieffer (1953), 51.1 μohm-cm obtained by L'vov, Nemchenko and Samsonov (1960), and a very early value of 150 μohm-cm by Friederich and Sittig (1925). With the absence of analytical data to establish purity and composition, it is impossible to resolve these differences.

A value for which an analysis is given was reported by Kolomoets and co-workers (1958). They give a specific resistance at 20° of 59 μohm-cm for $NbC_{0.99}$ containing 0.17 wt % free carbon and a Nb + C summation of 99.69%. The values show a linear increase with temperature with a slope of 0.0635 μohm-cm/deg.

Superconductivity

According to Giorgi and co-workers (1962), the transition temperature of NbC varies with composition, dropping from 11.1°K at $NbC_{0.977}$ to 1.05°K at $NbC_{0.829}$. In a later publication Giorgi and co-workers (1963) show that Nb_2C is not superconducting down to 2.0°K and that the previous value of 9.18° (Hardy and Hulm, 1954) was probably due to Nb metal in their sample. The transition temperature for the metal is 9.465°K (De Sorbo and Nichols, 1961).

Thermodynamic Properties

The heat of formation of NbC at 298°K has been measured as a function of composition by Huber and co-workers (1961). The equation $\Delta H°_{298} = 6.60 - 70.95\ (C/Nb) + 30.75\ (C/Nb)^2$ was used to fit experimental values obtained from combustion calorimetry. During the same study, the heat of formation of Nb_2C was found to vary from -43.1 ± 1.7 kcal/mole to -46.6 ± 1.2 kcal/mole over its homogeneity range. Kusenko and Gel'd (1960) also obtained $\Delta H°$ values for NbC as a function of composition. However, their data suffer from the uncertainty created by not being able to correct for the large amount of oxygen present. A recent measurement by Kornilov and co-workers (1962), using a sample of $NbC_{0.915}$, is in excellent agreement with Huber and co-workers (1961) if the same heat of formation for Nb_2O_5 is used in the calculations.

High temperature molar heat contents (cal/mole) have been reported by Gel'd and Kusenko (1960) as a function of temperature between 300° and 1800°K and at various compositions as follows:

$NbC_{0.50}(H_T - H_{298}) = 7.94T + 0.750 \times 10^{-3}T^2 + 1.025 \times 10^5T^{-1} - 2776$

$NbC_{0.749} = 8.95T + 1.127 \times 10^{-3}T^2 + 1.26 \times 10^5T^{-1} - 3190$

$NbC_{0.867} = 9.70T + 0.995 \times 10^{-3}T^2 + 2.15 \times 10^5T^{-1} - 3485$

$NbC_{1.00} = 10.79T + 0.863 \times 10^{-3}T^2 + 2.15 \times 10^5T^{-1} - 4013$

The composition cited for the last equation is probably nearer $NbC_{0.98}$, in view of the phase limit at $NbC_{0.99}$. Heat capacity measurements have been reported between 1490° and 2256°C. An impure sample of $NbC_{0.99}$ (0.22 wt % O, 0.47 wt % N) showed a peak in the heat capacity at 2164°C (Barriault et al., 1961).

Low temperature measurements by Sandenaw and Storms (1964) have produced the following values:

$NbC_{0.702}$ C_p = 7.89 cal/mole-deg; S°(298.15) = 7.41 e.u.

$NbC_{0.825}$ = 8.47 = 7.78

$NbC_{0.980}$ = 8.62 = 8.05

Recent heat content measurements by Neel and co-workers (1960) and Levinson (1963) have extended the range to about 2800°K. These studies are compared in Figure I.2.5 after being corrected to a common basis.

Vaporization

The vaporization of NbC becomes noticeable in vacuum only above 2500°C. If the material is allowed to remain hot for a sufficient time, the composition will change until a congruent composition of $NbC_{0.748}$ at 2635° is reached. At higher temperatures the composition shifts to lower values, being $NbC_{0.735}$ at 2860° (Storms, 1963[b]). Fries (1962), in a rather complete study of the vaporization behavior by the Langmuir method, obtained a congruent composition of $NbC_{0.747}$ at 2670°. His data give a value of 189 kcal/mole of carbon for the heat of vaporization from compositions near $NbC_{1.0}$ and a carbon pressure according to the equation $\log P_C(\mathrm{atm}) = 5.296 - 3.27 \times 10^4/T$. He observed that the mass evaporation rate becomes greater at lower carbon contents.

In a recent paper, Bolgar, Verkhoglyadova and Samsonov (1961) state that NbC evaporates through a molecular species. This conclusion was based on their impression that the composition of congruent vaporization is at $NbC_{1.0}$. This premise does not lead to such a conclusion; furthermore, the congruent composition is, in fact, not at the 1:1 ratio. Although a conclusive study has not been made, present evidence leads to just the opposite conclusion, that the niobium and carbon evaporate from NbC in an unbound state. The same authors gave 167 kcal/mole as the heat of evaporation, in poor agreement with Fries, and the rates of evaporation are much too high, by a factor of at least 10.

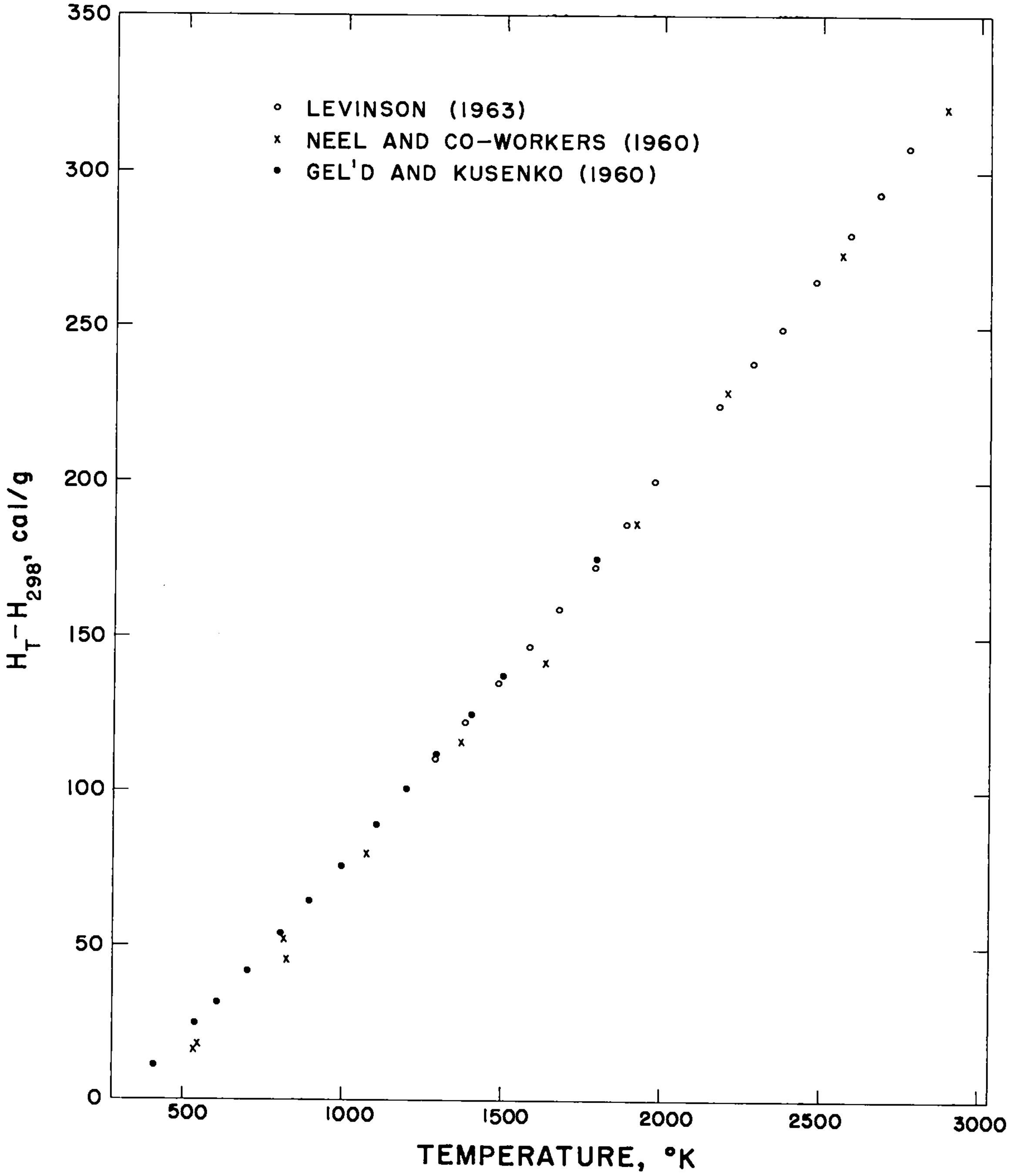

Figure I. 2. 5 The Heat Content of $NbC_{0.99}$ as a Function of Temperature

I. 2.3 The Tantalum-Tantalum Carbide System

Preparation

Tantalum carbide was first prepared by Joly in 1876 by heating the pentoxide or tantalites and Na_2CO_3 with carbon at about 1500°C. The pentoxide is a common starting material for modern investigations, but, as with the other carbides, heating the elemental powders together leads more quickly to a pure product. A procedure adopted by Lesser and Brauer (1958) gives satisfactory results. They heated the outgassed powdered elements in a graphite crucible in vacuum until, at about 1000°, the materials began to react, producing an evolution of gas and heat. After the reaction had subsided, the temperature was raised to about 2000° and held for about 15 min. Heatings were continued, with intermittent grindings, until a homogeneous and pure product was obtained. Reducing the compact to a powder between heatings helps overcome the slow rate with which carbon diffuses into the carbide. Naturally, the higher the temperature the more quickly will equilibrium be obtained. A hydrogen atmosphere will also help.

Although TaC cannot be deposited directly on a W wire from a hydrocarbon + $TaCl_5$ + H_2 vapor--because of the immediate formation of Ta metal--the carbide can be obtained by a subsequent heating in a hydrocarbon atmosphere. (Moers, 1931[a]; Becker and Ewest, 1930). Eliminating the first step, Robins (1959) produced TaC by heating Ta wires in methane. He also prepared TaC by melting iron or aluminum containing tantalum and carbon in a graphite crucible. The TaC crystals were separated by dissolving the menstruum in HCl.

Arc-melting techniques have also been employed. This, however, tends to produce carbon-deficient TaC.

Phase Relationships

The phase relationships reported for this system are in disagreement. Ellinger (1943), the first to publish a complete phase diagram, gives the following major features: eutectic melting at 2800° between Ta and Ta_2C, peritectic melting of Ta_2C at 3400°, TaC with a broad range between about $TaC_{0.79}$ and $TaC_{1.0}$, with a maximum melting temperature of about 3800°, and a TaC-C eutectic melting at 3300°. Later work has shown that the melting temperatures are too low, although the general shape of the phase diagram is essentially correct. Smirnova and Ormont (1954, 55, 56[a]) gave the range of Ta_2C as $TaC_{0.38}$ to $TaC_{0.50}$ and that of TaC as $TaC_{0.58}$ to $TaC_{0.91}$, although this range is inconsistent with their data. In addition, their material suffered from the absence of equilibrium. Lesser and Brauer (1958) found a somewhat wider range for Ta_2C, namely $TaC_{0.41}$ to $TaC_{0.50}$. Unfortunately, this was based on one sample in which they failed to detect the presence of Ta, but which had the same lattice parameter as samples which did contain Ta. This value should therefore be taken as a lower limit. They also found that TaC lies between $TaC_{0.74}$ and $TaC_{1.00}$. McMullin and Norton (1953) placed the upper limit of the Ta_2C phase at $TaC_{0.46}$ instead of $TaC_{0.50}$, and the limits of TaC at $TaC_{0.67}$ and $TaC_{0.988}$. Bowman (1961) agrees with the TaC range, giving limits of $TaC_{0.71}$ and $TaC_{0.99}$ at 2400°, with a trend to lower carbon content at higher temperatures. Robins (1959) also was not able to reach the 1:1 ratio, having been stopped at $TaC_{0.96}$. In view of the lattice parameter and his method of preparation, the highest composition in his sample was probably above this value. Sara and co-workers (1963) have confirmed that the range of TaC lies between $TaC_{0.72}$ and $TaC_{0.98}$ at 2250°. The range of Ta_2C is still in doubt. however.

With the above results in mind, coupled with the phase relationships known to exist in the two similar systems, Nb-NbC and V-VC, a tentative phase diagram has been constructed as Figure I. 2. 6. The eutectic and peritectic melting temperatures have been taken from

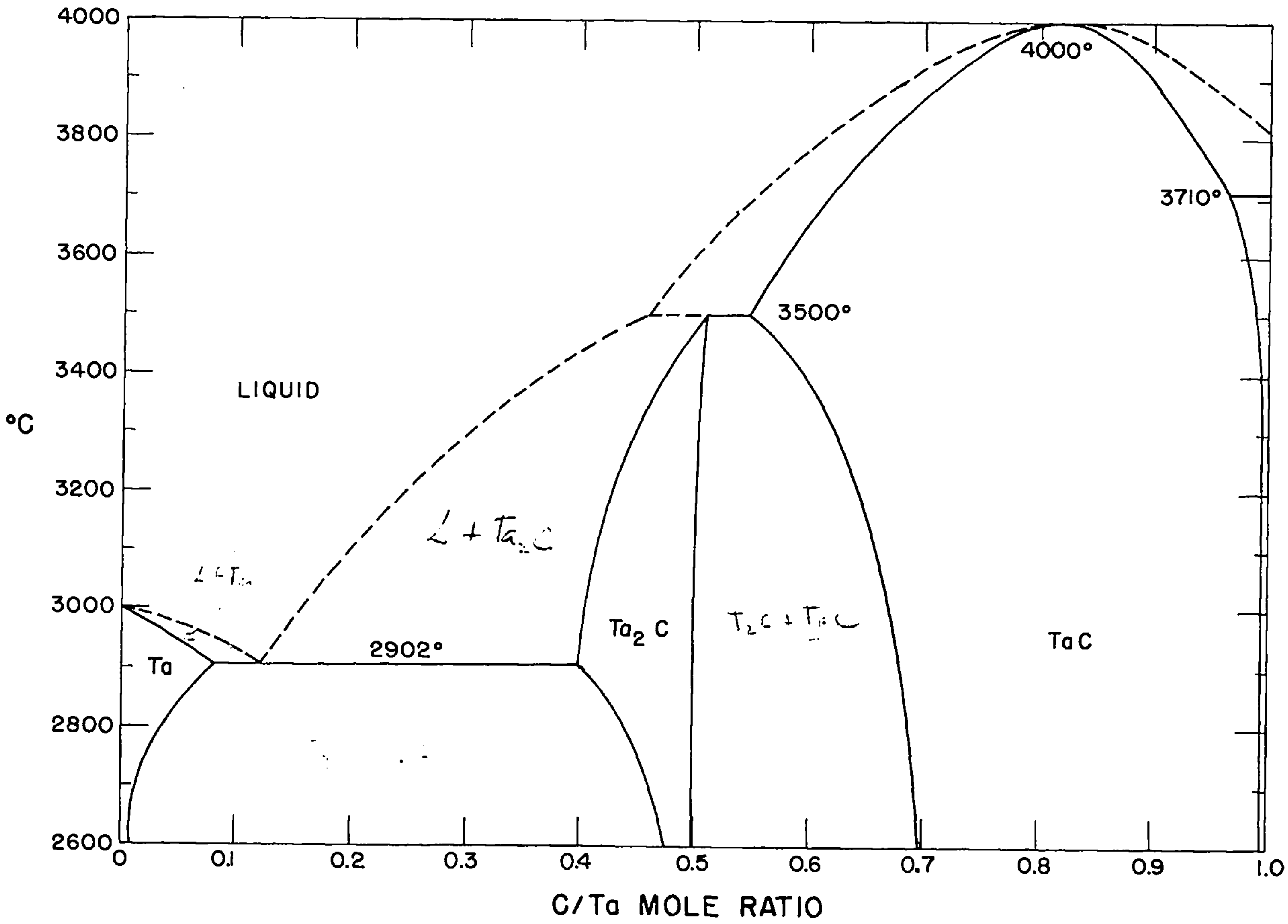

Figure I. 2. 6 Phase Diagram of the Ta-TaC System the work of Nadler and Kempter (1960). The eutectic composition at $TaC_{0.12}$ is based on the work of Pochon and co-workers (1959). By drawing the solidus to match the same general shape as that found for NbC, the temperature of the melting point maximum at about $TaC_{0.85}$ has been estimated. None of the measured values are this high for a good reason; near this temperature the rapid loss of carbon can scarcely be suppressed even by a hydrocarbon atmosphere, with the resulting shift to lower compositions (Zalabak, 1961).

Not shown on the diagram is a low temperature zeta phase reported by Lesser and Brauer. In all powder patterns prepared from samples between $TaC_{0.5}$ and $TaC_{0.73}$, they discovered extra lines which grew in very slowly, always with the lines of either Ta_2C or TaC or both present. At 2000° there was some evidence for its partial decomposition. How this phase should be related to the others has not yet been determined.

Lattice Parameter and Structure

The structure and lattice parameters for the phases, Ta, Ta_2C and TaC are shown in Table I. 2. 4. Bowman (1961) found that the lattice parameter of the TaC phase changes with composition according to the equation $a_o = 4.3007 + 0.1563\,(C/Ta)$ as shown in Figure I.2.7. Previous work of Lesser and Brauer (1958) and recent data of Sara and co-workers (1963) completely support the variation found by Bowman (1961). In view of the close agreement between the various measurements and the simple relationship exhibited by this property, one can use the lattice parameter to determine the composition with a good deal of confidence. It is necessary, though to apply the cautions discussed in the Chapter I.2. 2, page 51.

Solution of the above equation for x-ray density leads to $\rho = 15.11 - 0.64\,(C/Ta)$. Thus the density is 14.48 g/cm^3 at $TaC_{0.99}$ and rises as carbon is removed.

TABLE I. 2. 4

Structure and Lattice Parameter of Ta, Ta_2C and TaC

Phases in Equilibrium	Composition of First Phase	Structure	Lattice Parameter, A	Investigator
Ta	pure	bcc	a = 3.296	Fansteel Metallurgical Corp. (1956)
Ta_2C + Ta	$TaC_{0.41}$	hcp	a = 3.101 c = 4.933	Lesser and Brauer (1958)
Ta_2C + TaC	$TaC_{0.50}$	hcp	a = 3.106 c = 4.945	Lesser and Brauer (1958)
TaC + Ta_2C	$TaC_{0.70}$	fcc	a = 4.4100 ± 0.0005	Bowman (1961)
TaC + C	$TaC_{0.99}$	fcc	a = 4.4555 ± 0.0003	Bowman (1961)

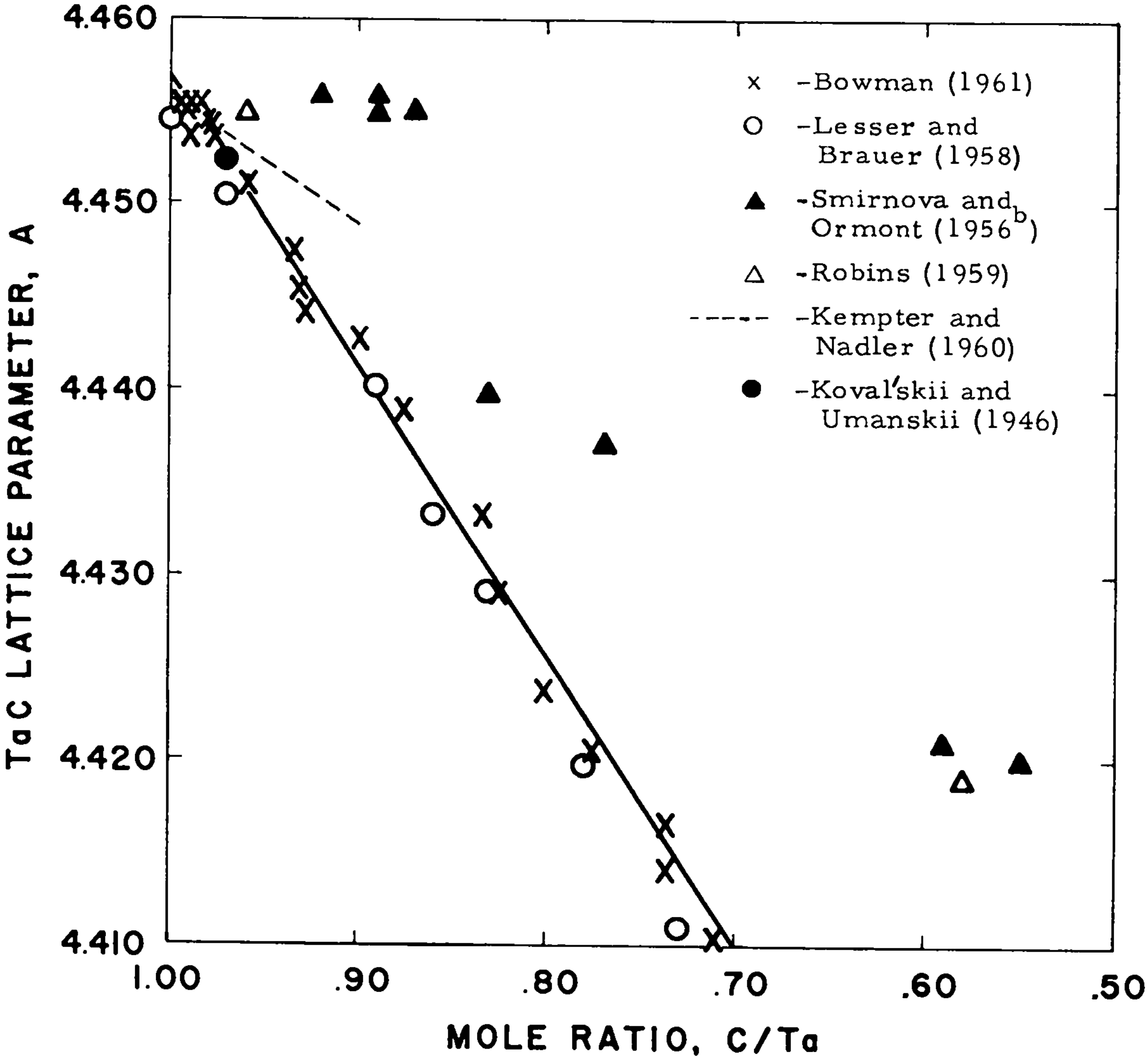

Figure I. 2. 7 Lattice Parameter of the TaC Phase as a Function of Composition

Appearance

From the metal to about $TaC_{0.85}$, the powder has a gray metallic color. At higher carbon contents, the material gradually assumes a brown cast which develops into the characteristic golden color at $TaC_{0.99}$.

Chemical Stability

Like NbC, tantalum carbide is very stable toward acids but will dissolve in a mixture of HNO_3 and HF. It is stable in N_2 up to 3315° provided no H_2 is present. In pure O_2, burning will result above 800°; small amounts of oxygen in the atmosphere will cause decarbonization. Water acts much the same way as oxygen at high temperatures.

Hardness

A number of measurements have been made using material of uncertain composition. Jones (1956) gives 1400 DPH for TaC in equilibrium with carbon (Table I. 3. 4); Meerson and Umanskii (1953) cite 1547 kg/mm^2; Kieffer and Kölbl (1949), using a 50 g load, obtained 1800 kg/mm^2; and Foster and co-workers (1950) measured a Knoop hardness of 1952 kg/mm^2 on a high carbon sample which probably contained some tungsten. This property has been measured as a function of composition, first by Samsonov and Rukina (1957) who observed a linear variation which extrapolated to 1600 kg/mm^2 at $TaC_{1.0}$, and recently by Santoro (1963) who found that the hardness maximized near $TaC_{0.83}$ at 2400 kg/mm^2 (100 g load) and 3000 kg/mm^2 (25 g load). The two works agree at the phase boundaries.

Ellinger (1943) placed the Knoop hardness value for Ta_2C at about 1000 kg/mm^2. Samsonov and Rukina (1957) give a value of 947 kg/mm^2.

Electrical Resistivity

The early measurements of specific resistivity yielded values near 170 μohm-cm (Friederich and Sittig, 1925; Moers, 1931[b]; Andrews, 1932). As the technique and material have improved, the values have dropped, the lowest being 25 μohm-cm reported by Rudy and Benesovsky (1960). The lack of analytical data leaves most values open to question. Kolomoets et al. (1958) give 44 μohm-cm at 25° using a material analyzing $TaC_{1.0}$ with 0.04 % C_f and a Ta + C_t summation of 99.85%. The values show a linear increase with temperature with a slope of 0.0667 μohm-cm/deg. This can be compared with the values: 40.6 μohm-cm (Samsonov, 1956[b]), < 34 μohm-cm (Samsonov and Rukina, 1957), and 42.1 μohm-cm (L'vov, Nemchenko and Samsonov, 1960).

Much of this inconsistency probably results because the specific resistance rises with decreasing carbon content. According to Andrews (1932), a maximum occurs at $TaC_{0.83}$, but later workers place it at Ta_2C (Smirnova and Ormont, 1956[b]). Three studies have been made of this property at various compositions (Samsonov and Rukina, 1957; Cooper and Hansler, 1963; and Santoro, 1963). Although there is some scatter, the resistivity was found to change in a nearly linear manner between ~25 μohm-cm at $TaC_{1.0}$ and 140 μohm-cm at $TaC_{0.70}$.

Superconductivity

Giorgi and co-workers (1962) have demonstrated that the superconductive transition temperature changes with composition, with values of 9.7°K at $TaC_{0.987}$ and 2.04°K at $TaC_{0.848}$. Their paper has resolved the previously conflicting reports ranging from normal conductivity above 1.2°K (Hardy and Hulm, 1954; Ziegler and Young, 1951) to a transition temperature of 9.2°K (Meissner and Franz, 1930) and has re-emphasized the importance of knowing the composition of the material measured.

Giorgi and co-workers (1963) have also shown that Ta_2C is not superconducting down to 2.0°K, in contrast to a transition temperature of 3.26°K given by Hardy and Hulm (1954). They suggest that this high value was due to the presence of Ta metal in the sample. The metal becomes superconducting at 4.457°K (Milne, 1961).

Thermodynamic Properties

The heat of formation, ΔH°_{298}, for TaC in equilibrium with carbon has been reported as -38.5 ± 0.6 kcal/mole by Humphrey (1954) and as -38 ± 5 kcal/mole by McKenna (1936). Smirnova and Ormont (1955) determined ΔH°_{298} as a function of composition. Unfortunately, because of serious disagreement over the position they found for the TaC-Ta_2C phase boundary (they give $TaC_{0.58}$) and the relationship between lattice parameter and composition (Figure I.2.7), there is considerable doubt about the correctness of the values reported.

Careful work by Huber and co-workers (1962) gives the following equation to express the variation of ΔH_{298} with composition:

$$\Delta H_f = 22.81 - 103.78\,(C/Ta) + 46.88\,(C/Ta)^2 \text{ kcal/mole.}$$

In the same work, the heat of formation of Ta_2C ($TaC_{0.485}$) was found to be -45.8 ± 3.4 kcal/mole. A recent measurement by Kornilov and co-workers (1962), using $TaC_{0.982}$, is in excellent agreement with Huber and co-workers (1962) if the same heat of formation for Ta_2O_5 is used in the calculations.

Low temperature heat capacity has been measured by Kelley (1940) using TaC containing 4.26% free carbon and less than 0.02% other impurities. He reports that $C_p(294.5) = 8.764$ cal/mole-deg and $S_{298} = 10.1 \pm 0.1$ e.u. Measurement of the high temperature heat content of $TaC_{0.99}$ by Levinson (1963) has yielded the following equation:

$$H_T - H_{310°K} = -2.407 + 5.942 \times 10^{-2}T + 3.442 \times 10^{-6}T^2 \text{ cal/g}$$

$$(1296 - 2843°K).$$

Vaporization

Above 2000°, vaporization of TaC becomes noticeable with the loss of carbon. According to Andrews (1932), there is virtually no loss of metal even at 3670°K, although as the composition approaches Ta_2C, metal does begin to evaporate (Coffman et al., 1960[b]). Hoch et al. (1955) gave an evaporation rate of 2.489×10^{-8} g/cm^2-sec at 2495°K, due solely to the loss of carbon. Using Langmuir techniques, Coffman and co-workers (1960[b]) calculate that carbon evaporates with a heat of 148 kcal/mole from a composition near $TaC_{1.0}$. They conclude that $TaC_{1.00}$ is thermodynamically stable above 2230°. This conflicts with the experimental results discussed previously. The very slow rate at which carbon diffuses through TaC can lead to errors in vaporization rate studies and should be kept in mind when these measurements are evaluated.

Lyon (1962) has shown that the congruent composition is somewhat below $TaC_{0.50}$.

Chapter I. 3

The Group-6a Carbides

The following compounds have been reported in the 6a Group: $M_{23}C_6$, M_7C_3, M_2C, M_5C_3, M_3C_2 and MC. If one wishes to believe the present literature, there is apparently only a slight similarity between the carbides of Mo and W and none between them and the Cr carbides. This is unusual in view of the marked similarities observed in the other Groups. The compounds $Cr_{23}C_6$, Cr_7C_3 and Cr_3C_2, each melting peritectically, are said to occur in the Cr-C system. In view of the methods used to obtain this information and the lack of similarity to the other systems in this group, further work should be done before conclusions are based on these observations. Both the Mo and W carbide systems form a hexagonal (metal lattice only) M_2C structure and a higher carbide structure having a hexagonal low temperature form which converts to a fcc lattice before melting. This compound occurs at Mo_3C_2 in the molybdenum system but, in the tungsten system, it is designated WC.

The metals exhibit higher melting points than the corresponding elements of the other Groups, and the dissolution of carbon causes a more drastic reduction in the melting point. Apparently, the strong metal-metal bonds, which are broken by dissolved carbon, are not replaced by stronger carbon-metal bonds in the carbide. The low heat of formation confirms this view and shows that these carbides are much less stable than those of Groups-4a and -5a.

In spite of this lower stability, the hardness of WC is quite high, sufficient to warrant its use in the hard metal industry.

I. 3.1 The Chromium-Chromium Carbide System

Preparation

The carbides of Cr have been observed since 1893[c] when Moissan prepared Cr_3C_2 and "Cr_4C" in the electric arc and blast furnace.

Because of the useful properties chromium imparts to steels, most of the knowledge about this system has been obtained by isolating the carbides from steels and other alloys. Even chromium metal is apt to have iron as a major impurity. Thus, many of the data to follow should be viewed with the reservation that they might better apply to the Fe-Cr-C system.

Technically, Cr_3C_2 is produced by heating a mixture of Cr_2O_3 and carbon in hydrogen at 1600° C. Below 1300°, Cr_7C_3 is the major product, while above this temperature Cr_3C_2 begins to form. Boiling HCl can be used to remove the lower carbides (Kosolapova and Samsonov, 1959). The thermodynamics of the carbon reduction of Cr_2O_3 can be found in a comprehensive paper by Kelley and co-workers (1944).

Layers containing Cr and Cr_3C_2 have been produced by the thermal decomposition of chromium carbonyl (Owen and Webber, 1948; Lander and Germer, 1948). The metal will react with methane at 600-800° (Campbell and co-workers, 1949).

These carbides can be prepared by reacting the powdered elements. However, because chromium has a very high vapor pressure at its melting point (3.9 torr), arc melting can result in a substantial loss of the metal.

Phase Relationship

The literature, at the present time, contains evidence for the three phases $Cr_{23}C_6$, Cr_7C_3 and Cr_3C_2. Early workers gave Cr_4C as the formula of the first phase. Epprecht (1951) reported a cubic CrC phase above about 2000°, but this is unconfirmed.

A phase diagram has been reported by Bloom and Grant (1950) which shows peritectic melting of each phase at 1520°, 1780° and 1895°, respectively, and a Cr-$Cr_{23}C_6$ eutectic which melts at 1498°. Friemann and Sauerwald (1932) give this latter temperature as 1515°, which was lowered to 1475° when the formation of $Cr_{23}C_6$ was suppressed by rapid cooling. Markovskiĭ and co-workers (1957) measured the melting point of Cr_3C_2 in contact with graphite at 1850°. The homogeneity range of these phases has not been reported.

The metal melts at 1915° with an allotropic transition at 1840° (Grigor'ev and co-workers, 1960). These workers also report a transition at 1650° which is still unconfirmed. However, Edwards (1960) concludes that the normal bcc form is the only one firmly established at the present time. According to Smith (1957), the solubility of carbon in Cr is very slight (0.32 wt %) even at the eutectic temperature. If this is true, the effect of carbon on the melting point of Cr is striking, amounting to about -13°/100 ppm C.

At the present time, there is insufficient information to construct a phase diagram that can be viewed with confidence.

Lattice Parameters and Structures

$Cr_{23}C_6$ is reported to be complex face-centered cubic (D_4^8 - type) with 116 atoms per unit cell and a = 10.66 A (Westgren, 1933). This is supported by the electron diffraction work of Brown and Clark (1951). When this phase was formed in steel, Allten and co-workers (1954) designated it $(Cr, Fe)_{23}C_6$ and gave a = 10.60 A. The Cr_7C_3 phase has also been found in steels (Crafts and Lamont, 1949). A hexagonal structure with a = 4.53, c = 14.01 A was reported by Westgren (1933). Kelley and co-workers (1944) gave parameters of a = 4.5, c = 13.98 A to this phase. Cr_3C_2 was first reported as orthorhombic by Hellström and Westgren (1933), and parameters of a = 2.82, b = 5.52, c = 11.46 A were reported by Kelley and co-workers (1944). This structure was later confirmed by Meinhardt and Krisement (1960), using thermal neutrons, and a space group D_{2h}^{16} - Pbnm (Pnma) was assigned.

Chemical Stability

In powdered form, all of the carbides begin to oxidize at 700°. However, massive samples of Cr_3C_2 and $Cr_{23}C_6$ remain practically unaffected up to 1000°. Cr_7C_3 is attacked at 800° (Kosolapova and Samsonov, 1961). These carbides are even more reactive in steam. Kelley and co-workers (1944) observed that Cr_3C_2 burned in O_2 below 1050° and was insoluble in hot H_2SO_4, but would dissolve in boiling perchloric acid; Cr_7C_3 required 1100-1150° to burn and would dissolve in hot dilute H_2SO_4; and Cr_4C gave incomplete combustion even at 1200° and was easily soluble in warm dilute H_2SO_4. Boiling 1:1 HCl will also dissolve $Cr_{23}C_6$ and Cr_7C_3 (Grigor'eva and Klimenko, 1959).

Hardness

Kieffer and Kölbl (1949) reported a hardness of 1300 kg/mm^2 for Cr_3C_2. Other workers have obtained values between 1000 and 1400 kg/mm^2. Westbrook (1957), from a study of the effect of temperature up to 800°, found room temperature values for Cr_7C_3 and $Cr_{23}C_6$ of 1600 kg/mm^2 and 1000 kg/mm^2, respectively.

Electrical Resistivity

Electrical resistivity and other electrical properties were determined by L'vov and co-workers (1961). They give the following values of the electrical resistivity:

$Cr_{23}C_6$ - (5.33 wt % C) = 127 ± 2 μohm-cm
C_7C_3 - (9.00 wt % C) = 109 ± 4
Cr_3C_2 - (13.33 wt % C) = 75 ± 5
Cr = 18.9

Superconductivity

Hardy and Hulm (1954) report that $Cr_{23}C_6$, Cr_7C_3 and Cr_3C_2 are normal conductors as low as 1.20°K. The metal is normal below 0.1°K (Hulm and Blaugher, 1961).

