AD NUMBER

482 360

CLASSIFICATION CHANGES

TO

FROM

AUTHORITY

WRDC/IST LTR dtd 21 MAR 89
(For Entries 11 thru)

AFML-TR-65-2
Part II, Volume VII

TERNARY PHASE EQUILIBRIA IN TRANSITION METAL-BORON-CARBON-SILICON SYSTEMS

Part II. Ternary Systems
Volume VII. The Ti-Si-C, Nb-Si-C, and W-Si-C Systems

C. E. Brukl

Aerojet-General Corporation

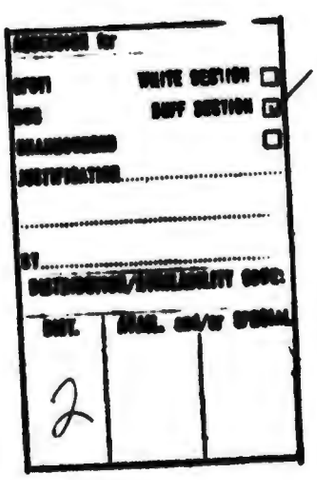
TECHNICAL REPORT NO. AFML-TR-65-2, Part II, Volume VII

December 1965

Air Force Materials Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation, whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.



Copies of this report should not be returned to the Research and Technology Division unless return is required by security consideration, contractual obligations, or notice on a specific document.

(18) AFML (19) TR-65-2-Pt-2-Vol-7
Part II, Volume VII

(6) TERNARY PHASE EQUILIBRIA IN TRANSITION METAL-BORON-CARBON-SILICON SYSTEMS.

Part II. Ternary Systems.
Volume VII. The Ti-Si-C, Nb-Si-C, and W-Si-C Systems,

(10) C. E. Brukl.

(11) Dec 65;
(12) 57p.
(15) AF 33(615)-1247
(16) AF-7350
(17) 735001

FOREWORD

The work described and illustrated in this report was performed at the Materials Research Laboratory, Aerojet-General Corporation, Sacramento, California under USAF Contract No. AF 33(615)-1249. The contract was initiated under Project No. 7350, Task No. 735001. The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division with Captain R. A. Peterson and Lt. P. J. Marchiando acting as Project Engineers, and Dr. E. Rudy, Aerojet-General Corporation as Principal Investigator. Professor Dr. Hans Nowotny, University of Vienna, Austria, served as consultant to the project.

The project, which includes the experimental and theoretical investigation of selected refractory ternary systems in the system classes Me_1-Me_2-C, Me-B-C, Me_1-Me_2-B, Me-Si-B and Me-Si-C was initiated on 1 January 1964.

The experimental program was laid out by E. Rudy, and the author wishes to acknowledge the assistance given by Dr. E.Rudy. D. Harmon, J. Hoffman, R. Radtke, R. Cobb and J. Pomodoro were of valuable assistance in the preparation of the experimental work.

Chemical analyses of the alloys was carried out under the supervision of Mr. W. E. Trahan, Metals and Plastics Chemical Testing Laboratory, Aerojet-General Corporation. The writers also wish to thank Mr.R. Cristoni, who prepared the many drawings, and Mrs. J. Weidner who typed the report.

Other reports issued under USAF Contract AF 33(615)-1249 have included:

Part I. Related Binaries

- Volume I. Mo-C System
- Volume II. Ti-C and Zr-C Systems
- Volume III. Mo-B and W-B Systems
- Volume IV. Hf-C System
- Volume V. Ta-C System. Partial Investigation of the Systems V-C and Nb-C.
- Volume VI. W-C System, Supplemental Information on the Mo-C System.
- Volume VII. Ti-B System
- Volume VIII. Zr-B System
- Volume IX. Hf-B System
- Volume X. V-B, Nb-B, and Ta-B Systems

Part II. Ternary Systems

- Volume I. Ta-Hf-C System
- Volume II. Ti-Ta-C System
- Volume III. Zr-Ta-C System

FOREWORD (Cont'd)

Volume IV. Ti-Zr-C, Ti-Hf-C, and Zr-Hf-C Systems
Volume V. Ti-Hf-B System
Volume VI. Zr-Hf-B System

Part III. Special Experimental Techniques

Volume I. High Temperature Differential Thermal Analysis.

Part IV. Thermochemical Calculations

Volume I. Thermodynamic Properties of Group IV, V, and VI Binary Transition-Metal Carbides

This technical report has been reviewed and is approved.

W. G. RAMKE
Chief, Ceramics and Graphite Branch
Metals and Ceramics Division
Air Force Materials Laboratory

ABSTRACT

Phase equilibria in isothermal sections of the ternary Ti-Si-C, Nb-Si-C, and W-Si-C systems were established with X-ray films employing the Debye-Scherrer powder technique. The Ti-Si-C system contains a new ternary phase near the composition "Ti_2SiC"; the Nb-Si-C system also has a known ternary phase near the Nb-Si binary, whereas the W-Si-C system exhibits no ternary compounds.

With the exception of the Ti_5Si_3 phase, the mutual solubilities of the binary carbide and silicide phases are exceedingly small or nonexistent.

The results of these investigations are compared with other previous investigations.

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

LIST OF ILLUSTRATIONS

LIST OF TABLES

I. INTRODUCTION AND SUMMARY

A. INTRODUCTION

In the continuing research on binary and ternary carbide, boride, silicide, borocarbide, silicocarbide, and silicoboride systems containing the refractory metals of the IVa-VIa periodic groups, solid-state sections of three silicocarbide systems have been investigated.

Although the exact constitution diagrams of the majority of refractory silicides, particularly in the high temperature regions, are not known, the information present is sufficient in most instances for solid-state interpretation of some ternary silicocarbide systems.

The oxidation resistance of some of the refractory silicides has been known for quite a while, and the oxidation resistance of silicon carbide is known to be quite good at temperatures below about 950°C. It is interesting, therefore, to gain an insight into the phase equilibria and mutual solubilities exhibited by the phases in various refractory silicocarbide systems, inasmuch as refractory silicide-refractory carbide mixtures could, and have, come into consideration in the oxidation protection of carbides. Refractory silicide impregnation and coating are also methods proposed for the protection of graphite; it is therefore beneficial to know the possible phase interactions of such combinations.

Not until detailed investigations of the binary silicide systems, in particular the group IVa metal-silicides are conducted, will we be able to completely interpret results in the solid-liquid region of such refractory silicocarbide ternary systems.

B. SUMMARY

Solid-state sections of the Ti-Si-C, Nb-Si-C, and W-Si-C ternary systems were investigated using X-ray powder patterns of heat

treated samples prepared by hot pressing. In isolated experiments, differential thermal analysis as well as melting point studies were conducted.

1. Binary Carbide Systems

The binary titanium-carbon and tungsten-carbon systems have been extensively investigated and recently described in previous reports[1,2] (Figures 1 and 4). A partial investigation of the Nb-C system has also been performed[3] (Figure 2). In investigations concerning this report, the basic findings of other authors[4-10] that NbC_{1-x} has a considerable homogeneous range, but that Nb_2C has a rather small single phase region at lower temperatures, were confirmed.

2. Binary Silicide Systems

At 1200°C no evidence of the existence of a proposed Ti_3Si phase[11] was detected in the titanium-silicon system; the existence of the other binary silicide phases Ti_5Si_3, TiSi, and $TiSi_2$ as well as the as yet unknown, U-1 was confirmed.

By the same token, the established binary silicide phases in the Nb-Si and W-Si systems were reconfirmed; a proposed Nb_3Si[11] as well as the high temperature Nb_4Si phase were not observed in samples sintered at 1300°C. It was proven that a proposed "W_3Si" phase[12] does not exist at high temperatures; the eutectic temperature in this region of the W-Si system is close to 2065°C.

3. Ternary Silicocarbide Systems

a. The Titanium-Silicon-Carbon System (Figure 13)

In investigations at 1200°C, a new ternary phase which lies close to the composition "Ti_2SiC" was found. This phase is in equilibrium with $TiSi_2$, SiC, TiC_{1-x}, and Ti_5Si_3(C). $TiSi_2$ is in equilibrium with SiC, the new ternary phase, and the solid solution of Ti_5Si_3 (C). There

is a rather wide two-phase region between TiC_{1-x} and $Ti_5Si_3(C)$. Ti_5Si_3 takes about 8 atomic percent carbon into solid solution; the other binary carbide and silicide phases show only an extremely small, or no, mutual solubility.

b. The Niobium-Silicon-Carbon System (Figure 16)

A ternary Nowotny-phase with a small homogeneous range is present relatively close to the Nb-Si binary; this phase is in equilibrium with α-Nb_5Si_3, $NbSi_2$, and NbC_{1-x} at 1300°C. NbC_{1-x} is in equilibrium with SiC, $NbSi_2$, the ternary Nowotny-phase, and α-Nb_5Si_3, whereas $NbSi_2$ is in equilibrium with NbC_{1-x}, SiC, and the ternary Nowotny-phase. All the binary silicide and carbide phases show virtually no, or at best, an exceedingly slight mutual solid-solubility.

c. The Tungsten-Silicon-Carbon System (Figure 20)

There are no ternary phases present in this system at 1800°C; the equilibrium is characterized by the binary silicide and carbide phases, none of which shows any solubility into the ternary region. WSi_2 is in equilibrium with SiC; W_5Si_3 with SiC, WC, and W_2C; WC with SiC and W_5Si_3; and α-W_2C with W_5Si_3.

II. LITERATURE REVIEW

A. BINARY SYSTEMS

1. The Titanium-Carbon System

There have been many investigations on the titanium-carbon system; all agree in general with the exception that additional investigations were necessary to ascertain the lower metal-rich limit of the monocarbide defect structure and to determine whether the β-Ti phase decomposes peritectically or forms a eutectic with the monocarbide. A complete listing

of the many older papers is found in M. Hansen's Constitution of Binary Alloys[13] and in Hartstoffe[14] by Kieffer and Benesovsky as well as in A Critical Review of Refractories[15] by E. K. Storms.

An exact determination of the constitution of the titanium carbon system was undertaken at this laboratory[1] to provide valid starting points for the ternary systems under investigation with the present Air Force contract.

The important features of this system at temperatures above 1200°C are: (Figure 1).

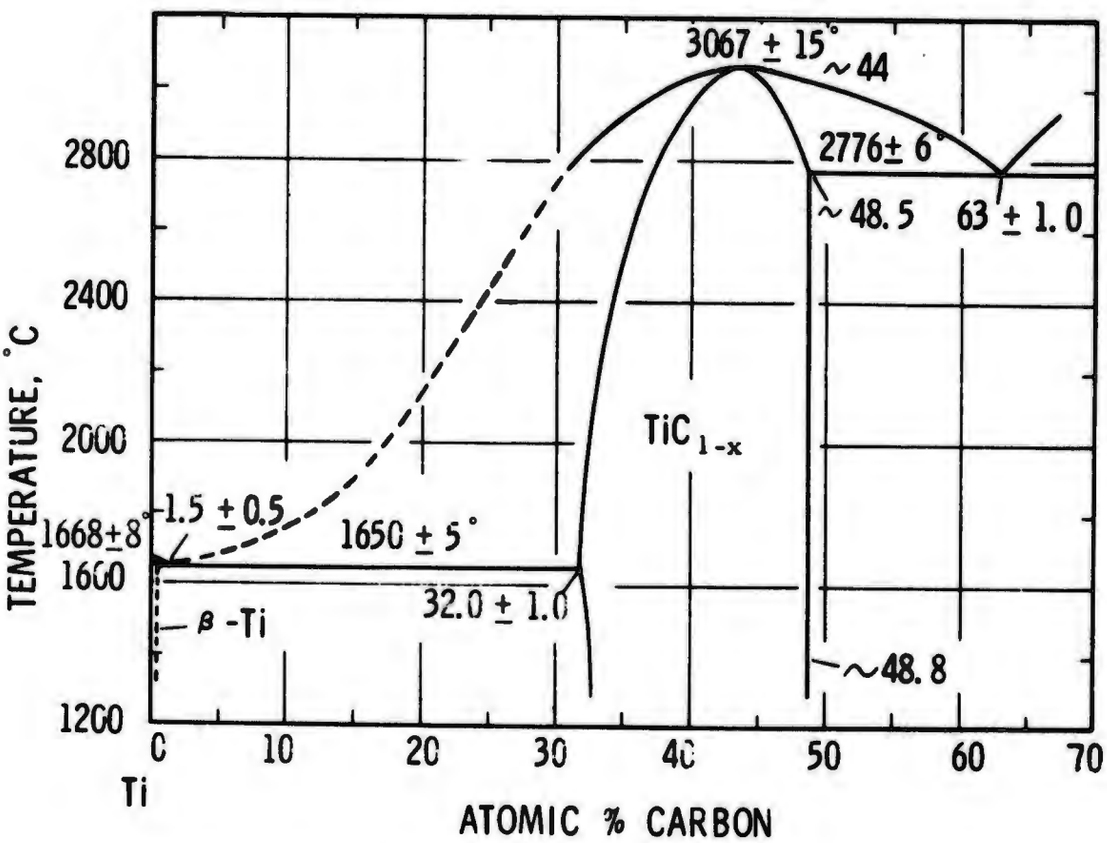


Figure 1. Ti-C: Constitution Diagram.