Thermodynamic Properties

A complete study of the thermodynamic properties of the chromium carbides was undertaken by Kelley and co-workers (1944). From the reaction between Cr_2O_3 and graphite, ΔH and ΔF° were measured as a function of temperature. High temperature enthalpy was also measured up to 1500°K. The values are shown in Table I.3.1. From these measurements, they concluded that each carbide is thermodynamically stable with respect to decomposition to the higher or lower carbide at room temperature. A more recent determination of high temperature enthalpy of Cr_3C_2 by Oriani and Murphy (1954) gave values which are somewhat below those of Kelley. This is due, they suggest, to the higher oxide content of Kelley's preparations. Using the same material, DeSorbo (1953) measured the low temperature heat capacity. He reports $S^\circ_{298.16} = 20.42 \pm 0.05$ e.u. and $C_p(298.16) = 23.53$ cal/mole-deg. The entropy value is in excellent agreement with that reported by Kelley et al. (1944) (20.4 e.u.).

TABLE I.3.1

Heat and Free Energy of Formation and Heat Content Values for the Chromium Carbides

Kelley and co-workers (1944)

$\mathrm{Cr_4C}$: $\Delta F^\circ_T = -16610 - 4.33T \log T + 1.535 \times 10^{-3}T^2 - 0.286 \times 10^5 T^{-1} + 10.14T$

$\Delta F^\circ_{298.16} = -16.74$ kcal/mole

$\Delta H_T = -16610 + 1.88T - 1.535 \times 10^{-3}T^2 - 0.572 \times 10^5 T^{-1}$

$\Delta H_{298.16} = -16.38$ kcal/mole

$H_T - H_{298.16} = 29.23T + 3.70 \times 10^{-3}T^2 + 5.018 \times 10^5 T^{-1} - 10{,}764$
(298 - 1700°K, ± 0.2% av)

$\mathrm{Cr_7C_3}$: $\Delta F^\circ_T = -42650 - 8.75T \log T + 2.615 \times 10^{-3}T^2 - 1.146 \times 10^5 T^{-1} + 18.44T$

$\Delta F^\circ_{298.16} = -43.76$ kcal/mole

$\Delta H_T = -42650 + 3.80T - 2.615 \times 10^{-3}T^2 - 2.291 \times 10^5 T^{-1}$

$\Delta H_{298.16} = -42.52$ kcal/mole

$H_T - H_{298.16} = 57.00T + 7.19 \times 10^{-3}T^2 + 10.104 \times 10^5 T^{-1} - 21024$
(298 - 1500°K, ± 0.1% av)

$\mathrm{Cr_3C_2}$: $\Delta F^\circ_T = -22330 - 9.90T \log T + 1.775 \times 10^{-3}T^2 + 0.296 \times 10^5 T^{-1} + 27.43T$

$\Delta F^\circ_{298.16} = -21.20$ kcal/mole

$\Delta H_T = -22330 + 4.30T - 1.775 \times 10^{-3}T^2 + 0.591 \times 10^5 T^{-1}$

$\Delta H_{298.16} = -21.01$ kcal/mole

Oriani and Murphy (1954)

$H_T - H_{298.16} = 26.19T + 4.74 \times 10^{-3}T^2 + 4.72 \times 10^5 T^{-1} - 9237$
(298 - 1200°K, ± 0.4%)

Vaporization

Vaporization produces a rapid preferential loss of Cr throughout the Cr-C system, and, according to Fujishiro and Gokcen (1961[b]), the vapor is mostly, if not all, chromium. Measurement of the dissociation pressure from a graphite Knudsen cell at 1900° to 2237°K by these workers led to the following equations for the pressure (atm) of Cr:

$$\log P_{solid} = -21.194/T + 6.525$$
$$\log P_{liquid} = -19.535/T + 5.76.$$

I. 3.2 The Molybdenum-Molybdenum Carbide System

Preparation

Like most of the other carbides, Mo_2C was prepared by Moissan (1893, 1895, 1897) in an electric arc. Later he and Hoffmann (1904) obtained "MoC" from an aluminum menstruum.

The reduction of MoO_3 by carbon leads to the carbide in two steps: between 420°and 640°MoO_2 is formed by an exothermic reaction, and above 820° the metal begins to form. The carbide Mo_2C results only after the oxide has been eliminated (Hegedüs and Neugebauer, 1960). This, however, does not preclude the possibility of a solid solution between the carbide and oxide. The reaction is promoted by the presence of hydrogen halides (Hüttig and co-workers, 1950).

Molybdenum metal can be converted to Mo_2C by the action of CO (Browning and Emmett, 1952; Hilpert and Ornstein, 1913); the reaction with CH_4 will produce Mo_2C and Mo_3C_2(Tutiya, 1932); and the direct reaction with graphite will lead, under the proper conditions, to both carbides. The latter reaction starts at about 1000° (Arkharov and co-workers, 1960; Hüttig and co-workers, 1950) forming the Mo_2C phase first. The thermodynamics of the CH_4 reaction have been studied by Browning and Emmett (1952).

Deposition from the gas phase can be accomplished by heating a wire to 300-800° in an atmosphere of molybdenum carbonyl and hydrogen (Lander and Germer, 1948; Campbell and co-workers, 1949) or by heating graphite in molybdenum chloride vapors (Pring and Fielding, 1909).

Fused-salt electrolysis of carbonate-borate-fluoride-metal oxide salt baths has produced both carbides, which deposit as silvery crystals on a graphite electrode (Weiss, 1946).

Phase Relationship and Lattice Parameters

The lower carbide has been established to have an integral stoichiometry of Mo_2C and an orthorhombic structure. The integral stoichiometry of the higher carbide, which has been referred to as MoC, has been placed in some doubt by the work of Rudy and co-workers (1961, 1962[a]). They report that this phase actually has a composition corresponding to Mo_3C_2, which is hexagonal at low temperatures but which converts to a cubic structure before it melts.

Of the known phases, only Mo_2C is thermodynamically stable at low temperatures and pressures (below about 1000°). Apparently it can have a composition between approximately $MoC_{0.44}$ and $MoC_{0.50}$ at about 1400° (Sykes and co-workers, 1935; Wallace and co-workers, 1963). $MoC_{0.50}$ melts peritectically at 2410 ± 15° (Nadler and Kempter, 1960; Sykes and co-workers, 1935; Friederich and Sittig, 1925). Between the Mo_2C phase and Mo there is a eutectic, melting at 2200 ± 25°, with a composition of about $MoC_{0.15}$ (Sykes and co-workers, 1935). Beyond Mo_2C, the melting point rises regularly to 2575° at Mo_3C_2 (Wallace and co-workers, 1963). The hexagonal structure, based on x-ray studies, has been modified by Parthé and Sadagopan (1963) using neutron diffraction techniques. They found that Mo_2C is orthorhombic (D_{2h}^{14}-Pbcn) with $a = 4.72_4$, $b = 6.00_4$, and $c = 5.19_9$. However, the hexagonal metal structure is normally seen when x-ray techniques are used. For this reason, the hexagonal parameters are listed in Table I. 3. 2.

There has been considerable controversy in the literature concerning the crystal structures that should be assigned to the compound Mo_3C_2. At least four structures have been observed, depending on the conditions of preparation. Kuo and Hägg (1952) observed a hexagonal structure

TABLE I.3.2

Structure and Lattice Parameter of the Molybdenum Carbides

Phases in Equilibrium	Composition of First Phase	Structure	Lattice Parameter, A	Investigator
Mo	pure	bcc	a = 3.1467	Speiser and co-workers (1952)
Mo + Mo_2C	$MoC_{0.0016}$	bcc	a = 3.1478	
Mo_2C +Mo	$MoC_{0.44}$	"hcp"	a = 2.994 ± 0.005 c = 4.722 ± 0.005	Wallace and co-workers (1963)
Mo_2C	$MoC_{0.48}$	"hcp"	a = 3.0028 ± 0.0001 c = 4.7288 ± 0.0001	Fries and Kempter (1960)
Mo_2C + Mo_2C_3	$MoC_{0.50}$	"hcp"	a = 3.012 c = 4.736	Rudy and co-workers (1961)
α -Mo_3C_2	$MoC_{0.67}$ (η)	hex, D_{6h}^{4}	a = 3.010 ± 0.002 c = 14.63 ± 0.01	Wallace and co-workers (1963)
β -Mo_3C_2	$MoC_{>0.67}$(α)	fcc	a = 4.2810 (quenched in value)	Rudy and co-workers (1962^{a})

(a = 2.932, c = 10.97A), designated γ', when Mo and CO were allowed to react at low temperatures. Above 800° it converted to another hexagonal structure a = 2.898, c = 2.809 A(WC-type), designated γ. Nowotny and co-workers (1954[b]), when they were unable to obtain the γ phase and found higher parameters for the γ' phase, suggested that the discrepancy might be due to oxygen contamination. Their preparation gave lattice parameters of a = 3.01, c = 14.61 A and was assigned to the space group D_{6h}^{4}. If only the strongest lines in the hexagonal pattern are considered, a cubic indexing results, and a = 4.27 can be calculated. With the addition of a little NbC (Rudy and co-workers, 1961), ThC, UC and VC (Rudy and co-workers, 1962[a]), ZrC (Wallace and co-workers, 1963), or WC (Dawihl, 1950), the cubic lattice can be stabilized. By employing a very rapid quench from the melt, Rudy and co-workers (1962[a]) were able to retain the cubic phase in the binary system. The use of high pressures will also produce the cubic form. At 0.6 kilobars and 1750°, only the hexagonal form was observed (Koval'skii and Semenovskaya, 1959), but at 40-70 kilobars and 1800-2500°, Clougherty and co-workers (1961) found that upon cooling the cubic form had been retained. From the analyzed compositions and the fact that the melting point is independent of composition beyond $MoC_{\sim 0.69}$ (Wallace and co-workers, 1963), one can conclude that the cubic form is a high temperature allomorph of Mo_3C_2 rather than an unstable form of MoC. With this in mind, the designation used to describe the hexagonal Mo_3C_2 (η) and the cubic form (α) might better be changed to (α) for the low temperature form and (β) for the cubic form, thus making this system consistent with the W-WC system.

The temperature of the hexagonal cubic transformation and the phase limits have not been reported for the Mo_3C_2 phase. This phase decomposes into Mo_2C and carbon below 1800° (Rudy and co-workers, 1962[a]). Melting point determinations of what was thought to be MoC have given values of 2870° (Engelke and co-workers, 1960) and 2692° (Agte and Alterthum, 1930). A melting point of 2575° for compositions beyond $MoC_{0.69}$, recently measured by Wallace and co-workers (1963), sheds doubt on the previous values.

The metal melts at 2620 ± 20° (Taylor and co-workers, 1961; Worthing, 1925) and apparently has only one crystal form up to at least 2250° (Demarguay, 1945).

The various lattice parameters and structures are summarized in Table I.3.2.

Appearance

All compositions have a metallic color which becomes darker as the carbon content increases.

Chemical Stability

The molybdenum carbides are rapidly attacked in air even at 700-800° (Powell and co-workers, 1955). According to Schwarzkopf and Kieffer (1953), the higher carbide is dissolved by concentrated HF, by cold HNO_3, and by boiling H_2SO_4, but concentrated HCl has very little effect. Also this carbide is attacked by the halogens to a varying degree.

The carbides are stable in H_2 below 2000° (Ohlinger, 1959[b]).

Hardness

The following values have been reported for the hardness of Mo_2C: 1479 kg/mm^2 (Meerson and Umanskii, 1953), 1500 kg/mm^2 (Kieffer and Kölbl, 1949) and 1550 DPH (Jones, 1956; Table I.3.4).

Schwarzkopf and Kieffer (1953) report that Bückle obtained a value of 1800 kg/mm^2. Mo_3C_2 is reported as being somewhat harder than Mo_2C, but no values have appeared.

Electrical Resistivity

According to Friederich and Sittig (1925), the specific resistivity of Mo_2C is 97.5 μohm-cm, and the value for Mo_3C_2 is 49 μohm-cm. A more recent determination gives 71.0 μohm-cm for Mo_2C (L'vov and co-workers, 1960).

Superconductivity

Matthias and Hulm (1952) have confirmed the early resistance measurements of Meissner and Franz (1930) with values of 2.78°K and 9.26°K for T_c of Mo_2C and Mo_3C_2, respectively.

Transition temperatures between 0.92 and 0.98 have been reported for pure Mo metal (Horwitz and Bohm, 1962; Hein and co-workers, 1963; Geballe and co-workers, 1962).

Thermodynamic Properties

The free energy of formation of Mo_2C and Mo_3C_2 has been estimated by numerous authors from equilibria in multicomponent systems. Some of this work is in error because the results are based on incorrect compositions for the equilibrium phases. These results have been recalculated in light of later findings.

Browning and Emmett (1952) measured the free energy by studying the equilibrium involving H_2 and CH_4. The following values at 950°K were calculated from their data after making appropriate corrections. It should be realized that most of the calculated values in their paper are in error, as noted by Kempter (1956).

(1) $2.27\ Mo + CH_4 = 2.27\ MoC_{0.44}(Mo_2C) + 2H_2\ \Delta F° = -12.3$ kcal/mole;

(2) $6.0\ MoC_{0.50}(Mo_2C) + CH_4 = 6.0\ MoC_{0.667}\ (Mo_3C_2) + 2H_2$
$\Delta F° = -2.2$ kcal/mole;

(3) $Mo + 0.44C = MoC_{0.44}(Mo_2C)$ $\Delta F° = -4.0$ kcal/mole.
If it is assumed that $\Delta F°$ for the reaction $MoC_{0.44} + 0.06C = MoC_{0.50}$ is small, then the following values can be calculated:

(4) $Mo + 0.667C = MoC_{0.667}(Mo_3C_2)$ $\Delta F° = -0.6$ kcal/mole;

(5) $MoC_{0.50}(Mo_2C) + 0.167C = MoC_{0.667}(Mo_3C_2)$ $\Delta F° = -0.2$ kcal/mole.
Thus both compounds are stable with respect to the elements, but Mo_3C_2 will decompose to give Mo_2C and C at 950°K, as has been observed.

Gleiser and Chipman (1962[a]) measured the pressure of CO and CO_2 over $MoO_2 + Mo_2C + Mo$ in the range 1200-1340°K and expressed the free energy of formation of Mo_2C as

$$\Delta F° = -11.710 - 1.83T \text{ cal/mole.}$$

However, they made no effort to determine or correct for possible oxygen contamination of the Mo_2C phase. It should be noted that the values were applied to $MoC_{0.5}$, not to the actual composition of the Mo_2C phase, i.e., $MoC_{0.44}$.

Alekseev and Shvartsman (1962), using the $Mo + Mo_2C + H_2 + CH_4$ equilibrium, obtained the formula

$$\Delta F° = +3800 - 14.84T \text{ cal/mole}$$

for the free energy of formation of Mo_2C in the range 873°- 1123°K. The free energy values from these studies are compared in Figure I.3.1.

$\Delta F_f°$ for Mo_3C_2 has been estimated from equilibrium studies within solid systems. By studying the Nb-Mo-C system, Rudy and co-workers (1961) proposed that the free energy of MoC_{1-x} was between -6 and -9 kcal/mole at 2120°K. Wallace and co-workers (1963) re-examined this value in light of a more reasonable composition for the equilibrium phases and suggested that the free energy of $MoC_{0.61}(Mo_3C_2)$ lies

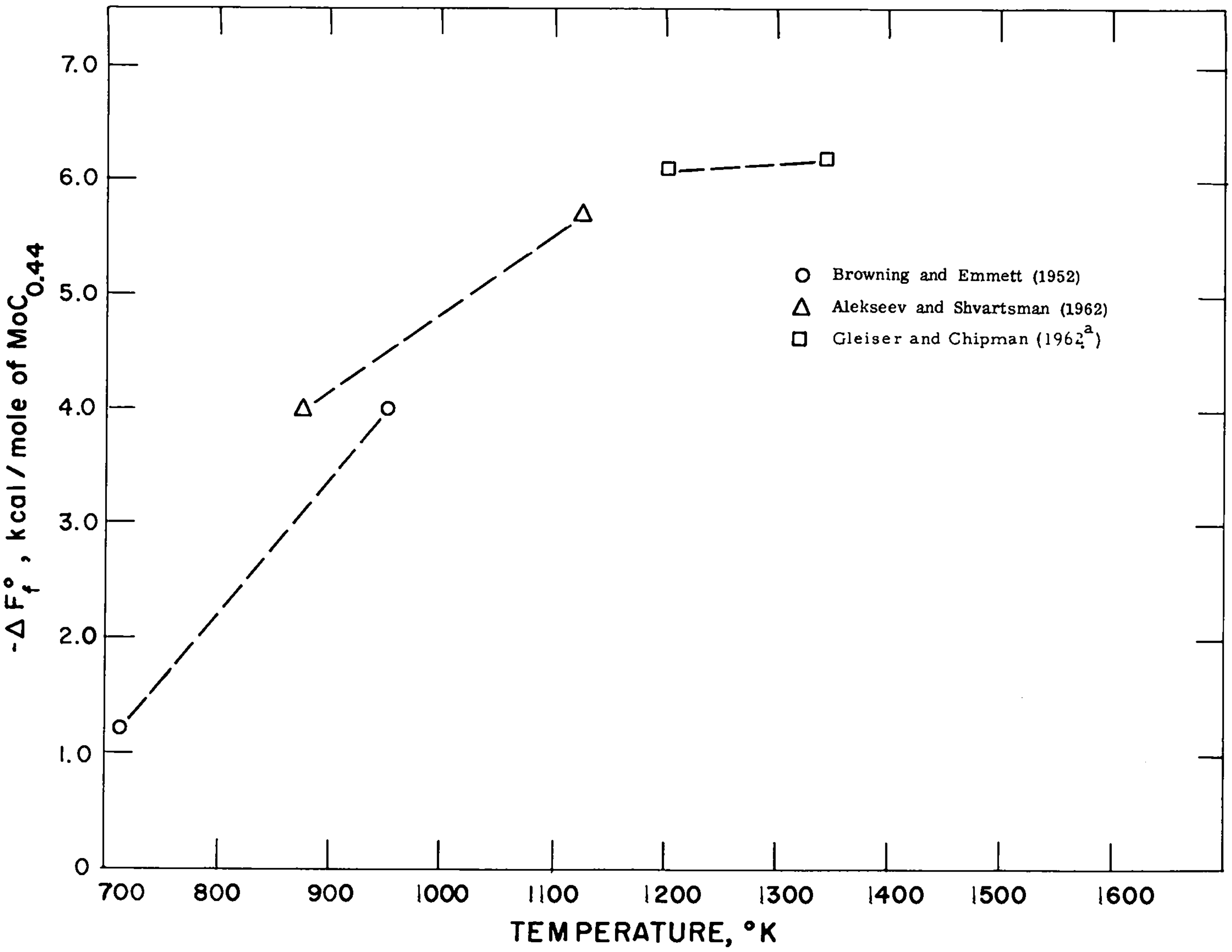

Figure I. 3. 1 A Comparison of the Reported ΔF° Values for Mo_2C

between -1 and -4 kcal/mole. Using a similar analysis of the Zr-Mo-C system, Wallace and co-workers (1963) obtained -2.6 ± 1.5 kcal/mole for ΔF_f° over the temperature range 1720-2370°K.

Mah (1963b) measured the heats of formation of Mo_2C and "MoC" by combustion calorimetry and obtained -11.0 ± 0.7 kcal/mole and -2.4 ± 1.0 kcal/mole, respectively. However, the "MoC" sample, for which analysis gave $MoC_{0.86}$, was assumed to be a mixture of MoC and Mo_2C. Since the high-carbon carbide actually has a stoichiometry of Mo_3C_2, the material was no doubt a mixture of Mo_3C_2 and free carbon. Any Mo_2C that might have been present would have resulted from the decomposition of the Mo_3C_2 into Mo_2C and C upon cooling. Therefore, the uncertainty for this value is a good deal larger than that indicated.

Workers at the Southern Research Institute (1963) have reported heat content values for Mo_2C above 533°K. Their least-squares fit of six points has been converted from Btu/lb to cal/mole in the following equation:

$$H_T - H_{273} = 3.09 \times 10^{-3} T^2 + 13.88T + 9360/(T-255) - 4538$$

$$(533 - 2200^\circ K).$$

Vaporization

No vaporization studies have appeared except the work of Bolgar and co-workers (1961).

I. 3.3 The Tungsten-Tungsten Carbide System

Preparation

Starting with Moissan (1893, 1896, 1897), the tungsten carbides have been prepared by melting together either W or WO_3, and carbon. Most later work has been based on preparations obtained by heating the powdered metal or tungsten compounds with carbon or CH_4, sometimes in the presence of H_2, but below the melting point.

WC can be prepared by heating tungstic acid (H_2WO_4) or ammonium paratungstate in a mixture of H_2 and CH_4 at 850° to 1000°. With tungstic acid, the reduction to W metal is complete before carbonization takes place (Newkirk and Aliferis, 1957).

The reaction between WO_3 and carbon proceeds in a similar fashion. Intermediate oxides are formed between W and unreacted WO_2, leading to the formation of the carbides only after the oxide has been eliminated (Hegedüs and Gadó, 1960).

Carbide formation from the powdered elements is possible at 1050° (Hüttig and co-workers, 1950). Below 650° this reaction leads mainly to W_2C, but above this temperature WC is formed (Kotö and Suzuki, 1948). The presence of H_2 or a hydrocarbon gas promotes this reaction. A final heating in vacuum above 1500° should be used to remove the last trace of oxygen.

Methods of producing carbide coats from the gas phase have been described by Campbell and co-workers (1949) and Lander and Germer (1948).

Phase Relationship

Numerous papers have established the existence of the two phases, W_2C and α-WC, and recently evidence for β-WC phase has been reported. Until recently, however, knowledge of the phase relationship has rested on the work of Sykes (1930) as modified by Norton (see Schwarzkopf and Kieffer, 1953). The latest work, by Sara and Dolloff (1962), has shown that the system is somewhat more complicated, and that the melting temperatures are much higher than thought.

Their phase diagram, Figure I.3.2, has the following features: eutectic melting between W and W_2C at 2710°; congruent melting of W_2C at 2795° and a composition of $WC_{0.43}$; a high temperature phase β-WC, which forms at 2525°; peritectic melting between β-WC and carbon at 2785°; and the dissociation of α-WC into β-WC and graphite at 2755°. The W-W_2C eutectic temperature agrees well with 2727° measured by Barnes (1929) and 2732° reported by Nadler and Kempter (1960). The latter authors also reported that a composition of $WC_{1.01}$ melts at 2720°.

The range of W_2C was shown by Sara and Dolloff (1962) to be wider than thought, from $WC_{0.39}$ to $WC_{0.50}$ at 2400°, and α-WC apparently has a negligible composition range. The β-WC, like the other cubic carbides, has a wide homogeneity range, but it is impossible to quench in by normal cooling. In addition, this phase was undoubtedly prepared by Lautz and Schneider (1961) although they refer to it as a cubic form of W_2C. By sparking two electrodes made of α-WC together under oil, they collected the pure phase, a = 4.25 A, as a fine powder. Goldschmidt and Brand (1963) also found a cubic phase by sparking W against graphite. Although they designated it β-W_2C, their evidence is not sufficient in view of the work of Sara and Dolloff (1962) to establish this phase as the high temperature form of W_2C rather than β-WC.

Tungsten, with a melting point of 3407° (Zalabak, 1961), is the highest melting metal. The dissolution of only 0.3 at.% carbon (Goldschmidt and Brand, 1963) is sufficient to lower the melting point to the eutectic temperature. The metal is bcc at room temperature.

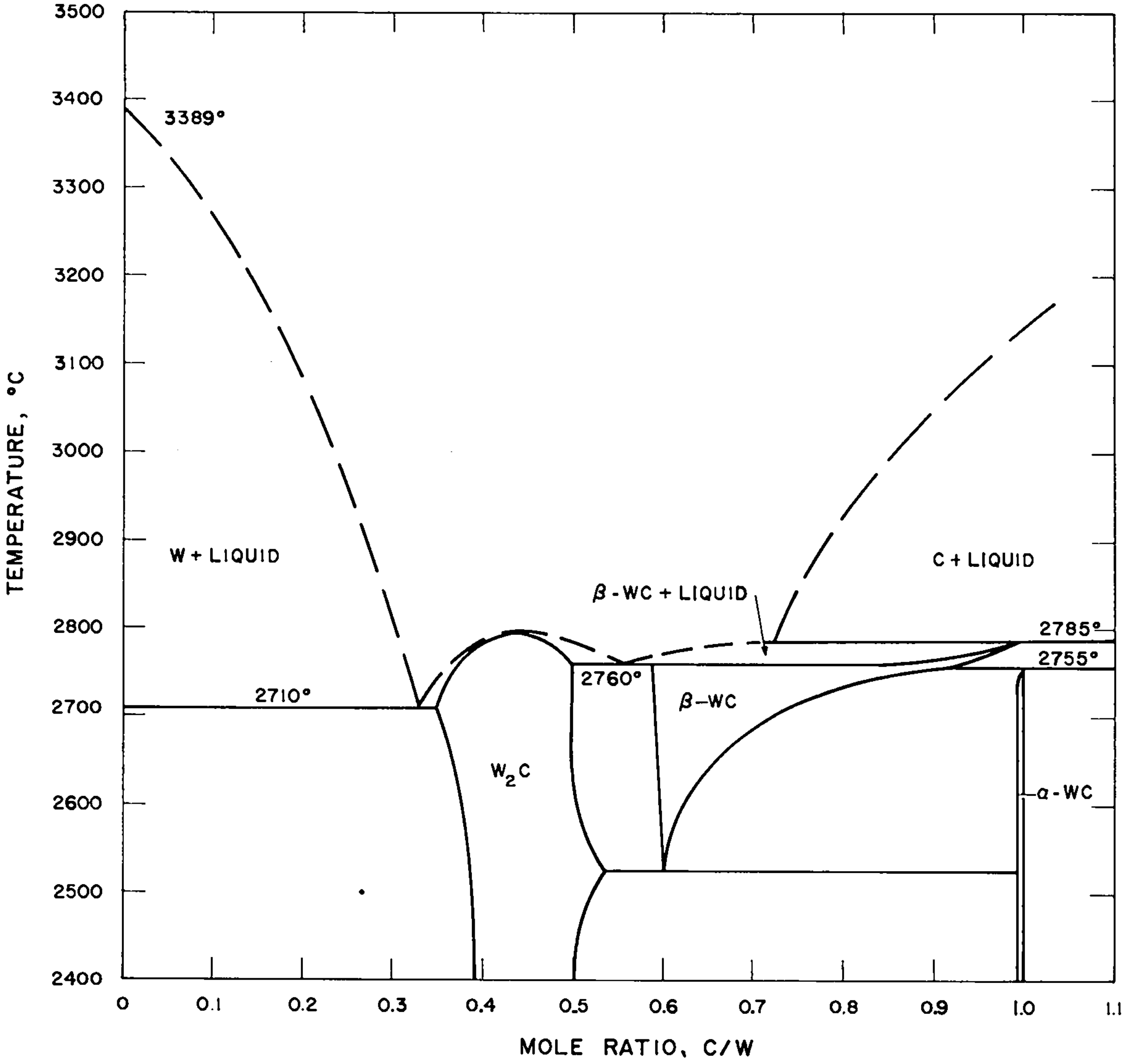

Figure I. 3. 2 Phase Diagram of the W-WC System (Sara and Dolloff, 1962)

Lattice Parameters and Structure

The structures of W_2C and α-WC are both simple hexagonal, and β-WC is fcc. Recent proposals that the cubic structure is a high temperature form of W_2C, as indicated by the initial work of Becker (1928), are without sufficient supporting evidence.

Until recently the exact crystal structure of α-WC was in doubt. The originally proposed structure of Westgren and Phragmén (1926) was questioned by Hägg (1931) who suggested that a NiAs-type structure would also fit the x-ray data. However, until neutron diffraction was used, it was not possible to assign an unambiguous structure. Using this technique, both Leciejewicz (1960) and Parthé (1961) assigned the space group D^1_{3h} - P6m2, corresponding to the structure proposed by Westgren and Phragmén (1926). Electron diffraction studies of Butorina (1960) gave the same result. The homogeneity range of this phase is unknown. For this reason, lattice parameters are listed in Table I.3.3 only for samples for which an indication of the composition was given. The trend in 'c' values suggests that the α-WC phase might have some width, in contrast to what has been assumed.

The newly found β-WC phase has a parameter of 4.215 A (Sara and Dolloff, 1962) which is remarkably close to the value obtained when the lattice parameter of the TiC-WC solid solution is extrapolated to pure WC (Metcalfe, 1946).

The W_2C phase (hcp, L'3-type) also shows a variation in 'c' across the single-phase region (Nowotny and co-workers, 1954[a]).

Chemical Stability

WC is stable in air to 700°, it is decarbonized when heated in hydrogen, and it is not attacked by N_2 even at high temperatures. W_2C is attacked by Cl_2 at 300-400°, but WC is unaffected.

TABLE I.3.3

Structure and Lattice Parameter of the Tungsten Carbides

Investigator	Lattice Parameter, A		Analysis or Phases in Equilibrium
	a	c	
α-WC			
Metcalfe (1946)	2.9063	2.8368	$WC_{1.0}$
Parthé (1961)	2.90	2.83	$WC_{0.986}$
Coffman and co-workers (1960[a])	2.906	2.823	$WC_{0.973}$
β-WC			
Sara and Dolloff (1962)	4.215		$WC_{0.82}$
W_2C			
Westgren and Phragmén (1926)	2.992	4.722	$WC_{0.52}$
Coffman and co-workers (1960[a])	3.028	4.729	$W_2C + WC$
Nowotny and co-workers (1954[a])	2.99	4.72	$W_2C + WC$
	2.99	4.69	$W_2C + W$
W			
Parrish (1960)	3.16522 ± 0.00009		pure

Dilute 1:4 HNO_3 + HF will dissolve W_2C at room temperature, and WC after the solution has been heated (Kachik et al., 1946).

Hardness

Most hardness values for these carbides were obtained in the middle 1940's when the technique was less accurate than now. Consequently there is rather poor consistency between the values. More recently, Jones (1956), Table I.3.4, reported 2250 DPH for WC when W_2C was present, while Kieffer and Kölbl (1949) reported 3000 kg/mm^2 (50g load) for W_2C when WC was present. On the other hand, Dolloff and Sara (1961) give 1450 and 2085 kg/mm^2 as being representative of W_2C and WC, respectively.

Electrical Resistivity

Three recent values for the room temperature resistivity of WC are 25 μohm-cm (Rudy and Benesovsky, 1960), 19.6 μ ohm-cm (L'vov and co-workers, 1960), and 50 μohm-cm with a linear slope of 0.240 μohm-cm / deg (Kolomoets and co-workers, 1958). The latter value applies to a sample of $WC_{0.99}$ containing 0.02 wt % free carbon and having zero porosity.

Recent values for W_2C are lacking. Becker (1928) reported a room temperature value of 80 μ ohm-cm and an increase in the resistivity-vs-temperature slope at about 2300°. From this he suggested that W_2C has a high temperature form. Andrews (1923) observed that the resistivity of W_2C is greater than that of WC.

Superconductivity

α-WC has been reported to be a normal conductor above 1.28°K (Ziegler and Young, 1953; Lautz and Schneider, 1961).

Lautz and Schneider (1961) found that a cubic form of "W_2C" became superconducting at 5.2°K (center). As discussed above, this material

TABLE I.3.4
Hardness of Group-4a,-5a and -6a Carbides
(Jones, 1956)

Compound	Impurities, wt %	Carbon, wt %	X-ray Analysis	Lattice Parameter, A	Hardness, DPH
TiC(a)	Zr : 0.001-0.01	20.2	graphite		3100
ZrC(b)	Hf : 1.0-10.0 Ti : 0.1-1.0 Si : 0.01-0.1 V : trace Cr : trace Mo: trace	12.5	graphite	4.698	2200
HfC(a)	Zr : ~1.0 Ti : trace V : trace	6.0	HfC only		1675
VC(a)	Ca : 0.01-0.1 Cr : trace Fe : trace Ba : trace	21.6	graphite + unidentified lines		2250
NbC(c)	Zr : 0.01-0.1 Ti : 0.01 Fe : trace Mo: trace	11.5	NbC only		1950
TaC(c)	Mo: ~0.1 Ti : ~0.01 Cr : trace Fe : trace	6.3	TaC only		1400
Cr_3C_2(a)	Al : ~1.0 Si : 0.01-0.1 Ca : ~0.01 Ti, V, Mn, Co, Cu: trace	13.1	mostly Cr_3C_2 or Cr_7C_3. No oxide		1860
Mo_2C(c)	Si : 0.01-0.1 Ti, Fe, Ni: trace	5.8	Mo_2C only, variable composition		1550
WC(c)	Fe : 0.1-1.0 Ti : 0.01 Cr : 0.01 Si, Mn: trace	5.8	WC + W_2C		2250

(a) Prepared from oxides
(b) Prepared from hydrides
(c) Commercial product

was no doubt β-WC. W_2C is superconducting below 2.74° K as confirmed by Matthias and Hulm (1952).

From a study of alloys, Hulm and Blaugher (1961) concluded that tungsten metal should have a negative transition temperature. No evidence of superconductivity has been seen above 0.035° K (Strongin and Fairbank, 1961).

Thermodynamic Properties

The combustion measurement of McGraw and co-workers (1947) was recalculated by Huff and co-workers (1948) to give a ΔH°_{298} value for α-WC equal to -8.4 ± 0.2 kcal/mole. Mah (1963^b) obtained ΔH°_{298} = -9.6 ± 0.4 kcal/mole for a sample of α-WC which was reported to contain 0.53% tungsten metal. A study of the system $WC + CO_2 = W + 2CO$ has yielded a value of -8.34 ± 0.3 kcal/mole for ΔF°_f between 1215° and 1266° K (Gleiser and Chipman, 1962^b).

Mah (1963^b) obtained ΔH°_{298} = -6.3 ± 0.6 kcal/mole by burning a sample of W_2C which contained both W and WC.

The high temperature heat content of α-WC has been measured by the Southern Research Institute (1963) and by Levinson (1964). The latter worker, using very pure $WC_{0.99}$, fit his data by the following equation:

$$H_T - H_{310^\circ} = -17.15 + 5.140 \times 10^{-2} T + 4.589 \times 10^{-6} T^2 \text{ cal/g}$$

$$(1276^\circ\text{-}2642^\circ K,\ \pm 2.0\%).$$

Vaporization

Both carbides lose carbon rapidly when heated above 2400°, leading eventually to the metal (Andrews and Dushman, 1921; Andrews, 1923). WC heated above 2000° will rapidly form a surface layer of W_2C through which the diffusion of carbon is not quite rapid enough to insure equilibrium (Coffman and co-workers, 1963). The evaporation rate studies of Hoch and co-workers (1955) and Coffman and co-workers (1963) show that the total pressure of carbon over $W_2C + \alpha WC$ is essentially equal to the C_1 pressure over graphite, and that no metal evaporates up to 2700° K.

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PART II

GROUP-4a, -5a AND -6a NITRIDES

INTRODUCTION TO THE GROUP-4a, -5a, AND -6a NITRIDE SYSTEMS

The attitudes developed in the general introduction are applicable to the nitrides. Briefly these are: The use of Greek letters to designate the phases has been avoided when the integral stoichiometry of the phase is known. Otherwise, the generally accepted nomenclature is used even though this may be inconsistent. Early papers have been largely ignored except when they were unique in either quantity or quality. And an effort has been made to understand the effect of oxygen contamination on the properties and how this can be avoided.

This last point cannot be too strongly emphasized. Oxygen in any form (except CO), either dissolved in the metal, as the oxide, or in the gas stream, will react and contaminate the sample. Unlike the corresponding carbides, the nitrides are only slightly self-purifying, if at all. To make matters worse, the amount of oxygen is difficult to determine analytically. For this reason, most investigators assume, with some justice, that the difference between 100% and the summation of metal % and nitrogen % is due to oxygen. This assumes, of course, that these analyses can be obtained with sufficient precision. It is worth noting in this regard that the Kjeldahl method for determining nitrogen has been found, on some occasions, to give values which are too low.