(E. Rudy, C.E. Brukl, and D.P. Harmon, 1965).

The only intermediate phase, titanium monocarbide, possesses a wide homogeneous range from 32 At.% C, at the eutectic temperature of 1650°C, to 48.8 At.% C; it melts congruently at 3067°C at 44 At.% C. Between β-Ti, whose carbon solubility is less than 1 At.%, and the carbon defect monocarbide there is a eutectic at 1.5 At.% C. The eutectic temperature is 1650°C. On the carbon-rich side of the monocarbide a eutectic exists at 63 At.% C between $TiC_{0.94}$ and graphite. This eutectic temperature is 2776°C. The maximum lattice parameter of the cubic monocarbide structure is 4.330 Å at 48.5 At.% C; the smallest is 4.285 Å on the metal-rich boundary (32 At.% C) of the homogeneous range.

2. The Niobium-Carbon System

There have been a considerable number of complete and partial investigations in the niobium-carbon system[4-9, 16-22]. In general, the constitution diagram appears to be quite similar to that of the tantalum-carbon system.

Two intermediate phases, Nb_2C and NbC, are definitely known to exist[16-18]. A third phase, the so-called Brauer ζ-phase[5] at a composition of about Nb_3C_2, has been observed and probably is the result of a non-equilibrium epitaxial precipitation from the carbon-defect monocarbide solid-solution. This would be similar to the findings in the Ta-C system[3, 23].

Niobium is reported[9] to take 100 ppm carbon into solid-solution at 1500°C, 2 At.% C at 2000°C[10], and about 7 At.% C at the eutectic temperature[9]. The eutectic existing between the niobium solid solution and the Nb_2C phase is reported to be[10] located near 13.5 At.% C. According to the literature cited, the eutectic temperature is: 2335°C[7, 8], 2340°C[10], 2335°C[20], and 2328°C[22]. There have been various values reported for the homogeneous range of the Nb_2C phase. Brauer and co-workers[4-6] report that the Nb_2C phase exists between 33 and 26 At.% C; these values were later slightly modified by the same author. On the other hand, Elliott[9] reported that the homogeneous range of Nb_2C lies between about 31 and

32.5 At.% C. Storms and Krikorian[7, 8] have shown that the homogeneous range of the Nb_2C phase is strongly temperature dependent. At the α-Nb-Nb_2C eutectic temperature the metal-rich boundary of the Nb_2C phase is at about 28 At.% C[7, 8], and at the peritectic decomposition temperature of Nb_2C the carbon-rich boundary is located at about 34.2 At.% C[7, 8]. Below about 2000°C the homogeneous range of the Nb_2C phase decreases rapidly and encompasses only a very narrow range about the stoichiometric Nb_2C composition[7, 8, 10].

The peritectic decomposition temperature of the Nb_2C is recorded as being 3090°C[7, 8] and 3080°C[22, 10].

The NbC phase also has a considerable homogeneous range. G. Brauer[4-6] has reported the single phase region to be between about 41.5 and 48.0 At.% C; Storms and Krikorian [7, 8] report 41.2 to 48.8 At.% C.

Due to the fact that both metal and carbon losses become appreciable at the high melting temperatures of the monocarbides, varying melting points have been reported for NbC. It is almost certain, however, that the maximum congruent melting point of NbC is not at the stoichiometric composition, but somewhere in the vicinity of 46 At.% C[15] the following melting points have been reported for NbC: 3500°C for $NbC_{0.86}$[7, 8], 3480°C[22], 3485°C for $Nb_{0.95}$[23], and 3600°C[10].

The monocarbide and graphite form a eutectic at 60.5 At.% C[10]. The eutectic temperature is reported as being 3220°[22], 3250°[7, 8], and 3300°C[10].

Since investigations in this laboratory of the melting behavior of ternary carbide systems with niobium indicated a higher melting point for NbC than reported in the majority of available literature, a partial investigation of the carbon-rich portion of the Nb-C system was made by E. Rudy[3]. The results are shown in Figure 2.

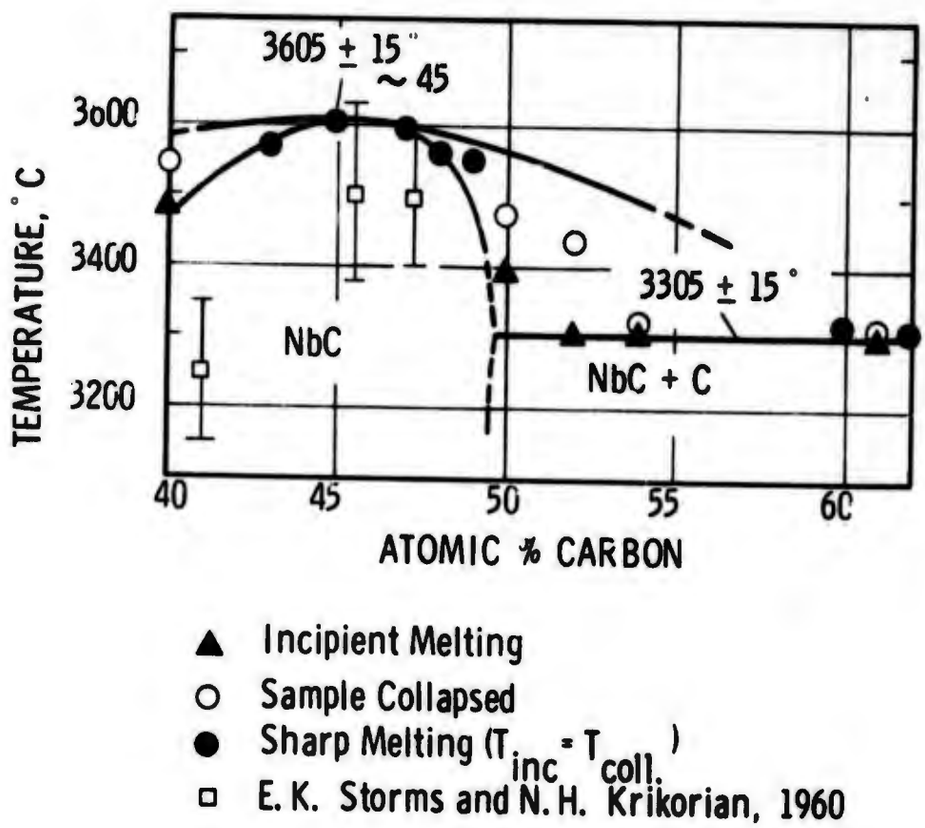


Figure 2. Nb-C: Melting Temperatures of the Monocarbide Phase and the Carbon-Rich Eutectic.

The monocarbide melts congruently at 3605°C at a composition near 45 At.% carbon. The carbon-rich eutectic isotherm is at 3305°C and the eutectic point is located near 60 At.% carbon. These results are in excellent accord with the values reported by Kimura and Sasaki[10].

In addition to the confirmed higher melting point for NbC_{1-x}, a structural phase transition, similar to that in the Ta_2C phase[3], was observed in the Nb_2C phase at approximately 2460°C. A paper by E. Rudy to be published shortly, will contain a modified version of the Nb-C system incorporating the latest experimental findings.

Because the most recent findings in this laboratory[3] have confirmed the higher melting point of NbC_{1-x}, and other cursory investigations in the Nb-C system have indicated that the phase diagram of the Nb-C system by Kimura and Saski[10] is the closest to being the true representation of the Nb-C system, it is depicted here in Figure 3.

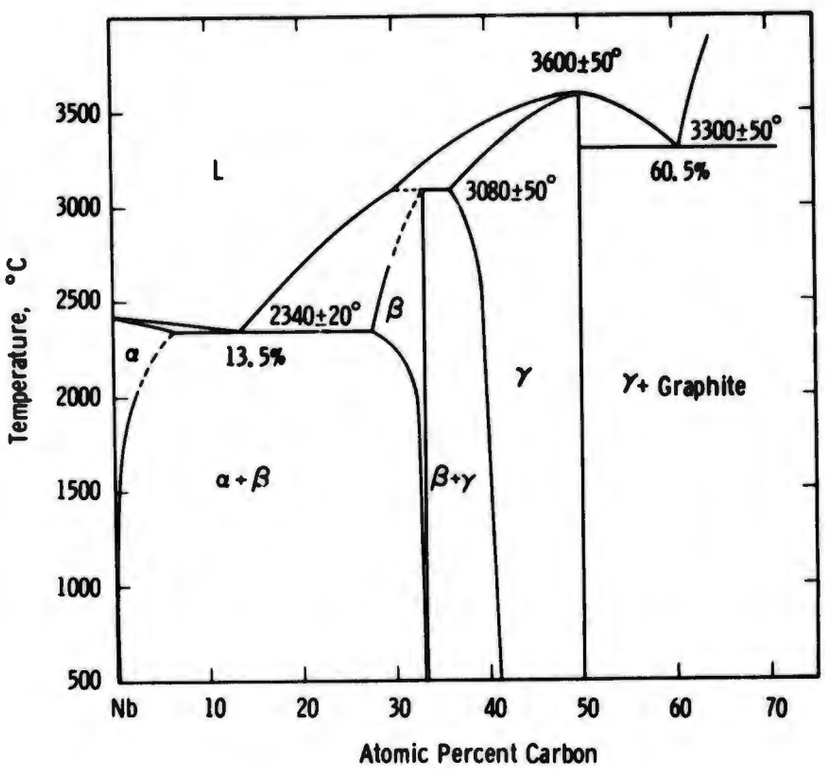


Figure 3. Nb-C: Constitution Diagram.
(H. Kimura and Y. Saski, 1961).

Table 1 shows the crystal structures and lattice parameters of the intermediate Nb-C compounds.

3. The Tungsten-Carbon System

Until quite recently the tungsten carbon system had been assumed to be quite well known and of a not too complex type. The constitution diagram of the tungsten-carbon system as proposed by W. Sykes[24] in 1930 was the accepted model. The phases known to exist at that time were

Table 1. Crystal Structures and Lattice Parameters of Intermediate Nb-C Phases

Phase	Crystal Structure and Type	Lattice Parameters in Å	Literature
α-Nb_2C	hexagonal, L'3	a = 3.117 - 3.126 c = 4.954 - 4.968	4
NbC_{1-x}	cubic, B-1	4.433 - 4.466	4
$Nb_3C_2(\zeta)$	unknown	-	4

W_2C and WC. Other investigations,[25-28] as well as more recent ones[29-33], have shown that other intermediate phases are indeed present, and that the high temperature behavior of this binary system is far more complex than originally contemplated. A suspected phase change (involving the carbon lattice) in the W_2C phase has been observed[25] and confirmed[26-28, 2]. There is a high temperature β-W_2C as well as the low-temperature α-W_2C. A face-centered-cubic high temperature phase at compositions somewhat carbon poorer than WC (designated as WC_{1-x}) has been discovered[29] and its existence confirmed[31-33, 2]

Using the findings of their recent, very extensive investigations, R. Doloff and R. Sara[32, 33] established a new phase diagram which incorporates the majority of the newer findings in the tungsten-carbon system.