The effect of dissolved oxygen has not been determined in most cases, studies in the Nb-N-O system by Brauer being a notable exception (see Brauer and Esselborn, 1961[a]). However, there are examples of marked differences in measured properties which can be attributed to the unrecognized presence of oxygen. Lattice parameter measurements of VN, shown in Fig. II.1.2, provide a good illustration. The earliest measurements, by Epel'baum and Ormont (1947), were made on material obtained by decomposing NH_4VO_3. Even though the oxygen content (from summation) was thought to be less than 0.5 wt %, it is clear that their nitrides were seriously contaminated. Hahn (1949) prepared purer samples by nitriding the metal, but the metal used contained at least 5% oxygen. In the most recent work, Schnell (1960) took great pains to exclude oxygen and obtained VN which contained less than 0.3 wt % oxygen by analysis. It is interesting to note that the presence of oxygen apparently widens the homogeneity range as well as raises the lattice parameter. But, in this system, all the measured parameters approach the same value at $VN_{1.0}$. This can be attributed to a decreasing oxygen solubility with increasing nitrogen content, as was observed by Schnell (1960). Although insufficient work has been done to know whether this is a general characteristic of all nitride systems, it should be kept in mind when interpreting experimental data.

Most of the cubic nitrides have been prepared with compositions higher than $MN_{1.0}$. The behavior of the lattice parameter and the density in this region indicates that the increase in stoichiometry is due to the formation of metal atom vacancies. This creates still another variable which must be considered when studying these materials, and it raises some interesting questions about the type of bonding in the nitride systems.

So far as is known, all of the cubic nitrides have a yellowish color. This deteriorates from rich, golden yellow in Group-4a to a bronze color for VN and pale yellow cast for NbN. The hexagonal forms are all gray or almost black, except for Cr_2N which is said to be yellow. Once a pure sample has been seen, the color provides a quick estimation of whether the material is pure and of the highest stoichiometry.

Chapter II. 1

The Group-4a Nitrides

The elements in this group form a single cubic nitride with a range of composition similar in width to the corresponding carbide. The lower phase limit lies below $MN_{0.50}$, and the upper limit may be over $MN_{1.1}$. Because of the very rapid loss of nitrogen at high temperatures, the melting points of these compounds are in doubt. Apparently nitrogen raises the melting temperature of the metal to produce a peritectic. In addition, the low temperature hexagonal form of the metal is stabilized so that it, too, melts peritectically. Formation of the compound produces an additional increase in melting point, but the amount of this increase will not be known with certainty until measurements are made under the equilibrium nitrogen pressure. However, the melting temperatures are at least as high as 3000°.

The lattice parameters of the ZrN and HfN phases have been observed to increase as the nitrogen content is reduced, while TiN is normal in this respect. It is possible that these compunds have a defective metal lattice as well as the familiar nonmetal defects. Thus, as the N/M ratio is decreased, vacancies in the metal lattice are filled by metal atoms, thereby causing sufficient expansion to compensate for the contraction attending the removal of nitrogen. This dual defect structure has been proposed by earlier investigators to explain how compositions beyond the 1:1 ratio can be obtained.

II. 1. 1 The Titanium-Titanium Nitride System

Preparation

Early workers prepared the nitride by heating TiO_2 with carbon under a nitrogen atmosphere. This technique, however, can lead to significant contamination by carbon and oxygen. TiO_2 can also be nitrided by NH_3, or by $N_2 + H_2$, but with a similar uncertainty as to the purity of the final product (Belyakova and co-workers, 1940). The reaction with NH_3 has been studied in detail by Douglass and co-workers (1961).

Pure TiN is best prepared by heating TiH or Ti in N_2 or NH_3. The reaction of TiH with N_2 produces TiN between 1800° and 1900° (Duwez and Odell, 1950). When NH_3 is used, the reaction will go at a lower temperature (1000°) (Verkhoglyadova and co-workers, 1961). A satisfactory method is to heat the pure metal for 24 hours at 1000° in a stream of pure NH_3, pulverize, then heat at about 2000° in pure N_2 (Gutierrez, 1963). The absence of impurities, such as CO_2, O_2, H_2O, or hydrocarbons, either in the metal or in the gas, is essential if a pure product is to be obtained. Even hot graphite near the sample will furnish carbon by gas transport (Arai and co-workers, 1960). In addition, because the metal can dissolve considerable amounts of oxygen without visible effect, it should be analyzed before use.* Once the TiN has been contaminated by carbon or oxygen, it is almost impossible to purify.

The reaction between $TiCl_4$, N_2 and H_2, on a hot W wire, first studied by van Arkel (1924), has been observed by Wilke (1960) to produce single crystals (2.5-70 microns x 0.7-1.5 mm) of TiN.

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*The purity of the metal can be estimated from the value of the 'c' lattice parameter (Ageev and Model', 1958). This method is applicable only after the metal has been heated in vacuum to bring the surface oxide into solution and to remove dissolved nitrogen.

Arc melting of Ti in a N_2 atmosphere has been used to produce TiN. Because of the rapid loss of nitrogen and Ti near the melting point, this method is apt to produce a nitrogen-deficient as well as an inhomogeneous sample (Palty and co-workers, 1954).

Phase Relationship

Titanium forms one nitride, TiN, with a cubic structure (NaCl-type) and a wide range of homogeneity. The lower phase limit is near $TiN_{0.38}$, as reported by Palty and co-workers (1954). The upper phase limit is generally assumed to be $TiN_{1.0}$, but it may be as high as $TiN_{1.18}$ (Brager, $1939^{a,b}$). According to Brager (1939^{a}), the upper limit is caused by vacancies in both the Ti and N lattices, as determined from density measurements. This is based on TiN samples prepared by heating $TiCl_4 + NH_3$ to 400°. When the material was heated to 1400-1600°, the composition shifted to $TiN_{1.0}$. No subsequent work has been done to show whether this behavior is typical of the system rather than due to the method of preparation, as Brager implied.

The phase diagram of Palty and co-workers* (1954), Figure II. 1. 1, shows that the melting point of the metal is raised rapidly by dissolved nitrogen to a peritectic at 2020 ± 25°. The α phase is stabilized by nitrogen and melts peritectically at 2350 ± 25°. In samples near the composition $TiN_{0.3}$, they observed additional lines in the diffraction pattern which could be indexed as tetragonal, $a = 4.92$, $c = 5.61$. Formation of this phase (ϵ) was incomplete even after 96 hours at 1000°.

The melting point of TiN is obscured by rapid decomposition into N_2 and Ti vapor at this temperature, but in spite of this, two early

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*A more complete description of this work can be found in Cadoff and Palty (1952). In Figure II. 1.1 the metal melting point used by these authors (1725°) was changed to a better value, 1660° (Schofield and Bacon, 1953).

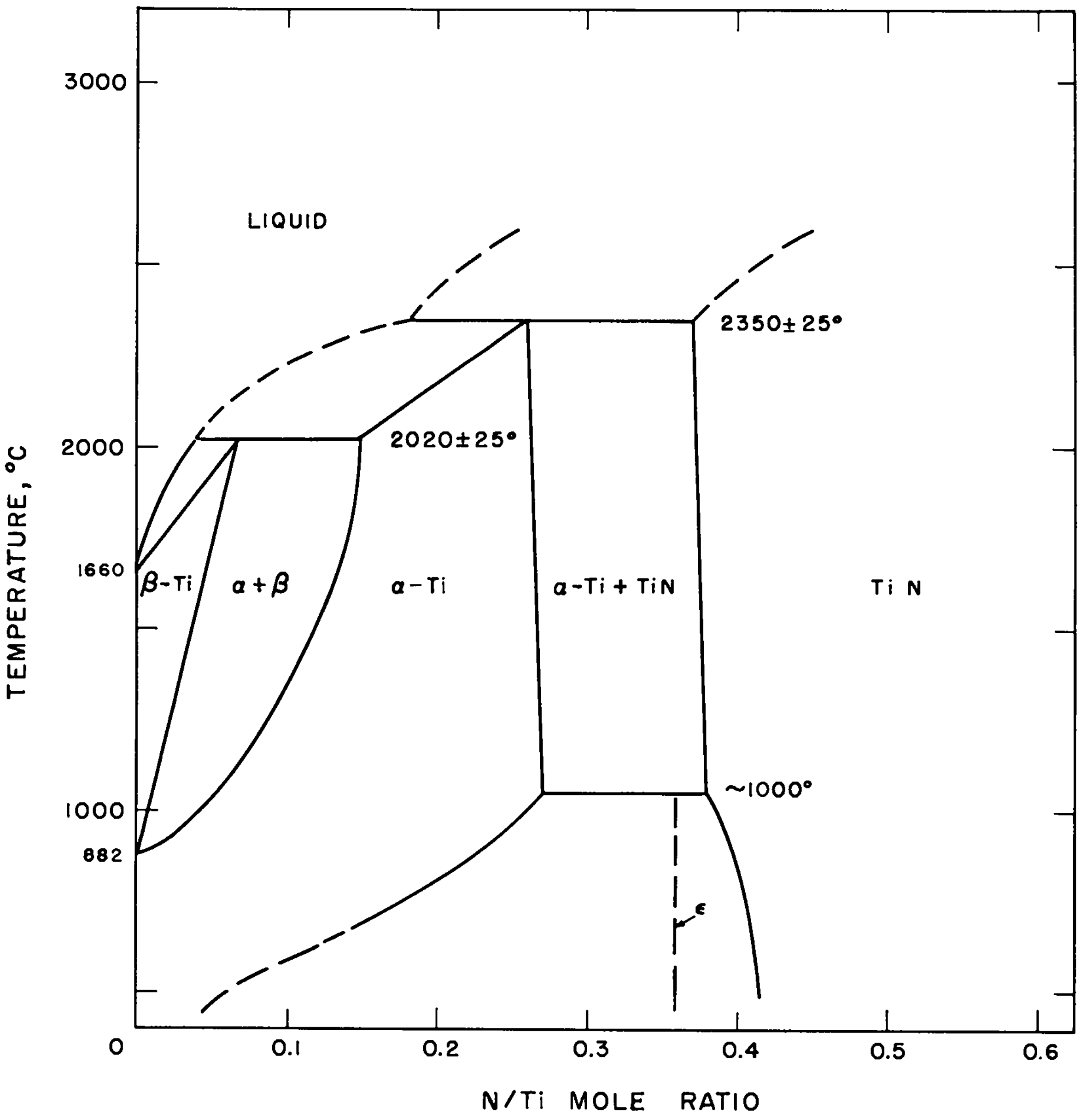

Figure II. 1. 1 Phase Diagram of the Ti-TiN System measurements place it near 3000° (Friederich and Sittig, 1925; Agte and Moers, 1931).

Lattice Parameter and Structure

Unlike the other nitrides in this group, the TiN lattice contracts as nitrogen is removed. Table II. 1. 1 summarizes the phase boundary compositions and lattice parameters. The lattice parameter varies almost linearly between the extremes (Ehrlich, 1949; Vainshtein et al., 1961). Beyond $TiN_{1.0}$ Brager (1939^{a}) reported a sharp drop in the parameter, to 4. 22 A at $TiN_{1.16}$.

Chemical Stability

According to Blocher (reported in Campbell, 1956), TiN is insoluble in HNO_3, HCl and H_2SO_4, but is dissolved by aqua regia, fused alkalies or boiling alkali solutions.

Pollard and Woodward (1950) found that TiN reacts rapidly with O_2 above 1400°, forming a stable oxide film (Wakelyn, 1961). TiN also reacts slowly with CO_2 at high temperatures. Both reactions eventually lead to TiO_2. There is apparently no reaction with CO or H_2 according to Pollard and Woodward (1950). On the other hand, May and Hoekstra (1961) reported considerable reaction with H_2.

The reaction with oxygen has been studied in some detail by Münster and Schlamp (1957) and by Samsonov and Golubeva (1956).

Appearance

Pure $TiN_{1.0}$ has a vivid yellow color. Deviations from this stoichiometry lead to a gray color. In small quantities, carbon produces a gray-lavender tint (Beattie and VerSnyder, 1953). Extreme contamination by oxygen or carbon can make the material black (Arai and co-workers, 1960).

TABLE II. 1. 1

Lattice Parameter and Structure of Ti and TiN

Phases in Equilibrium	Composition of First Phase	Structure	Lattice Parameter, A	Investigator
α-Ti	pure	hcp	a = 2.95111 ± 0.0006 c = 4.68433 ± 0.00010	Wood (1962
β-Ti	pure	bcc	a = 3.280 ± 0.003	Rare Metals Handbook (1961)
α-Ti + TiN	$TiN_{0.014}$	hcp	a = 2.9510 c = 4.6920	Clark (1949)
TiN + Ti	$TiN_{0.45}$	fcc	a = 4.221	Vainshtein et al. (1961)
$TiN + N_2$	$TiN_{0.99}$	fcc	a = 4.244	Vainshtein et al. (1961)

Hardness

The hardness of TiN is related directly to the nitrogen content. Measurements by Samsonov and Verkhoglyadova (1961[a]) give 1200 kg/mm^2 at $TiN_{0.59}$ and 1900 kg/mm^2 at $TiN_{0.97}$ (50 g load). In a previous paper, Samsonov (1952) gives 2160 kg/mm^2 for $TiN_{1.0}$.

Electrical Resistivity

Early measurements of resistivity have produced a wide range of values for TiN, from 21.7 μohm-cm (Moers, 1931[b]) to 130 μohm-cm (Friederich and Sittig, 1925). Later work indicates that this variation is probably due to an extreme difference in the nitrogen content of the measured samples.

Dissolution of nitrogen in the metal causes the resistivity to rise from 42 μohm-cm (McQuillan, 1950-51) through 55.8 μohm-cm at 0.293% N (Jaffee and Campbell, 1949). Measurements by Samsonov and Verkhoglyadova (1961[b]) show that once the TiN phase forms, the resistivity becomes much greater, being 113 μohm-cm at $TiN_{0.56}$, with a decrease as more nitrogen is added. Near $TiN_{1.0}$ it approaches 27 μohm-cm. Between these extremes, the variation has a negative variation from linearity. This can be compared with the value of 60 μohm-cm reported by Kolomoets and co-workers (1958) for a material containing 79.95% Ti, 22.3% N and 0.65% free carbon ($TiN_{0.95}$).

The temperature coefficient of resistivity for $TiN_{1.0}$ is positive from liquid air temperature (Moers, 1931[b]) through 1000°, with a value of 0.0621 μohm-cm/deg between room temperature and 1000° (Kolomoets et al., 1958). However, at lower nitrogen contents a wide and variable maximum forms which shifts toward 900° as nitrogen is removed (Samsonov and Verkhoglyadova, 1961[b]).

Superconductivity

The early resistance measurements of superconductivity by Meissner and Franz (1930) have been confirmed by Hardy and Hulm (1954), and by Münster and Sagel (1956) using magnetic susceptibility measurements. They report TiN to have a transition temperature of 5.6°K. In addition, this is lowered by dissolved oxygen which, in some cases, results in a double break in the permeability curve.

In view of the experience with ZrN and HfN, it would be desirable to measure this property as a function of stoichiometry before the above value is accepted as correct.

Thermodynamic Properties

The high temperature heat capacity has been measured by Naylor (1946) with the following results:

$$H_T - H_{298.16} = 11.91T + 4.7 \times 10^{-4}T^2 + 2.96 \times 10^5/T - 4585$$

$$(298\text{-}1800°\text{K} \pm 0.5\%) \text{ cal/mole.}$$

This is compared with the more recent work of Neel and co-workers (1960) in Figure II.1.2. Specific heat measurements at low temperature (Shomate, 1946) give $S°_{298.16} = 7.20 \pm 0.04$ e.u. and $C_{p(298.16)} =$ 8.86 cal/deg-mole.

Using the same material as Naylor, Humphrey (1951) obtained -80.5 ± 0.3 kcal/mole as the heat of formation of $TiN_{1.0}$. This agrees well with an earlier value of -80.3 kcal/mole (Neumann and co-workers, 1931). If Humphrey's value for the heat of formation of TiO_2 is used (225.52 kcal/mole), the values become identical. A study by Knudsen effusion techniques has led to $\Delta H°_{298} = -79.4$ kcal/mole (Hoch and co-workers, 1955) for a composition of about $TiN_{0.79}$.

Vaporization

Vaporization of TiN results in both gaseous Ti and N_2. According

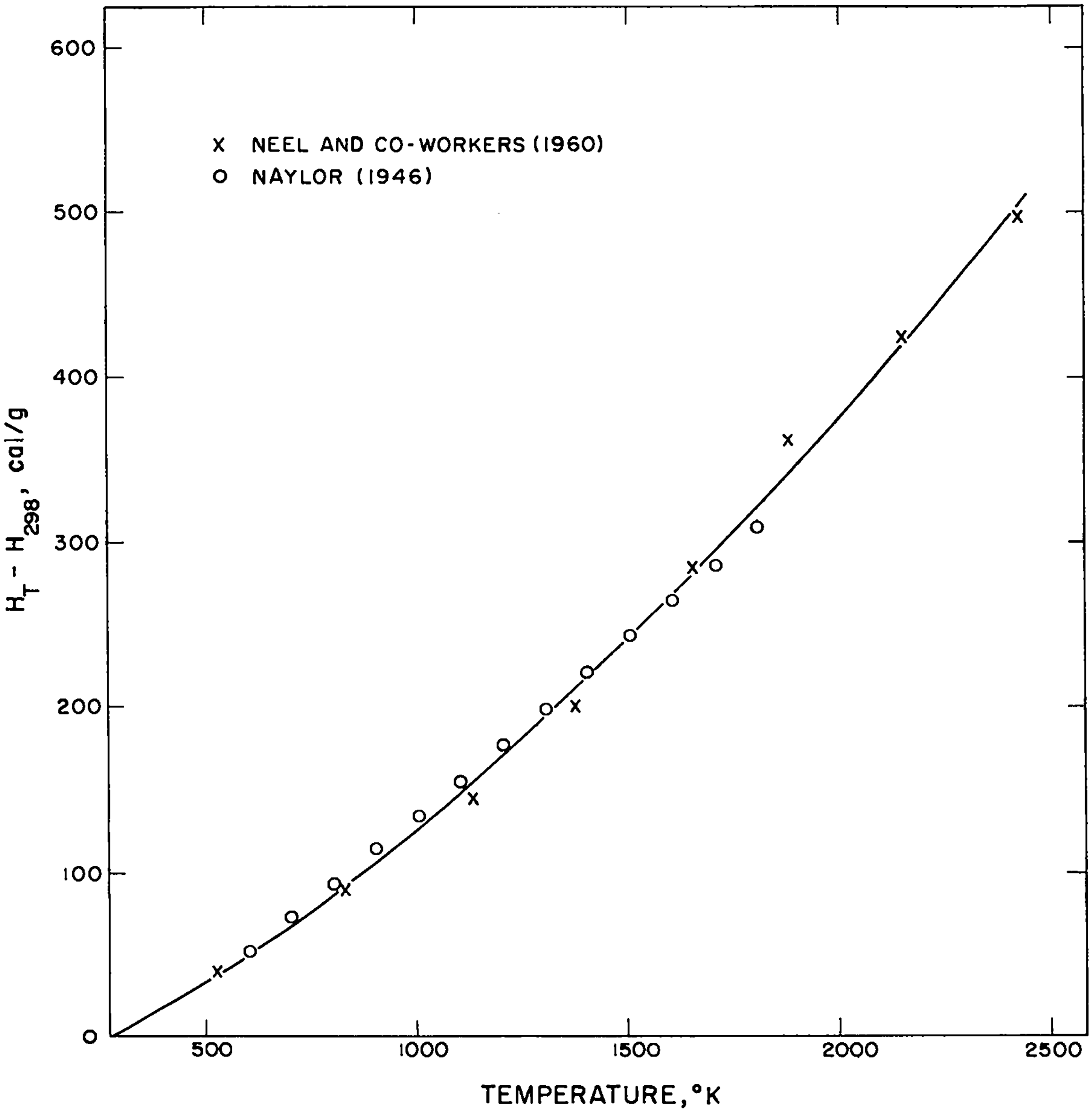

Figure II. 1. 2 Heat Content of TiN as a Function of Temperature to Dreger and Margrave (1960), the heat of decomposition is 143.1 kcal/mole if the evaporation coefficient is 0.155. Starting with a sample of $TiN_{0.79}$ Hoch and co-workers (1955) measured the evaporation rate from a Knudsen crucible. They report the following pressures over $TiN_{\sim 0.79}$:

$$\log P_{Ti} = -2.7859 \times 10^{4}/T - 0.40 \times 10^{-4}T + 8.263 \text{ (atm)}$$

$$\log P_{N_2} = -2.7859 \times 10^{4}/T - 0.40 \times 10^{-4}T + 7.963.$$

The manner in which the evaporation rates change with composition has not been determined. In any case, since this system apparently does not vaporize congruently, the pressures given above apply to non-equilibrium conditions.

II.1.2 The Zirconium-Zirconium Nitride System

Preparation

ZrN is more difficult to obtain free of oxygen than is TiN when starting with the oxide. Even when starting with the metal, precautions ought to be taken to see that the metal is oxygen free.*

As with TiN, the pure nitride has been prepared by heating the metal or hydride in NH_3 or N_2. When Zr and N_2 react, the stoichiometry of the product depends on the temperature and pressure, as can be seen from Figures II.1.6 and II.1.7, as well as the heating time (Kibler and co-workers, 1962). These measurements show that the highest nitrogen content results at low temperatures and high N_2 pressures. By heating the metal in N_2 (1 atm) between 1300° and 1400° for 5 hours, Mah and Gellert (1956) produced what they called $ZrN_{1.0}$. At lower temperatures Domagala and co-workers (1956) observed a much lower composition limit, probably because of incomplete reaction. For example, at 800° $ZrN_{0.34}$ was the limit, and at 1000° $ZrN_{0.5}$ resulted. Even heating at 1200° for 12 hours did not raise the composition above $ZrN_{0.76}$. An additional factor influencing the reaction rate, as well as the purity of the product, is the presence of O_2 and H_2, in trace amounts, in the gas stream (Gulbransen and Andrew, 1949).

Arc melting has been used to prepare materials in this system (Domagala and co-workers, 1956), but the rapid evolution of nitrogen leaves a nitrogen-poor and inhomogeneous sample.

The deposition from $ZrCl_4$ vapor onto a heated wire has been described by van Arkel and DeBoer (1925), Moers (1931^a) and

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*Under suitable conditions the hardness of the metal might be useful as a rough criterion of purity (Kearns and Chirigos, 1962).

Campbell and co-workers (1949). Single crystals as well as polycrystalline layers result.

Phase Relationship

Cubic ZrN is the only compound found in this system, but the limits of this phase are not well known.

Domagala and co-workers (1956) have studied the system in detail below $ZrN_{0.42}$, using x-ray, metallographic, and incipient melting techniques. Dissolved nitrogen raises the melting point of Zr from 1855° to 1880° and stabilizes α-Zr to 1985°, where it melts peritectically. From diffusion measurements, Mallett and co-workers (1954) have determined the solubility of N_2 in β-Zr to be log (wt % N) = $\frac{-2810}{T} + 1.42$. This is somewhat higher than that found by Domagala and co-workers (1956).

The homogeneity range of ZrN is somewhat narrower than that of TiN. Although the data are meager, the lower limit is no higher than $ZrN_{0.55}$ at about 1500° (Rudy and Benesovsky, 1961; Smagina and co-workers, 1960), and probably lower at the peritectic temperature. Early measurements place the melting point of $ZrN_{1.0}$ near 3000° (Friederich and Sittig, 1925; Agte and Moers, 1931; Becker, 1933). This information is summarized in Figure II.1.3 as a probable phase diagram.

No mention has been made of an ϵ phase, as was found in the Ti-N system by Palty and co-workers (1954).

Lattice Parameter and Structure

The effect of composition on the lattice parameter is somewhat unusual. Above $ZrN_{0.78}$ it is constant at 4.577 A, but as more nitrogen is removed the lattice expands. At the lower phase boundary, the parameter is 4.584 A. This is shown in Figure II.1.4. The wide

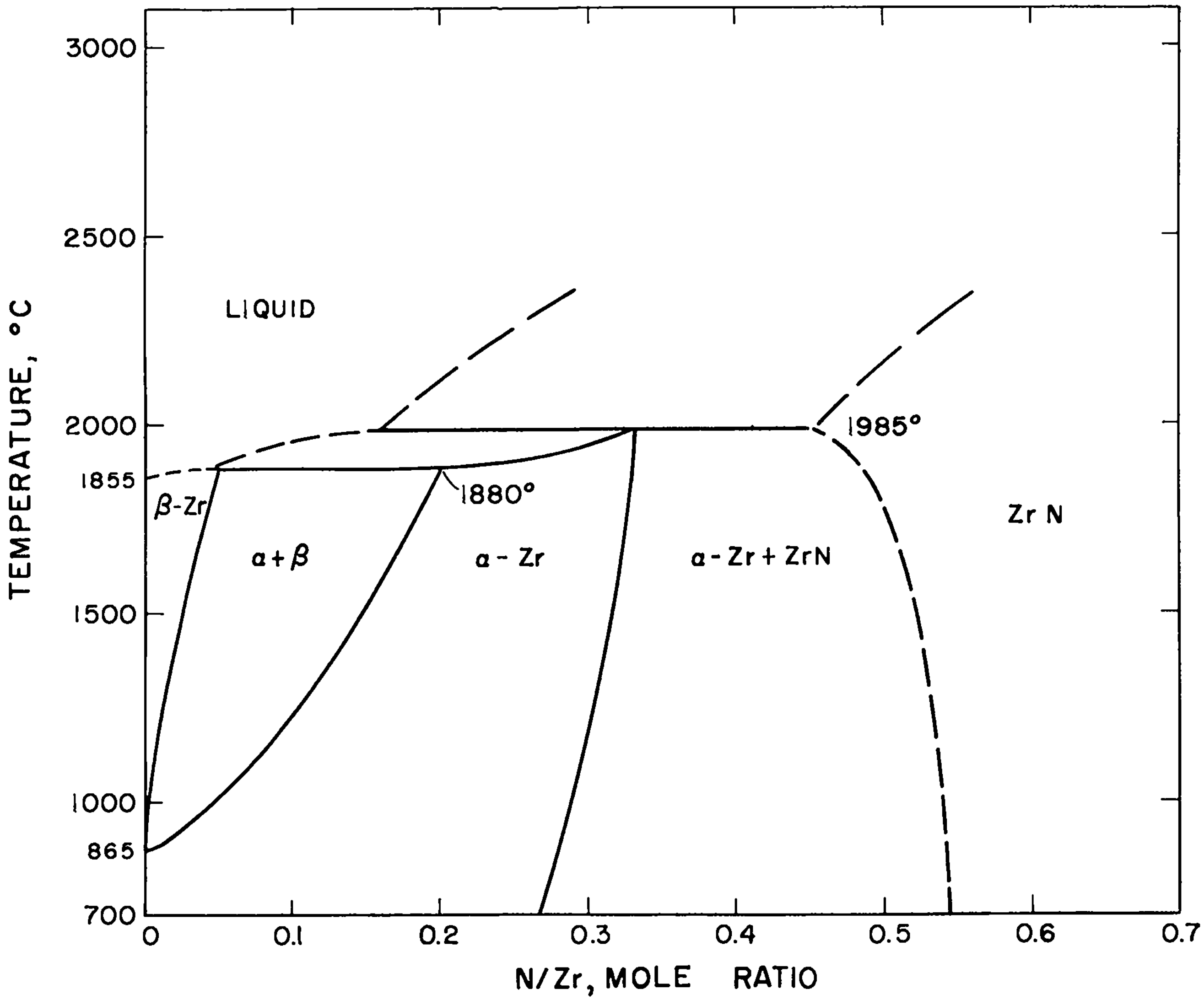

Figure II. 1. 3 Phase Diagram of the Zr-ZrN System

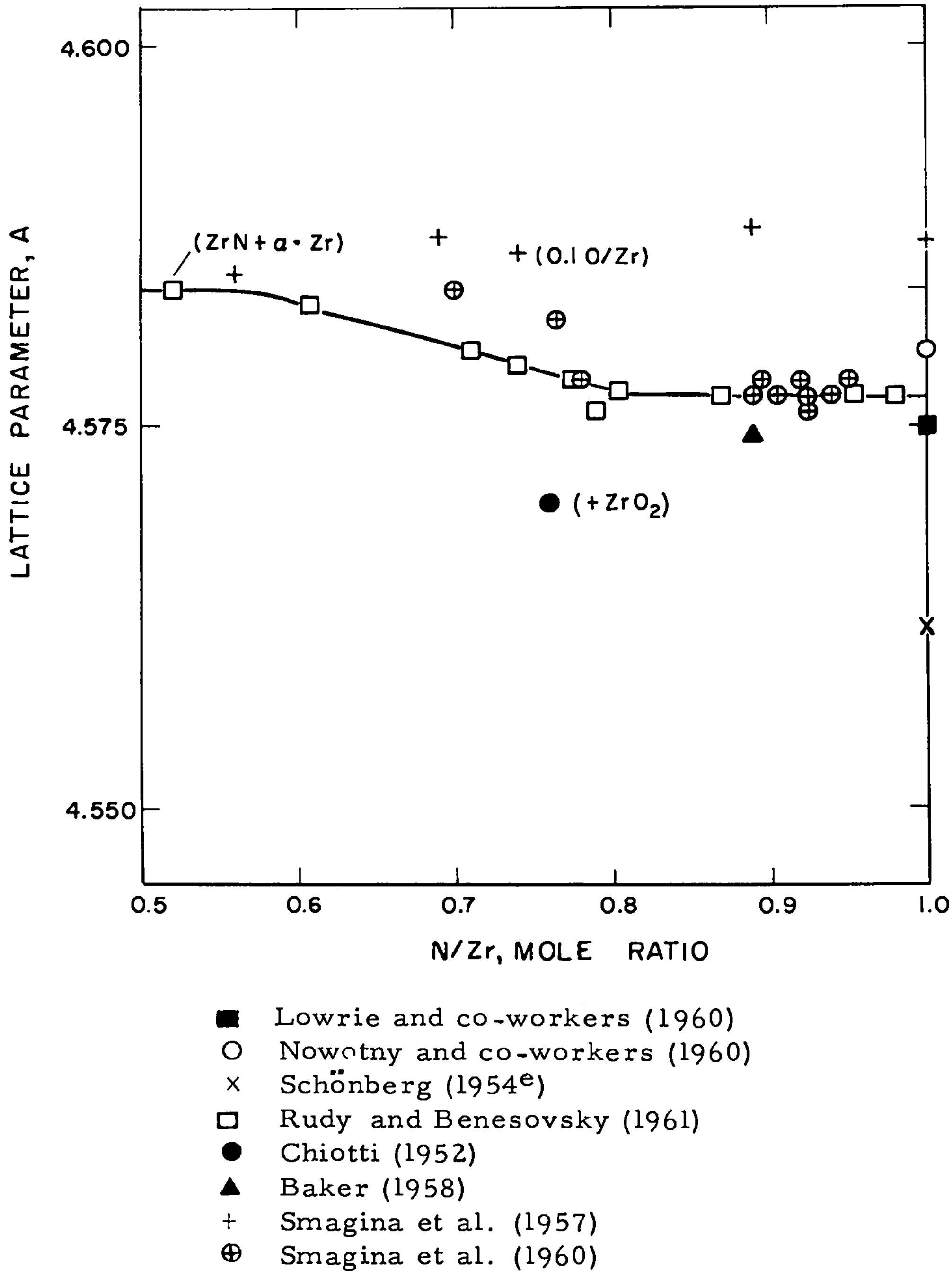

Figure II.1.4 Lattice Parameter of the ZrN Phase as a Function of Composition scatter would appear to be due to something besides dissolved oxygen.

Chemical Stability

ZrN is insoluble in HNO_3 but will dissolve in concentrated H_2SO_4. Heated alkalies or boiling solutions thereof dissolve the nitride with the formation of NH_4 (Schwarzkopf and Kieffer, 1953). The oxidation resistance of ZrN is generally considered to be poor.

Appearance

$ZrN_{1.0}$ has a yellow color when pure. A lower stoichiometry or impurities lead to a darkening until a gray or black color results.

Hardness

A hardness of 1510 kg/mm^2 (100 g, Knoop) has been given by Schwarzkopf and Kieffer (1953) for ZrN (composition unstated), and 1983 kg/mm^2 (30 g load) was measured by Samsonov (1952). On the other hand, $ZrN_{0.91}$ is reported to have a hardness of 1480 ± 85 kg/mm^2 (Samsonov and Verkhoglyadova, 1961[a]). As with TiN, the hardness is expected to be a function of composition.

Electrical Resistivity

The following room temperature resistivity values have been reported: 160 μohm-cm (Friederich and Sittig, 1925), 13.6 μohm-cm (Moers, 1931[b]), 11.52 μohm-cm (Clausing, 1932), and 21.1 μohm-cm (L'vov and co-workers, 1960). The temperature coefficient is positive.

It would be interesting to see this property measured as a function of composition.

Superconductivity

Hardy and Hulm (1954) have confirmed the early resistivity measurements of Meissner and Franz (1930) with a transition temperature of 8.9°K. The composition of the material was not given. Recent work by Szklarz and Giorgi (1962) has shown that the transition temperature of $ZrN_{1.0}$ is higher than 10°K and is a function of composition.

Thermodynamic Properties

High temperature heat contents have been measured by Coughlin and King (1950) using a nitride containing 86.75% Zr and an undetermined amount of nitrogen. Their values fit the following equation:

$$H_T - H_{298.16} = 11.10T + 8.4 \times 10^{-4}T^2 + 1.72 \times 10^5 T^{-1} - 3961$$

$$(298\text{-}1700°K, \pm 0.4\%) \text{ cal/mole.}$$

This is compared to the work of Neel and co-workers (1960) in Figure II.1.5.

Using the same material as Coughlin and King (1950), Todd (1950) calculated the following values at 298.16°K from measurements at low temperatures:

$$S° = 9.29 \pm 0.05 \text{ e.u.}, \quad C_p = 9.655 \text{ cal/deg-mole.}$$

Measurements of the heat of formation, by combustion calorimetry, have given $\Delta H°_{298} = -87.3 \pm 0.4$ kcal/mole* (Mah and Gellert, 1956) and -85.5 kcal/mole* (Neumann and co-workers, 1934). This property varies with composition, from -56.1 kcal/mole* at $ZrN_{0.56}$ to -87.9 kcal/mole* at $ZrN_{1.0}$, with a slight positive deviation from a straight line between these limits (Smagina and co-workers, 1957, 1959). Hoch et al. (1955) have calculated, from their Knudsen effusion studies, a value of -80.43 kcal/mole

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*Calculated using the same heat of formation value for ZrO_2 (-261.5 ± 0.2 kcal/mole) (Humphrey, 1954).

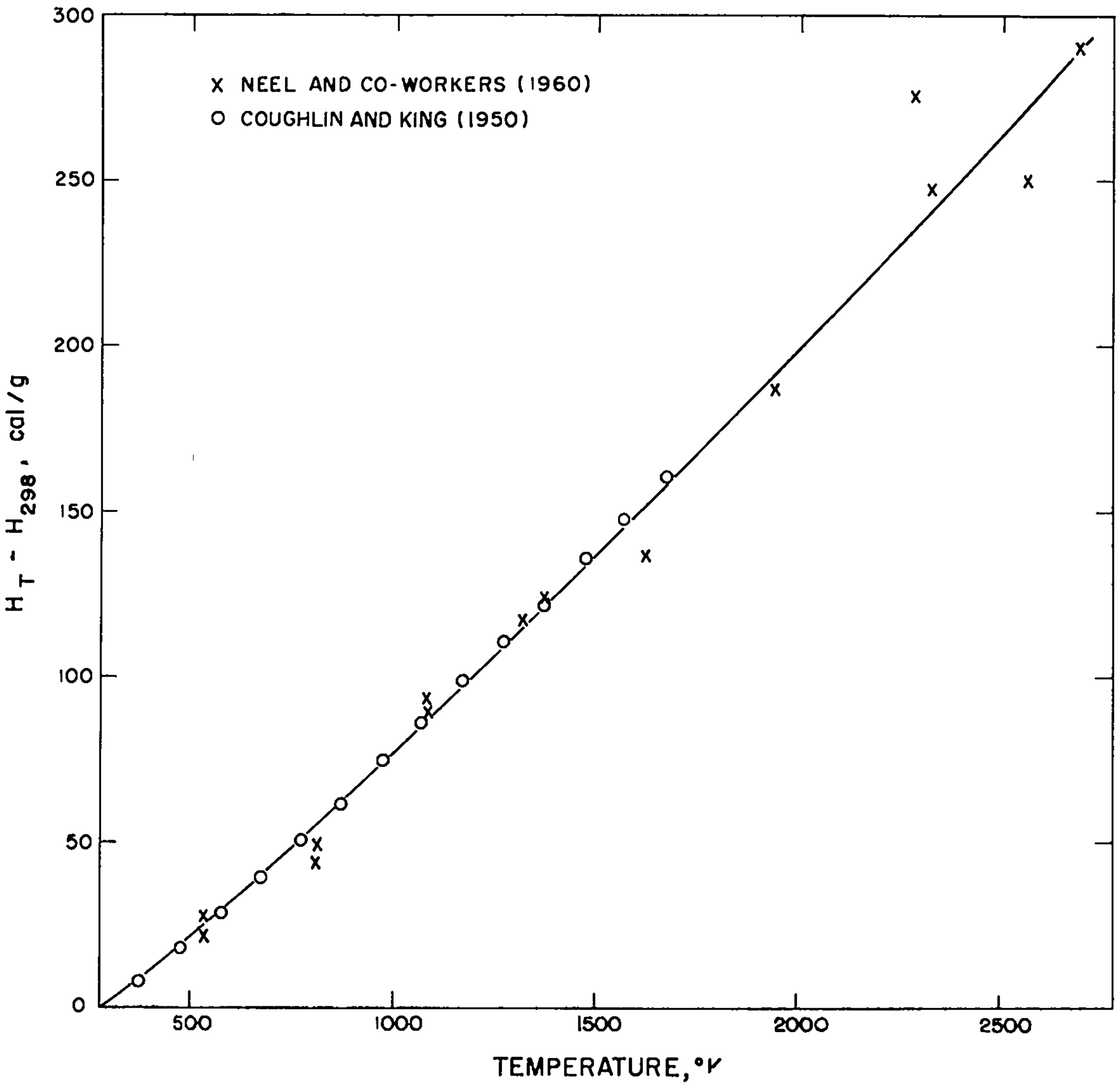

Figure II.1.5 Heat Content of ZrN as a Function of Temperature for what they considered to be $ZrN_{0.97}$. Results by Kibler et al. (1962) indicate (see below) that this material was nearer the composition $ZrN_{0.82}$.

Vaporization

The equilibrium N_2 pressures over this system have been measured on two occasions by Knudsen effusion and by a tensi-volumetric method. The most recent work, by Kibler, Lyon and DeSantis (1962), shows that the pressure of N_2 increases dramatically as the nitrogen content of the solid increases (Figure II. 1. 6). Thus, not only are vapor pressure measurements complicated because of the wide composition range, but considerable errors can result as the composition changes. This is apparent in the work of Hoch et al. (1955). Even though an initial analysis showed their material to be $ZrN_{0.97}$, a comparison with the results of Kibler and co-workers (1962) in Figure II. 1. 7 suggests that the final composition was near $ZrN_{0.82}$. With this assumption, the results are in good agreement. The dashed line corresponds to an equation for N_2 pressure based on thermodynamic arguments by Hoch et al. (1955). Kibler and co-workers have refrained from making thermodynamic calculations until the nitrogen content of their samples is better known. Measurements by Smagina and co-workers (1960), using the tensi-volumetric method, gave pressures several orders of magnitude higher than those reported above, although the same general trends with composition were noted.

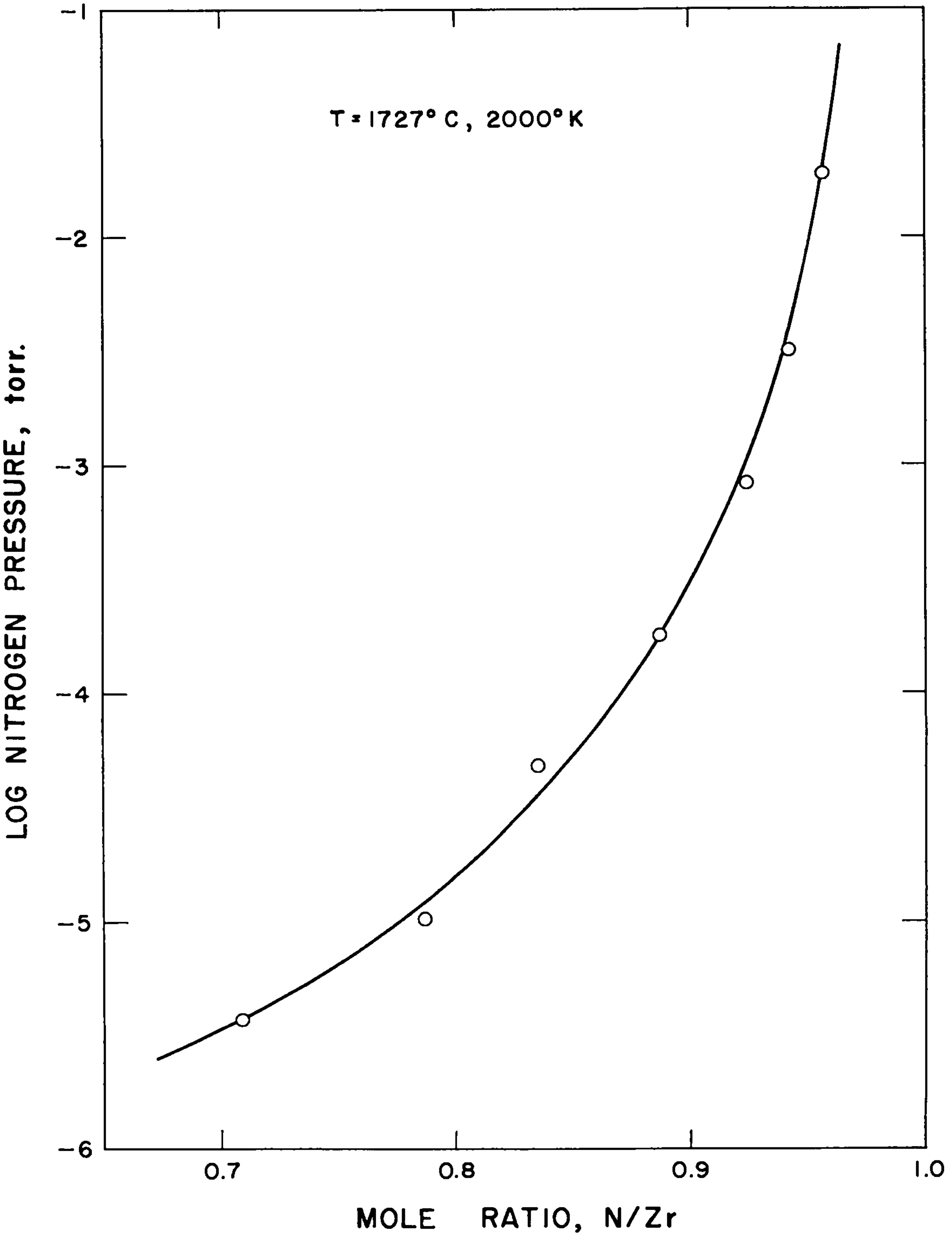

Figure II. 1. 6 Pressure of Nitrogen over ZrN as a Function of Composition

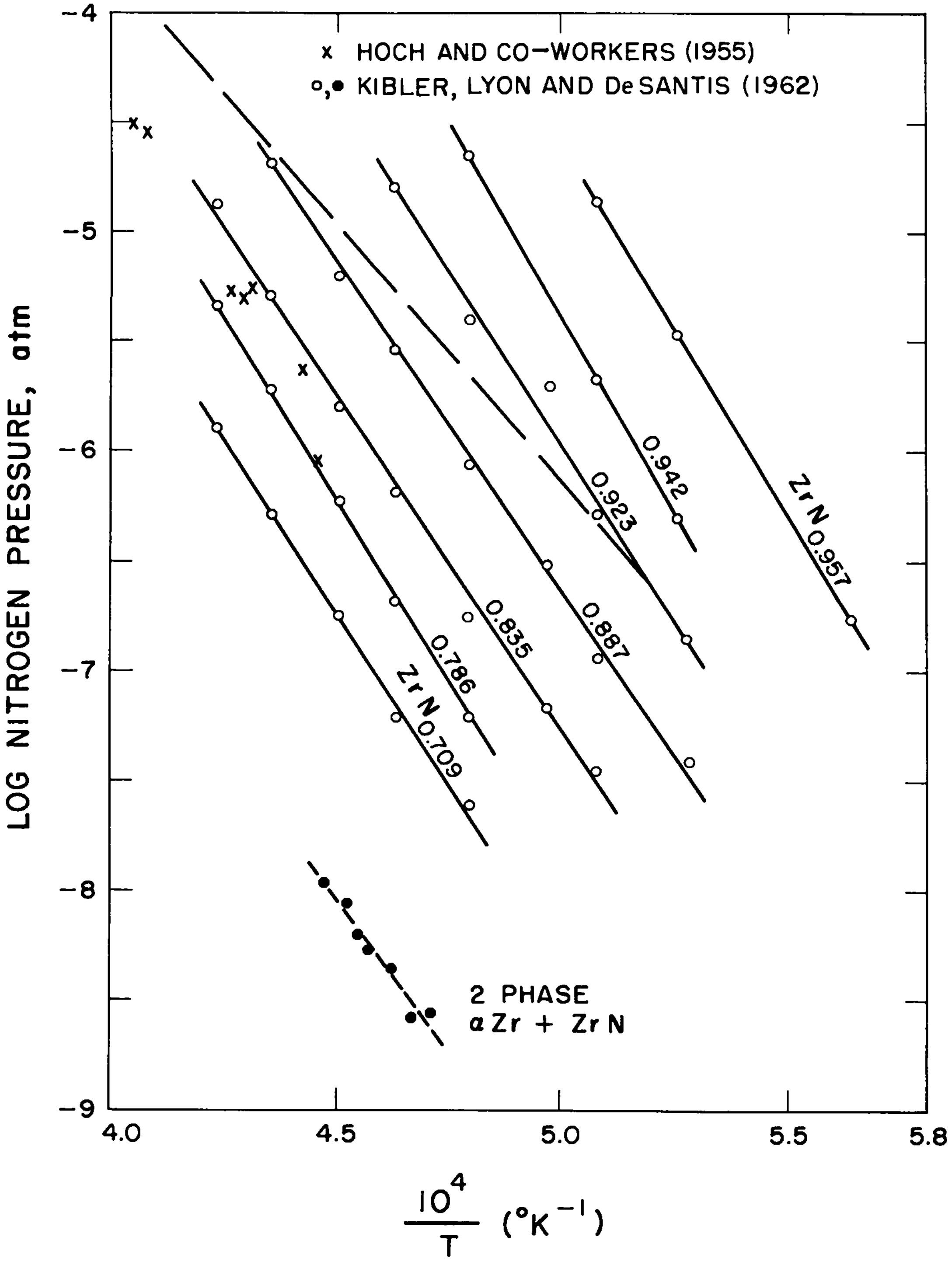

Figure II. 1. 7 Pressure of Nitrogen over ZrN as a Function of 1/T

II.1.3 The Hafnium-Hafnium Nitride System

Preparation

From the sparse descriptions in the infrequent studies of this system, one can assume that HfN can be prepared by the same methods used to produce TiN and ZrN. Humphrey (1953) made a composition slightly above $HfN_{1.0}$ by heating the metal in N_2 at 1400-1500° for 10 hours with intervening grindings. Glaser et al. (1953) found that HfN would also result if the temperature was raised to 2000°. The reaction rate has been studied by Edwards and Malloy (1958).

Preparation by vapor-phase deposition has been described by Moers (1931^a) and Campbell and co-workers (1949).

Phase Relationship

Very little information has been published about this system. According to Rudy and Benesovsky (1961), α-Hf dissolves nitrogen to give $HfN_{0.41}$ at 1700°. The fcc HfN phase extends from about $HfN_{0.74}$ to beyond $HfN_{1.0}$. Like TiN, HfN apparently can form a defect metal lattice so that the cubic phase is stable to at least $HfN_{1.13}$ (Wallace, 1962). However, observations of this phenomenon are still very sparse.

Rudy and Benesovsky (1961) also suggested a Hf_2N phase which as yet has not been verified.

Lattice Parameter and Structure

The lattice parameters at the phase boundaries are listed in Table II.1.2. The unknown purity of the samples with respect to oxygen makes the listed values open to question. It should be noted that the lattice parameter increases as nitrogen is removed from the HfN lattice. This same effect has been noted in the Zr-N system.

TABLE II.1.2

Lattice Parameter and Structure of Hf and HfN

Phases in Equilibrium	Composition of First Phase	Structure	Lattice Parameter, A	Investigator
α-Hf	pure	hcp	a = 3.187 c = 5.041	Fast (1953)
β-Hf	estimated	bcc	a = 3.50	Duwez (1951)
α-Hf + HfN	$HfN_{0.41}$	hcp	a = 3.2215(a) c = 5.157	Rudy and Benesovsky (1961)
HfN + α-Hf	$HfN_{0.74}$	fcc	a = 4.524(a)	Rudy and Benesovsky (1961)
HfN + N_2	$HfN_{1.0}$	fcc	a = 4.518(a)	Rudy and Benesovsky (1961)

(a) Contains 2 wt % Zr

Chemical Stability

The chemical properties are assumed to be similar to those of ZrN.

Appearance

Like the other nitrides in this group, pure HfN has a yellow color. Deviation from this color is a good indication of oxygen or carbon contamination, or that the material is deficient in nitrogen. Compositions beyond the 1:1 ratio have been reported to be olive-drab.

Hardness

Samsonov and Verkhoglyadova (1962) give 1640 ± 161 kg/mm^2 as the hardness of $HfN_{0.86}$. No other values could be found in the literature.

Electrical Resistivity

A value of 33 ± 5 μohm-cm for $HfN_{0.86}$ has been reported by Samsonov and Verkhoglyadova (1962).

Superconductivity

Recent work by Szklarz and Giorgi (1962) has shown that Zr-free $HfN_{1.0}$ has a transition temperature of 6.2°K.

Thermodynamic Properties

A heat of formation for $HfN_{1.03}$ of -88.24 ± 0.34 kcal/mole has been given by Humphrey (1953).

Neel and co-workers (1960) have measured the high temperature heat content up to 2500°C, as shown in Figure II.1.8. The material contained 3.4 wt % Zr. S°_{298} has been estimated by Kelley and King (1960) to be 10.9 ± 0.3 e.u.

Vaporization

Preliminary measurements of N_2 pressures over HfN between $HfN_{0.82}$ and $HfN_{1.0}$ have been reported by Kibler and Lyon (1962).

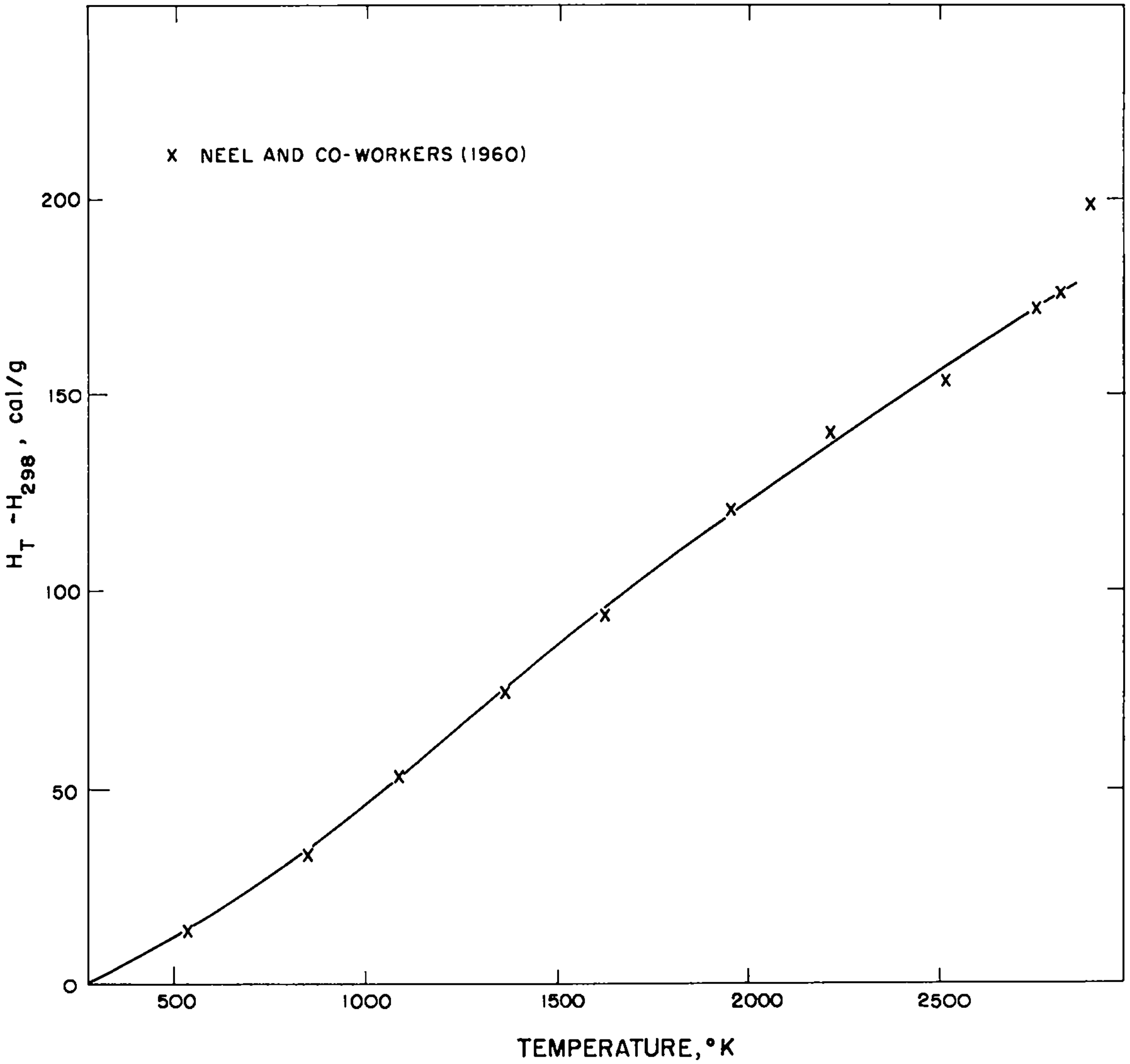

Figure II. 1. 8 Heat Content of HfN as a Function of Temperature

Chapter II. 2

The Group-5a Nitrides

The nitride systems in this group are somewhat more complex than the corresponding carbide systems. These elements all form a hexagonal M_2N compound; however, at higher compositions this simple pattern breaks down. VN is fcc over a wide composition range while NbN exhibits a fcc structure at high temperatures and a hexagonal configuration, having a narrow composition range, at lower temperatures. Other crystal structures have been observed in this system, but, as yet, their relationship is poorly understood. TaN also has a hexagonal structure with a narrow range of composition, but no cubic form has been observed. It is not unreasonable to suggest that each MN compound exhibits an allotropic transition, but that the transition temperature for VN is too low for the hexagonal phase to be seen readily, and too high, in the case of TaN, for the cubic form to have been quenched in.

The melting temperature of these nitrides is in serious doubt because of the very rapid loss of nitrogen from even the metal-rich materials.

Characteristically, the cubic phases have a wide composition range over which the lattice parameter decreases as nitrogen is removed from the lattice. The VN phase, under certain conditions, can have a composition above the 1:1 ratio, and cubic NbN terminates at about $NbN_{1.05}$ under 40 atm pressure. A tetragonal modification of the cubic

NbN has been observed near $NbN_{0.75}$. The hexagonal MN phases are stable only very near $MN_{1.0}$, although NbN has been found to have a composition up to $NbN_{1.018}$.

The high superconductivity transition temperature of cubic NbN prompted many studies of this compound in the 1940's; at that time it had the highest known transition temperature, 16.2° K(onset). Cubic VN is also superconductive below 8.3° K(center). On the other hand, a superconducting state has not been observed in the hexagonal forms of NbN and TaN.

The preparation of these nitrides free of oxygen should not be difficult, provided pure N_2 is used and the metals have been outgassed in vacuum (10^{-6} torr) at 500° below the respective melting points for several hours. If the reaction is carried out in a tube furnace, it is essential to prevent diffusion of oxygen through the ceramic by using, for example, a double-walled tube with pure N_2 flowing between the walls.

II. 2. 1 The Vanadium-Vanadium Nitride System

Preparation

Impure VN has been prepared by heating V_2O_5 with carbon in flowing nitrogen (Friederich and Sittig, 1925; Dawihl and Rix, 1940) and by decomposing NH_4VO_3 in NH_3 at 1100° (Epel'baum and Breger, 1940[a,b]; Epel'baum and Ormont, 1947; Hahn, 1949). If pure material is desired, it is important to avoid both carbon and oxygen in the reactants. Contamination by carbon, however, can be removed by heating the powdered VN in H_2 at about 1100° (Shomate and Kelley, 1949). In fact, the carbide can be converted completely to the nitride by a mixture of N_2 and H_2 at 1200° (King, 1949).

More recent investigators have heated pure vanadium in N_2 or NH_3. Duwez and Odell (1950) heated the metal in N_2 at 1650°; Schnell (1960) found that a temperature of 1250° held for 24 hours was sufficient to produce $VN_{1.0}$. The kinetics of the nitration reaction have been studied by Gulbransen and Andrew (1950[b]).

Low nitrogen alloys have been prepared by arc melting techniques (Rostoker and Yamamoto, 1954).

Deposits of VN result when an object is heated in a mixture of VCl_4, N_2 and H_2 (Moers, 1931[a]; Campbell and co-workers, 1949; Pollard and Fowles, 1952).

Phase Relationship

Although a complete phase diagram has not been reported, it is now certain that two nitrides exist: a hexagonal V_2N and fcc VN.

Schnell (1960), using pure material, places the V_2N phase between $VN_{0.48}$ and $VN_{0.50}$ and the VN phase between $VN_{0.72}$ and $VN_{1.0}$, whereas Hahn (1949) gives $VN_{0.37}$-$VN_{0.43}$ and $VN_{0.71}$-$VN_{1.0}$ as the respective limits. The difference between these measurements can be attributed to the presumably high but variable oxygen content of the material studied by Hahn (1949). A comparison between the reported lattice parameters in Figure II. 2. 1 supports this view. The amount of oxygen in Schnell's material, although small, also was variable, increasing from 0.1% to 0.3% with decreasing nitrogen.

Compositions above $VN_{1.0}$ have been claimed when NH_4VO_3 is decomposed at low temperatures in $H_2 + N_2$ (Epel'baum and Ormont, 1947). Although this phenomenon has been observed under similar conditions in other nitride systems and is assumed to result from vacancies in the metal lattice, later papers have given no evidence to show that it is characteristic of this system.

The melting point of $VN_{1.0}$ is still in considerable doubt. Friederich and Sittig (1925) reported 2050° for very impure material, while Strasser (1956) lists 2360° without giving a source.

Lattice Parameter and Structure

The a_o values for VN obtained by Schnell (1960), Hahn (1949), and Epel'baum and Ormont (1947) are compared in Figure II. 2. 1. Oxygen contamination of Hahn's samples is highly suspect both because he worked under conditions that would lead to this and because his data are displaced toward higher vanadium content compared to the work of Schnell. This comment also applies to the work of Epel'baum and Ormont (1947) even though they report only 0.5 wt % oxygen. A curve has been drawn, based on Schnell's data, that can be represented by the equation:

$a_o = 0.261\ (N/V) + 3.878$, which gives 4.139 A for $VN_{1.0}$.

The lattice parameters of V_2N also change with composition. Phase boundary values are listed in Table II.2.1 along with parameters of the other phases in this system.

Schnell also observed the extra lines between $VN_{0.22}$ and $VN_{0.16}$ which were assigned previously to a tetragonal phase by Rostoker and Yamamoto (1954), but he assumed that these were due to oxygen.

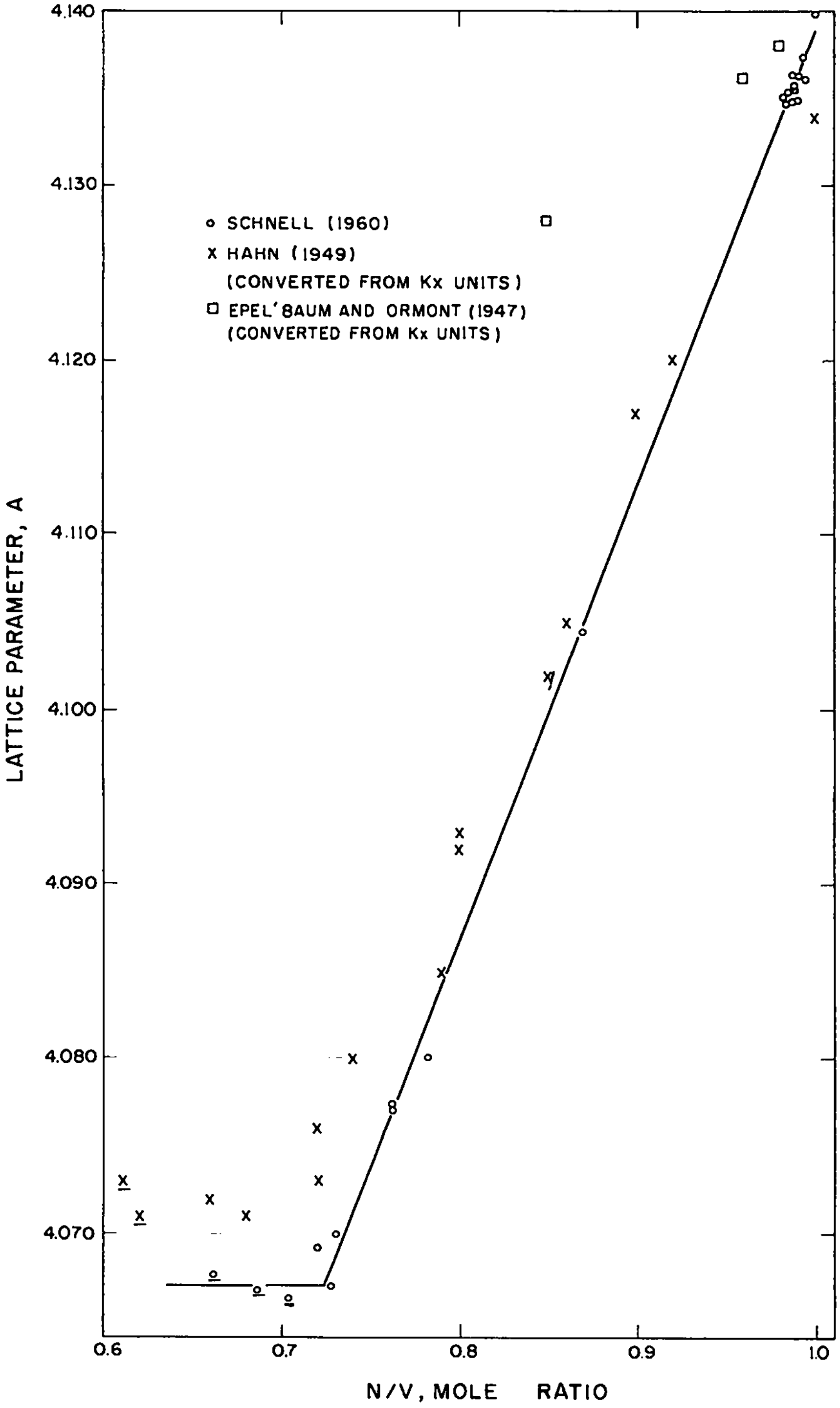

Figure II. 2. 1 Lattice Parameter of the VN Phase as a Function of Composition

TABLE II.2.1

Lattice Parameter and Structure of V, V_2N and VN

Phases in Equilibrium	Composition of First Phase	Structure	Lattice Parameter, A	Investigator
V	pure	bcc	a = 3.0240 ± 0.0003	James and Straumanis (1961)
$V + V_2N$	$VN_{<<0.15}$	bcc	a = 3.0344	Schnell (1960)
$V_2N + V$	$VN_{0.48}$	hcp	a = 2.823 c = 4.545	Schnell (1960)
$V_2N + VN$	$VN_{0.50}$	hcp	a = 2.839 c = 4.560	Schnell (1960)
$VN + V_2N$	$VN_{0.72}$	fcc	a = 4.066	Schnell (1960)
VN + N	$VN_{1.0}$	fcc	a = 4.139	Schnell (1960)

Chemical Stability

VN is insoluble in HCl and dilute H_2SO_4, but will dissolve in HNO_3. However, the nitride will gradually dissolve in boiling concentrated H_2SO_4, with the liberation of N_2. Strong alkalies will dissolve VN with the liberation of NH_3.

Appearance

Pure $VN_{1.0}$ has a dark bronze-yellow cast which becomes metallic gray as the nitrogen content is reduced.

Hardness

Hardness values of 1900 ± 102 kg/mm^2 (50 g load) and 1520 ± 115 kg/mm^2 have been reported for $VN_{0.338}$ and $VN_{0.74}$, respectively (Samsonov and Verkhoglyadova, 1961[a]).

Electrical Resistivity

The following room temperature resistivity values have been reported for VN: 200 μohm-cm (Friederich and Sittig, 1925); 85.9 μohm-cm (Moers, 1931[b]); 85.0 μohm-cm (L'vov and co-workers, 1960); and 123 ± 10 μohm-cm and 85 ± 4 μohm-cm for $VN_{0.338}$ and $VN_{0.93}$, respectively (Samsonov and Verkhoglyadova, 1962).

Superconductivity

The early resistivity measurements of Meissner and Franz (1930) have been confirmed by Hardy and Hulm (1954) with a transition temperature of 8.3°K. They also demonstrated that dissolved oxygen lowers the transition temperature. Since none of their samples were oxygen free or of the 1:1 composition, the reported transition temperature is a lower limit. A composition of $VN_{0.4}$ was not superconducting down to 1.2°K.

Thermodynamic Properties

Measurement of the high temperature heat content of $VN_{1.0}$ has led to the following equation (King, 1949):

$$H_T - H_{298.16} = 10.94T + 1.05 \times 10^{-3}T^2 + 2.21 \times 10^5 T^{-1} - 4096$$
(400 - 600°K, ± 0.3%) cal/mole.

Shomate and Kelley (1949) have obtained 8.91 ± 0.04 e.u. for S°_{298} and 9.080 cal/mole-deg for C_p (298.16) from low temperature heat capacity measurements. The heat of formation has been measured by combustion calorimetry (Mah, 1963). A value of -51.88 ± 0.20 kcal/mole was obtained for $VN_{1.0}$ (determined from V analysis only).

Vaporization

Schnell (1960) has measured the nitrogen pressure over $V_2N + VN$ between 1573-1873°K. His data can be best represented by the equation:

$$\log P_{N_2} \text{ (atm)} = -2.916 \times 10^3/T + 0.521.$$

The pressure over $VN_{0.44}$ (V_2N only) is about 100 times lower. Because the composition of the solid phases will change with temperature in an unknown manner, this equation cannot be used to calculate an unambiguous enthalpy value.

II. 2. 2 The Niobium-Niobium Nitride System

Preparation

Except for some early work in which Nb_2O_5 was used as the starting material (Friederich and Sittig, 1925), most preparations have resulted from the reaction between Nb and N_2. Various conditions have been used, but a temperature near 1300° and 1 atm of N_2 seems to be best. At lower temperatures the heating time becomes excessively long; at higher temperatures the equilibrium pressure becomes inconveniently high. Below 850° the stable nitride film essentially prevents further nitriding (Gulbransen and Andrew, 1950[a]). Between 1250° and 1300° after 30-50 hours, with intermediate grindings, the highest nitrogen content (ϵ-$NbN_{1.01}$) was obtained. At 1400° and 1 atm of N_2, δ-$NbN_{0.92}$ was the equilibrium composition. These observations and further details can be found in the paper by Brauer and Esselborn (1961[b]). Between the composition extremes, samples can be prepared by adjusting the temperature followed by a sinter in argon. Unfortunately, little is known concerning the pressures necessary to produce various compositions near NbN, although equilibrium pressures over the metal phase have been reported (Cost and Wert, 1962; Albrecht and Goode, 1959; Pemsler, 1961). Nb_2N is the first compound to form (Cost and Wert, 1962).

Although NbH and NH_3 have also been used as starting materials, little detailed information is available. Verkhoglyadova and co-workers (1961) observed that the formation of NbN is delayed in the presence of hydrogen. On the other hand, Brauer and Esselborn (1961[b]) found the reaction of N_2 with NbH to be faster than with Nb, possibly, as they suggest, because the NbH was more finely divided.

Phase Relationship

The Nb-N system is still not well known in spite of several extensive papers on the subject. Therefore, the following analysis will attempt to state the basic and generally confirmed relationships, and pose some questions that may be best answered by future work.

Nb metal dissolves only a trace of nitrogen at low temperatures, but as the temperature increases, the solubility becomes much greater. At 2400°, where the nitrogen-saturated metal is said to melt, Elliott and Komjathy (1961) gave 2.5 wt % ($NbN_{0.17}$) as the terminal solubility. Studies between 1100° and 2000°, by Cost and Wert (1962), have led to a terminal solubility which can be represented by the equation:

$$\log N_2(\text{at. }\%) = -4.464 \times 10^3/T + 2.995.$$

This equation gives 3.8 wt % ($NbN_{0.26}$) at 2400°, but below 1100° the observed solubility becomes progressively higher than that predicted by the equation. At 300° Cost and Wert (1962) found 0.006 wt % N_2 ($NbN_{0.0004}$). Their measurements are in quantitative agreement with those of Ang and Wert (1953), Albrecht and Goode (1959), and Elliott and Komjathy (1961).

Single-phase Nb_2N (hexagonal) has been found between $NbN_{0.40}$ and $NbN_{0.50}$ (Brauer and Esselborn, 1961^b). The temperature to which this range should apply and the manner by which the phase limits change with temperature were not reported.

Five phases have been reported in the vicinity of NbN (Table II. 2. 2). Of these, only the tetragonal γ phase, the cubic δ phase, and the hexagonal ϵ phase are stable and will be considered part of the system. A metastable δ' phase has been observed by several investigators, but apparently it occurs only during preparation or when the δ phase converts to the ϵ phase. Schönberg (1954^c) described a hexagonal (WC-type) phase occurring between $NbN_{0.8-0.9}$, but efforts by Brauer and Esselborn (1961^b) to confirm this were unsuccessful. It was presumed that this phase was due to oxygen contamination.

The δ phase is stable only above 1370°, but it can be easily retained upon cooling. Brauer and Esselborn (1961^b) place the phase limits between $NbN_{0.88-0.98}$ for their particular cooling rate (unknown).