An excellent literature review on the many papers concerned with the investigations of the tungsten-carbon system is given by E. Rudy, St. Windisch, and Jr. R. Hoffman in their report on the Tungsten-Carbon system[2].

To be able to interpret the complicated behavior in some ternary carbide systems with tungsten which are being investigated under the present Air Force Contract, this laboratory undertook an exhaustive

investigation of the tungsten-carbon system[2]. The results of these studies are presented in the constitution diagram of the system shown in Figure 4.

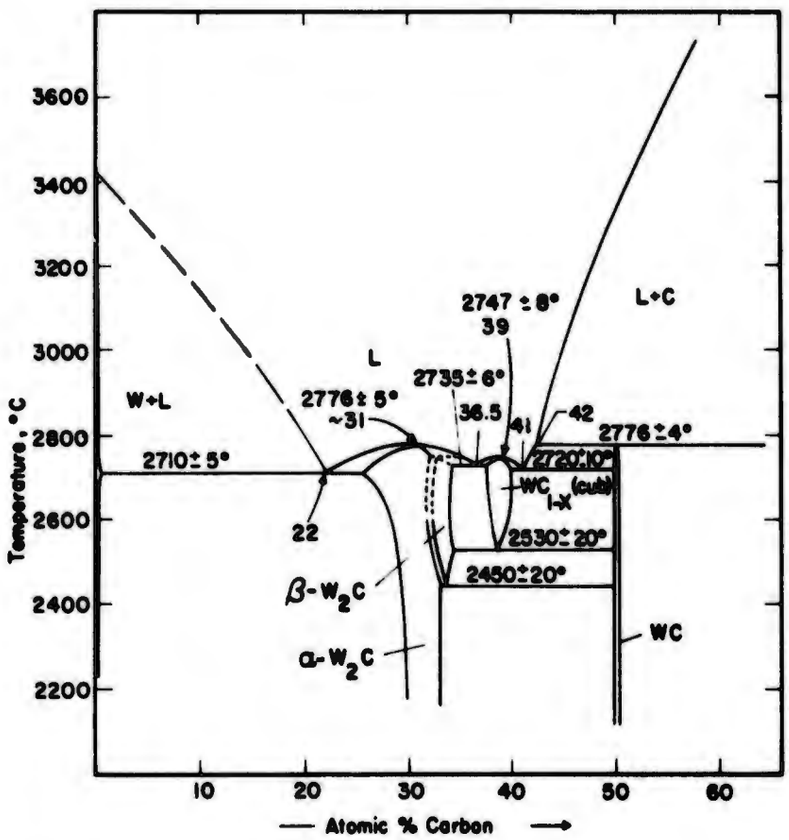


Figure 4. W-C: Constitution Diagram.
(E. Rudy, St. Windisch, and J. R. Hoffman, 1965).

The results of these investigations agree in general quite well with the previous results of Doloff and Sara[32, 33] with the exception of the α-β phase separation of the W_2C phase, the homogeneous range of the WC_{1-x}(cubic) phase, and the decomposition of the WC phase.

Four intermediate phases are present: α-W_2C, β-W_2C, α-WC_{1-x} (cubic) and WC (hexagonal).

The α-W_2C, the low temperature form of the subcarbide exists in the temperature range 2776° - 1250°C. At low temperatures, this

phase spans a composition range of 29.2 to 33.3 At.% carbon; at 2710° the homogeneous range is 25.6 to 32 At.% carbon. α-W_2C melts congruently at 2776°C and decomposes in a very slow eutectoid reaction to WC and W at temperatures below and about 1250°C. This phase forms a eutectic with tungsten; the eutectic temperature is 2710°C, and the eutectic point is located at 22 At.% carbon.

The β-W_2C, which differs only in the degree of order of the carbon lattice, exists between about 2750° and approximately 2450°C over the composition range of 32-35 At.% carbon. It decomposes peritectically into a α-W_2C and melt at 2750°C, and also decomposes eutectoidally into α-W_2C and WC at about 2450°C as well as undergoing a continuous phase change to α-W_2C at substoichiometric compositions in the given temperature range.

The cubic high temperature α-WC_{1-x} phase melts congruently at 2747°C at 39 At.% C and rapidly decomposes eutectoidally into β-W_2C and WC at 2530°C. This high temperature phase exists between 37.5 and 40 At.% carbon and furthermore forms eutectics with both β-W_2C (2735°C) at 36.5 At.% C) and WC (2720°C at 41 At.% C).

The other remaining phase in the W-C system, WC, possesses a very slight homogeneous range and decomposes peritectically (42 At.% C) into melt and graphite at 2776°C. The WC phase is stable at all temperatures up to its decomposition point.

Table 2 lists the intermediate compounds in the W-C system and gives their crystal structures with lattice parameters.

4. Silicon-Carbon System

In spite of the fact that silicon monocarbide is the basis of many commercial abrasive items by virtue of its high hardness, as well as being used in many high temperature applications, the constitution diagram of the silicon-carbon system has never been completely established.

Table 2. Crystal Structures and Lattice Parameters of the Tungsten-Carbon Intermediate Compounds.

Phase	Crystal Structure	Lattice Parameter	Literature
α-W_2C	hexagonal	a = 2.985 - 3.001Å c = 4.717 - 4.728Å	2
	anti-hexagonal cadmium- (C6)		34
		a = 2.993Å c = 4.727Å	35
β-W_2C	hexagonal	a = 3.002Å c = 4.75 - 4.76Å	2
α-WC_{1-x}	cubic NaCl Type(B-1)	a = 4.220Å	2
		a = 4.23Å	29
		a = 4.25Å	31
		a = 4.215 Å	32, 33
WC	hexagonal(Bh)	a = 2.906Å c = 2.837Å	2
		a = 2.907 Å c = 2.837Å	36
		a = 2.9063 c = 2.8368	37

Many different, but closely related, crystal polymorphs of SiC, (apparently the only intermediate compound observed in this system) have been observed, isolated, and their crystal structures determined[38]. These so called α-forms have either hexagonal or rhombohedral symmetry, and the various polymorphs are based on different atom stacking sequences[39]. A lengthy listing of the many works is given in Constitution of Binary Alloys[13]. A face-centered cubic form, the β-SiC (B3-type), a low temperature modification with a lattice parameter of 4.349 Å, has also been observed[39].

H. Nowotny and co-workers[40] performed exploratory investigations in the silicon-carbon system using X-ray, chemical, and thermal analyses. On the basis of these experiments, two possible phase diagrams for the silicon-carbon systems were developed. Figure 5 presents the version containing a eutectic-similar reaction involving liquid silicon with carbon in solution, solid SiC, and vapor. The other version proposes a

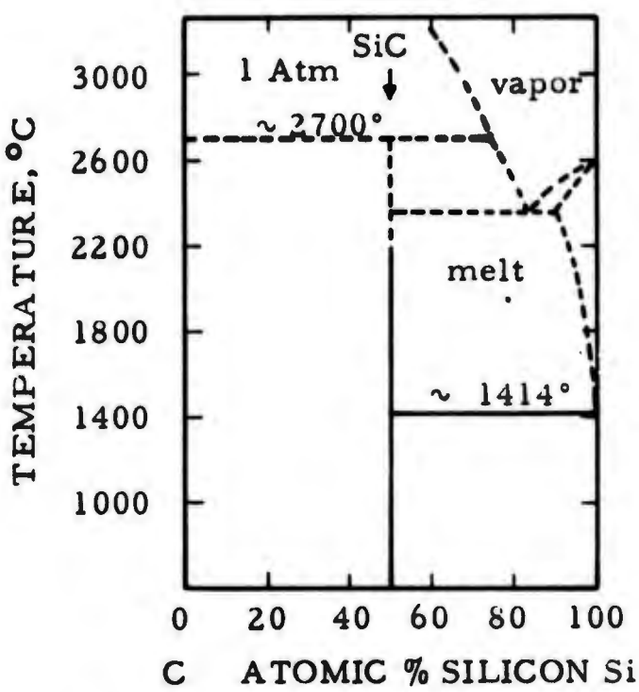


Figure 5. Si-C: Possible Constitution Diagram.
(H. Nowotny, et al., 1954).

peritectic-similar decomposition of liquid silicon with carbon in solution into solid SiC and vapor. Due to the small temperature difference between the melting point of pure silicon and silicon-carbon alloys lying between Si and SiC, it was not possible to determine whether a eutectic or peritectic reaction is present at lower temperatures. Both proposed diagrams display the decomposition of SiC into graphite and vapor at about 2700°C. This decomposition temperature of SiC has also been independently reported by O. Ruff[41].

5. The Titanium-Silicon System

Of the IVa group metal-silicon systems, Ti-Si, Zr-Si, and Hf-Si, the titanium-silicon system appears to be the least complicated although all details of the constitution diagram have not yet been completely clarified.

Three compounds are definitely known to exist; they are $TiSi_2$[43-45], TiSi[46, 47], and Ti_5Si_3[48-50]. Fairly recent publications show that K. Schubert[11] has found a Ti_3Si phase existing in the Ti_3P crystal structure; H. Nowotny[51] and co-workers have ascertained that another intermetallic phase is present in the titanium-silicon system at about 45 At.% silicon; this phase is isostructural with phases of similar composition in the Zr-Si and Hf-Si systems; the crystal structure and exact characteristics of this phase have not been determined.

In an extensive investigation M. Hansen[46] and co-workers have investigated the titanium-silicon system by means of micrographic, thermal analysis, melting point, and X-ray analysis methods; the phase diagram presented by these authors is reproduced for temperatures above 1000°C in Figure 6. β-titanium dissolves about 5 At.% silicon at the

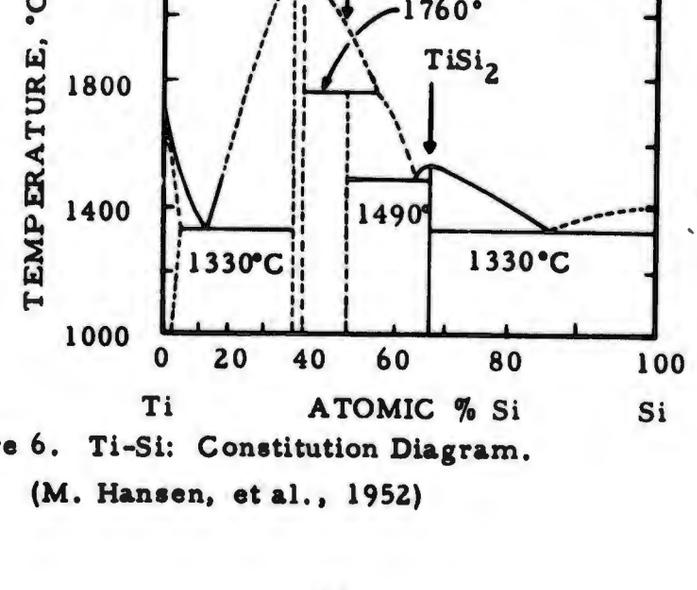


Figure 6. Ti-Si: Constitution Diagram.
(M. Hansen, et al., 1952)

eutectic temperature; β-titanium and Ti_5Si_3 form a eutectic at 13.6 At.% Si and 1330°C. The Ti_5Si_3 phase has a small range of homogeneity and melts congruently at 2120°C. TiSi decomposes peritectically to Ti_5Si_3 and liquid at 1760°C; a eutectic exists between TiSi and $TiSi_2$ at about 64.4 At.% Si — the eutectic temperature is 1490°C. $TiSi_2$ melts congruently at 1540°C and forms a eutectic at 85.8 At.% Si with silicon metal at 1330°C. There is virtually no titanium solubility in solid silicon.