TABLE II.2.2

Lattice Parameter and Structure of the Niobium Nitrides

Phases in Equilibrium	Composition of First Phase	Structure	Lattice Parameter, A	Investigator
Nb	pure	bcc	a = 3.3000 ± 0.0003	Seybolt (1954)
Nb + Nb_2N	?	bcc	a = 3.303	Brauer and Jander (1952)
Nb_2N + Nb	$NbN_{\sim 0.40}$	hcp	a = 3.056 c = 4.957	Brauer and Jander (1952)
Nb_2N + γ-NbN	$NbN_{0.50}$	hcp	a = 3.056 c = 4.995	Brauer and Jander (1952)
γ-NbN + Nb_2N	$NbN_{0.75}$	tetragonal deformed NaCl type	a = 4.385 c = 4.310	Brauer and Esselborn (1961[b])
γ-NbN + δ-NbN	$NbN_{0.79}$	tetragonal	a = 4.386 c = 4.335	Brauer and Esselborn (1961[b])
δ-NbN + γ-NbN	$NbN_{0.88}$	fcc	a = 4.381	Brauer and Esselborn (1961[b])
δ-NbN + N_2	$NbN_{0.98}$	fcc	a = 4.392	Brauer and Esselborn (1961[b])
ϵ-NbN + N_2	$NbN_{1.00}$	hexagonal, 10% $P\bar{6}c2$ 90% $P6_3/mmc$	a = 2.9591 ± 0.0002 c = 11.2714 ± 0.0006	Brauer and Esselborn (1961[b])
δ'-NbN	$NbN_{\sim 0.95}$	hcp, anti NiAs	a = 2.968 c = 5.549	Brauer and Esselborn (1961[b])
	$NbN_{0.80}$	hexagonal, WC type	a = 2.950 c = 2.772	Schönberg (1954[c])
	$NbN_{0.90}$	hexagonal, WC type	a = 2.958 c = 2.779	Schönberg (1954[c])

By heating under 40 atm N_2 and at 1460°, a composition as high as $NbN_{1.05}$ has been observed (Brauer and co-workers, 1953). At lower temperatures, the ϵ phase is the stable form. This phase has a very narrow homogeneity range close to $NbC_{1.0}$ that apparently extends up to $NbN_{1.018}$ (Brauer and Esselborn, 1961^b). The role of the tetragonal γ phase is somewhat in doubt. Brauer and Esselborn (1961^b) found it to be single phase between $NbN_{0.75-0.79}$ and to occur with the δ or ϵ phases at higher compositions. Elliott and Komjathy (1961), by metallographic examination, demonstrated that the γ phase precipitates within the δ phase upon cooling. This was also observed by Rögener (1952). Furthermore, after the sample had been annealed at 1200°, producing a total conversion to the ϵ phase, the γ phase had disappeared. Since both the γ and δ phase have a superconducting state (the more nitrogen-deficient γ phase has the lower transition temperature) and have almost the same lattice parameter, it is probable that these are not independent phases. For example, it has not been shown that the slight tetragonal distortion is not due to an increased solubility of oxygen as the structure becomes more deficient in nitrogen. Attempts to resolve this problem are further complicated because none of the studies using x-ray analysis have shown that quench from the heating temperature was successful.

Melting of the Nb_2N phase has been observed at 2400° (Elliott and Komjathy, 1961), somewhat below the melting point of the metal--2468° (Schonfield, 1956-57; Pemsler, 1961), and NbN is said to melt at 2050° (Friederich and Sittig, 1925).

Lattice Parameters and Structure

A summary of the lattice parameters and structures found in this system is given in Table II. 2. 2. The phase designations assigned by Brauer and Esselborn (1961^b) have been followed. Only the most recent or most reliable values are listed and are self explanatory, but in a few cases additional comment is necessary.

Lattice parameters for the ϵ phase have been reported on two previous occasions to be a = 2.956, c = 11.275 A(Brauer and Jander, 1952) and a = 2.9513, c = 11.248 A(Schönberg, 1954[c]). Schönberg (1954[c]) assigned a $P6_3/mmc$ structure to this compound, but Brauer and Esselborn (1961[b]) found a better fit between observed and calculated intensities if a slight distortion to this structure was assumed. Thus, they proposed that 90% of the lattice is arranged in the $P6_3/mmc$ configuration and the rest can be described as P6c2.

The δ' phase is said to be metastable. Earlier measurements of lattice parameters have resulted in a = 2.94, c = 5.46 A(Brauer and Jander, 1952), a = 2.968, c = 5.535 A(Schönberg, 1954[c]), and a = 3.017, c = 5.580 A(Umanskii, 1940).

The lattice parameters of both the δ phase and the β phase have been given as a function of composition (Brauer and Esselborn; 1961[b]).

Chemical Stability

Both Nb_2N and cubic NbN are insoluble in HCl, HNO_3, and H_2SO_4 (Friederich and Sittig, 1925; Brauer and Jander, 1952). NbN dissolves in strong alkalis, evolving NH_3, but the Nb_2N, under similar conditions, evolves N_2 (Schwarzkopf and Kieffer, 1953).

Appearance

Like the other nitrides, cubic NbN has a yellow cast which becomes gray at lower nitrogen contents. ϵ-NbN is almost black.

Hardness

Samsonov and Verkhoglyadova (1961[a]) have given a hardness of 1720 ± 100 kg/mm^2 for $NbN_{0.46}$ and 1396 ± 26 kg/mm^2 for $NbN_{0.96}$ (hex), both measured with a 50 g load.

Electrical Resistivity

A resistivity of 200 μohm-cm has been reported by Friederich and

Sittig (1925) for $NbN_{0.98}$; and L'vov and co-workers (1960) found 60 μohm-cm for an unspecified composition. From the work of Rögener (1952) it is clear that the resistivity is a function of both nitrogen and oxygen content. A value of 40 μohm-cm can be proposed for $NbN_{0.60}$, while within the cubic phase region the resistivity can be considered constant at about 80 μohm-cm. Oxygen contamination can raise this value to above 200 μohm-cm. Samsonov and Verkhoglyadova (1962) list 142 ± 6 μohm-cm, 85 ± 2 μohm-cm, and 78 ± 4 μohm-cm for $NbN_{0.5}$, $NbN_{0.96}$, and $NbN_{1.0}$, respectively.

Superconductivity

Discovery of a rather high transition temperature for NbN has prompted many studies of this property. Although general trends have been indicated, most measurements have shown broad transition regions and scattered transition values. This is not surprising because both the presence of oxygen and the absence of nitrogen lower the transition. The presence of metal atom vacancies, a phenomenon which is common in the nitride systems, might also play a part. Unless the material is heated for a sufficient time under the equilibrium pressure of oxygen-free N_2 there can be no guarantee of composition uniformity, an essential condition for accurate measurements.

In addition, the measurements have not been reported in a consistent way. Sometimes the temperature at the first indication of superconductivity is given (onset); in other cases, the center of the transition range is reported (center). Recently still another method is used--the linear portion of the transition curve is extrapolated in order to intersect an extension of the normal state base line, and this temperature is reported (extrapolated). These temperatures should be essentially the same for a pure, uniform sample; but, for many actual materials, they are several degrees apart. Lack of information often prevents a correction to a common basis; and, even if this were done, the additional values might lead to confusion. For these reasons only the reported temperatures are quoted with the basis indicated.

A transition temperature for δ-NbN near 16°K, found first by Aschermann and co-workers (1941), has been supported by later work. Horn and Ziegler (1947) found 15.25°K (onset) for $\delta\text{-NbN}_{0.90}$, which at that time was the highest transition observed for any material. Cook and co-workers (1950), by going to a higher nitrogen content ($\delta\text{-NbN}_{0.97}$), increased the temperature to 16.2°K (onset). Two years later, Rögener (1952) verified that this property is a function of composition, although he obtained his highest T_c (15.98°K, center) for $\delta\text{-NbN}_{0.87}$. The tetragonal phase was also found to be superconducting, but at a lower temperature. Hardy and Hulm (1954) confirmed this and, in addition, reported that Nb_2N was normal above 1.2°K. The hexagonal ε-NbN is normal above 1.94°K, (Schröder, 1957). Other studies have supported these results (Sellmeier, 1955; Lautz and Schröder, 1956).

Thermodynamic Properties

Values for $\Delta H^\circ_{298.16}$ have been obtained from combustion calorimetry by Mah. For $NbN_{1.0}$ (presumably the hexagonal form) a heat of formation of -56.8 ± 0.4 kcal/mole was reported (Mah and Gellert, 1956), while a rather impure Nb_2N (7.67 mole % Nb_2O) gave -61.1 ± 1.0 kcal/mole (Mah, 1958). This latter value can be compared to -67 ± 2 kcal/mole obtained from gas pressure measurements by Cost and Wert (1962).

A rather limited and rough measurement of high temperature heat content has been made by Sato and Sogabe (1941), resulting in the following equation:

$$H_T - H_{298} = 8.69T + 2.70 \times 10^{-3}T^2 - 2831$$

$$(298\text{-}600°K, \pm 5\%) \text{ cal/mole.}$$

Kelley and King (1961) have estimated $S^\circ_{298.15}$ of NbN to equal 9.0 ± 0.5 e.u.

Vaporization

The very limited pressure studies by Brauer and Esselborn (1961[b]) can be summarized as follows: the decomposition pressure at 1400° and at the upper phase limit of the δ phase ($NbN_{0.98}$) is considerably above 1 atm. With decreasing nitrogen content, the pressure first drops steeply then more slowly until it equals about 200 torr at the lower phase boundary ($NbN_{0.88}$). They also observed a nitrogen loss when the ε phase decomposes into the δ phase.

II. 2. 3 The Tantalum-Tantalum Nitride System

Preparation

The preparation of TaN is similar to that of NbN and most of the comments made in the previous section are applicable here. Most investigators have prepared the nitrides by heating the metal in purified nitrogen, although Schönberg (1954[a]) suggests that the use of ammonia is better because it is easier to purify. Several extensive studies have appeared concerning the conditions under which compositions up to Ta_2N will form (Albrecht et al., 1961; Gulbransen and Andrew, 1950[a]; Pemsler, 1961; Andrews, 1932), but equilibrium conditions in the region of TaN are not known with certainty. However, at 1 atm pressure and about 1300°, compositions near TaN can be obtained after several hours if powdered, outgassed Ta is heated in flowing nitrogen. Past experience has clearly demonstrated that if an oxygen-free nitride is to be obtained, the oxygen content of the gas and the metal must be reduced to a very low level. At a temperature at least as high as 850°, reaction with oxygen is much faster than the reaction with nitrogen (Albrecht et al., 1961).

Phase Relationship

The two compounds found in this system, Ta_2N and TaN, are both hexagonal. Several additional crystal structures have been reported, but these are unconfirmed. In particular, Schönberg (1954[a]) reported seeing evidence for a simple hexagonal structure in the region between $TaN_{0.80}$ and $TaN_{0.90}$.

The solubility of N_2 in the metal is slight at low temperatures but rapidly increases and reaches about $TaN_{0.24}$ at the melting temperature (Gebhardt and co-workers, 1961; Pemsler, 1961). However, it is not possible to quench in compositions higher than $TaN_{0.05}$ by cooling in vacuum. At very low nitrogen contents there is apparently an ordering phenomenon which has been reported by Schönberg (1954[a]) and Seraphim and co-workers (1962). The latter authors propose that the nitrogen atoms occupy the tetrahedral rather than the usual octahedral sites.

The homogeneity region of Ta_2N also broadens with increase in temperature. According to Gebhardt and co-workers (1961), the lower phase boundary goes from $TaN_{0.36}$ at 1000° to $TaN_{0.30}$ at 2000°, while the upper boundary, although it has not been studied as completely, is assumed to remain constant at $TaN_{0.50}$. This range is consistent with the results of Brauer and Zapp (1954). The melting point of this phase is unknown.

The hexagonal form of TaN has been reported to lie between $TaN_{0.98}$ and $TaN_{1.00}$ (Brauer and Zapp, 1954). If this system is similar to the Nb-N system, this phase should convert to a cubic form before melting; but no evidence for this has been reported. However, a cubic structure has been found in material heated at high pressures (~45 kilobars) and ~1400°C; and from the variation in lattice parameter it can be assumed that a homogeneity range exists (Giardini and Kohn, 1962). Melting temperatures of 2890° (Friederich and Sittig, 1925) and 3090° (Agte and Moers, 1931) have been observed. Because of the rapid evolution of nitrogen at these temperatures, it is very likely that these melting points represent the melting point of the nitrogen-free metal.

Lattice Parameter and Structure

Dissolution of N_2 in Ta causes the lattice parameter to increase almost linearly with a slope of 0.0053 A/at. % N_2 (Gebhardt and co-workers, 1958).

The hexagonal structure now known to be due to Ta_2N was assigned to TaN by an early investigator (van Arkel, 1924). However, later workers found that TaN is also hexagonal in its own right (D_{6h}^{1}-P6/mmm) (Brauer and Zapp, 1953, 1954; Schönberg, 1954^{a}), although the structure does not appear to correspond to its counterpart in the NbN system (ϵ-NbN).

Meager evidence for an additional phase (δ phase) between $TaN_{0.80}$ and $TaN_{0.90}$, given by Schönberg (1954[a]), has never been confirmed, and the briefly stated experimental methods do not allow an explanation to be given.

The observed phases are summarized in Table II.2.3, with the most probable lattice parameters.

Chemical Stability

In the absence of measurements, it can be assumed that the chemical behavior of this system is similar to the niobium nitrogen system.

Appearance

Hexagonal TaN is reported to have a blue-gray cast. This is similar to the color exhibited by the hexagonal form of NbN. The cubic form, found by Giardini and Kohn (1962), has a yellow color similar to the other cubic nitrides.

Hardness

According to Samsonov and Verkhoglyadova (1961[a]), the Ta_2N phase in $TaN_{0.58}$ has a hardness of 1220 ± 120 kg/mm^2, and $TaN_{1.01}$ gave a value of 1060 ± 72 kg/mm^2, both measured with a 50 g load. In a previous paper, Samsonov (1952) listed 3236 kg/mm^2 as the hardness of TaN. Gebhardt and co-workers (1961) found the Ta_2N phase in $TaN_{0.31}$ to have a hardness of 1820 kg/mm^2 (300 g, Vickers).

Electrical Resistivity

An early value of 135 μohm-cm was reported for TaN of dubious quality by Moers (1931[b]). Samsonov (1956) reported a value of 1650 μohm-cm. But in a later paper (Kolomoets et al., 1958), this same number is given as the temperature coefficient (μohm-cm/deg). More recently,

TABLE II. 2. 3

Lattice Parameter and Structure of Ta, Ta_2N and TaN

Phases in Equilibrium	Composition of First Phase	Structure	Lattice Parameter, A	Investigator
Ta	pure	bcc	a = 3.296	Fansteel Metallurgical Corporation (1956)
Ta + Ta_2N	$TaN_{0.047}$	bcc	a = 3.323	Gebhardt and co-workers (1958)
Ta_2N + Ta	$TaN_{0.41}$	hcp	a = 3.048 c = 4.915	Brauer and Zapp (1954)
Ta_2N + TaN	$TaN_{0.50}$	hcp	a = 3.042 c = 4.923	Brauer and Zapp (1954)
TaN + Ta_2N	$TaN_{>0.98}$	hexagonal (D_{6h}^{1}-P6/mmm)	a = 5.192 c = 2.911	Brauer and Zapp (1954)
TaN + N_2	$TaN_{1.00}$	hexagonal	a = 5.1913 c = 2.9108	Brauer and Zapp (1954)
δ-TaN	$TaN_{\sim0.80-\sim0.90}$	hexagonal (D_{3h}^{1}-P$\bar{6}$m2)	a = 2.925 - 2.938 c = 2.876 - 2.883	Schönberg (1954[a])
β-TaN	?	fcc	a = 4.315 - 4.375	Giardini and Kohn (1962)

Samsonov and Verkhoglyadova (1962) list 263 ± 22 μohm-cm for $TaN_{0.45}$ and 128 ± 15 μohm for $TaN_{1.01}$.

Superconductivity

Neither Hardy and Hulm (1954) nor Horn and Ziegler (1947) were able to detect superconductive behavior above 1.2° and 1.88°K, respectively. Apparently the hexagonal forms of TaN and NbN are similar in this respect. It would be very interesting to examine the cubic form of TaN.

Ta_2N is not superconducting down to 1.2°K (Hardy and Hulm, 1954).

Thermodynamic Properties

Mah and Gellert (1956) have measured the heat of formation of TaN by combustion calorimetry. A sample containing 3.55%TaO (assumed from summation only) gave -60.0 ± 0.6 kcal/mole* for $\Delta H^\circ_{298.15}$. This can be compared to an earlier value of -53.0 kcal/mole* (Neumann and co-workers, 1934) based on material of unknown purity.

Impure Ta_2N (3.31 mole % Ta_2O_5 + 5.34 mole % Ta, assumed from summation) was burned by Mah (1958) from which a tentative value of -64.7 ± 3.0 kcal/mole* was given for $\Delta H^\circ_{298.15}$.

The following equation was given by Sato (1939) to represent the high temperature heat content of TaN (cal/mole):

$$H_T - H_{298.16} = 7.73T + 3.90 \times 10^{-3}T^2 - 2652 \ (\pm 5\%,\ 298\text{-}800^\circ K).$$

Workers at the Southern Research Institute (1963) have measured the high temperature heat content of a very impure sample of Ta_2N ($TaN_{0.42}$). Their data, converted from Btu/lb-°F, are fit by the following equation:

$$H_T - H_{273} = 3.33T + 2.63 \times 10^{-3}T^2 - 7.23 \times 10^4/1.8T-459 + 2336$$

cal/deg-mole of $TaN_{0.42}$.

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*Calculated using Humphrey's (1954) value for the heat of formation of Ta_2O_5(-488.8 ± 0.5 kcal/mole).

Vaporization

At sufficiently high temperatures in vacuum, TaN will rapidly lose all of the combined nitrogen and revert to the metal. Andrews (1932) has noticed this to occur at 2100°K. Equilibrium pressures have been determined in the composition range below Ta_2N by Gebhardt and coworkers (1961), Pemsler (1961), and Kibler and Lyon (1962).

Chapter II. 3

The Group-6a Nitrides

The Group-6a nitrides are characterized by their great instability. In fact, they are not considered as refractories by some authorities. Nevertheless, the compounds are of theoretical interest and the elements, particularly tungsten, furnish useful construction materials which are inert to nitrogen at high temperatures.

These elements form compounds having the compositions M_2N and MN. In the Cr system, the first is hexagonal and the second is cubic, but the reverse is true for the Mo and W systems. In addition, tungsten forms WN_2 in the gas phase. In all cases, the solubility of nitrogen in the metal is slight.

These nitrides become progressively less stable as one goes from Cr to W. Indeed, tungsten is inert in N_2 up to its melting point, and the nitride can be prepared only at low temperatures in NH_3. This instability has led to a lack of interest in these compounds and, as a result, very little is known about their properties.

Because of the very limited data, the effect of oxygen on the properties has not been revealed. Therefore, until more information is available, most of the observations are open to some question.

II. 3. 1 The Chromium-Chromium Nitride System

Preparation

The direct reaction of the metal, either with N_2 or NH_3 at atmospheric pressure, has been used almost exclusively to prepare both nitrides. Verkhoglyadova and co-workers (1961) formed CrN by heating the metal powder in N_2 for 1-2 hours at 900°, and obtained Cr_2N by heating to 1200° for 1-4 hours followed by a rapid quench to avoid the precipitation of CrN. Using NH_3, Corliss and co-workers (1960) heated the metal at 1100°, with intermittent grindings, and obtained CrN containing a trace of Cr_2N. Caplan and Fraser (1955) also heated Cr in NH_3 between 950° and 1250°C to obtain CrN. The compositions of phases so prepared were not stated. Kiessling and Liu (1951) found that the nitrides would result if the chromium borides were heated in NH_3.

Phase Relationship

Chromium forms the two compounds Cr_2N and CrN. The first is hexagonal and the second is face-centered cubic, but very little else is known about these phases.

The solubility of nitrogen in the metal is slight at room temperature but increases rapidly as the temperature is increased. For example, Seybolt and Oriani (1956) give the terminal solubility as 0.028 wt % at 1000° and 0.26 wt % at 1400°. At the melting point of the metal under 1 atm of N_2, the solubility increases to roughly 4 wt % (Brick and Creevy, 1940; Adcock, 1926).

The hexagonal Cr_2N is said to exist between $CrN_{0.38}$ and $CrN_{0.50}$ (Eriksson, 1934). Very little has been reported about this compound, but the observation by Verkhoglyadova and co-workers (1961) that Cr_2N had to be cooled rapidly to prevent the precipitation of CrN suggests that either the compound or the high temperature composition is unstable at lower temperatures.

The homogeneity range of the cubic CrN is not known. However, one might assume, from the range of lattice parameters reported, that it is probably not a line compound.

No melting temperatures have been reported for this system.

Lattice Parameter

A lattice parameter for the CrN phase containing Cr_2N has been measured as low as 4.13 A (Corliss and co-workers, 1960), and Schönberg (1954[d]) reported a = 4.149 for $CrN_{1.0}$. Other reported values for materials of dubious purity fall within this range.

Parameters for the hexagonal Cr_2N phase have been reported to fall between a = 4.805 and 4.786, c = 4.480 and 4.463 A, depending on the temperature of preparation (Kiessling and Liu, 1951). These values apply to material prepared by heating chromium borides in ammonia. Eriksson (1934) gives a = 4.806-4.760 and c = 4.479-4.438 A as the range.

Chemical Stability

No information could be found.

Appearance

Both nitrides are said to be yellow. It is unusual that Cr_2N should be yellow because all other hexagonal nitrides in these groups are either gray or black.

Hardness

The hardness of $CrN_{0.99}$ and $CrN_{0.47}$ is 1083 ± 93 kg/mm^2 and 1571 ± 49 kg/mm^2, respectively, according to Samsonov and Verkhoglyadova (1961[a], 1962).

Electrical Resistivity

Samsonov and Verkhoglyadova (1962) list the electrical conductivity of $CrN_{0.497}$ and $CrN_{0.926}$ as 79 ± 5 μohm-cm and 640 ± 40 μohm-cm, respectively.

Superconductivity

Matthias and Hulm (1952) found CrN of unstated composition to exhibit no superconductivity down to 1.28° K.

Thermodynamic Properties

From combustion data, Mah (1960) found the heat of formation of Cr_2N to be -30.8 ± 1.1 kcal/mole, at 298.15° K.

The heat of formation of CrN was obtained by heating the metal in N_2 under pressure and measuring the heat produced by the reaction (Neumann and co-workers, 1931). This method gave -29.5 kcal/mole. Measurements of nitrogen pressure in the temperature interval 1100-1400° K have led to the following thermodynamic values (Sano, 1937):

	ΔH_{298}	ΔF_{298}	ΔS_{298}
Cr_2N	-20.6 kcal/mole	-17.3 kcal/mole	-11.2 e.u.
CrN	-24.3	-19.5	-16.0

Vaporization

The above study (Sano, 1937) gave the following formulas for the N_2 pressure over the indicated system:

$Cr_2N + Cr + N_2$ $\log P = -9558/T + 8.103$ (torr)

$CrN + Cr_2N + N_2$ $\log P = -12071/T + 10.65$

Valensi (1929) states that the N_2 pressure over Cr_2N at 1000° is about 400 torr.

II. 3. 2 The Molybdenum-Molybdenum Nitride System

Preparation

Because of the very slow rate at which Mo reacts with nitrogen, the molybdenum nitrides have been prepared almost exclusively from the reaction with NH_3. Although it is best to start with the pure metal, the metal oxide will also produce the nitrides when heated in ammonia (Uhrlaub, 1857; Matthias and Hulm, 1952).

In order to produce the mononitride from Mo and NH_3 at atmospheric pressure it is necessary to keep the reaction temperature below 725° and to heat for extended periods of time (Hägg, 1930). Compositions near MoN were produced after 5 days at 700° (Hägg, 1930). Slow cooling from 800° over a period of 4 weeks also resulted in $MoN_{\sim 1.0}$ (Schönberg, 1954[b]). The lower compositions can be prepared by heating for a proportionately shorter time or at a higher temperature. Verkhoglyadova and co-workers (1961) produced Mo_2N by heating 4 hours at 700°. Arkharov and co-workers (1960) found that a reaction is noticeable at 700° and follows a parabolic rate law up to 1150°. Above this temperature, neither nitride is formed. The paper by Hägg (1930) should be consulted for detailed information.

Phase Relationship and Lattice Parameter

Three compounds have been reported to occur in this system: a face-centered tetragonal structure (β) near $MoN_{0.39}$ which is stable only above 600°, a face-centered cubic phase (γ) with a narrow homogeneity range at Mo_2N, and a compound at $MoN_{1.0}$ with a simple hexagonal lattice (δ).

The solubility of nitrogen in Mo is quite small even at high temperatures (Norton and Marshall, 1944; Sieverts and Zapf, 1936).

The tetragonal β phase, first reported by Hägg (1930), was also observed by Schönberg (1954[b]). This phase is found only in samples which have been quenched from above 600°, in the region near $MoN_{0.39}$. Lattice constants of a = 4.188 and c = 4.024 A were measured by Hägg (1930). On the other hand, Sieverts and Zapf (1936) found only Mo and the β phase in a sample of $MoN_{0.44}$ after slow cooling from 820°. It is possible that this tetragonal distortion was due to dissolved oxygen acquired at the higher temperature.

Mo_2N is unusual in that it is cubic rather than hexagonal, a property it shares with W_2N. Although the homogeneity range is narrow at low temperatures, it widens as the temperature is increased. Troitskaya and Pinsker (1959), from electron diffraction studies of a thin nitride film on a crystal of sodium chloride, state that this compound can have a deficiency in the Mo lattice, depending on the conditions of formation. They have assigned lattice positions to the atoms and have given a lattice parameter of a = 4.165 A. On the other hand, Hägg (1930) concludes that the structure becomes deficient in nitrogen at high temperatures and finds lattice parameters of a = 4.136 and 4.185 A for the terminal compositions quenched from 1000°. At 600° the parameter at the Mo-Mo_2N boundary had increased to 4.163 A.

MoN apparently has a very narrow range at $MoN_{1.0}$, and is unstable above about 750°. Structurally, this compound is hexagonal, but the presence of a series of weak superlattice reflections, first seen by Hägg (1930), prompted Schönberg (1954^b) to make a more complete study. From powder patterns, he assigned a space group of D_{6h}^4 and lattice parameters of a = 5.725, c = 5.608 A. Troitskaya and Pinsker (1961), using the same methods which they applied to the γ phase, observed two hexagonal lattices, differing slightly in lattice parameter.

Because of the very poor thermal stability of these nitrides, melting points would be difficult to obtain and would be of little practical interest.

However, nitrogen at 1 atm pressure does lower the melting point of Mo from 2620° to 2450° or below (Ol'shanskiǐ, 1948).

Chemical Stability, Appearance, Hardness and Electrical Conductivity

No information could be found in the literature.

Superconductivity

Matthias and Hulm (1952), using materials prepared from the oxide, found hexagonal MoN to have a transition temperature of 12.0°K. Cubic Mo_2N became superconducting at 5.0°. According to a previous publication (Hulm and Matthias, 1951) these measurements were made on a sample containing all three phases, Mo, Mo_2N, and MoN.

Thermodynamic Properties

Heat of combustion measurements have led to a heat of formation for Mo_2N equal to -19.5 ± 0.3 kcal/mole at 298.1° (Mah, 1960).

Vaporization

Sieverts and Zapf (1936) measured a nitrogen pressure of 362 mm at 820° over $MoN_{0.44}$. From this they estimated an equilibrium pressure of 1 atm at 860°.

II. 3. 3 The Tungsten-Tungsten Nitride System

Preparation

Tungsten is inert towards nitrogen at all temperatures, and even NH_3 reacts very slowly. Hägg (1930) was able to obtain only $WN_{0.22}$ by heating the metal for 48 hours at 750° in 1 atm of NH_3. Kiessling and Liu(1951) obtained W_2N by heating at 825-875°; at 900° the material decomposed into W and N_2. Schönberg (1954^b) cooled W in NH_3 from 800° over a period of 4 weeks and found W_2N and WN ($WN_{0.72}$) in the product. The WN decomposed into W_2N and N_2 at 600°. This reaction has been studied in more detail by Mittasch and Frankenburger (1929).

The nitride will also result when the oxide is heated in NH_3 at 700° (Matthias and Hulm, 1952) and when ammonium tungstate is decomposed in NH_3 (Neugebauer and co-workers, 1959).

Phase Relationship and Lattice Parameter

The W-N system consists of a cubic W_2N, a hexagonal WN, and a WN_2 phase. Other phases have been reported, depending on the method of preparation, but these may not be typical of the system.

Tungsten absorbs essentially no nitrogen at atmospheric pressure. Norton and Marshall (private communication to S. Dushman, 1949) could find only 3.8×10^{-4} wt % N_2 at 2400° and less at lower temperatures.

The W_2N, first prepared by Hägg (1930), is isomorphous with the cubic Mo_2N phase. Hägg (1930) calculated a parameter of a = 4.126 A when W was present. This was confirmed by Kiessling and Liu (1951). These workers also found that W_2N converted to a simple cubic structure, a = 4.130, upon heating at 850° in flowing NH_3. This γ phase was later shown by Kiessling and Peterson (1954) to be an ordered defective structure containing both nitrogen and oxygen. Electron diffraction studies of a very thin film have revealed a cubic structure (NaCl-type) with a = 4.12-4.14 (Khitrova and Pinsker, 1959). Previously, Pinsker and Kaverin (1957) obtained a = 4.118 for W_2N from x-ray diffraction patterns.

WN is hexagonal and, according to Schönberg (1954^b), the lattice constants are a = 2.893 and c = 2.826A when W_2N is present. Electron diffraction studies by Khitrova and Pinsker (1961) of very thin films on rock salt have led to parameters of a = 2.89, c = 22.85 and a space group of $C\bar{3}$. Earlier (1958), these workers reported a = 2.89, c = 15.30 A and a space group of D_{6h}^4-$P6_3/mmc$ for a composition believed to be $WN_{0.87}$.

Langmuir (1913) observed that tungsten vapor, from a hot tungsten wire, would react with N_2 gas and form WN_2. The composition of this brown compound was later confirmed by Smithells and Rooksby (1927). Electron diffraction studies of a thin nitride film revealed a rhombohedral phase,. a = 2.89, c = 16.40 A, in the thinnest parts (Khitrova, 1962). A composition of W_3N_6 was assigned on the basis of the crystal structure and D_{3d}^5 was given as the space group. Khitrova and Pinsker (1962) have recently published a summary of their electron diffraction studies in the W-N system.

Chemical Stability, Appearance, Hardness and Electrical Resistivity

No information could be found in the literature.

Superconductivity

Matthias and Hulm (1952) found that W_2N (prepared from the oxide) was normal down to 1.28° K. In view of the superconducting behavior of Mo_2N, it would be of interest to measure W_2N, which is known to be oxygen free.

Thermodynamic Properties

Brewer and co-workers (Quill, 1950) list -17 kcal/mole as the heat of formation of W_2N.

Vaporization

No measurements of the equilibrium vapor pressures could be found in the literature.

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PART III

THORIUM, URANIUM AND PLUTONIUM CARBIDES AND NITRIDES

Chapter III. 1

The Th, U and Pu Carbides

The fcc MC and a MC_2 compound are both common to the Th, U and Pu carbide systems. In the U and Th systems the MC_2 structure converts to a cubic lattice which can form a continuous solid solution with the MC phase. PuC_2 apparently has but one crystal form and does not form a solid solution with PuC. Below ~1750° PuC_2 decomposes into Pu_2C_3 and C; UC_2 gives U_2C_3 and C below 1500°; and ThC_2 has not been observed to decompose above ~1000°. In addition, the M_2C_3 phase has not yet been found in this system. The melting point of the MC_2 phase increases in a regular way in going from PuC_2, reaching 2650° at ThC_2.

There are within this group several isolated differences which do not fit a general pattern. ThC_2 is the only compound to exhibit a color (pale yellow); only ThC has been found to show superconducting behavior. $PuC_{0.87}$ behaves as a semiconductor, whereas the other compounds are apparently metallic conductors.

In general, these carbides show a much more complicated phase relationship then do the other refractory carbides and, because of their high reactivity, are much harder to investigate. The U-C system has been studied extensively but is still not completely known. The other two systems are known only in their general aspects.

III. 1.1 The Thorium-Thorium Dicarbide System

Preparation

Most recent studies have used material prepared by either arc melting the unpowdered elements together or by heating the powdered elements at a temperature below the melting point. Because of the ease with which Th metal, especially the powder, reacts with oxygen and nitrogen, the arc-melting technique should be used if the highest purity is desired.

ThO_2 will react with C at 1800-1900° to give ThC or ThC_2 of uncertain purity (Samsonov et al., 1960). According to Scaife and Wylie (1958), 99% of the ThO_2 can be converted to the carbide after 30 minutes at 2130°C. This reaction also has been studied by Prescott and Hincke (1927).

Phase Relationships

Two compounds comprise this system: a fcc ThC phase, and ThC_2 which is monoclinic at low temperatures but which converts to a cubic form at high temperatures.

The solubility of C in Th has been measured on a number of occasions but there is little agreement (Peterson and Mickelson, 1954; Smith and Honeycombe, 1959; Peterson, 1961). This measurement is made difficult by the ease with which oxygen and nitrogen enter the lattice thereby changing the solubility of carbon. Thorium metal transforms from fcc to bcc near 1360° (Chiotti, 1954, 1955; McMasters and Larsen, 1961), and this temperature is raised by the addition of carbon (Chiotti, 1954, 1955). Recent work by Reid and co-workers (1963) places the transition at 1325 ± 10°C. The pure metal melts near 1725° (Chiotti, 1954; Thompson, 1933; McMasters and Larsen, 1961).

The fcc (NaCl-type) ThC phase can have a defect structure, the range of which increases with temperature (Wilhelm and Chiotti, 1950; Benesovsky and Rudy, 1961^b). However, as pointed out by Hansen and Anderko (1958), the structure should not extend to α-Th as was initially proposed. Rudy and co-workers (1962) placed the range between $ThC_{0.61}$ and $ThC_{1.0}$ at 1500°, but Henney and co-workers (1963^a) found single-phase ThC only between $ThC_{0.8}$ and $ThC_{1.0}$ at 1600°. The latter workers noted that the range was apparently widened by the presence of oxygen. At high temperatures ThC forms a solid solution with β-ThC_2, but, similar to the UC-UC_2 relationship, it breaks into a bell-shaped miscibility gap somewhere above 1500° (Brett, Law and Livey, 1960; Benesovsky and Rudy, 1961^b). $ThC_{1.0}$ apparently melts near 2625° (Wilhelm and Chiotti, 1950).

The low temperature form of ThC_2 is monoclinic (Hunt and Rundle, 1951). This compound is assumed to convert to the same high temperature form as does UC_2 (Brett, Law and Livey, 1960). Using thermal analysis techniques, Langer and co-workers (1962) observed thermal breaks at 1430° and 1480° when free carbon was present. Marchal and Accary (1963) found that electron beam melted ThC_2 (probably carbon deficient) showed a thermal expansion increase upon heating at ~1290° and contracted upon cooling at ~1240°. Hill and Cavin (1964) have shown that ThC_2 converts to a cubic phase at 1415 ± 10°. The presence of ThO_2 caused a large heat effect at 1470° to 1500°. The composition range of the monoclinic form is quite narrow but, as yet, the limits have not been established. ThC_2 apparently melts at $\leqq$2655° and forms a eutectic with carbon which melts at ~2500° (Wilhelm and Chiotti, 1950; Langer, 1963).

Although a number of phase diagrams have been drawn based on the initial work of Wilhelm and Chiotti (1950) (Rough and Bauer, 1958; Rough and Chubb, 1960; Hansen and Anderko, 1958; Langer, 1963), additional data are needed before a complete phase diagram can be constructed for this system.

It is surprising, in view of the similarity to the U-C and Pu-C systems, that a Th_2C_3 phase has not been seen. N. H. Krikorian (1963) attempted to form this phase by heating the indicated compositions in vacuum at the following temperatures and times: $ThC_{1.91}$, 1200° for 69 hr, 1000° for 168 hr, 750° for 168 hr; and $ThC_{0.99}$, 700° for 477 hr. These heatings resulted only in a sharpening of the diffraction pattern of the initial carbide.