The crystal structures and lattice parameters of the titanium-silicon intermediate phases are presented in Table 3.

Table 3. Crystal Structures and Lattice Parameters of Ti-Si Intermediate Compounds.

Phase	Crystal Structure	Lattice Parameter	Literature
$TiSi_2$	Orthorhombic C54 $TiSi_2$-type	a=8.252Å, b=4.783Å c = 8.540Å	43
TiSi	Orthorhombic, B27 FeB-type	a=6.53$_1$Å, b=3.63$_1$Å c=4.98$_7$Å	47, 52
Ti_5Si_3	Hexagonal, $D8_8$ Mn_5Si_3-type	a=7.465Å, c=5.162Å	48
$Ti_{\sim 55}Si_{\sim 45}$	Unknown but isostructural with Hf-Si and Zr-Si phases	- -	51
Ti_3Si	Tetragonal, DO_e Ti_3P-type	a=10.39Å, c=5.17Å	11

It has been shown[51] that one of the structure determinations[45] of $TiSi_2$ was incorrect, and the findings that $TiSi_2$ possesses the $ZrSi_2$-C49 type were due to aluminum contamination stemming from the aluminothermic reduction of the silicon used.

Inasmuch as two new phases have been found recently in the titanium-silicon system[11, 51] it seems apparent that a reinvestigation of the Ti-Si system is necessary. Furthermore, the question of whether or not the Ti_5Si_3 compound is definitely a pure binary phase, or just a metalloid stabilized ternary phase has not been completely clarified.

6. The Niobium-Silicon System

Because carbon stabilizes a ternary phase in the region around 38 At.% silicon in the niobium-silicon system[53-56], clarification of the exact characteristics of the central portion of this system was difficult. In addition, due to the pecularities of the phase Nb_4Si, many investigations[56-62] have been concerned with alloys in this region.

There are three intermediate phases which have been shown to exist in the Nb-Si system; one of these, the Nb_5Si_3 phase, undergoes a high temperature transformation[57, 60]. The known phases are $NbSi_2$[63] α-Nb_5Si_3[57, 60], β-Nb_5Si_3[57, 60], and Nb_4Si[56-60].

It would seem possible that the Nb_4Si phase, which has always been denoted by the approximate formula at 20 At.% Si, is in reality the Nb_3Si phase identified recently by K. Schubert[11].

Although the crystal structure of $NbSi_2$ was ascertained at an early stage[63], the structures of the two forms of Nb_5Si_3 were determined at a much later date[57, 60]. Original studies by Brauer and Scheele[64] showed a "Nb_2Si" which existed in two modifications; in addition to the two modifications mentioned above, a further modification was found at Nb_5Si_3 by L. Brewer and O. Krikorian[56].

It was subsequently shown by H. Nowotny[53-55] and co-workers as well as by A. G. Knapton[65] that the binary phase discovered by Brewer and Krikorian[56] was in reality a ternary $D8_8$ phase stabilized by carbon. A. G. Knapton[65] was able to prove that the "Nb_2Si" phases of Brauer and Scheele[64] were the α- and β-forms of Nb_5Si_3. The crystal structures of the α and β forms of the Nb_5Si_3 phase were determined by R. Kieffer and co-workers[57]. The phase relationships in the region of

Table 4 shows a compilation of the niobium-silicon intermediate phases and their crystal structures.

Table 4. Niobium-Silicon Intermediate Compounds and Crystal Structures

Phase	Crystal Structure	Lattice Parameter	Literature
$NbSi_2$	hexagonal-C40 $CrSi_2$-type	a=4.795Å, c=6.589Å	57, 63
α-Nb_5Si_3	Tetragonal-$D8_8$ (T-2) Cr_5B_3-type	a=6.57$_0$Å, c=11.88$_4$Å	54, 55, 57
β-Nb_5Si_3	Tetragonal-$D8_m$ (T-1) W_5Si_3-type	a=10.01$_8$Å, c=5.07$_7$Å	54, 57
Nb_4Si	Hexagonal-DO_{19} Ni_3Sn-type	a=3.59Å, c=4.96Å	59-62
Nb_3Si	Tetragonal-DO_e Ti_3P-type	a=10.23Å, c=5.19Å	11

20 to 25 At.% silicon were rather complicated, in fact there is no direct confirmation, as yet, as to whether the Nb_4Si and Nb_3Si phases are identical. Knapton[58,65] stated that Nb_4Si is only found in melted samples while R. Kieffer[57] and co-workers as well as L. Brewer and O. Krikorian[56] could not find evidence of this phase in sintered samples. An explanation for this was given by H. J. Goldschmidt[60] who stated, in concurrence with Knapton[58], that the Nb_4Si phase exists only at high temperatures and decomposes below about 1900°C. Once the Nb_4Si has decomposed, it is not able

to reform in the solid state. It is suspected that the decomposition of the Nb_4Si is somehow related[60] to the α-β transformation of the Nb_5Si_3 phase.

Figure 7 depicts the constitution diagram of the Nb-Si system by R. Kieffer[66] and co-workers; it has been modified by these authors to include the fact that the Nb_4Si phase is present and stable above about 1600°C. The solubility of silicon in niobium is about 5 At.% Si at the

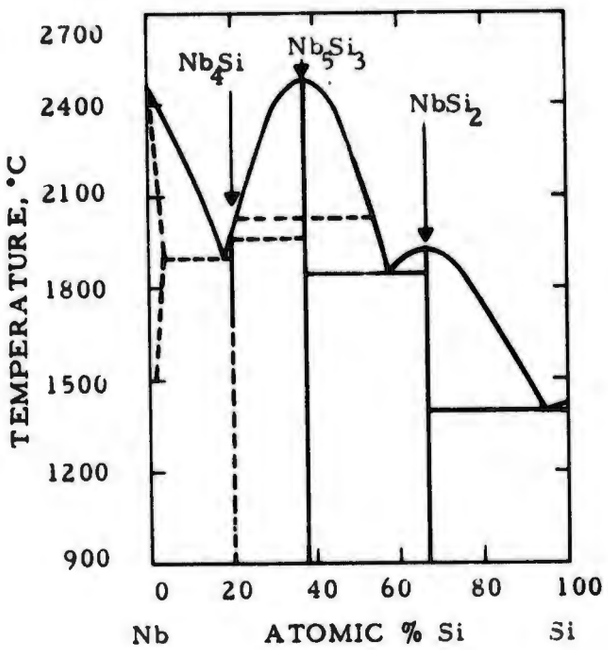


Figure 7. Nb-Si: Constitution Diagram
(R. Kieffer, et al. 1956 and 1963).

eutectic temperature of about 1900°C; the eutectic is between niobium and Nb_4Si, and the eutectic point lies about 18 At.% Si. Nb_4Si decomposes peritectically at about 1950°C into α-Nb_5Si_3 and liquid. The Nb_5Si_3 phase, which melts congruently at 2480°C, undergoes a transformation at about 2000°C. α-Nb_5Si_3 and $NbSi_2$ form a eutectic at about 58 At.% Si and at approximately 1850°C. $NbSi_2$ melts congruently at 1950°C and forms a eutectic at about 93 At.% Si at approximately 1400°C. There is no solubility of niobium in solid silicon.

7. The Tungsten-Silicon System

The tungsten-silicon system contains the fewest number of intermediate phases of the 4a, 5a, and 6a refractory-metal silicide systems. Only the phases WSi_2[82, 67] and W_5Si_3[55, 68, 69] are known to exist. A phase "W_3Si", claimed to have been found by Russian authors[12] in air-diffusion-studies is most probably an oxygen stabilized cubic structure[70].

The compound WSi_2 was discovered many years ago and its structure determined[82, 67]. In 1950 L. Brewer and co-workers[68] found a silicide of the approximate composition "W_3Si_2". This same silicide prepared by H. Nowotny[55] as well as by Blanchard and Cueilleron[69]; the crystal structure was determined. B. Aronsson[71] also determined the crystal structure; the correct formula of this phase is W_5Si_3. R. Kieffer,

Table 5 gives the intermediate tungsten-silicon phases.

Table 5. Intermediate Compounds and Crystal Structures in the Tungsten-Silicon System

Phase	Crystal Structure	Lattice Parameter	Literature
WSi_2	Tegragonal C11b $MoSi_2$-type	a=3.212Å, c=7.880	,67
W_5Si_3	Tetragonal $D8_m$(T-1) W_5-Si_3-type	a=9.605Å, c=4.964Å	68, 71

F. Benesovsky, and E. Gallistl[72], thoroughly investigated the tungsten-silicon systems by means of thermal, microscopical, and X-ray diffraction techniques; a constitution diagram was established (Figure 8). In a later work by Blanchard and Cueilleron[69], the constitution diagram of E. Gallistl[72] and the findings concerning melting temperature and eutectic compositions were confirmed.

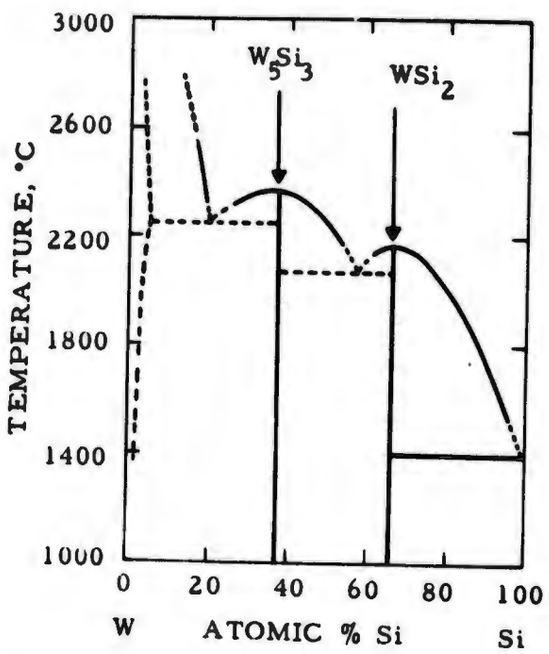


Figure 8. W-Si: Constitution Diagram .
(E. Gallistl, 1952).

There are three eutectics in the tungsten-silicon system: W-W_5Si_3 at about 20 At.% Si and 2290°C. W_5Si_3-WSi_2 at about 57 At.% Si and 2080°C; WSi_2-Si at approximately 99 At.% Si and 1400°C. Both compounds, WSi_2 and W_5Si_3 have extremely narrow ranges of homogeneity and melt congruently at 2320° and 2165°C respectively. The solubility of silicon in tungsten is approximately 5 At.% Si at the eutectic temperature 2290°C; silicon shows no solubility for tungsten in the solid state. W. Obrowski[73] states that W_5Si_3 is formed peritectically and furthermore has a slight homogeneous range; these facts, however, have not been confirmed.

Other investigations by R. Kieffer[70] on Mo-W-Si and W-Cr-Si alloys as well as by H. Nowotny, F. Benesovsky, and C. Brukl[74] on the W-Si-Ge system have shown no indications of the presence of a "W_3Si" compound as reported by Russian investigators[12].

B. TERNARY SYSTEMS

1. The Titanium-Silicon-Carbon System

Exploratory investigations in the titanium-silicon-carbon system by L. Brewer and O. Krikorian[49] have resulted in the schematic diagram reproduced in Figure 9.