Lattice Parameter

Because the lattice parameter of α-Th increases with dissolved carbon, nitrogen and oxygen, the value listed in Table III. 1. 1 is the lowest reported.

The lattice parameter of cubic ThC varies in an essentially linear manner between the extremes shown in Table III. 1. 1 (Henney and co-workers, 1963[a]). These terminal compositions, however, do not necessarily apply to the temperature from which they were cooled. X-ray powder patterns have been published by Kempter and Krikorian (1962).

The structure of α-ThC_2 has been established as monoclinic by the neutron diffraction studies of Hunt and Rundle (1951). Recent work by Kempter and Krikorian (1962) has shown that the structure also can be indexed as pseudo-orthorhombic. When this was done, they found that their parameters for pure, arc-melted $ThC_{2.0}$ differed significantly from the recalculated values of Hunt and Rundle (1951), but agreed reasonably well with those found by Baenziger (see Wilhelm and Chiotti, 1950). The pseudo-orthorhombic parameters of Kempter and Krikorian, (1962) are therefore listed in Table III. 1. 1. These workers also gave the powder pattern data for ThC_2 and transformation equations for the two indexings.

Appearance

Compositions below ThC_2 are metallic gray, whereas freshly broken surfaces of ThC_2 have a very pale metallic yellow color which darkens with time.

TABLE III. 1. 1

Structure and Lattice Parameter of Th, ThC and ThC_2

Phases in Equilibrium	Composition of First Phase	Structure	Cooled From	Lattice Parameter, A	Investigator
α-Th	pure	fcc	at 25°	a = 5.0842 ± 0.0002	Evans and Raynor (1959)
β-Th	pure	bcc	at 1450°	a = 4.11	Chiotti (1954)
α-Th + ThC	$ThC_{0.06}$	fcc	1500°	a = 5.12	Benesovsky and Rudy(1961[b])
ThC + Th	$ThC_{0.80}$	fcc	1600°	a = 5.305 ± 0.002	Henney and co-workers (1963[a])
ThC + ThC_2	$ThC_{0.99}$	fcc	melt	a = 5.346 ± 0.002	Kempter and Krikorian(1962)
α-ThC_2	$ThC_{2.0}$	monoclinic C2/c	2450°	a = 6.53 a = 4.24 c = 6.56 β = 104°	Hunt and Rundle (1951)
		pseudo-orthorhombic	melt	a = 10.555 b = 8.233 c = 4.201	Kempter and Krikorian (1962)
β-ThC_2		cubic	at 1500°	a = 5.808	Hill and Cavin (1964)

Chemical Stability

The metal and especially the carbides are so reactive to water vapor that they should be handled either in a nonreactive atmosphere or under a dry liquid. Both carbides can be dissolved by H_2O, 1:1 HCl, H_2SO_4, HNO_3, 25% tartaric acid, and 5% NaOH (Samsonov and co-workers, 1960). The reaction with water has been studied on a number of occasions, the most recent being a work by Kempter and Krikorian (1962).

ThC_2 forms only a thin coat of ThO_2 after 24 hr at 300° in pure O_2, while at 500° it is fully oxidized (Brett, Law and Livey, 1960). In moist air it reacts ten times faster than UC_2, being completely converted to the oxide after ~10 hours at 30°C. The carbon-deficient material is somewhat less reactive. Although there is no reaction with nitrogen at room temperature, there is a slight reaction in dry air (Engle, 1961).

Hardness

The only reported measurement of microhardness was made by Kempter and Krikorian (1962). $ThC_{0.99}$ gave 850 kg/mm^2 (200 g, DPH), and ThC_2 gave 600 kg/mm^2. Because of the uncertain chemical form of the analyzed oxygen, these compositions might be somewhat lower than indicated.

Electrical Resistivity

Using rods of the above composition, Kempter and Krikorian (1962) measured values at 25° of 25 μohm-cm and 30 μohm-cm for ThC and ThC_2, respectively. On the other hand, Chiotti (1950) observed that the resistance of ThC is about 5 times that of ThC_2.

Superconductivity

Hardy and Hulm (1954) could find no evidence for superconductivity above 1.2°K in a sample of ThC of unstated purity and composition. Recently, however, Costa and Lallement (1963) found that ThC became superconducting at 9 ± 1°K. ThC_2 apparently has not been measured.

Thermodynamic Properties

Huber and Holley (1962) measured the heat of formation of $ThC_{0.99}$ by combustion calorimetry and calculated a value of $\Delta H°_{298} = -7 \pm 6$ kcal/mole. The large uncertainty was believed due to the high percentage of unburned material found after combustion.

Using the values which Prescott and Hincke (1927) obtained from the ThO_2-CO-C system, combined with estimated free energy functions and a more recent value for the heat of formation of ThO_2, Krikorian (1955) estimated that $\Delta H_f^\circ(298) = -33 \pm 8$ kcal/mole for ThC_2. Egan (1964) using emf values from the cell Th, $ThF_4/CaF_2/$ ThF_4, ThC_2, C calculated $\Delta H_f = -37.1$ kcal/mole and $\Delta F_f = -29.4 \pm 0.3$ kcal/mole, both at 800°C.

On the basis of equilibria in the Th-W-C system, Rudy and co-workers (1962) gave a range of -32 to -23.3 kcal/mole for ΔF of ThC_2 at 1500°C. The thermodynamics of ThC_2 have been reviewed recently by Lofgren and Krikorian (1963).

Vaporization

Using a mass spectrometer, Jackson and co-workers (1962) found that between 2000° and 2422°K the pressure of $Th_{(g)}$ and $ThC_{2(g)}$ are of comparable magnitude above $ThC_{2(s)} + C_{(s)}$. The pressure of these species was described by the following equations:

$$ThC_{2(g)},\ \log P_{atm} = -39364\ (\pm 163)/T + 7.20\ (\pm 0.65)$$

$$Th_{(g)},\ \log P_{atm} = -36025\ (\pm 144)/T + 5.74\ (\pm 0.57)$$

Lonsdale and Graves (1962) studied this system,using target collection. In view of the above results, their calculated thorium pressures should be somewhat higher than the sum of the ThC_2 and Th pressures. By comparing the results of Jackson and co-workers (1962) with the equation obtained by Lonsdale and Graves (1962), $\log P_{atm} = -37600\ (\pm 1000)/T + 7.39\ (\pm 0.39)$, one finds that the latter workers obtained pressures which were consistently high by a factor of 4.4. Lofgren and Krikorian (1963) suggest that the temperature measurements of Lonsdale and Graves (1962) were too low because the hole in their target was too small to allow the light from the crucible to completely fill their pyrometer lens.

The pressure of Th over $ThC_2 + C$ has been studied by emission spectrometric techniques (Lofgren and Kirkorian, 1963). Although some difficulty was experienced in obtaining consistent data, a heat of formation value near -23 kcal/mole was reported.

pp 182-212 from
LA-2942, "A Critical Review of Refractories" by Erk and K. Storms

III. 1. 2 The Uranium-Uranium Dicarbide System

Introduction

An enormous amount of work has been directed, of late, to those properties of UC and UC_2 which are important to high temperature power reactor technology. Most of this work has been done under conditions dictated by economy rather than purity, and much of the emphasis has been placed on the engineering aspects of the problem. While such information is necessary and valuable, it adds little to a basic understanding of the pure U-C system, and, therefore, is beyond the scope of this discussion.

In spite of this great interest, the complete phase diagram is still not known. Although this is partly due to the complexity of the system, the main problem stems from the almost unavoidable presence of dissolved oxygen and nitrogen. These elements can seriously affect the properties of the carbides and, unless their presence is taken into account, there is little hope of consistency between independent measurements. It is therefore worthwhile to consider, first, the changes produced when carbon is replaced by nitrogen and oxygen.

A. Nitrogen:

Above 1200°, the lowest temperature reported, all or part of the carbon atoms in UC can be replaced by nitrogen. This substitution results in a contraction of the lattice (Austin and Gerds, 1958; Williams and Sambell, 1959). Indeed, if UC having a parameter of 4.9605 A, indicating integral stoichiometry, is used, the lattice parameter versus nitrogen content is almost linear. On the other hand, by starting with UC having a parameter of 4.9544, a variation is produced which is almost independent of nitrogen content at first, but then approaches the value for UN as the nitrogen content is increased (Williams and Sambell, 1959). Austin and Gerds (1958) noted that when UC_2 was present, the UC-UN solid solution assumed an equilibrium composition of about 35 mole % UN + 65 mole % UC at 1800°. They also found that nitrogen is essentially insoluble in UC_2 and U_2C_3. However, the presence of nitrogen does seem to inhibit the formation of U_2C_3 (Henney and co-workers, 1963). According to Rough and Chubb (1959), nitrogen reacts with the molten carbide to displace carbon from the monocarbide to produce some UC_2. Thus, if only the carbon content is considered, attempts to locate the high carbon UC phase boundary could result in an erroneously low composition. Such a contamination can result during arc-melting if N_2 is present in the gas (Brown, 1963). Chubb and Keller (1963) found that $UC_{1.0}$, after being melted in a partial pressure of 0.01 atm of N_2, contained 700 ppm nitrogen. The amount increased with nitrogen pressure and as the carbon content was reduced. Atoda and co-workers (1963) observed that the reaction with N_2 (1 atm) started at 600°, increased rapidly up to 1100°, and became almost constant between 1100° and 1250°. The nitrogen combined with the uranium, producing free carbon and U_2N_3 with a composition between $UN_{1.4-1.6}$, depending on the temperature.

B. Oxygen:

The solubility of oxygen in UC and the ease with which this solution can take place depend on a number of factors, the more important being the stoichiometry, the annealing temperature and the CO pressure. Even though there is no agreement in the literature as to the role each plays, a brief discussion will be attempted,based largely on the excellent work of Anselin and co-workers (1963). In order to simplify the presentation, the composition extremes of the UC phase will be handled separately beginning with hypostoichiometric UC.

Since UO_2 is insoluble in UC, the amount of dissolved oxygen in a particular sample will depend largely on the rate at which the UO_2 can be converted to the easily soluble but unstable UO. If free uranium is present, the reduction can take place above 1200° by the reaction $UO_2 + U = 2[UO]$.* Because no gas is evolved it makes no difference whether heating is carried out in vacuum or in argon. On the other hand, above 1600° in vacuum, the reaction $2UO_2 + UC = 3[UO] + CO$ can proceed with the removal of CO. Now the gaseous environment is important. When heating is done in argon there is a less efficient removal of CO, partly because the sample will sinter and partly because of the accumulation of CO in the gas. If the CO pressure is sufficiently high to stop or reverse this reaction, the UC phase will contain less dissolved oxygen than if the CO pressure were lower. Thus, it has been proposed that a lower CO pressure leads to an apparently higher solubility of oxygen (Sano and co-workers, 1963; Brett and co-workers, 1963). In the absence of UO_2 the reaction $U(C,O) = [U] + CO$ can lower the oxygen content if the CO pressure is sufficiently low. This reaction can produce free U or just a lower stoichiometry, depending on the conditions. The CO pressure over $U(C_{0.75}O_{0.25})$ has been measured by Stoops and Hamme (1964). The evaporation of UO can also reduce the oxygen content.

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* Brackets are used to indicate that the material is dissolved in the carbide phase.

When U_2C_3 or UC_2 are present with UO_2, the initial reaction in vacuum produces UC with the evolution of CO. After all of the higher carbide has been removed a reaction takes place between the UC and the remaining oxide (Harrison and co-workers, 1963). If the CO pressure is too high to allow these reactions, additional U_2C_3 might result above 1400° according to the reaction

$$3\ UC + UO_2 = 2\left[UO\right] + U_2C_3\ .$$

In the absence of UO_2, the carbide can self-purify through the loss of U_2C_3 if the CO pressure is not high.

Below 1400° the terminal composition of U(C, O), in equilibrium with UO_2 and U, lies near $UC_{0.65}O_{0.35}$ (Anselin and co-workers, 1963; Brett and co-workers, 1963; Accary, 1963). Values for this composition as low as $UC_{0.75}O_{0.25}$ (Stoops and Hamme, 1964) and as high as $UC_{0.2}O_{0.8}$ (Namba, Imoto and Sano, 1962; Sano and co-workers, 1963) have been reported. On the other hand, UC in equilibrium with U_2C_3 and UO_2 can dissolve only a little oxygen, no more than 5 at. % (Anselin and co-workers, 1963). UC_2 and U_2C_3 dissolve essentially no oxygen.

The effect of this impurity on the various properties is complicated by being dependent on the carbon content of the material as well as on the presence of vacancies. Although there is presently insufficient information to evaluate these variables, they should be kept in mind when interpreting experimental data. Dissolved oxygen causes the lattice parameter of UC to go through a maximum. Accary (1963) was first to report that the extrapolated parameter for pure UC rose from 4.9598 A to a maximum of 4.9613 A at 1800 ppm oxygen. Witteman (1963) noted an increase to 4.9625 A when small amounts of UO_2 were added to hyperstoichiometric UC. A similar maximum has been reported recently by Brett and co-workers (1963) (4.9625 A) and by Anselin and co-workers (1963). As the oxygen content is increased beyond the maximum, the lattice parameter decreases rapidly to a saturation value of 4.9519 ± 0.0001 A (Witteman, 1963; Stoops and Hamme, 1964). Values as high as 4.9568 A (Anselin and co-workers, 1963) and as low as 4.9490 A (Vaughn and co-workers, 1957) have been reported.

The formation of U_2C_3 is apparently inhibited by the presence of dissolved oxygen as well as nitrogen according to Henney and co-workers (1963^b). Although U_2C_3 is the stable phase in contact with graphite below ~1500°, it did not form when the nitrogen-oxygen concentration was in excess of ~100 ppm. Instead, the samples consisted of $UC_{1-x}N_x$ and α-UC_2 containing a small amount of oxygen. In their case, self-purification was claimed when annealing was done at 1300° for times up to 70 hr in a vacuum of 10^{-5} torr. On the other hand, both Anselin and co-workers (1963) and Brett and co-workers (1963) observed the presence of U_2C_3 in their material even though an oxide phase was present.

A study of these carbides is made even more difficult because they hydrolyze so easily. For this reason, it is difficult to know whether the oxygen content is dissolved in the carbide or has been acquired as a surface film during handling. For example, Keller and co-workers (1961) report that 25 micron UC powder is pyrophoric and that a slightly coarser powder, stored in argon for 2 months, increased in oxygen content from 790 ppm to 1200 ppm.

Preparation

A great deal of attention has been given to ways of preparing the carbides economically and in large quantities. These techniques are, in general, unsuitable for the preparation of small, pure research specimens, and will not be discussed in any detail except to acquaint the reader with their limitations.

Experience at Los Alamos and elsewhere has shown that the carbides of uranium can be prepared easily, and, under the proper conditions, to a high degree of purity by arc melting the elements together. If a graphite electrode is used, the melt tends to pick up additional carbon, and, for this reason, a tungsten electrode is sometimes preferred. Reports of contamination by W or by Cu from the water-cooled hearth usually give low values, unless the melt was allowed to overheat and sputter. A satisfactory procedure is as follows: The proper amount of uranium, as a freshly cleaned rod, and graphite, as spectroscopic rods, are placed in a shallow depression in the copper hearth. Air is evacuated, and the system is back-filled with purified helium or argon. The use of helium, although it produces a more unstable arc, allows a shorter melting time which results in less carbon pickup from the electrode. A zirconium button is melted to further purify the gas, after which the arc is transferred to the uranium rod. By playing the arc over the melt, the carbon can be dissolved quite easily. The button is then turned on edge several times and remelted. A current between 400 and 600 amps is sufficient to melt a charge of about 100 grams (Stone, 1962).

Uranium will react with hydrocarbon gases to produce UC at low temperatures and UC_2 when the temperature is raised. However, because carbon diffusion is slow through the initial carbide film, the metal is normally reduced to a fine powder by converting it to the hydride previous to carbiding. Methane will give mainly UC below

650°, and mainly UC_2 above 900° (Kalish, 1960). Propane and butane will react much more rapidly than methane, but the conditions are more critical to prevent the deposition of free carbon. For these gases, UC is the major product below 750°. UC can even be produced at 10° in propane, if the system is exposed to a gamma flux (Sano and co-workers, 1960). In general, this method has led to an impure product because of the difficulties in obtaining pure gases. Furthermore, the resulting fine powder is very reactive and must be handled with special care.

Economically, the reaction between the uranium oxides and carbon is very attractive. However, unless considerable time is invested in high vacuum purification or unless the product is arc melted, impure material is certain to result. There have been reports that the oxygen level can be reduced to a low level by heating in flowing argon, but experience by others (Stoops and Hamme, 1962) have shown that there are some difficulties connected with this procedure. Unless great pains are taken to remove all oxygen (free or combined) from the argon, the net removal of oxygen from the carbide may be quite small.

The preparation of UC from a liquid metal system has been studied by Johnson and co-workers (1963). A mixture of powdered uranium and charcoal in liquid Mg-Zn alloy at 800° gave UC as a precipitate after 2-5 hours. However, they found oxygen was a serious impurity in the final product.

Not only are the powdered uranium carbides pyrophoric in air, but even if left in an inert atmosphere for any length of time, they will acquire what little oxygen is present in the gas. It is advisable, therefore, to store the material as large pieces and, if necessary, make a powder immediately before use.

Phase Relationships

The three compounds, UC, U_2C_3 and UC_2, make up the U-C system. Fcc UC is stable from room temperature to its melting temperature; bcc U_2C_3 decomposes at about 1800° without melting; and UC_2 is stable from about 1500° to its melting point. UC_2 converts from a tetragonal (α) to a cubic (β) lattice at about 1785°. These are the major, well-known features of the diagram. Many of the details are still in doubt. A tentative equilibrium phase diagram is shown in Figure III. 1. 1. The positions of many of the phase boundaries are in doubt and are therefore represented as dashed lines. Insufficient information has been reported to allow the region near UC_2 to be defined. Rather than add to the already considerable speculation, this area has been left blank.

Pure uranium has at least three crystal forms. The α-β transition occurs at 667 ± 1.3°, the β-γ transition takes place at 774.8 ± 1.6° (Blumenthal and co-workers, 1960), and the metal melts at 1132.3 ± 0.8° (Blumenthal and co-workers, 1960; Udy and Boulger, 1954). A low temperature phase change has been observed at 42°K (Fisher and McSkimin, 1961). The presence of carbon lowers the transition temperatures to eutectoids at 665.9° and 771.8°, respectively, and the melting point of the metal is lowered slightly to 1116.6° (Blumenthal, 1960). This author also reports that the solubility of carbon in solid uranium is no higher than 185 ppm even at the eutectic temperature.

The formation of UC causes the melting point to rise to 2560 ± 50° at $UC_{1.1}$ (Witteman and Bowman, 1963). Earlier measurements of

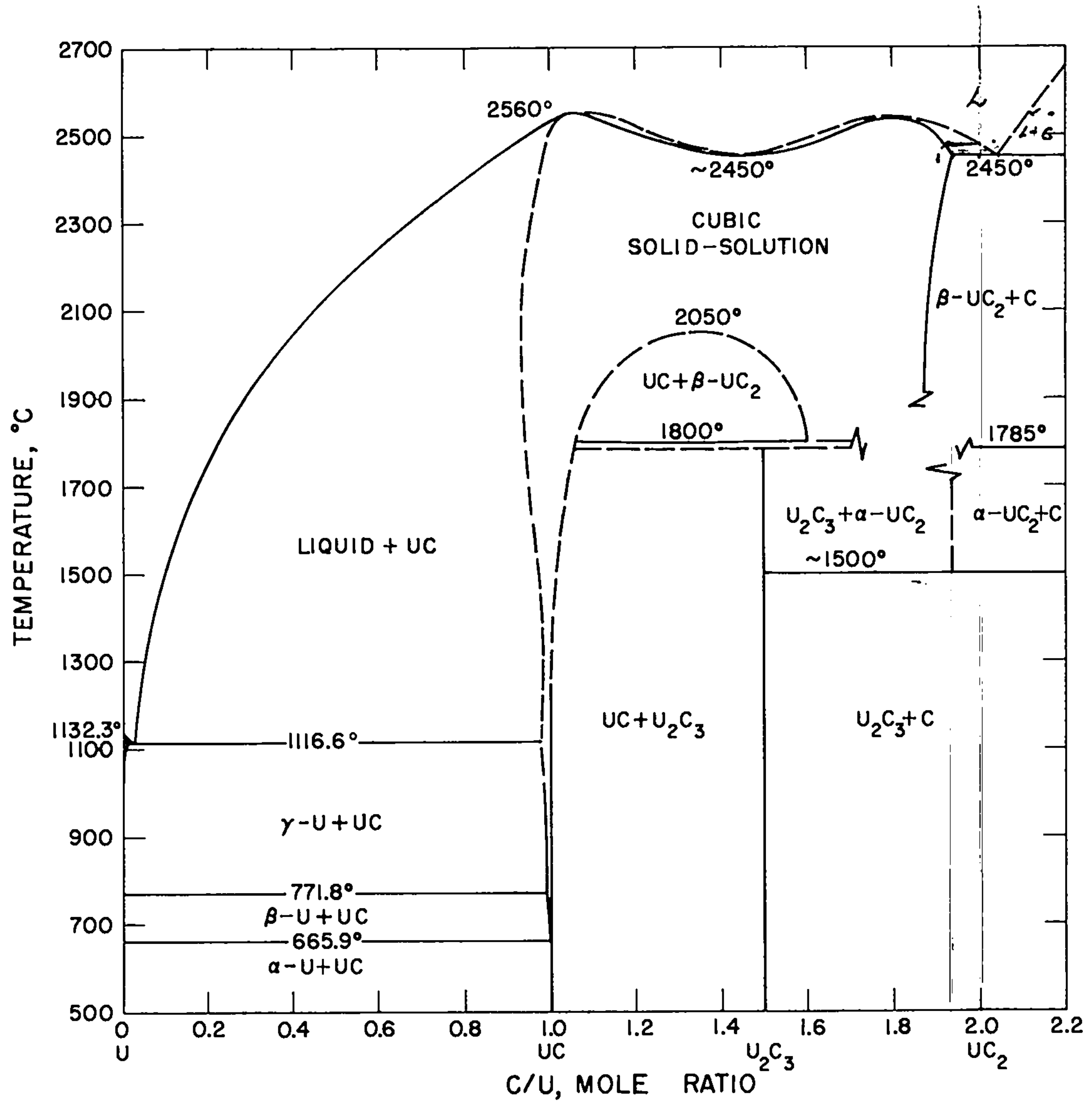

Figure III. 1. 1 Tentative Phase Diagram of the Uranium-Uranium Dicarbide System this temperature include values of 2590 ± 50° (Chiotti, 1952), 2350° to 2400° (Mallett and co-workers, 1952), 2520° (Brownlee, 1958), 2275° (Rundle and co-workers, 1948), and 2280° (Newkirk and Bates, 1959). This last measurement was made using a tungsten vee to hold the melt and the value is near those found in the W-UC system. Unlike the other cubic carbides, UC has only a slight homogeneity range, which at first was thought to be negligible (Rundle and co-workers, 1948). With the lattice parameter behavior first noted by Williams and co-workers (1960), a composition range at higher temperatures was suspected. In an effort to clarify these observations, Buckley (1961) examined quenched alloys containing various impurities as well as various amounts of free uranium. He found that the lattice parameter of quenched UC goes through a minimum when the total composition is below $UC_{0.8}$, in agreement with Williams and co-workers (1960). When a sample containing a small amount of free uranium was quenched from various temperatures, a similar minimum was observed upon cooling from about 2000°. An anneal at 1300° caused the lattice parameter to increase to 4.959 A, and small cubic particles of uranium appeared within the grains. From this Buckley (1961) concluded that rapidly cooled UC retains a defect structure which is characteristic of some higher temperature. By applying the equation

$$\ln C_s = \frac{T_m}{T}\left[\ln (C_s^\circ / C_l^\circ) - \frac{S}{R}\right] + \frac{S}{R} + \ln C_l$$

where C_s = apparent excess of U in $UC_{1.0}$ at the solidus boundary,
C_l = uranium concentration in the liquidus (values attributed to Rundle et al.),
C_s° and C_l° = respective values at the melting point of pure $UC_{1.0}$,
T_m = melting point of $UC_{1.0}$ (a value of 2350° was used),
T = temperature at which C_s and C_l are measured,

R = gas constant, and

S = entropy of fusion of pure uranium (value calculated from the data of Rauh and Thorn, 1954),

and reasoning from the behavior of the lattice parameter, he concluded that the solidus must be retrograde with a lower limit at $UC_{0.94}$ and about 2000°. Magnier and Accary (1963), and Kerr (1963) recently confirmed this observation but the former workers placed the limit at $UC_{0.96}$ and 1700°. They suggest this "nose" in the low carbon boundary is caused by the peritectic formation of an unidentified compound at this temperature. No experimental support for this interpretation has been reported. Therefore, the shape of the phase boundary in Figure III. 1. 1 has been based on the work of Buckley (1961) and its position was calculated from the above equation, using preliminary liquidus values of Storms (1964), a melting point of 2560° for $UC_{1.0}$, and a value for C_s°/C_1° to make C_s equal to $UC_{0.980\pm0.005}$ at 1300° (Witteman and Bowman, 1963). This leads to a minimum in the solidus at $UC_{0.93}$ and 2000°. It is important when evaluating experiments in this region of the phase diagram to consider the effect of dissolved oxygen. The presence of free uranium increases the ease with which oxygen will dissolve and, if the UO_2 phase is absent, heating the U(C, O) solution in vacuum can lead to the formation of free uranium with the evolution of CO.

The high carbon boundary, below 1800°, approaches $UC_{1.0}$ when a sample is cooled in vacuum (Witteman and Bowman, 1963). Burdick and co-workers (1955) placed the boundary at $UC_{1.12}$ when an oil quench from 1700° was used.

In the region between UC and UC_2, the diagram shows several very interesting features which are still not completely understood. In 1952, Mallett and co-workers proposed that a solid solution exists between UC and UC_2 in the region between about 2020° and the melting point, and that this broke into a two phase field of UC and UC_2 below 2020°. Their diagram shows termination of the miscibility gap at 1800° by the formation of U_2C_3. These conclusions were based on metallographic examination of alloys quenched from between 1700° and the melting point. However, they were unaware of the α-β transition of UC_2. Nine years later, Chubb and Phillips (1961), using the same technique, presented evidence to challenge this interpretation. Their diagram shows a miscibility gap which extends to the solidus, forming a eutectic between UC and β-UC_2. They proposed also that UC_2 converts from cubic to tetragonal at a temperature above that at which U_2C_3 forms. Recently Witteman and Bowman (1963) reported evidence, based on thermal analysis,* which completely supports the initial ideas of Mallett and co-workers (1952). Alloys cooled from just below the melting temperature show a break in the cooling rate where the solid solution breaks into UC + β-UC_2, followed by a thermal arrest where cubic UC_2 converts to the tetragonal form. Thus, it is proposed that the hat-shaped miscibility gap has a critical temperature of 2050 ± 50° at $UC_{1.35 \pm 0.05}$, and the lower boundary, at 1800°, extends between $UC_{1.06-1.12}$ and $UC_{\sim 1.6}$.

U_2C_3 has been a very elusive compound which is not normally found in material quenched from above 1800°. Early workers at Iowa State College suggested, as one explanation for the Widmänstatten structure exhibited by material quenched from the melt, that a U_2C_3 phase existed at high temperature, but it could not be retained upon cooling (Rundle

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* Details of this technique can be found in a paper by Rupert (1963).

and co-workers, 1948; Wilhelm and co-workers, 1949). Later, Mallett and co-workers (1952) showed that the actual situation was just the opposite, that U_2C_3 was not stable at high temperatures but was formed only very slowly at lower temperatures. They found this phase required some mechanical stress to initiate its formation. Later workers also noted this behavior, but it is clear that other factors are involved. Recent work at Harwell (Henney, Hill and Livey, 1962) demonstrates that dissolved nitrogen and oxygen influence the ease with which U_2C_3 will form. Using very pure material, Witteman and Bowman (1963) observed that it would form easily during cooling, when the composition was near $UC_{1.5}$, and when the material had been cycled across the decomposition temperature several times. Heating within the solid solution region was found to reduce the ability of U_2C_3 to re-form upon cooling. Using material of unknown purity, Chubb and Dickerson (1963) found that formation was complete within 15 minutes at 1600°. Norreys and co-workers (1963) and Imoto and co-workers (1963) concluded that a time delay, depending on temperature, precedes its formation. The decomposition temperature was placed at 1840° by Wilson (1960), but this temperature is probably too high. The phase is apparently very close to a line compound (Mallett and co-workers, 1952; Witteman, 1963).

Although many features of the UC_2 phase are still open to discussion, it is generally agreed that UC_2 has a melting point in excess of 2450° and a transition from cubic to tetragonal at 1800°. There is no doubt that UC_2 decomposes into U_2C_3 and carbon at low temperatures, but this temperature is still somewhat uncertain. Each of these features will be discussed separately.

Work at Los Alamos has shown that a melting point minimum of $\sim$2450° exists between UC and UC_2 and that UC_2 melts at 2450 ± 50° in contact with graphite. In addition, metallographic examination of small beads of $UC_2 + C$, which were cooled very rapidly from the melting point, has revealed a eutectic structure (Hoffman; see, Witteman and Bowman, 1963). Thus, the maximum melting point of the UC_2 phase must be in excess of 2450°. Mallett and co-workers (1952) gave a range of 2450 - 2500°. The very low value of 2200°, reported by Wilson (1960), was probably due to tungsten contamination. The proposal that UC_2 melts peritectically in contact with carbon (Chubb and Phillips, 1961) has not been supported.

The polymorphic transition at 1800° is so rapid that the cubic form of UC_2 cannot be quenched in. Using a high temperature x-ray camera, Wilson (1960) observed the transition at 1820°. However, thermal arrest work at Los Alamos has placed this temperature nearer to 1800° (Witteman 1963; Rupert, 1963). The transition is 15-20° higher when UC is present than when carbon is the second phase (Wilson, 1960; Witteman, 1963).

Under equilibrium conditions UC_2 will decompose into U_2C_3 and carbon below 1500° (Leitnaker and Witteman, 1962). Temperatures of 1500-1600° (Imoto and co-workers, 1963), 1750° (Henney and co-workers, 1962), 1600° (Rudy and Benesovsky, 1963) and $< 1550°$ (Huddle and co-workers, 1962) also have been reported. However, because this reaction is very slow, pure UC_2 can be retained from the melt provided the composition is near $UC_{1.94}$. At lower compositions UC will form in addition to UC_2 upon cooling and, if the carbon content is sufficiently high, graphite will be present as the second phase. When heatings are carried out below 1500°, or below 1800° when the composition is lower than $UC_{1.94}$, it is not unusual to find the nonequilibrium mixture $UC + U_2C_3 + UC_2 + C$ at room temperature.

UC_2 is never obtained with an integral stoichiometry. This defect structure was first noted by Mallett and co-workers (1952) and many others since then. Depending on the amount of free carbon present and the thermal history, compositions centering around $UC_{1.88}$ and $UC_{1.95}$ have been found. It has been observed by Witteman and Bowman (1963) that the composition $UC_{1.94}$ can be retained from the melt provided free carbon is largely absent. Otherwise a composition of $UC_{1.89}$ results. Finely divided free carbon is thought to act as a precipitation center allowing the β-UC_2 to acquire a lower composition which is representative of some lower temperature. During a rapid quench, the α-β transition takes place without a change in composition. Imoto and co-workers (1963) observed that material containing free carbon had a composition of α-$UC_{1.86}$ after being quenched from 2200°. However, if graphite-free $UC_{1.86}$ were allowed to cool slowly from 2200° the presence of UC was detected. In this case the α-UC_2 acquired its equilibrium composition. From the amount of UC formed, they were able to calculate that α-UC_2 has an equilibrium composition of $UC_{1.96\pm0.04}$.

Lattice Parameter and Structure

UC is fcc, as found first by Litz and co-workers (1948). According to Figure III. 1. 2, the best parameter for hyperstoichiometric UC is 4.9605 ± 0.0005 A. The higher parameters reported by other workers are no doubt due to dissolved oxygen. At the low carbon boundary, the parameter depends on the thermal history as well as on the almost unavoidable presence of oxygen. By removing the oxygen with Be, Anselin and co-workers (1963) obtained a value of 4.956 A. Carniglia (1963) found the same value after zone refining a single crystal which was reported to be $UC_{1.0}$

U_2C_3 was found to be bcc (I43d) from x-ray (Mallett and co-workers, 1952) as well as from neutron diffraction studies (Austin, 1959). A lattice parameter of 8.088 A has almost always been found, regardless

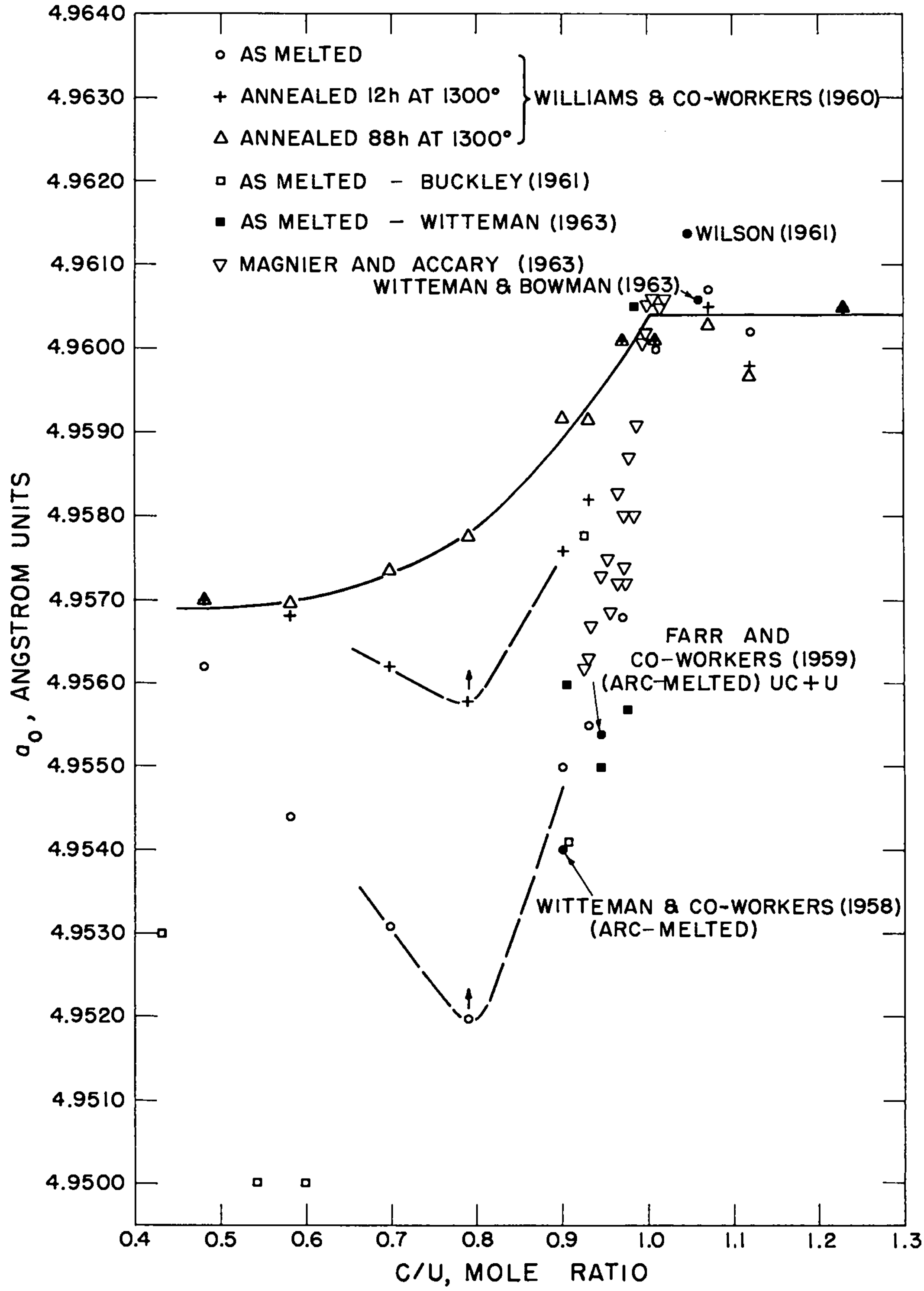

Figure III. 1. 2 The Effect of Heat Treatment on the Lattice Parameter of UC of the conditions of preparation. The compound is known to dissolve essentially no nitrogen and is a line compound; this suggests that the solubility of oxygen is equally low. It has been suggested that the formation of U_2C_3 from UC_2 occurs through a slight shift in the uranium positions and that the transformation is martensitic in nature (Gillam, 1962). The movement of the carbon atoms by interstitial diffusion could then account for the slowness of formation. Magnier and co-workers (1963) observed that U_2C_3 forms from UC_2 by nucleation and growth.

The structure of α-UC_2 has been determined on two occasions by neutron diffraction studies (Atoji and Medrud, 1959; Austin, 1959). Both assigned the CaC_2-type structure (I4/mmm). Numerous values for the lattice parameter have been reported but with rather poor agreement. Very pure arc-melted samples of $UC_{1.91-1.94}$ have given a value of $a = 3.5241 \pm 0.0005$, $c = 5.9962 \pm 0.0008$ A with a decrease to $a = 3.519 \pm 0.001$, $c = 5.979 \pm 0.002$ for a composition of $UC_{1.89}$ containing free carbon (Witteman, 1963). These values are in good agreement with those of Imoto and co-workers (1963). Since slow cooling allows $UC_{1.86}$ to decompose into α-$UC_{1.94}$ and $UC_{1.0}$, it is possible for α-UC_2, after being cooled slowly, to have a higher parameter than after being quenched. In addition, if the free carbon content is low, slow cooling can result in an unexpected high parameter with UC as the second phase.

It is interesting to note that, whereas the C-C distance in CaC_2 is equal to the triple bond, this distance in α-UC_2 is essentially that of a double bond. Above 1800° this tetragonal structure converts to a cubic form. Starting with the high temperature x-ray studies by Wilson (1960), most workers have assumed that the cubic form is the

CaF_2 type. Recent work at Los Alamos, using high temperature neutron diffraction, has ruled out this possibility (Bowman et al., 1964). They found that the high temperature form has the pyrite structure, as has been argued from indirect evidence (Bredig, 1960; Chang, 1961; Accary, 1963).

Chemical Stability

The very high reactivity of the uranium carbides has been,a limitation to their application and a nuisance to those attempting to prepare pure materials. No attempt has been made to compile all of the chemical properties exhibited by these carbides; only those reactions which would hamper the production of pure materials have been discussed. Additional information can also be found in the introduction.

Fine UC is pyrophoric and in larger pieces it will slowly react with oxygen at room temperature. For example, storage of powdered UC in Ar containing 200 ppm O_2 will result in a stable oxygen content of 0.2-0.4 wt %(Sowden and co-workers, 1963). Oxidation of arc-melted buttons by CO_2 is measurable above 350° and no protective film is formed up to at least 700° (Brown and Stobo, 1961; Atoda and co-workers, 1963). At low temperatures free carbon accumulates as the uranium reacts to form an oxide. Although the reaction of UC with H_2O at room temperature is slow, at 95° the reaction becomes violent. $UC_{0.75}O_{0.25}$ is much more stable under these conditions (Stoops and Hamme, 1964). Grossman (1963) observed that the surface film, which was produced when UC was exposed to air, could be removed by heating to above 1530° in vacuum. At temperatures below 1430° this film would re-form even in a vacuum of 5×10^{-7} torr.

Mallett and co-workers (1952) observed no reaction between U_2C_3 and water at 75° unless the solution was made strongly acid.

Borchardt (1959) found that $UC_{1.69}$ reacted with oxygen between 150°and 680° to give UO_2 and carbon. At higher temperatures, the reaction led to U_3O_8.

According to Brett and co-workers (1960), UC_2 is stable in water vapor at room temperature, and is stable in air up to 200°. At 300° it reacts to form U_3O_8. The reaction of UC_2 with water has been studied recently by Kempter (1962). He confirmed the observation that UC_2 hydrolyzes faster than UC. Tripler and co-workers (1959) found that the reaction rate with N_2O_2 and H_2O increased in this order. UN_x was the end product of the reaction with N_2. UC_2 is apparently slightly more reactive to oxidation by CO_2 than is UC (Atoda and co-workers, 1963).

Appearance

All of the uranium carbides are gray when powdered and metallic looking when seen as an arc-melted button.

Hardness

The apparent hardness of these carbides naturally depends on the composition and purity if cast materials are measured, and on the annealing temperature if the pieces were sintered from powders. Because these variables cannot be easily related to the fundamental property of the material, only microhardness values of reasonably well characterized material have been listed.

A Knoop hardness of 935 Kg/mm^2 (100 g load) has been reported for UC (Tripler and co-workers, 1959). Measurements reported by Chubb and Dickerson (1962), although they show a good deal of scatter, center around 600 kg/mm^2. More recently, these authors (1963) gave 650 kg/mm^2 DPH as the room temperature value for both $UC_{1.02}$ and $UC_{0.98}$ with a decrease in hardness at higher temperatures.

Workers at Battelle have consistently reported 1100 kg/mm^2 (both Knoop and DPH) for U_2C_3 and 500 kg/mm^2 for UC_2 (Tripler and co-workers 1959; Chubb and Dickerson, 1962, 1963; Chubb and Rough, 1960). Jones (1956) found 700 kg/mm^2 DPH for UC_2. Norreys and co-workers (1963) observed 1500 kg/mm^2 (50 g load) as the hardness of U_2C_3.

Electrical Resistivity

The following room temperature resistivity values have been reported for UC: 35-40 μohm-cm (Chubb and Rough, 1960); 35 μohm-cm for $UC_{1.0}$ (Chubb and Dickerson, 1963); 50-56 μohm-cm for UC of 90-92% density (Regan and Hedger, 1961); 40.5 μohm-cm (Norreys and Wheeler, 1963); 33-44 μohm-cm (Smith and Rough, 1959); <69 μohm-cm (Leary and co-workers, 1963). The latter value may be too high because it was obtained by the eddy current method (Leary, 1964).

Measurements have been made at higher temperatures on a number of occasions; Norreys and Wheeler (1963) found a gradually decreasing slope from room temperature to a value of 277 μohm-cm at 2252°K. Griffiths (1962) found a change in slope at 525° which he showed was due to dissolved oxygen. A vacuum anneal for 24 hr at 1400° under 10^{-6} torr pressure apparently removed sufficient oxygen to eliminate the break. Regan and Hedger (1961) quote Griffiths as obtaining a linear temperature coefficient of 0.15 μohm-cm/°C between -180° and 400°C. Grossman (1963) has made measurements between 927° and 1777°C and fit them to the following equation:

$$\rho = 20.4 \times 10^{-6} + 114.8T \times 10^{-9} \text{ ohm-cm}$$

The U_2C_3 phase apparently has a resistivity of 210 μohm-cm (Chubb and Dickerson, 1962).

Recent work by Chubb and Dickerson (1963) shows a room temperature resistivity for $UC_{1.96}$ of 120 μohm-cm, with an arrest in the curve at 200 μohm-cm and about 1000°. Above this temperature, the resistivity continues to increase in a normal manner. They suggest that this behavior denotes a change in state. No other support for this conclusion has been reported.

Superconductivity

Hardy and Hulm (1954) found that UC was not superconductive down to 1.2°K. In view of the preparation procedure and lattice constant, the presence of UO_2 is indicated. Using pure materials supplied by Witteman, Giorgi (1962) could find no indication of superconductivity above 4°K for $UC_{1.91} + C$, $UC_{1.16}$ and U_2C_3.

Thermodynamic Properties

At the present time, the great activity in measuring and estimating thermodynamic properties of the uranium carbides would quickly render any review obsolete. In addition, several excellent critical evaluations have already appeared (Henney and co-workers, 1962; Rand and Kubaschewski, 1960; Huber and Holley, 1963; Cunningham and co-workers, 1962; Vienna Panel, 1963). With this in mind, the following was written to give only a cursory view of the data. The reader might wish to consult the report of the Vienna Panel (1963) for a more complete evaluation.

A. Uranium Monocarbide, UC:

The heat of formation of UC has been measured by combustion calorimetry on two occasions. Farr and co-workers (1959) obtained -21.0 ± 1.0 kcal/mole after correcting for about 4% free uranium and 850 ppm oxygen. Droege and co-workers (1959) gave -20.0 ± 5.0 kcal/mole, but corrections were not made for 1450 ppm oxygen and the uranium metal present. In addition the conversion from constant volume to constant pressure was not indicated. If a common heat of formation for U_3O_8 is used, this value becomes -19.7 kcal/mole.

Because of the difficulty in correcting for oxygen, the value of Farr and co-workers (1959) is considered better. A recent recalculation of this measurement by Huber and Holley (1963) has led to a value of -21.7 ± 1.0 kcal/mole. This was subsequently accepted by the Vienna Panel.

A number of heat capacity studies have been reported to date. These are compared in Figure III. 1. 3. Boettcher and Schneider (1958) obtained a C_p of 12.00 ± 0.75 cal/mole-deg and 13.25 ± 0.75 cal/mole-deg at 398°K and 523°K, respectively. Mukaibo and co-workers (1962) fit the equation $C_p = 5.01 + 2.63 \times 10^{-2}T - 1.92 \times 10^{-5}T^2$ (cal/mole-deg) to their data and claim an accuracy of ±3% up to 673°K. The material used in this study probably contained some uranium metal according to the lattice parameter. To plot the data of Combarieu and co-workers (1963), it was necessary to lift the values from a graph and, therefore, some error might have been introduced. Low temperature measurements by Westrum, and Martin and co-workers (reported in Vienna Panel Report, 1963) give $C_p(298.15) = 12.10$ cal/mole-deg, $S^\circ_{298} = 14.29$ e.u. and C_p (298) = 11.9 cal/mole-deg, $S^\circ_{298} = 14.07$ e.u., respectively. Harrington and Vozzella (1963), using an ice drop calorimeter, obtained the equation $C_p = 14.223 + 1.574 \times 10^{-3}T - 4.118 \times 10^{5}T^{-2}$ for the molar heat capacity between 273° and 1475°K. As can be seen from Figure III. 1. 4, this measurement is in excellent agreement with Krikorian's estimation (Krikorian, O. H., 1962) but differs significantly from the values adopted by the Vienna Panel. High temperature measurements by Levinson (1963^b) have resulted in the following equation:

$H_T - H_{310\,^\circ K} = 4.082 + 3.515 \times 10^{-2}T + 9.204 \times 10^{-6}T^2$ cal/g of $UC_{0.99}$. The reason for the apparent lack of agreement between

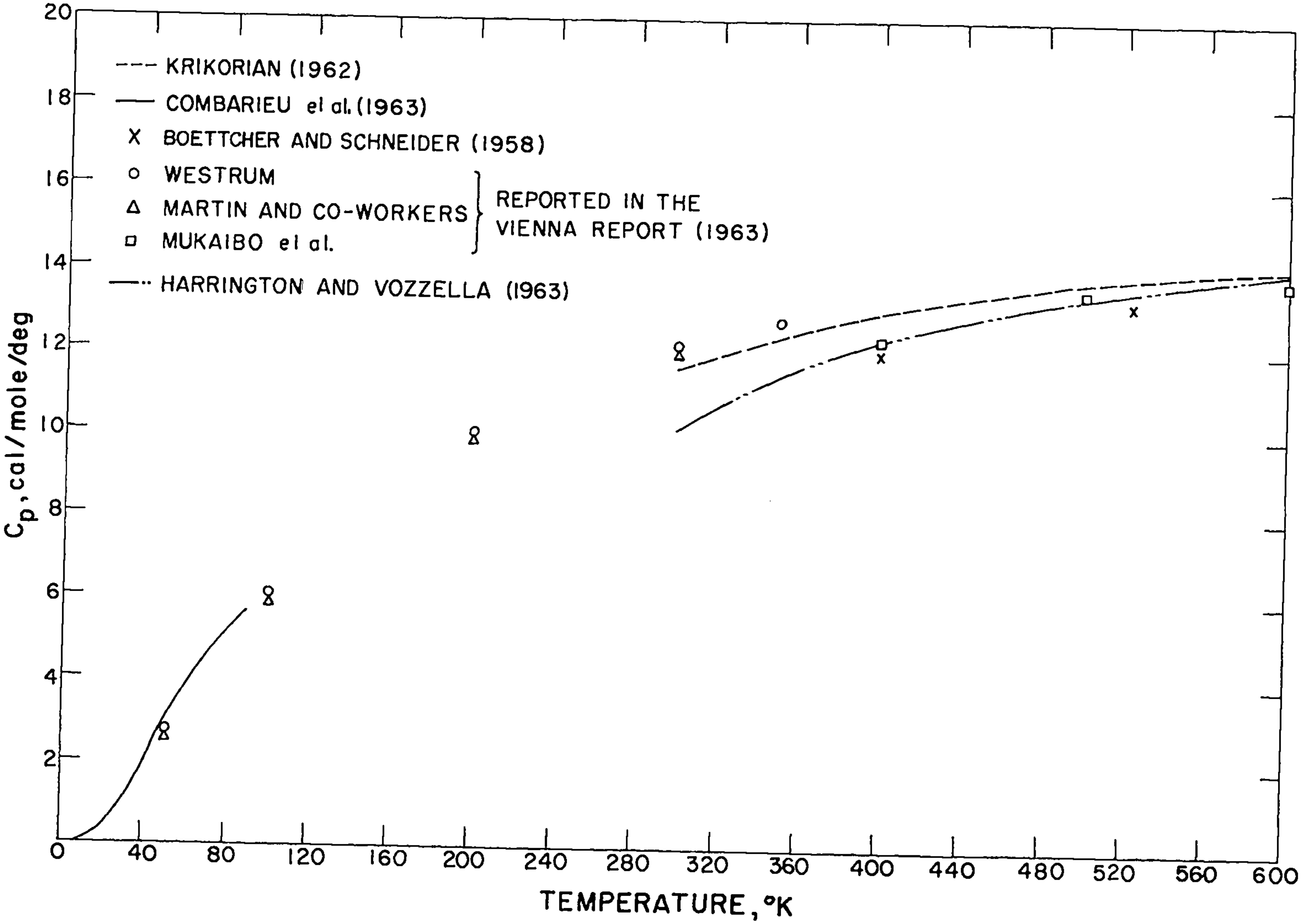

Figure III. 1.3 Low Temperature Heat Capacity of UC

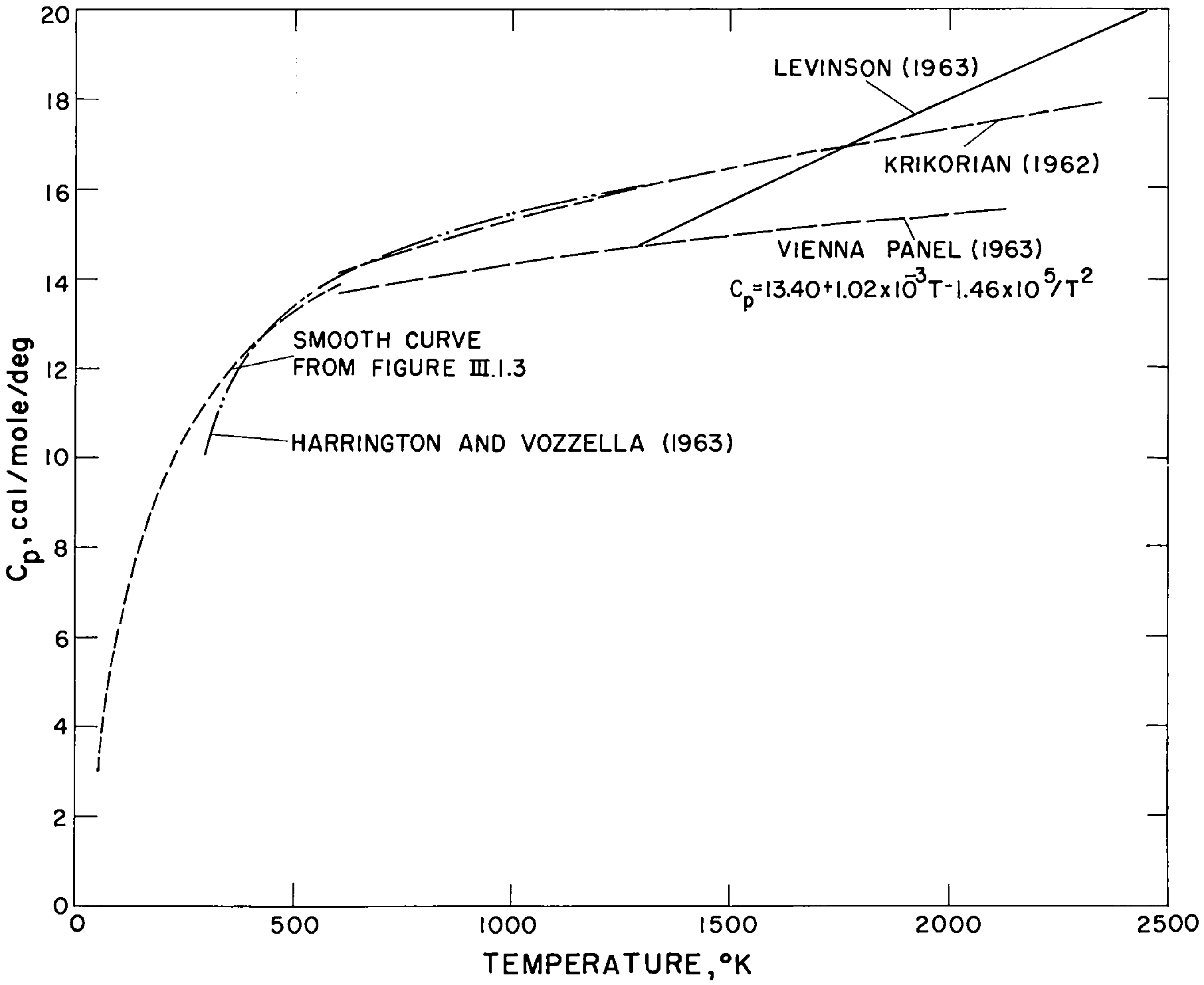

Figure III. 1. 4 High Temperature Heat Capacity of UC

Levinson's data and what one would reasonably expect is not clear at the present time.

B. Uranium Sesquicarbide, U_2C_3:

The heat of formation is -49 ± 4 kcal/mole according to combustion measurements by Huber and Holley (1962). No other direct thermodynamic measurements have been reported.

C. Uranium Dicarbide, UC_2:

A recent redetermination of the heat of combustion (Huber and Holley, 1963) has yielded -21.1 ± 2 kcal/mole as the heat of formation of $UC_{1.90}$ at 298°K. The Vienna Panel adopted a value of -23 ± 2 kcal/mole.

Measurements of the low temperature heat capacity, reported by Westrum (Vienna Panel, 1963), are compromised somewhat by the uncertain composition of his material. By assuming, however, that the sample analyzing $UC_{1.79}$ contained the appropriate amounts of $UC_{2.0}$ and $UC_{1.0}$, he calculated C_p (298) = 14.65 and S° (298) = 16.18 e.u.

Using a high temperature drop calorimeter, Levinson (1963^a) obtained data which fit the following equations:

$$H_T - H_{310°K} = 20.21 + 7.978 \times 10^{-4}T + 3.024 \times 10^{-5}T^2 \text{ cal/g} \quad \text{tetragonal}$$

$$H_T - H_{310°K} = 67.91 - 9.113 \times 10^{-3}T + 2.629 \times 10^{-5}T^2 \text{ cal/g} \quad \text{cubic.}$$

If a recent value of 1800°C for the α-β transition temperature is used, (Witteman and Bowman, 1963), Levinson's data give 10.2 cal/g or 2.66 kcal/mole as the heat of transition. The various heat capacity measurements and estimations are compared in Figure III. 1. 5. The Vienna Panel gave the following equation for the heat capacity of UC_2:

$$C_p = 29.90 + 3.06 \times 10^{-3}T - 3.71 \times 10^5/T^2 \text{ cal/mole-deg and}$$

$$S°_{298} = 16.2 \pm 0.5 \text{ e.u.}$$

Besides the above more or less direct measurements, thermodynamic information has been obtained from the U-C-Bi system (Rice

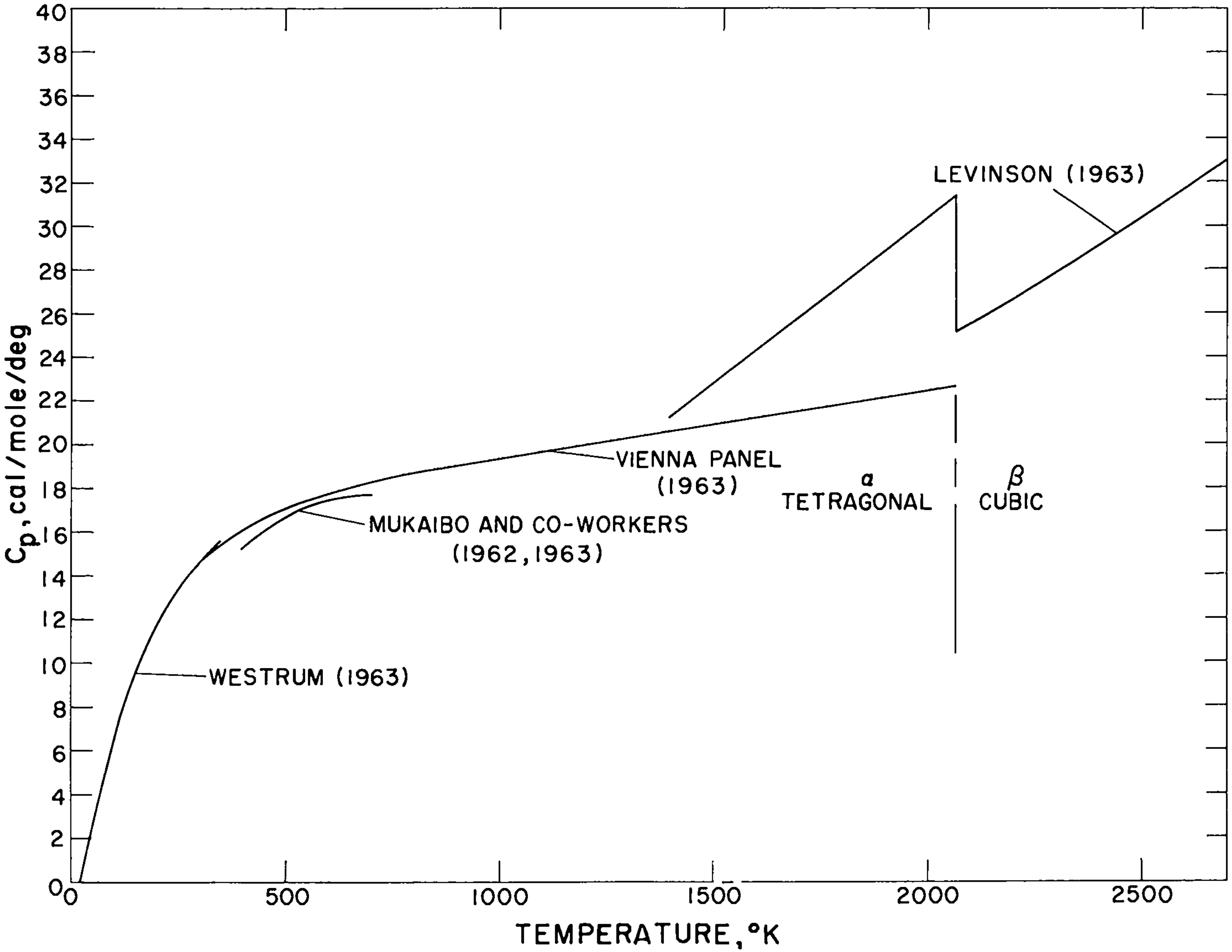

Figure III. 1. 5 High Temperature Heat Capacity of UC_2

and co-workers, 1962), the U-C-Au system (Alcock and Grieveson, 1962), and U-(Hf, Zr, Nb, Ta)-C systems (Rudy and Benesovsky, 1963). Most of this work is open to question because of oxygen contamination as well as possible solution of the solvent metal in the uranium carbide. In addition, the basis of the calculations by Rudy and Benesovsky (1963), i.e.,that a miscibility gap exists in the UC-HfC system, has been shown to be false by Krikorian, N. H. and co-workers (1963).

Vaporization

The very high reactivity of the uranium carbides and the high temperature at which measurements must be made have added many unresolved difficulties to a study of their vapor pressure. As a result, although numerous values have been reported, there is rather poor agreement. Until the reasons for this poor agreement are determined, thermodynamic calculations based on the data can only be viewed as rough approximations.

When heated under Langmuir conditions, the uranium-carbon system exhibits congruent vaporization. This observation was first reported by workers at Los Alamos (Leitnaker and Witteman, 1962) and later confirmed by Krupka (Bowman and Krupka, 1963) and Vozzella and co-workers (1963). These measurements place the congruent composition between $UC_{1.07-1.10}$ in the temperature range 2400-2600°K. Recent work by Carniglia (1963) indicates that the congruent composition lies near $UC_{1.32}$ at the melting point. This observation is so clear-cut, it can be used to provide a basis on which to evaluate the more uncertain pressure data. To do this, the reported vapor pressures have been plotted in Figure III. 1.6 as log g-atom/sec-cm^2 vs 1/T. When the individual data points were given, they were plotted; otherwise the reported straight lines have been drawn. Also included is the evaporation rate of carbon (as C_1, C_2 and C_3) from graphite (Stull and Sinke, 1956).

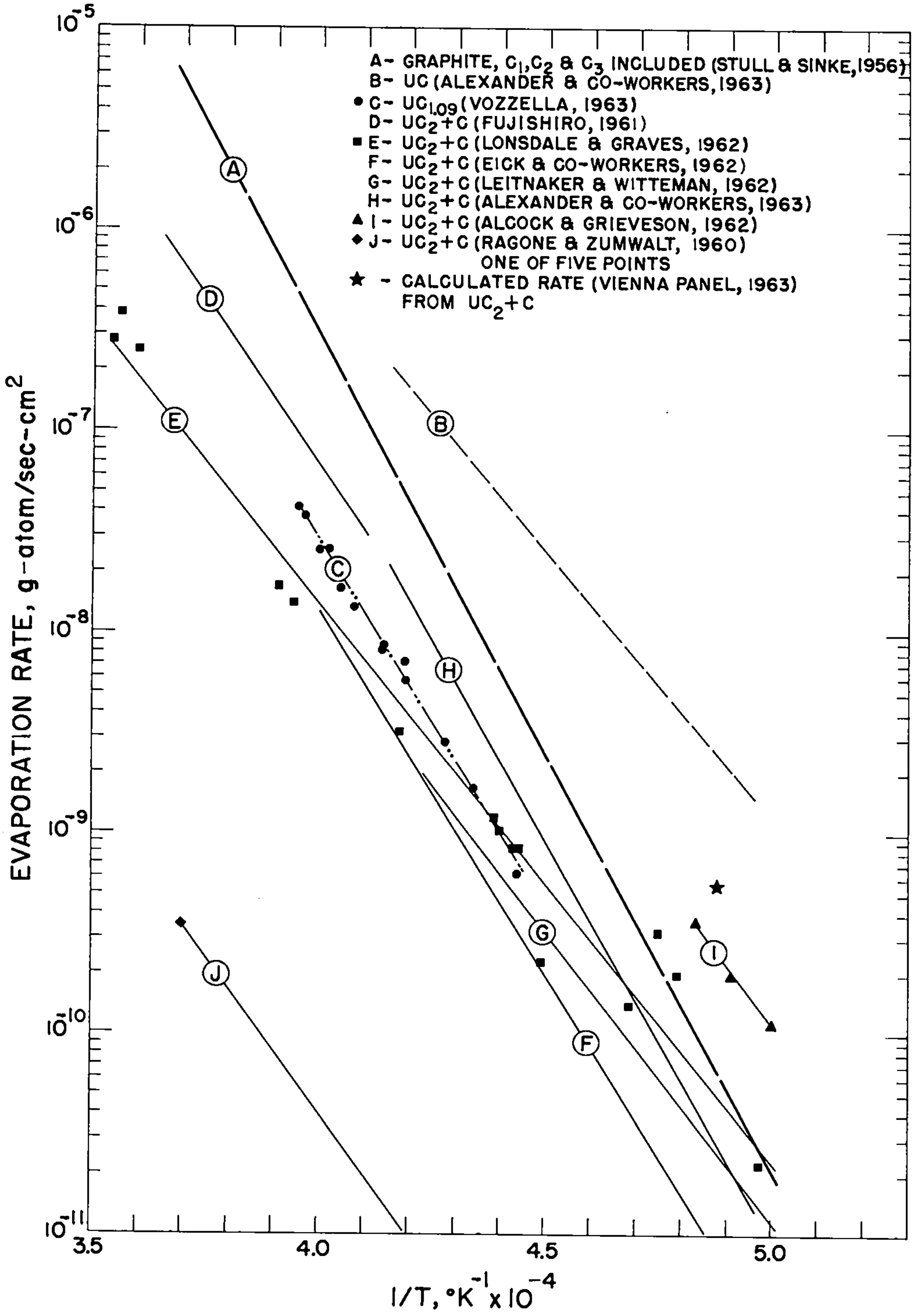

Figure III. 1. 6 Evaporation Rate of UC and UC_2

Since these calculations were made by assuming unity accommodation coefficients, in the strictest sense, the conclusions can only be applied to Knudsen measurements. However, Langmuir-type experiments can also be discussed if the effect of the accommodation coefficient is kept in mind.

A. Uranium Monocarbide, UC:

Two measurements of the uranium pressure over UC have been reported. Vozzella (1963) calculated evaporation rates, shown as Curve C in Figure III. 1. 6, from the amount of weight lost by a plug of $UC_{1.10}$ while being heated in vacuum. From this data one can conclude that the pressure of $U_{(g)}$ is only slightly higher over $UC_{1.10}$ than over UC_2 + C. The carbon pressure, of course, must be significantly lower. Earlier work by Vozzella and co-workers (1963) gave a somewhat higher pressure.

Alexander and co-workers (1963[a]) have measured the uranium pressure over UC contained in a Knudsen cell. Although the crucible material was not indicated in this paper, previous work by these authors (1963[b]) using a W crucible gave essentially the same pressures. Experience at Los Alamos (Krupka, 1963) has shown that W removes carbon from UC leading to a uranium-rich composition. Therefore, their measurements should not be applied to $UC_{1.10}$, but to some unknown lower composition. They conclude that under equilibrium conditions no congruent composition exists; but under steady-state conditions, the constant evaporating composition would be near $UC_{1.1}$.

B. Uranium Dicarbide, UC_2:

As shown in the figure, numerous measurements of the uranium pressure over UC_2 + C have been reported, but with generally poor agreement. The three most complete studies (Curves, E, F and G), all employing target collection from a graphite Knudsen cell, show agreement within a factor of two above 2300 °K, but at lower temperatures the slopes are such as to give increasingly poor agreement. An average curve through these measurements predicts that UC_2 + C will lose carbon preferentially above ~2000°K from an equilibrium cell, and below this temperature, graphite will accumulate as uranium is lost. Because of the low accommodation coefficient of carbon evaporating from graphite, this temperature will be somewhat higher under Langmuir conditions. This is not inconsistent with the congruent studies of Leitnaker and Witteman (1962). On the other hand, the thermodynamic values adopted by the Vienna Panel (1963) predict a uranium pressure which is not only significantly higher than the measured pressures, but one that would predict a preferential loss of uranium from UC_2 + C. Clearly, additional work must be done before any of the data can be considered reliable.

Mass spectrometer studies of UC_2 have shown the presence of UC_2 molecules in the gas phase, (Lonsdale and Graves, 1962; Eick, Rauh and Thorn, 1962). At 2800°K the ratio of U^+ to UC_2^+ of 4 was observed by the latter workers. Preliminary work by Storms (1964) has shown that this ratio is unity at 2700°K when the UC_2 is in equilibrium with carbon. Since $UC_{2(g)}$ is a significant fraction of the gas phase at temperatures of interest, the uranium pressures obtained by total collection must be lowered somewhat.

III, 1.3 The Plutonium-Plutonium Dicarbide System

Preparation

Studies involving plutonium are a difficult undertaking. Besides the health hazard associated with its high alpha activity, the element is very reactive to air. These properties require that all work be done in a dry-box with the attending difficulties and limitations. The carbides, although less reactive, must also be handled in a dry atmosphere.

The plutonium carbides have usually been prepared by arc melting either the elements or PuO_2 and carbon together. By starting with the pure elements and remelting the buttons at least six times, pure homogeneous materials are said to result. Unfortunately, alloys near the composition Pu_2C_3 are very sensitive to thermal shock and cannot be melted conveniently using the arc. Mulford and co-workers (1960) mentioned this difficulty but avoided it by melting these compositions in a previously carbided tantalum crucible, where the heating and cooling rates were much slower. PuO_2 can be substituted for the element if purity is not important. Palfreyman and Keig (1962) frequently found the oxide phase in carbides so prepared. On the other hand, because the oxide and carbide form a solid solution, the absence of the oxide phase does not necessarily mean that the sample is oxygen free.

Powder metallurgical techniques using Pu, $PuH_{2.8}$ or PuO_2

powders have also been employed. However, the resulting porous plugs appear to be more reactive with air than the dense alloys prepared from the melt (Kruger, 1962; Drummond and co-workers, 1957). Mulford and co-workers (1960) observed that the reaction between PuO_2 and C became appreciable at 1100° and was essentially complete after the temperature had reached 1600°. They also report that the reaction between molten Pu metal and graphite is undetectable below 1200°.

Under certain conditions, the carbides are pyrophoric (Ogard and co-workers, 1961). Even a normally inert dry-box atmosphere will oxidize the powders (Palfreyman and Russell, 1961).

Phase Relationships

The plutonium-carbon system is composed of the following phases: plutonium metal with its six crystal forms; a zeta phase at Pu_3C_2; PuC with a defective cubic NaCl-type structure; another cubic compound at Pu_2C_3; and an unidentified high temperature compound at PuC_2. This is shown as a tentative phase diagram in Figure III. 1. 7.

Although the transition temperatures of the metal appear to be unaffected by carbon (Elliott and Larson, 1961; Mulford and co-workers, 1960), the melting point is depressed to 630°. Recent work by Rosen and co-workers (1963) place this eutectic at $637 \pm 1°$.

Each of the allotropes of Pu transforms in contact with Pu_3C_2 (zeta phase). These have been measured by Hill (1962) for pure Pu. Thermal analysis studies by Mulford and co-workers (1960) have shown that Pu_3C_2 decomposes into ϵ-Pu + PuC at 575°. Metallographic studies by Rosen and co-workers (1963) place this temperature at $558 \pm 2°$. Pu_3C_2 is apparently a line compound.