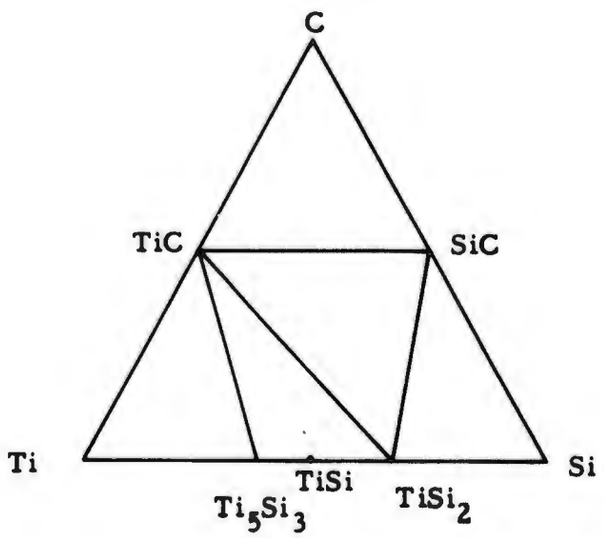


Figure 9. Ti-Si-C: Schematic Section.
(L. Brewer and O. Krikorian, 1954).

No ternary phases were observed and the phase-fields of the ternary are governed by the binary phases[49].

Brewer and Krikorian[49], using the heats of formation of the carbides, have calculated ranges of the heats of formation of the binary silicides. These results are reproduced in Table 6.

Table 6. Ti-Si: Heats of Formation of Binary Silicides in Kcal/gram-atom Si.

Phase	ΔH_{298} of Formation Kcal/gram-atom Si
1/2 $TiSi_2$	<-15.4 >-34.9
1/2 Ti_5Si_3	<-15.4 >-86.1

2. The Niobium-Silicon-Carbon System

H. Nowotny and co-workers[53, 75] have found a ternary $D8_8$ phase which lies in the vicinity of 38 At.% silicon near the Nb-Si binary. With increasing carbon concentration, the a axis of this ternary compound remains almost constant at 7.52 Å while the c axis varies from 5.23 to 5.27 Å[75]. This ternary phase was also observed by Brewer and Krikorian[49] as well as by G. Knapton[65]. Brewer and Krikorian[49] presented a schematic section of the Nb-Si-C ternary which is reproduced in Figure 10.

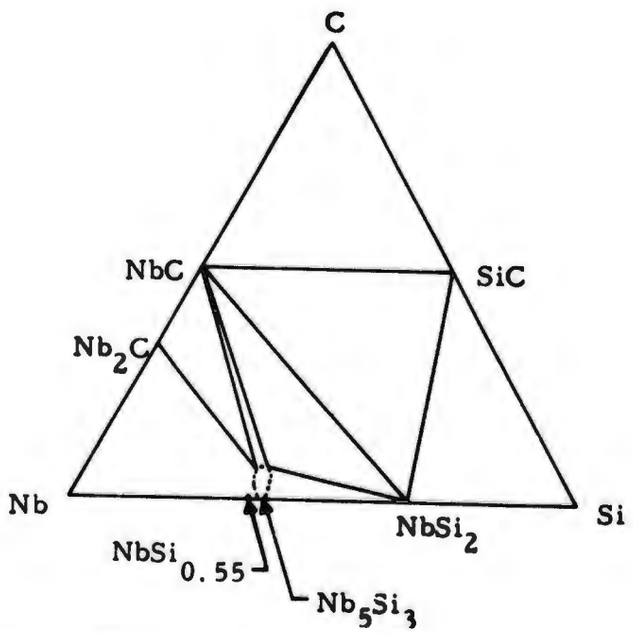


Figure 10. Nb-Si-C: Schematic Section.
(L. Brewer and O. Krikorian, 1954).

The same authors[49] have given limits for the heats of formation of the niobium-silicide phases; these values are displayed in Table 7.

Table 7. Nb-Si: Heats of Formation of Niobium-Silicides.

Phase	ΔH°_{298} of Formation Kcal per gram-atom Silicon	
1/2 $NbSi_2$	< -8.5	> -28
1/3 Nb Si_3	< -8.5	> -48
20/11 $NbSi_{0.55}$	< -8.5	> -48

H. Nowotny[75] has further found evidence of a second less stable ternary phase in the vicinity of $(Nb_2Si)_3C$ which was not able to be identified.

3. The Tungsten-Silicon-Carbon System

L. Brewer and O. Krikorian[49] did not find a ternary phase in this system; H. Nowotny and co-workers[75] were also not able to find a ternary phase in the W-Si-C system, but another publication[76] reported that in the presence of N_2, O_2, and sufficient carbon (< 10 At.%) a $D8_8$ phase was observed in the W-Si-C system.

L. Brewer and O. Krikorian[49] have given a schematic diagram for the W-Si-C system; this diagram is shown in Figure 11.

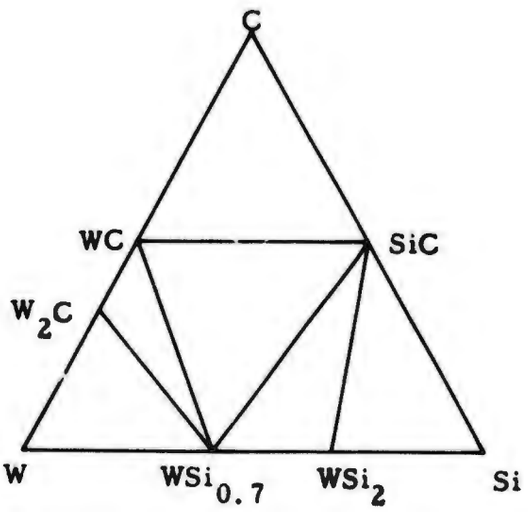


Figure 11. W-Si-C: Schematic Section.
(L. Brewer and O. Krikorian, 1954).

Table 8 lists the heats of formation of tungsten silicides as presented by Brewer and Krikorian[49].

Table 8. W-Si: Heats of Formation of Tungsten Silicides

Phase	$\Delta H°_{298}$ of Formation Kcal/gram-atom Silicon	
1/2 WSi_2	<-1.6	>-17.2
10/7 $WSi_{0.7}$	<-4.6	>-25.0

III. EXPERIMENTAL PROGRAM

A. EXPERIMENTAL PROCEDURES

1. Starting Materials

Elemental as well as hydride powders were used for the majority of samples prepared; however, pre-prepared carbide and silicide master alloys were used as starting materials for a few specific experiments.

Titanium metal powder was obtained from the Var-Lac-Oid Chemical Company, New York, and had the following impurities (in ppm): C-1300, H-1500, N-50, Fe-500 and Cl-1200. The lattice parameters of this starting material, as determined with CuKα, were a = 2.94$_9$ Å and c = 4.68$_8$ Å. The particle size was smaller than 74 micrometers.

Titanium dihydride, purchased from Metal Hydrides, Inc., Beverly Mass., had the following impurities (in ppm): Al-1000-3000, C-1000 max., Ca-500 max., Fe-1000 max., Mg-500 max., N-2000 max., Si-1000 max., and Zr-1000 max.; the hydrogen content was 3.99% by weight. This titanium hydride had an average particle size of 7.3 micrometers. A Debye-Scherrer powder diagram of this material showed only the face centered cubic dihydride structure. Spectrographic analysis at the Aerojet Metals and Plastics Chemical Testing Laboratory resulted in the following data (in ppm): Cr-400, Al-10, Fe-100, Zr-50, and Ca-100.

Two batches of niobium metal powder were used; both lots were supplied by the Wah Chang Corporation, Albany, Oregon. The first lot had the following impurities (in ppm): Al-<20, C-80, Fe-310, H-180, N-35, O-590, Si-<50, Ta-<500, and Ti-<40. The particles were sized less than 44 micrometers. Quality control analyses performed at the Aerojet Metals and Plastics Chemical Testing Laboratory yielded the following spectrographic

results for this niobium (in ppm): C-120, Si-<20, N-120, Ta-<1000, and W-not detected. Vacuum fusion analysis by the same laboratory gave these results for interstitial impurities (in ppm) H-27, O-655, and N-741. The lattice parameter of this powder as determined with CuK_α radiation was 3.30$_3$Å.

The vendor supplied the following analysis for the second batch of niobium powder (in ppm): Al-<20, C-100, Fe-58, H-18, N-130, O-750, Si-<50, Ta-<500, and Ti-<40. The metal powder was sized between 149 and 44 micrometers. Spectrographic quality control analysis gave the following values (in ppm): C-100, Si-<20, N-160, Ta-<1000, and W-not detected. Vacuum fusion analysis of this material gave the following values for the interstitials (in ppm): H-203, O-3775, and N-700. The lattice parameter of this starting material was 3.30$_4$Å.

Again, two batches of tungsten powder were used as starting materials for these investigations; both were supplied by the Wah Chang Corporation, Glen Cove, New York. The vendor's analysis for the first batch was (in ppm): Al-<10, C-27, Co-<10, Cr-<10, Fe-40, Mg-<10, Mn-<10, Mo-50, Ni-20, O-360, Pb-<10, Si-<10, Sn-<10, and non volatile material-100.

The average particle size of this tungsten powder was 6.8 micrometers. Aerojet's spectrographic analysis gave these values for the tungsten powder, (in ppm): C-130, Si-50, Cr-<20, Mo-<50, Ni-<50, Cu-<10, Al-80, Fe-80, Ti-<20, Co-<50, and Pb-<20. The lattice parameters of this tungsten powder was 3.166$_5$ Å.

The following vendor's values accompanied the second batch of tungsten powder (in ppm): Al-<10, C-20, Ca-<10, Co-<10, Cr-10, Cu-<10, Fe-40, Mg-<10, Mn-<10, Mo-80, O-200, Pb-<10, Si-<10, Sn -<10, Ni-15, and non volatile materials-100. The average particle size was 6.2 micrometers. The results of the spectrographic analysis at Aerojet was (in ppm): C-not detected, Si-20, Cr-<20, Mo-<50, Ni-<50, Cu-<10, Al-10,

Fe-100, Ti-<20, Co-<50 and Pb-<20. Vacuum fusion analysis results from the Aerojet Quality Control Laboratory were (in ppm): H-54, O-1081, and N-430. The lattice parameter of this material was 3.166 Å.

The silicon used in these investigations was supplied by the Var-Lac-Oid Chemical Company, New York, and had the following vendor's analysis (in ppm): Fe-500, Al-100, Ca-200, Ti-10, Cr-50, Mn-30, Cu-10, Ni-trace. The particles were sized smaller than 44 micrometers. The Aerojet's Metals and Plastics Chemical Testing Laboratory's spectrographic analysis of this material was (in ppm): C-80, Cr-100, Ni-<10, Cu-800, Al-1000, Fe-250, Ti-400, Mg-<10, B-10, and Ca-500. The lattice parameter of this starting material was 5.429 Å.

Carbon was used in two forms. The lampblack powder, supplied by Monsanto Chemical Co., had 99.57% free carbon and the following impurities (in ppm): H_2O-400, benzol extract-3000, ash-300, and volatiles-3600. The particle size was 0.01-0.1 micrometers. Spectrographic analysis at the Aerojet Metals and Plastics Chemical Testing Laboratory gave the following results (in ppm): Si-20, Mg-<10, Cu-<10, Al-10, Fe-10.

Graphite powder was obtained from the National Carbon Company and had the following typical impurities (in ppm): S-110, Si-46, Ca-44, Fe-40, Al-8, Ti-4, Mg-2, V-trace, and ash-800 max. 99% of the graphite was smaller than 74 micrometers. Highly overexposed X-ray films of these materials showed no traces of any impurities.

a. Pre-prepared Carbide and Silicide Master Alloys

A tungsten silicide with 39 At.% Si nominal and one with 67.5 At.% Si nominal were prepared in the following manner:

The fine powders were well mixed by hand; 20 ml. of a 10% camphor in ether-solution was mixed in as a binder; the powders were cold pressed into a 3 inch diameter cylindrical form at 1.1 tons/cm^2

in a Mannesmann press. The compacts were then heated to 110°C for 48 hours under a 30" Hg vacuum to remove the camphor. The compacts were reacted in a molybdenum boat in a muffle furnace under hydrogen at 1250°C and subsequently heat-treated at 1250°C for two hours in a hydrogen atmosphere. The reacted and sintered silicides were broken up and ground in a agate mortar and sieved to <44 micrometers.

The tungsten carbide master alloy was pressed as described above, but reacted under argon at 2100°C. The final powder was sieved to <66 micrometers. The preparation of the silicon carbide alloy also followed the steps outlined above, but was reacted and sintered for 1 hour at 1350°C under hydrogen.

Table 9 shows the nominal and chemically analyzed values of the pre-prepared carbides and silicides.

Table). Nominal and Chemical Analysis Values of Pre-prepared Carbides and Silicides Master Alloys

	Nominal Composition in At.%		Analyzed Composition in At.%	
Alloys	Si	C	Si	C
W-C	-	50.0	-	48.4
Si-C	53.0	47.0	balance	47.4
W-Si	39.0	-	39.0	0.2
W-Si	67.5	-	67.5	0.3

2. Alloy Preparation and Heat Treatment of Alloys

The alloys for the solid-state studies in the Ti-Si-C, Nb-Si-C, and W-Si-C ternary systems were all prepared by carefully weighing and hand mixing the elemental or hydride powders. The mixtures were

then hot pressed in graphite dies at temperatures varying between about 1300 and 1800°C. After removal of any carbide surface layer formed during hot pressing, the samples were given long time heat-treatments. Table 10 gives the heat treatment particulars of each of the three ternary systems.

Table 10. Solid-State Heat Treatment Conditions of Ti-Si-C, Nb-Si-C, and W-Si-C Samples

System	Heat Treating Temperature Centigrade	Duration	Atmosphere
Ti-Si-C	1200°	50-87 hrs	Helium
Nb-Si-C	1300°	64-65 hrs	Helium
W-Si-C	1800°	16 hrs	Helium

3. Differential Thermal Analysis

The high temperature differential thermal analysis equipment, which has been amply described and discussed in other reports[77, 78] under the present Air Force contract, was used only on a specifically selected alloy in the W-Si-C system. In this case an uncertainty existed in regard to correct equilibria as presented by the Debye-Scherrer powder X-ray patterns of the solid-state samples. In this instance a type of "Gürtler's Klär-Kreuz" method was used with the DTA to observe the formation of the correct equilibria. The details of these experiments are described in the Experimental Results Section (pages 48 and 49).

4. X-Ray Analysis

Chips of the solid-state samples, which had undergone heat treatment, as well as those few samples which were differentially thermally analyzed, were ground to fine powder and X-rayed with copper and chromium K_α radiation using the Debye-Scherrer powder technique.

To eliminate the film-blackening caused by titanium fluorescence radiation, induced by the CuK_α, a cover film, which absorbed this soft white radiation was used over the films during the exposure.

In the three ternary systems investigated, the majority of the crystal structures are known; the exceptions are: a phase in the titanium-silicon binary at about 40-45 atomic percent silicon, a new ternary phase in the titanium-silicon-carbon system near the composition "Ti_2SiC", and a very evasive ternary phase in the Nb-Si-C system near the composition $Nb_4Si_{1.7}C$.

The Debye-Scherrer patterns of the phases present in the Ti-Si-C system were exceedingly complex owing to the fact that these crystal structures give rise to numerous diffraction lines; further complications were present due to the difficulty of not being able to obtain even remotely usable powder diagrams with the longer chromium radiation. Almost all of the many line-coincidences were unresolved under the forced choice of copper radiation.

5. Chemical Analysis

Spectrographic analyses were carried out on the starting elemental powders as a check control of the vendor's own analyses. These results showed no excess contamination by any metallic impurity; the results corresponded rather well to the vendor's original analysis. In some cases the interstitial impurities (H_2, N_2, O_2) of the starting materials, as well as of a select few of the prepared ternary alloys were determined in a platinum bath using a vacuum fusion method. The results of the analyses on the interstitial impurities tended to be somewhat higher than those reported by the vendor. In no case, however, was any exceedingly large amount of interstitial impurity detected.

Carbon and silicon analyses were carried out post-experimentally on a few randomly selected ternary silicocarbide samples to check the nominal compositions.

Carbon analyses were performed using the standard direct combustion method, and either trapping the evolved carbon dioxide on sodium-hydroxide and computing carbon content by weight gained, or by measuring the thermal conductivity of the combusted CO_2-O_2 gas mixture in a Leco carbon analyzer.

Silicon was determined by fusing the sample in a sodium hydroxide-sodium peroxide mixture, dissolving the melt in perchloric acid and volatilizing the silicon as SiF_4 with a hydrofluoric-sulfuric acid mixture. In all cases the analysis values of carbon and silicon checked quite closely with the nominal values.

B. EXPERIMENTAL RESULTS

1. The Titanium-Silicon-Carbon System

Seventy-one samples were made by hot pressing and sintering at 1200°C under helium. After heat treatment, the samples were X-rayed with CuK_α radiation using the Debye-Scherrer powder method. Figure 12 shows the location of the samples as well as the qualitative X-ray evaluation of these samples.

The few binary titanium-silicon samples which were made showed no phases present other than those already known. Traces of a phase of unknown crystal structure, which has been reported by H. Nowotny[51], were also observed. This phase probably lies in the vicinity of 40-45 atomic percent silicon. No samples were placed in the titanium-silicon binary near 25 atomic percent silicon, the region where a Ti_3Si phase has recently been reported[11], but powder diagrams of ternary Ti-Si-C samples near the Ti-Si binary showed no extraneous lines which might be attributed to this phase. Apparently, at 1200°C no evidence of this Ti_3Si phase is present. The lattice parameters of the binary Ti-Si phases as determined in this investigation are listed in Table 11. Because of the strong X-ray absorbtion by titanium, the lattice parameters were obtained by extrapolation to $\theta = 90°$; they are in good accord with the published literature. The range of values for the Ti_5Si_3

phase indicates that this phase has a homogeneous range — a fact which has previously been reported[46].

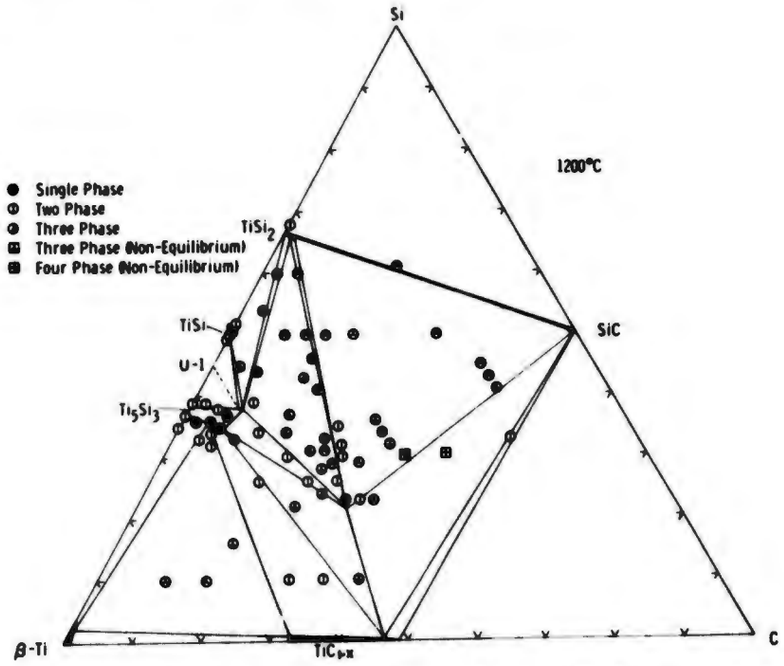


Figure 12. Ti-Si-C: Location and Qualitative X-ray Analysis of 1200°C Samples.

Table 11. Lattice Parameters and Crystal Structures of Titanium Silicides

Phase	Crystal Structure	Lattice Parameters
$TiSi_2$	Orthorhombic (C-54)	a=8.23$_5$Å ; b=4.77$_5$Å c=8.54$_9$Å
TiSi	Orthorhombic (B-27)	a=6.53$_7$Å ; b=3.63$_8$Å c=5.01$_3$Å
Ti_5Si_3	Hexagonal ($D8_8$)	a=7.44$_9$ - 7.45$_4$Å c=5.14$_9$ - 5.14$_4$Å

The interesting characteristic of the ternary Ti-Si-C system is the appearance of a previously undetected ternary phase near the composition "Ti_2SiC". Earlier investigations in the ternary Ti-Si-C system[49] have dealt mainly with the region near the binary phase Ti_5Si_3. This fact, along with the additional complication that many lines of the powder diagrams of this phase coincide, or very nearly coincide, with the diffraction lines of binary Ti-Si phases may have prevented this phase's earlier detection. As closely as can be estimated from the X-ray films, this new ternary phase does not have an appreciable homogeneous range and is located close to the composition $Ti_{48}Si_{21}C_{31}$. An alloy with a nominal composition of Ti-Si-C, 47-23-30 At.%, which showed this phase with but traces of $TiSi_2$ and Ti_5Si_3 (C), was analyzed at Ti-Si-C, 48.8 - 23.5 - 27.7 At.%. This sample was also analyzed for its H_2, N_2, and O_2 contents; the results were: H_2-40 ppm, N_2-2100 ppm, and O_2-28 ppm.

In view of the fact that it is still suspected that the Ti_5Si_3 binary phase may be stabilized by extremely small amounts of N_2 and O_2 impurities (the isostructural phases in the Zr-Si and Hf-Si systems are definitely ternary phases), it is conceivable that this new ternary phase might also be similarly stabilized and in reality be a quaternary or higher order phase. The relatively low content of interstitials (as analyzed) indicate very strongly, however, that the new phase is a genuine ternary phase.

Table 12 gives the measurement of the Debye-Scherrer powder pattern of the new ternary phase.

The pattern of this new phase appears to have certain similarities with a previously reported Ti_2GeC[79], but neither the line intensity nor indices match close enough to conclusively decide that the two phases are isostructural.

Table 12. Measurement of Powder Diagram of the Ternary Ti-Si-C Phase near the Composition "Ti_2SiC".

CuK_α Radiation Observed $Sin^2\theta$	Intensity Observed
.0682	vw
.0859	m
.0911	vvw
.1012	vvw
.1135	st
.1222	m
.1318	mst
.1773	w coincid. $TiSi_2$
.2059	w
.2385	m
.2530	mst-
.2747	vw
.3208	vvw
.3620	mw
.3689	mw-
.3741	mw+
.3846	vw
.4060	mw-
.4913	mw dif.
.5918	vvw
.6232	mw dif.
.6375	mw-dif.
.7423	m dif.
.7590	w + dif
.8453	mw dif.
.8654	mw dif.

st = strong mst = medium strong m = medium
w = weak vw = very weak vvw = very, very weak
dif = diffuse mw = medium weak

At 1200°C the ternary phase forms two-phase equilibria with TiC_{1-x}, SiC, $TiSi_2$, and the solid solution Ti_5Si_3 (C) (Figure 13).