Cubic PuC extends from $PuC_{0.77}$ to $PuC_{0.92}$ at ~570° (Rosen and co-workers, 1963; Mulford and co-workers, 1960), and its range becomes more narrow at lower temperatures. Kruger (1963) placed the PuC-Pu_3C_2

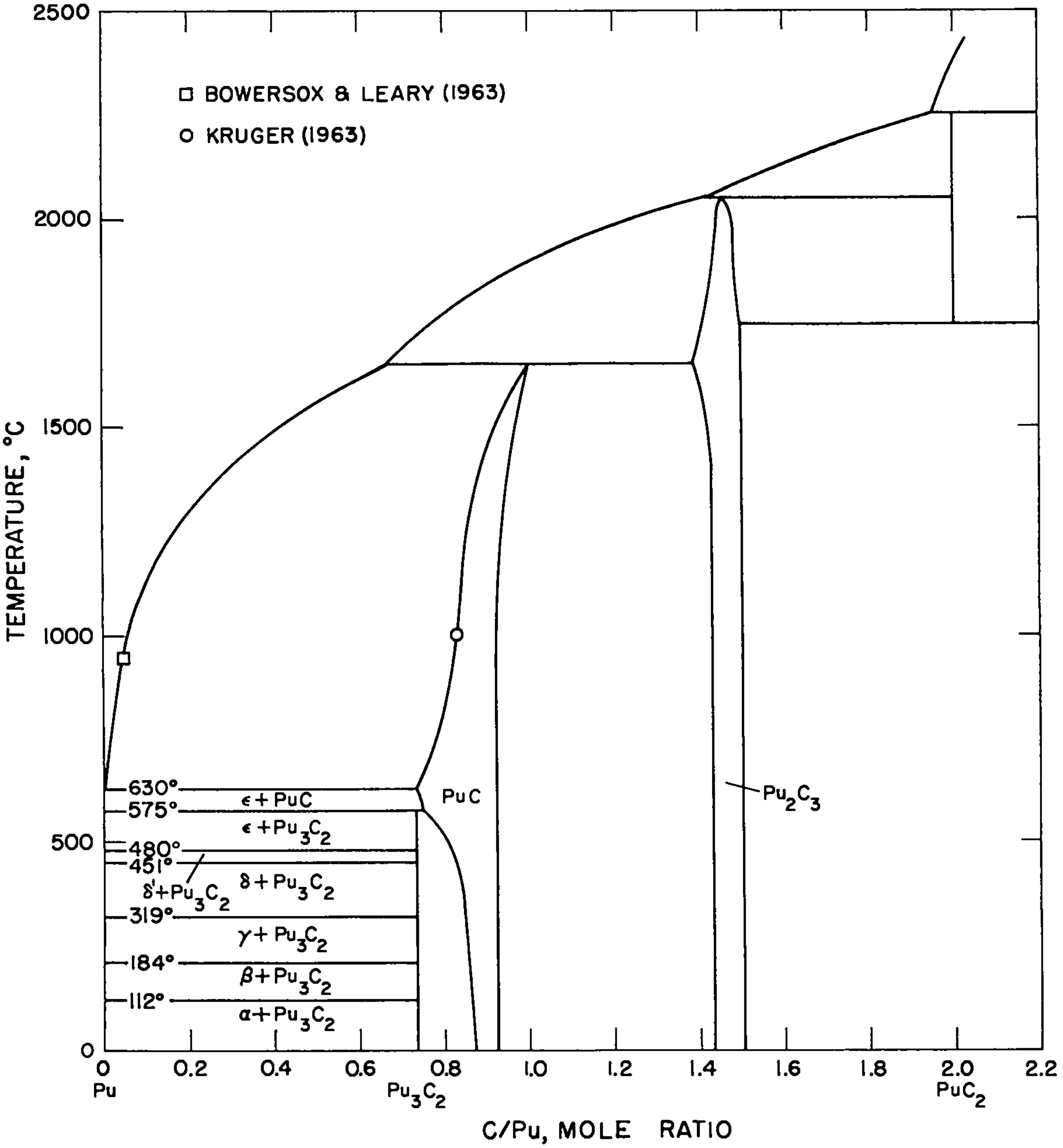

Figure III. 1. 7 Tentative Phase Diagram of the Pu-PuC_2 System boundary between $PuC_{0.83-0.88}$ on the basis of a metallographic examination of alloys which had been held at 400° for 25 days. A recent report from Los Alamos (Quarterly Status Report, 1962) places the boundary between $PuC_{0.72-0.79}$ and $PuC_{0.75-0.79}$ when alloys were quenched from 610° and 555°, respectively. Chikalla (1962) found the homogeneity range of arc-melted samples to lie between $PuC_{0.66-0.96}$. It should be noted, however, that Kruger (1963) observed a thermal break which extended over the range from 560° to 425° when samples of $PuC_{0.80}$ were cooled. Thus, it is not certain that the above composition ranges were successfully quenched-in and may, therefore, depend on the cooling rate employed. Although it is well established that PuC, like VC, does not extend to the integral stoichiometry at low temperatures, recent evidence has been presented to suggest that it does approach $PuC_{1.0}$ before it melts (Rosen and co-workers, 1963). According to Mulford and co-workers (1960), the PuC phase melts peritectically at 1654°. This observation was confirmed by additional work at Los Alamos (Quarterly Status Report, 1962). Rosen and co-workers (1963) place the low-carbon limit of the peritectic line at about $PuC_{0.63}$. Material cooled from the melt shows a cored structure rather than that typical of peritectic melting. This has led to speculation that either diffusion is very rapid at the peritectic temperature or that the PuC composition at this temperature is very near the liquidus composition. (Kruger, 1963; Palfreyman and Keig, 1962).

Cubic Pu_2C_3 also has a homogeneity range. Between 610° and 555°, the lower phase limit is between $PuC_{1.41-1.46}$ (Los Alamos Quarterly Status Report, 1962) while the upper limit is assumed to lie at $PuC_{1.50}$. This phase melts peritectically at 2050° (Mulford and co-workers, 1960).

Above ~1750°, a PuC_2 phase forms, then melts upon heating to ~2250° (Mulford and co-workers, 1960). The phase limits and crystal structure of this phase have not been reported, although it can be retained in almost pure form.

Lattice Parameter and Structure

The allotropic configurations of pure Pu metal are listed in Table III. 1. 2 with their lattice parameters. In view of the low solubility of carbon in Pu, one would expect these parameters to remain unchanged in the carbide system.

No crystal structures have been assigned to Pu_3C_2 or PuC_2.

PuC, with a NaCl-type lattice, shows a linear variation of lattice parameter with composition between the limits indicated in Table III. 1.2 (Kruger, 1963; Rosen and co-workers, 1963). Agreement between the various values for the low-carbon limit of PuC is poor. Perhaps, as Mulford and co-workers (1960) point out, this is due to the presence of oxygen. The effect of oxygen is to cause the parameter to go through a maximum as the oxygen content is increased. This occurs at 20 at.% dissolved PuO and a = 4.973 A (Anselin and co-workers, 1963). Measurements by Chikalla (1962) show that the parameter at this boundary is lowered by repeated arc meltings. In addition there is a minimum in the lattice parameter variation at $PuC_{0.66}$, similar to the effect observed in the UC system by Williams and co-workers (1960) (Fig. III. 1. 2). Rand and Street (1963) observed that $PuC_{0.63}$ showed an irreversible lattice parameter increase at 215°, 320° and 400° C. The parameter went from 4.9710 to 4.9780 A. $PuC_{0.84}$ was normal in this respect. An additional factor in choosing a correct value for the lattice parameter is radiation self-damage which causes the parameter to increase with time (Rand, Fox and Street, 1962). Chikalla (1962) also observed this effect.

Although the composition range of bcc Pu_2C_3 is quite narrow, a higher lattice parameter has been observed when the second phase is PuC_2 instead of PuC, as shown in Table III. 1. 2.

TABLE III.1.2

Structure and Lattice Parameter of Plutonium Metal and its Carbides

Phases in Equilibrium	Composition of First Phase	Structure	Lattice Parameter, A	Investigator
α-Pu	pure at 21°	simple monoclinic $P2_1/m$	a = 6.183 ± 0.001 b = 4.822 ± 0.001 c = 10.963 ± 0.001 β = 101.79° ± 0.01°	Zachariasen and Ellinger (1963[a])
β-Pu	pure at 190°	monoclinic I2/m	a = 9.284 ± 0.003 b = 10.463 ± 0.004 c = 7.859 ± 0.003 β = 92.13° ± 0.03°	Zachariasen and Ellinger (1963[b])
γ-Pu	pure at 235°	orthorhombic Fddd	a = 3.159 ± 0.001 b = 5.768 ± 0.001 c = 10.162 ± 0.002	Zachariasen and Ellinger (1955)
δ-Pu	pure at 320°	face-centered cubic	a = 4.6371 ± 0.0004	Ellinger (1956)
δ'-Pu	pure at 465°	body-centered tetragonal	a = 3.327 ± 0.003 c = 4.482 ± 0.007	Ellinger (1956)
ε-Pu	pure at 490°	body-centered cubic	a = 3.6361 ± 0.0004	Ellinger (1956)
$PuC + Pu_3C_2$	$PuC_{0.74}$	fcc (NaCl-type)	a = 4.954	Kruger (1962)
$PuC + Pu_2C_3$	$PuC_{0.94}$	fcc	a = 4.9730 ± 0.0001	Kruger (1962)
$Pu_2C_3 + PuC$	$PuC_{\sim 1.5}$	cubic, $I\bar{4}3d$-T_d^6	a = 8.1210 ± 0.0001	Kruger (1962)
Pu_2C_3	$PuC_{\sim 1.5}$	cubic	a = 8.1258 ± 0.0003 a = 8.1256 ± 0.0001	Mulford and co-workers (1960) Kruger (1962)
$Pu_2C_3 + PuC_2$	$PuC_{\sim 1.5}$	cubic	a = 8.1317 ± 0.0003	Mulford and co-workers (1960)
$Pu_2C_3 + C$	$PuC_{\sim 1.5}$	cubic	a = 8.1330 ± 0.0010	Chikalla (1962)

Appearance

All compositions in the Pu-C system appear to be gray metallic.

Chemical Stability

According to Drummond and co-workers (1957), PuC will oxidize slowly when heated to 200-300° in air, and will burn brightly in O_2 at 400°. A clean, dense surface was observed to remain bright after 2 months in air at room temperature. It was not attacked by cold water but effervesced steadily in hot water. Cold, dilute HCl or H_2SO_4 caused hydrolysis, although HNO_3 showed only a slight action.

Pu_2C_3 was somewhat more stable to acids than PuC.

The above authors also observed that PuC_2 was much less stable in moist air than the other carbides but was more stable to oxidation.

It appears that if metal is present or if the material is porous, chemical attack will be much more rapid.

Hardness

The hardness of PuC has been observed to vary between 600 and 1000 DPH as the carbon content of the phase increases (Quarterly Status Report, 1962). Mulford and co-workers (1960) reported that the hardness of PuC in contact with Pu_3C_2 was between 500 and 600 DPH and that the Pu_3C_2 phase gave a value between 70 and 90 DPH. Palfreyman and Russell (1961) give 750 kg/mm^2 and 900 kg/mm^2 as being the DPH of PuC and Pu_2C_3, respectively. Kruger (1962) reported that arc-melted PuC had a hardness of 860 ± 25 DPH.

Electrical Conductivity

PuC prepared from the oxide and of unstated composition gave a resistivity of 230 μohm-cm (Pascard, 1961). Leary and co-workers (1963) reported an average value of 269 μohm-cm for $PuC_{0.87}$, and 274 μohm-cm for $PuC_{1.00}$. In the range 25-830°C $PuC_{0.87}$ behaved as a semiconductor.

Superconductivity

No measurements have been reported.

Thermodynamic Properties

Huber and Holley (1962) have measured the heat of formation of PuC and Pu_2C_3 by combustion calorimetry. Assuming that the PuC phase had a composition of $PuC_{0.77}$ and contained ~10% Pu_2C_3, they calculated a value of $\Delta H^\circ_f = +3.7 \pm 3.1$ kcal/mole. On the basis of the lattice parameter (a = 4.9646) and the phase diagram, it is more probable that the composition was $PuC_{0.85}$ containing a small amount of $PuC_{1.43}$ (Pu_2C_3).

Their very preliminary value for Pu_2C_3 is $\Delta H^\circ_f = -1.7$ kcal/mole. No other measurements have been reported.

Vaporization

By measuring the weight loss from a graphite Knudsen effusion cell, Mulford and co-workers (1962) gave the following equation to express the pressure of Pu over PuC_2:

$$\log P\,(\mathrm{atm}) = -17920\,(\pm 250)/T + 2.779\,(\pm 0.11)$$
$$(2000\text{-}2500^\circ\mathrm{K}).$$

They found that PuC_2 loses Pu preferentially, and therefore no congruent composition for vaporization exists in this system.

Palfreyman and Potter (1963) measured the vapor pressure of $PuC_{0.898}$ by a transpiration method and gave the relationship

$$\log P(\mathrm{atm}) = -51,100/T + 22.3$$

for the range 1773° to 1838° K.

Chapter III. 2

The Th, U and Pu Nitrides

The nitrides of U and Th are very much alike in that they both form compounds having a stoichiometry of MN and M_2N_3. As yet, only the MN compound of Pu has been reported. In each case, the MN compound is fcc (NaCl-type), but this simple relationship is not carried over to the M_2N_3 compound. Th_2N_3 is hexagonal (La_2O_3-type), whereas U_2N_3 shows, besides this structure, a bcc form at a lower temperature. The bcc structure (Mn_2O_3-type) is a distorted fluorite lattice which becomes perfect at UN_2.

In each system, MN is the most stable compound and can be obtained from the other compounds by heating them at high temperatures or at low pressures.

The MN compounds have a narrow composition range at low temperatures, but this probably widens at higher temperatures. The melting point of the MN phases is pressure dependent, but in excess of 2500° C at 1 atm.

Although these compounds are good getters for oxygen, the solubility of oxygen is generally low. Nevertheless, until the effect of oxygen has been determined, all of the reported observations should be taken with some reservation.

III.2.1 The Thorium-Nitrogen System

Preparation

Although few procedures have been described, the thorium nitrides can be prepared in essentially the same way as the uranium nitrides. The reaction rate between N_2 and Th has been studied by Gerds and Mallett (1954).

Phase Relationship and Lattice Parameters

Two phases have been identified in this system: ThN and Th_2N_3.

ThN is fcc (NaCl-type) (Rundle, 1948) with a lattice parameter of a= 5.20 A (Rundle, 1948; Chiotti, 1952). ThN is sufficiently stable at high temperatures that a melting temperature of 2630 ± 50 °C has been observed (Chiotti, 1952). However, this temperature probably changes with pressure as does the melting temperature of UN. Chiotti (1952) found that after melting, the lattice parameter had dropped to a = 5.144. Street and Waters (1962) found a parameter of a = 5.1593.

Th_2N_3 is hexagonal (La_2O_3-type) with a = 3.883 ± 0.002, c = 6.187 ± 0.004 (Zachariasen, 1948; Chiotti, 1952) for a composition analysing $ThN_{1.57}$. Like the counterpart in the uranium system, Th_2N_3 is not stable in vacuum above approximately 1500 °C (Chiotti, 1952).

The solubility of N_2 (1 atm) in Th can be expressed by the following formula (Gerds and Mallett, 1954):

$$\log c \text{ (wt \%)} = -2405/T + 0.9115 \text{ (1118 - 1763°K)}.$$

Both nitrides will react rapidly at high temperatures with oxygen containing gases, and will hydrolyze in air at room temperature. All of the above work should be viewed with this in mind.

Appearance

Gerds and Mallett (1954) found that ThN formed as a golden-yellow film. Th_2N_3 was dark gray.

Chemical Stability

The thorium nitrides appear to be more reactive than the corresponding uranium compounds.

Hardness and Electrical Resistivity

No measurements could be found in the literature.

Superconductivity

Hardy and Hulm (1954) found that a composition of $ThN_{1.3}$ was not superconducting at 1.2°K. No analysis was given.

Thermodynamic Properties and Vaporization

No measurements could be found in the literature.

III .2. 2 The Uranium-Nitrogen System

Preparation

Of the many possible reactions (Taylor and McMurtry, 1961), the best and most widely used method of preparation is the direct reaction between the metal or UH_3 and N_2 or NH_3. Although the powdered metal will react rapidly with these gases, only the massive form can be freed of the inevitable oxide film by a nitric acid wash. After this treatment a powder can be obtained by heating first with NH_3 or H_2, then N_2 (Dayton and Tipton, 1956; Chiotti, 1952). Since the nitride is an excellent getter at the preparation temperature, it is essential to remove oxygen as well as H_2O and CO_2 from the gas stream (Newton, 1949; Francis and Hodge, 1961). The reaction rates of N_2 with U have been measured by Mallett and Gerds (1955).

If the reaction is carried out at ordinary pressures (~1 atm) and between 800° and 1000°, U_2N_3 forms with a composition approaching $UN_{1.75}$ (Rundle and co-workers, 1948). This can easily be converted to UN by heating in vacuum between 1300° and 1600° until the evolution of nitrogen has essentially ceased (Rundle and co-workers, 1948; Tripler and co-workers, 1959; Kempter and co-workers, 1959; Chiotti, 1949; and Olson and Mulford, 1963). By heating in 1 atm of helium previous to the vacuum treatment or by slowly raising the temperature, the rapid evolution of nitrogen can be controlled. The preparation of UN by arc melting, even under N_2, has been found unsatisfactory

(Williams and Sambell, 1959). In order to prepare UN_2, high pressures (126 atm) have been found necessary (Rundle and co-workers, 1948; Eding and Carr, 1961). UN_2 has also been observed as a minor contaminate in UN (Kempter and co-workers, 1959; Mallett and Gerds, 1955).

Powdered materials above the composition $UN_{\sim 1.0}$ are pyrophoric (Kempter and co-workers, 1959; Olson and Mulford, 1963; Eding and Carr, 1961).

Phase Relationship

A partial phase diagram is shown in Fig. III.2.1. Besides the phases UN and U_2N_3, a rather unstable UN_2 phase has been reported, but its relationship to the others is still largely unknown.

The transition temperatures of uranium metal are unaffected by the presence of nitrogen, and the melting point of the metal is reduced only slightly to a eutectic at 1130° (Benz and Bowman, 1964). These workers also found that UN is very similar to UC in that the lower phase boundary shows retrograde behavior with an upper limit of $UN_{0.96}$ at 1500° and $UN_{0.80}$ at 2000°. However, because the defect structure cannot be quenched in, UN appears as a line compound at room temperature. The upper boundary lies at $UN_{1.01 \pm 0.02}$ at 1600°.

The melting temperature of UN is strongly dependent on the nitrogen pressure, thus accounting for the rather scattered values reported in the past (Rundle and co-workers, 1948; Newkirk and Bates, 1959). According to Olsen and Mulford (1963), the congruent melting point of UN occurs only above 2.5 atm of N_2 at 2850 ± 30°C. Below this temperature the pressure at the first appearance of liquid can be determined from the following equation:

$$\log P(\mathrm{atm}) = 8.193 - 29.54 \times 10^3/T + 5.57 \times 10^{-18} T^5 \quad (1406\text{-}3125°\mathrm{K}).$$

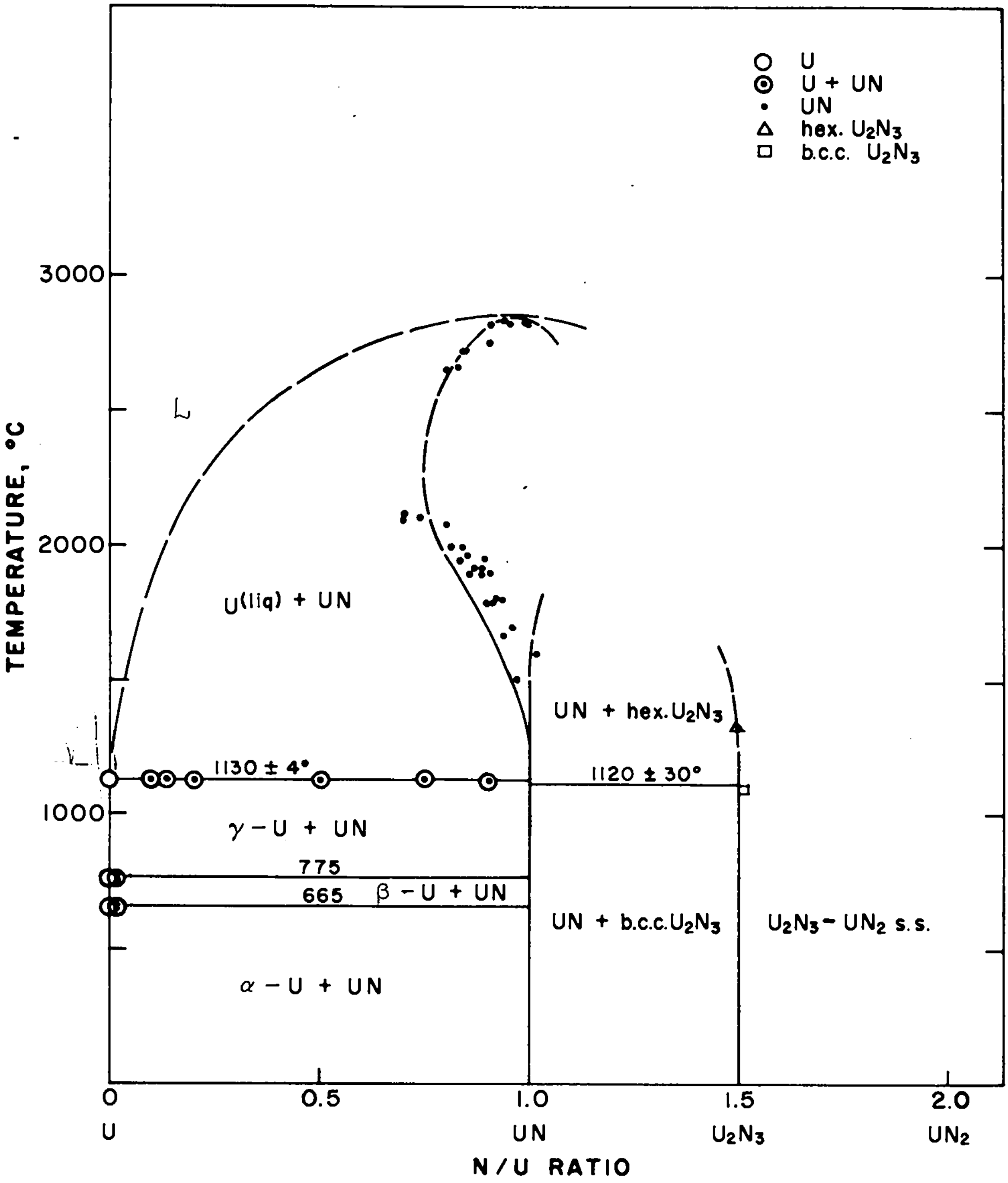

Figure III. 2. 1 A Partial Phase Diagram of the Uranium-Nitrogen System (Benz and Bowman, 1964)

Keller (1962) found higher melting points than those found by Olsen and Mulford (1963). These two studies are compared in Fig. III. 2. 2. Benz and Bowman (1964) observed congruent melting at 2835 ± 30° under 2 atm of nitrogen.

The phase relationships of the other phases will be discussed, to the extent that they are known, in the next section.

Lattice Parameter and Structure

UN is face-centered cubic (NaCl-type), according to both x-ray and neutron diffraction patterns (Mueller and Knott, 1957; Rundle and co-workers, 1948). A lattice parameter of $a = 4.8897 \pm 0.0005$ A represents the most probable value based on recent data (Kempter and co-workers, 1959; Williams and Sambell, 1959; Street and Waters, 1962; and Olson and Mulford, 1963). It should be remembered, though, that oxygen dissolves in UN and causes the lattice to expand.

U_2N_3 has a body-centered cubic structure (Mn_2O_3-type) which, if only the principal lines are considered, can be indexed as fcc (Rundle and co-workers, 1948). As nitrogen is added to the structure, the lattice parameter decreases from a value of $a = 10.68$ A at the UN-U_2N_3 phase boundary to $a = 10.58$ at $UN_{1.75}$ (Katz and Rabinowitch, 1951). At the same time the weak diffraction lines disappear, being apparently gone at $UN_{1.75}$. This is interpreted to mean that the distortion in the basic fcc lattice is reduced by the addition of nitrogen until at UN_2 the structure becomes totally fcc. Unfortunately, this process has not been followed above $UN_{1.75}$. Not only does this view require an initial lattice contraction as nitrogen is added, but a minimum in the bond distances in the region between $UN_{1.75}$ and $UN_{2.0}$ as well. On the other hand, Keller (1962) found two phases present at room temperature in

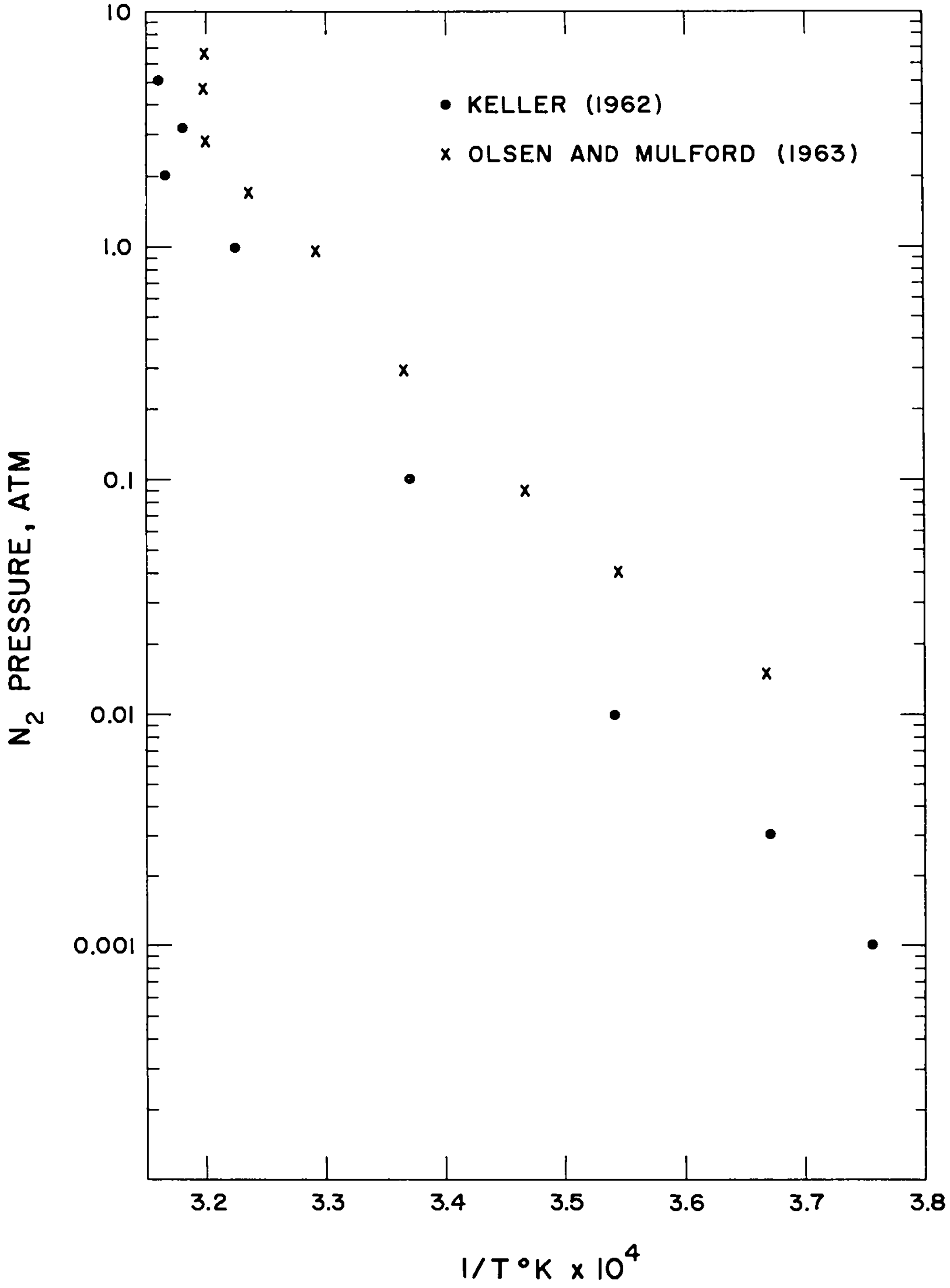

Figure III. 2. 2 The Melting Point of UN as a Function of Nitrogen Pressure samples of a composition between $UN_{1.62}$ and $UN_{1.75}$. At 800°, however, the change in N_2 pressure with composition indicates that a solid solution exists (Keller, 1963).

After examining surface layers of the uranium nitrides, prepared by Mallett and Gerds (1955), Vaughan (1956) proposed a new phase isomorphous with Th_2N_3. Recently, Trzebiatowski and co-workers (1962) found this phase in material which was quenched from 1000°, but not in samples containing more nitrogen than $UN_{1.50}$. This phase, designated β, has lattice constants of $a = 3.700$, $c = 5.826$ A (hexagonal) and shows ferromagnetic properties at low temperatures, a behavior which is completely different from the normal bcc α-U_2N_3. Benz and Bowman (1964) found the transition temperature at 1120 ± 30°. At 1315°, the region between UN and U_2N_3 consists of a two-phase mixture of $UN_{1.0}$ and $UN_{1.49 \pm 0.02}$. In view of this work, the doubts concerning the existence of the β form expressed by Evans (1962) do not seem justified.

Rundle and co-workers (1948) gave UN_2 a lattice parameter of $a = 5.301$ A.

Appearance

All of the uranium nitrides appear to have a gray to black color when pure.

Chemical Stability

The nitrides are easily oxidized, U_2N_3 in particular. At 150-200° the powder will burn in air. Reaction with O_2 begins at 250°, with H_2O at 230°. There is apparently no reaction with H_2 (Francis and Hodge, 1961).

UN is attacked by concentrated HNO_3, but cold HCl, H_2SO_4 or NaOH solution are without effect (Kohlschütter, 1901). Molten alkali, however, will liberate NH_3. The water corrosion resistance of UN is superior to UC. Specimens held in degassed, deionized water at 26°C showed only a slight weight loss (Speidel and Keller, 1963).

Hardness

Tripler and co-workers (1959) reported a hardness of 542 (100 g Knoop) for UN which probably contained some UO_2 phase. Speidel and Keller (1963) observed a hardness of 580 (100 g Knoop).

Electrical Resistivity

Taylor and McMurtry (1961) report a value of 208 μohm-cm at room temperature for UN with 18% porosity. Work reported by Speidel and Keller (1963) yielded a value of 176 μohm-cm at 200° and a positive temperature coefficient.

Superconductivity

Hardy and Hulm (1954) found that their sample of UN was not superconducting at 1.2°K. However, the preparation procedure was not described and an analysis was not given.

Thermodynamics

The heats of formation of UN and U_2N_3 have been measured by the direct reaction of the elements in a heated calorimeter (Gross and co-workers, 1962). The values obtained were $\Delta H° = -69.6 \pm 0.4$ kcal/mole for the reaction $U + 1/2\ N_2 = UN$ and -29.15 ± 0.5 kcal/mole for the reaction $2UN + 1/2\ N_2 = U_2N_3$. Using oxygen combustion, Hubbard (1962) obtained $\Delta H^\circ_{f298} = -70.95 \pm 0.67$ kcal/mole. These measurements can be compared to an early value of -68.5 kcal/mole (Neumann et al., 1932) and a value of -74.5 kcal/mole obtained from vapor pressure measurements (Vozzella and co-workers, 1964).

Speidel and Keller (1963) have reported the following equation for the heat content of UN between 422° and 3098°K:

$$H_T - H_{273} = 13.3211T + 5.9302 \times 10^{-4}T^2 + 2.1025 \times 10^5 T^{-1} - 4437.2$$

Vaporization

Approximate measurements of the nitrogen pressures over $UN_{1.56}$ to $UN_{1.65}$ at various temperatures, made at Battelle (BMI-CC-2700, 1945; BMI-CT-1697, 1944), are reported in the survey by Katz and Rabinowitch (1951).

Using Knudsen effusion, Vozzella and co-workers (1964) have measured the pressure of N_2 and U over $UN_{(s)}$. The N_2 pressure was found to vary from 1.5×10^{-7} to 5×10^{-5} atm over the temperature range 1910 to 2265°K, and the uranium pressure was about a factor of two below that reported by Rauh and Thorn (1954) for pure $U_{(l)}$. The condensation coefficient for N_2 on UN was estimated from a Langmuir experiment to be 0.01.

Benz and Bowman (1964) found that below 2115°C, a bare plug of UN vaporized congruently.

A mass spectrometric study by Cavett and Bonham (1963) gave a ratio of vaporization rates, Q_{N_2}/Q_U, of 2.0×10^4 at 1800°C from a W Knudsen cell. No vapor species other than U and N_2 were reported.

III. 2.3 The Plutonium-Nitrogen System

Preparation

The scarcity of Pu metal and its high level of alpha activity have severely limited the work done on this system. Brown and co-workers (1955) have described in some detail a preparation procedure. They found that Pu metal reacts only slowly with N_2 even at 1000°C. However, the hydride will react with N_2 at 230° to form pure PuN. Their procedure was to convert the metal to $PuH_{2.7}$ by heating in H_2, then, after the reaction was complete, slowly raise the temperature to 800° while the H_2 was flushed out with pure N_2. After 2 hr the sample was cooled. Rand and Street (1962) note that with only a trace of H_2 in the N_2, Pu metal could be converted to the nitride at 600°. They subsequently heated the product in vacuum at 1500° to decompose any hydride. PuN has also been made by heating the hydride in NH_3 at 650°C and 250 torr (Westrum, 1949). Attempts to prepare PuN by arc melting resulted in only an 80% conversion to the nitride (Olson and Mulford, 1964).

Phase Relationship and Lattice Parameter

Nothing is known concerning the phase relationship in this system, and only the compound PuN has been reported.

PuN is fcc (NaCl-type) (Zachariasen, 1949) with a lattice parameter of $a = 4.906 \pm 0.001$ (Carroll, 1962; Brown and co-workers, 1955). Because of radiation damage, this value will increase with time (Rand et al., 1962). Studies of thermal expansion have revealed no phase change up to 1000° (Carroll, 1962; Rand and Street, 1962). Rand and Street (1962) found that $PuN_{0.907}$, prepared at 1500°, exhibited a lattice contraction after being held above 900° in a silica tube. It was suggested that this was due to the formation of a more nearly stoichiometric nitride which was characteristic of the lower temperature. Olsen and Mulford (1964) could find no difference in lattice parameter between samples quenched rapidly from 1500° or 2700°. Their samples had an average analysed composition of $PuN_{0.955}$. Anselin and co-workers (1963) observed that PuN cooled from 1400° had a higher parameter than that cooled from a higher or lower temperature. They also found that the presence of oxygen raised the parameter. More work is clearly needed before any conclusions can be made concerning the homogeneity range of PuN.

Olsen and Mulford (1964) have measured the apparent melting point of PuN as a function of nitrogen pressure. Their data can be fit by the following equation:

$$\log P\ (\text{atm}) = 8.193 - 29.54 \times 10^{3}/T + 11.28 \times 10^{-18} T^{5} \quad (2563\text{-}3043\,°\text{K})$$

Congruent melting was not observed up to 25 atm.

Appearance

Brown and co-workers (1955) found that freshly prepared PuN was black but, it should be noted, turned brown after a few days due to hydrolysis.

Chemical Stability

PuN hydrolyzes in moist air and cold water. Hot water causes an immediate decomposition. HNO_3 attacks the nitride only upon heating (Brown and co-workers, 1955). PuN is such a good getter that even a normally good vacuum will not protect it while hot (Carroll, 1962). Olsen and Mulford (1964) observed that PuN powder if exposed for only a brief time to air would acquire up to 0.9% oxygen. Also freshly prepared PuN powder was found to be pyrophoric in air.

Hardness, Electrical Resistivity, Superconductivity, Thermodynamic Properties

No measurements could be found in the literature.

Vaporization

PuN held at 1700° for 30 min was found to have lost 58% of the original plutonium and produced a condensate which was a mixture of PuN and Pu (Anselin and Pascard, 1962).

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