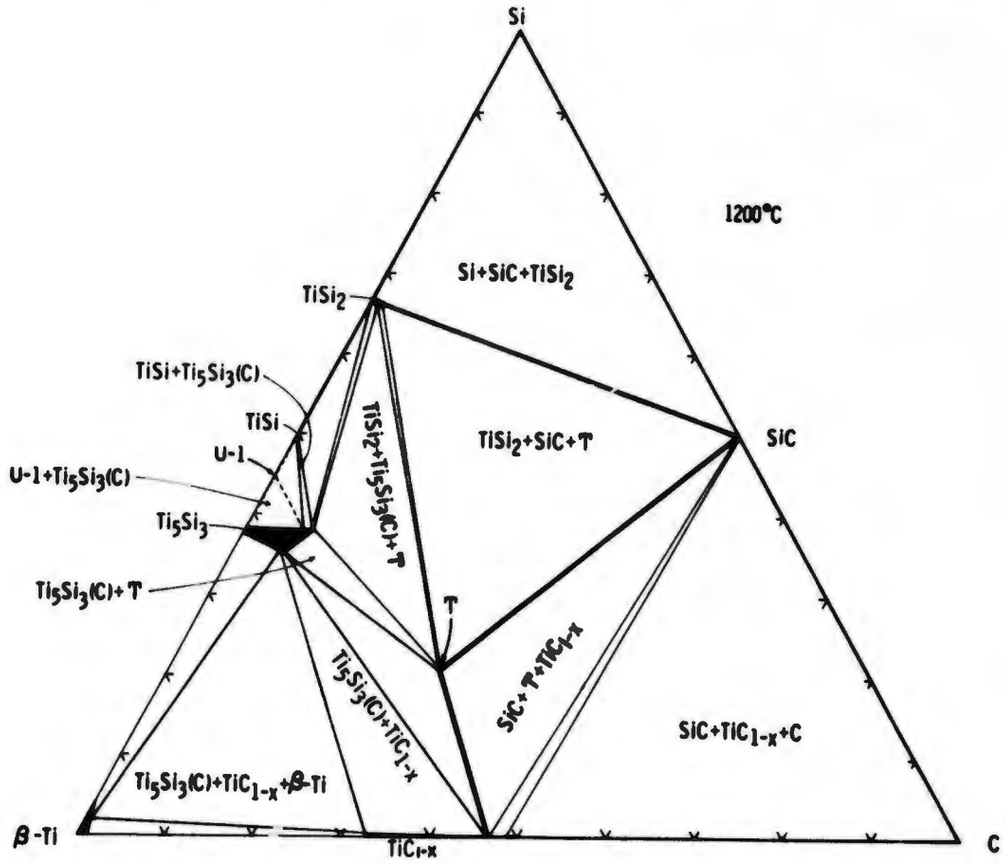


Figure 13. Ti-Si-C: Section at 1200°C.

From the roentgenograms of the numerous samples placed in the immediate vicinity of the Ti_5Si_3 phase in the ternary, the homogeneous range of the $D8_8$ phase was determined. It stretches toward the Si-C binary as well as toward slightly lower silicon concentrations. The maximum solubility for carbon is about 8 At.%.

Table 13 shows the variance of the lattice parameters of the $D8_8$ phase at various compositions in the ternary field.

Table 13. Lattice Parameters of the Binary Ti_5Si_3 and Ternary Ti_5Si_3 (C) Phase

Nominal Composition in Atomic Percent			Lattice Parameters in Å	
Ti	Si	C	a	c
61	39	0	7.44_9	5.14_4
63	37	0	7.45_3	5.14_5
65	35	0	7.45_4	5.14_9
62	36	2	7.44_7	5.14_3
63	33	4	7.43_9	5.14_6
62	32	6	7.44_9	5.15_8
60	36	4	7.43_4	5.14_9
61	34	5	7.44_5	5.16_6

The solid solution of Ti_5Si_3 (C) is in equilibrium with β-Ti, TiC_{1-x}, the ternary phase T, TiSi, $TiSi_2$, and the as yet unidentified binary Ti-Si phase U-1.

The U-1 phase, which undoubtedly has a rather low stability forms,two-phase equilibria with only its adjoining phases, i.e. TiSi and Ti_5Si_3 (C). The diffraction patterns of U-1 are extremely weak and diffuse, and it was not possible to determine whether it possesses a homogeneous range. TiSi on the other hand shows no solubility whatsoever for carbon or the carbide phases; the lattice parameters of the TiSi phase contained in ternary samples are the same as those in binary samples. TiSi also, forms equilibria with only its neighboring binary phases (Figure 13).

The $TiSi_2$ phase, which is in equilibrium with TiSi, Ti_5Si_3 (C), the ternary phase T, and SiC shows a slight enlargement of the lattice parameters in ternary samples containing this phase. The lattice parameters of the binary $TiSi_2$ phase were $5 = 8.23_5$ Å, $b = 4.77_5$ Å, and $c = 8.54_9$ Å while the lattice parameters of a sample with 20 At.% Ti, 61 At.% Si

and 19 At.% C were calculated to: a = 8.26_1 Å, b = 4.78_6 Å, and c = 8.57_0 Å; this corresponds to a volume increase in the unit cell of 0.8%. The solubility of carbon in $TiSi_2$ is therefore quite small and probably of the order of 1-2 At.%C.

Debyeograms of ternary alloys containing the β-form of SiC showed no change at all in the lattice parameter of this phase. The binary β-SiC had a lattice parameter of 4.35_8 Å, while those parameters obtained from ternary Ti-Si-C alloys varied between 4.35_8 and 4.35_7 Å. There is, therefore no solid-solubility in β-SiC.

Titanium monocarbide, which has a wide homogeneous range with the carbon defect structure, forms equilibria with β-SiC, the new ternary phase, and the solid solution of Ti_5Si_3 (C). The two-phase regions with β-SiC and T are very narrow as judged from the qualitative analysis of the X-ray powder diagrams; the lattice parameters of the TiC_{1-x} phase as measured in samples lying in the TiC_{1-x} -β-SiC, TiC_{1-x} -T, and TiC_{1-x} -T-β-SiC regions are somewhat smaller than the value of a binary TiC_{1-x} with the smallest carbon defect: 4.32_{0-3} vs. 4.33_0 Å[1]. This indicates that a small range of TiC_{1-x} is in equilibrium with stoichiometric β-SiC. The lattice constants of the monocarbide phase measured in ternary samples in the Ti_5Si_3 (C)-TiC_{1-x} region decrease with decreasing carbon content; however, these values, as well as those lattice parameters taken from samples in the three phase field β-Ti-Ti_5Si_3(C)-TiC_{1-x} are slightly larger than those of the appropriate tie-line-connected-binary-base-point concentrations indicating a very slight solubility of silicon in the extreme defect monocarbide lattice.

The solubility of silicon in β-titanium was not specifically investigated; the solubility for silicon was taken from the literature[46] and the solubility for carbon from a previous publication[1]. Figure 13 shows the phase equilibria of the Ti-Si-C system at 1200°C.

A few selected ternary Ti-Si-C and binary Ti-Si alloys were analyzed post-experimentally for their silicon and carbon contents. These values are shown in Table 14. The analyzed values are very close to the nominal compositions and show only a slight compositional shift.

Table 14. Chemical Analysis Values of Some Ti-Si and Ti-Si-C Samples.

Atomic Percent						
Nominal				Analyzed		
Ti	Si	C		Ti *	Si	C
32	68	0		31.9	67.5	0.6
57	37	6		58.9	34.9	6.2
59	35	6		59.5	34.8	5.7
47	23	30		48.8	23.5	27.7

*By Difference

2. The Niobium-Silicon-Carbon System

A total of 70 solid state samples were made to ascertain the solubilities and phase equilibria at 1300°C; of these, four were binary Nb-C samples and three were binary Nb-Si samples. Figure 14 shows the qualitative X-ray findings as well as the compositional locations of the samples at 1300°C.

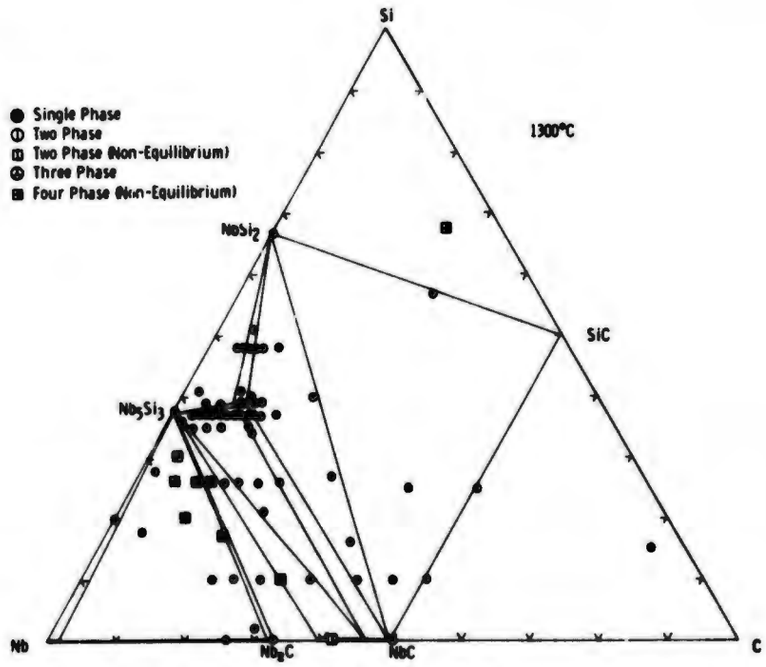


Figure 14. Nb-Si-C: Location and Qualitative X-ray Analysis of 1300°C Samples.

The results of the niobium-carbon samples are in accord with the findings of many other authors[4-7, 19]; they showed that NbC_{1-x} has a considerable homogeneous range. A sample with 50 atomic percent carbon was single phase monocarbide with a lattice parameter of 4.46_6 Å, whereas a sample with 41 atomic percent carbon had a lattice parameter of 4.43_4 Å and showed traces of the Brauer-Nb_3C_2 [5] zeta phase which is metastable and, in analogy to the findings in the Ta-C system[3] probably is the result of a nonequilibrium precipitation in the presence of the carbon defect niobium monocarbide. Two samples in the vicinity of α-Nb_2C, the low temperature form[3], showed that this phase has, at best, a very small homogeneous range 1300°C. The specimen with 27 At.% carbon was two-phased (α-Nb_2C and Nb): the α-Nb_2C had lattice parameters of $a = 3.11_9$ Å and $c = 4.96_3$ Å; the sample with 33 At.% C showed α-Nb_2C lattice parameters of $a = 3.11_9$ Å and $c = 4.96_5$; the X-ray film of this sample showed a trace of the NbC_{1-x} cubic phase next to the subcarbide pattern.

The binary Nb-Si X-ray films showed the presence of only two intermediate phases at 1300°C. The disilicide, $NbSi_2$, had lattice parameters of $a = 4.79_5$ Å and $c = 6.59_0$ Å while the T-2, low temperature form of Nb_5Si_3 had $a = 6.56_9$ Å and $c = 11.87_3$ Å.

A sample was placed at 25 At.% silicon in the Nb-Si binary to check for the presence of the Nb_4Si phase[56-60] and for the more recently described[11] Nb_3Si phase. The X-ray pattern of the hot pressed sample which was sintered at 1300°C showed no signs of any patterns other than Nb and α-Nb_5Si_3. A Nb_4Si or Nb_3Si phase or phases do not exist at 1300°C — at least not in sintered samples (see literature review, page 17).

The principal characteristic of the ternary Nb-Si-C system is the formation of a ternary phase[53, 55, 65] at the composition of approximately $Nb_{11}Si_{4.1}C_2$. This "Nowotny Phase" has the $D8_8$ hexagonal structure and possesses a rather small homogeneous range as determined by qualitative X-ray analysis of many powder diagrams of samples in its vicinity. The $D8_8$ phase forms two-phase equilibria with $NbSi_2$, α-Nb_5Si_3, and NbC_{1-x}.

Although its homogeneous range is rather small, a noticeable variation is present in the lattice parameters. Table 15 gives the lattice parameters of the ternary $D8_8$ phase.

Table 15. Lattice Parameters of the $D8_8$ Phase in Ternary Alloys

Nominal Composition in Atomic Percent			Lattice Parameters in Ångstroms		
Nb	Si	C	a	c	c/a
53	34	13	7.52_7	5.31_5	.706
53	35	12	7.52_3	5.30_9	.705
59	37	4	7.53_7	5.25_2	.696
58	37	5	7.54_4	5.25_6	.696
57	37	6	7.54_6	5.25_9	.696
56	37	7	7.54_2	5.26_4	.697
54	37	9	7.53_3	5.30_5	.704
53	37	10	7.53_1	5.31_6	.705
52	37	11	7.52_9	5.31_6	.706
50	37	13	7.52_8	5.31_4	.705
48	37	15	7.52_6	5.31_2	.705
52	39	9	7.52_6	5.31_3	.705
50	39	11	7.53_1	5.31_6	.705
49	39	12	7.52_9	5.31_7	.706

$NbSi_2$ forms two-phase equilibria with the ternary $D8_8$ phase, NbC, and β-SiC. A visual comparison of the X-ray patterns of $NbSi_2$ in ternary samples with the pattern of a pure binary $NbSi_2$ showed no discernable lattice parameter change. Exact measurement of these same films, however, led to the detection of a very, very slight change in the c parameter of the $NbSi_2$ phase. The pure binary values were $a = 4.79_5$ Å and $c = 6.59_0$ Å while the average results of several values taken from ternary samples were $a = 4.79_5$ Å and $c = 6.58_7$. According to these results there is an almost negligible carbon solubility in $NbSi_2$.

As in the ternary Ti-Si-C system, the β-SiC phase in the Nb-Si-C system shows no solubility for any of the other binary phases. The lattice parameters of the pure binary β-SiC phase was 4.35_8Å while the values taken from samples in the ternary Nb-Si-C area were between 4.35_7 and 4.35_8Å. The β-SiC phase is in equilibrium with $NbSi_2$ and NbC.

Lattice parameter measurements of the NbC phase, as well as qualitative X-ray analysis of samples located in the NbC-SiC, $NbSi_2$-NbC, NbC-SiC-$NbSi_2$, $NbSi_2$-NbC-$D8_8$, and NbC_{1-x}-$D8_8$ regions, were used to locate the three-phase base points along the NbC_{1-x} defect carbon region. SiC and $NbSi_2$ are in equilibrium with a practically stoichiometric NbC. Figure 15 shows the phase-field divisions and the niobium monocarbide lattice parameters in the monocarbide region.

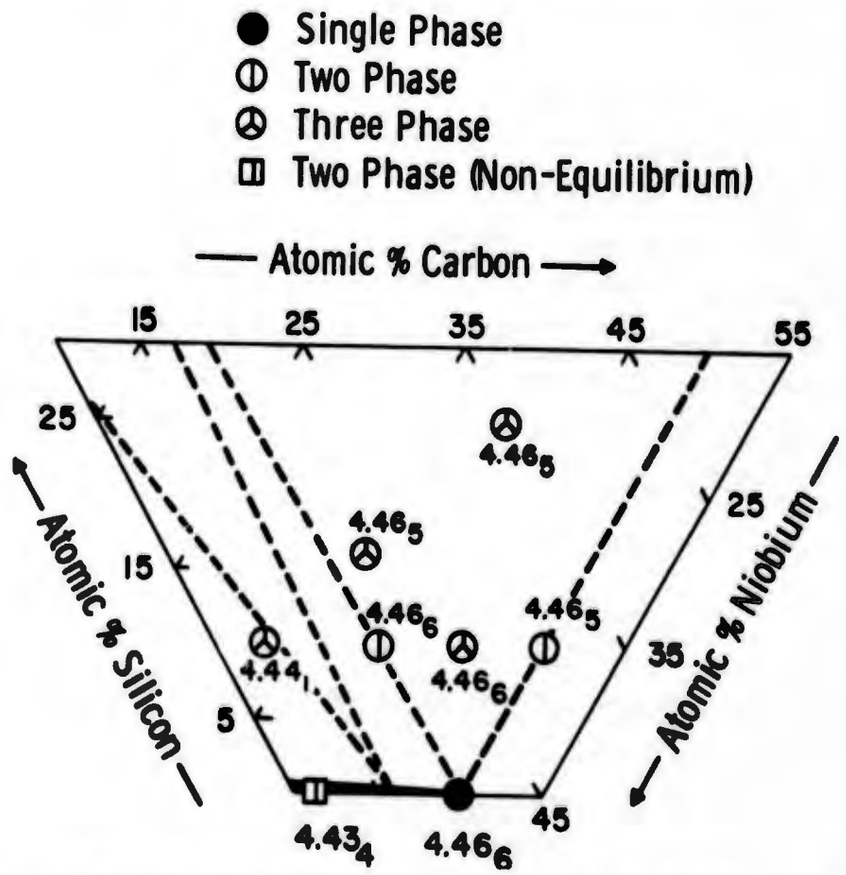


Figure 15. Nb-Si-C: Lattice Parameters of the NbC_{1-x} Phase With Location of Ternary Alloys.

The smallest lattice parameter obtained for the NbC_{1-x} phase in a binary sample was 4.43_4 Å; the lattice parameters of this same phase taken from samples in the $D8_8$- α-Nb_5Si_3-NbC_{1-x} region were on the average slightly larger with 4.43_7 Å. On the basis of this observation, an extremely small solubility, probably less than 1 At.% silicon, may be assigned to the high carbon-defect end of the niobium monocarbide homogeneous range at 1300°C.

Based on the powder diagram X-ray findings, the NbC_{1-x} phase is in equilibrium with SiC, $NbSi_2$, $D8_8$, and α-Nb_5Si_3.

The α-Nb_2C phase, which has a very small homogeneous range in the Nb-C binary system[10], is in equilibrium with α-Nb_5Si_3 and of course, Nb and NbC_{1-x}.

All X-ray results, as determined by the presence or absence of the pertinent phases in the Nb-α-Nb_5Si_3-$D8_8$-NbC_{1-x}-Nb_2C region indicate, without a doubt, that the Nb_2C - α-Nb_5Si_3 two-phase equilibria exists at 1300°C. However, due to nonequilibrium conditions, the presence of four and sometimes five phases was noted in the area between α-Nb_5Si_3 - $D8_8$ - NbC_{1-x} and Nb_2C indicating that at some temperature close to 1300°C, either above or below, a two-phase equilibria $D8_8$-Nb_2C might replace the NbC_{1-x} - α-Nb_5Si_3 two phase region. The majority of evidence points to the definite existence of the NbC_{1-x} -α-Nb_5Si_3 equilibrium at 1300°C as indicated in Figure 16.

The lattice parameters of the α-Nb_2C phase, as taken from silicon containing ternary samples, were a=3.11_9Å and c=4.96_7Å; the c value is only a slight bit larger (compared with lower temperature values) than the corresponding binary value (see page 9) and speaks for only a barest solubility of α-Nb_5Si_3 in α-Nb_2C. α-Nb_5Si_3 forms two-phase equilibria into the ternary Nb-Si-C field with the $D8_8$ ternary phase, NbC_{1-x}, and Nb_2C. There is no change whatsoever in the lattice parameters of the α-Nb_5Si_3 phase which was observed in ternary carbon containing alloys, and therefore no solubility or homogeneous range is exhibited by this binary silicide phase into the ternary Nb-Si-C region.

Roentgenograms in the region Nb: 58-70, Si: 20-26, and C: 6-15 atomic percent showed varying small amounts of a ternary phase which was not able to be identified or specifically located. The X-ray pattern, which was too weak to be measured with any degree of accuracy, appeared on the films of 1300°C samples containing all the other binary carbide and silicide phases as well as the ternary $D8_8$ phase. The presence of this second ternary phase, which appears to be not very stable at the temperature (1300°C) investigated, is most probably connected in some manner with the difficulty in attaining equilibrium shown by many samples in this region; in this respect, some X-ray films presented somewhat misleading evidence concerning the possible existence of the $D8_8$-Nb_2C equilibrium.

A complete clarification of the characteristics of this portion of the Nb-Si-C system will only be possible with extensive investigations over a wide temperature range up to and including liquid-solid equilibria.

Because of the small amounts present, the evasiveness, and uncertainties involving this unknown ternary phase, which has also been observed in trace amounts, but not closer defined, in this same region by H. Nowotny[75], none of the possible equilibria involving this phase is depicted in the 1300°C isothermal section of the Nb-Si-C system displayed in Figure 1 . In addition, those ternary samples showing nonequilibrium conditions at 1300°C are designated in an appropriate manner in Figure 14.

The solubility of carbon and silicon in niobium was not specifically investigated; the values portrayed in the isothermal section was taken from the literature[64, 10].

Post experimental chemical analysis of silicon and carbon was performed on two randomly selected ternary samples to check the nominal compositions. The niobium content was calculated by difference. The nominal values of these two samples were: Nb-Si-C 54-37-9 and 53-37-10 atomic percent; the analyzed values were: Nb-Si-C 54.1-37.1-8.8 and 53.5-36.5-10.0 atomic percent. The results are in excellent accord, and it is safe to assume

that no great concentration shifts occurred in the rest of the ternary Nb-Si-C samples.

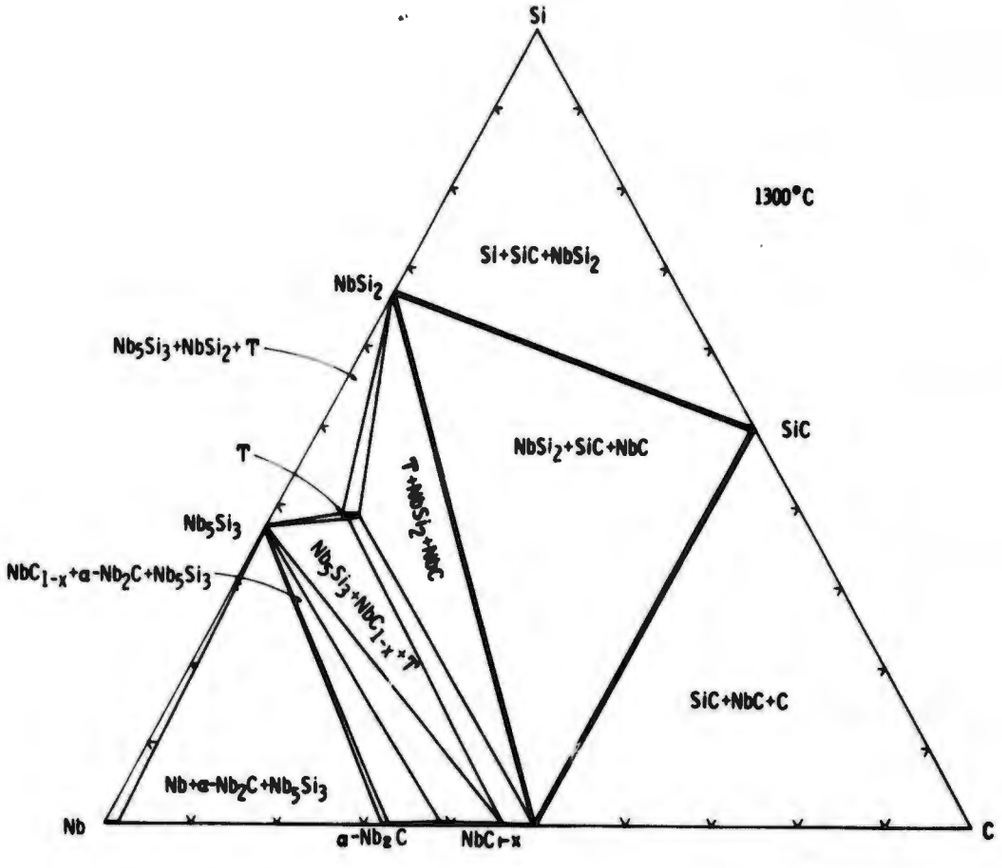


Figure 16. Nb-Si-C: Section at 1300°C.

3. The W-Si-System (Partial Investigation)

To verify or disclaim recent findings concerning the possibility of the existence of a "W_5Si" phase in the tungsten-silicon binary system[12], the melting point of a W-Si alloy with 25 atomic percent silicon was measured using the Pirani technique. Duplicate samples melted fairly sharply at 2065°C and 2062°C.

Subsequent metallography of the molten portions of these samples showed only two phases present, although a eutectic was hard to discern.

Figure 17 portrays the two phased metallographic picture of this W-Si sample.

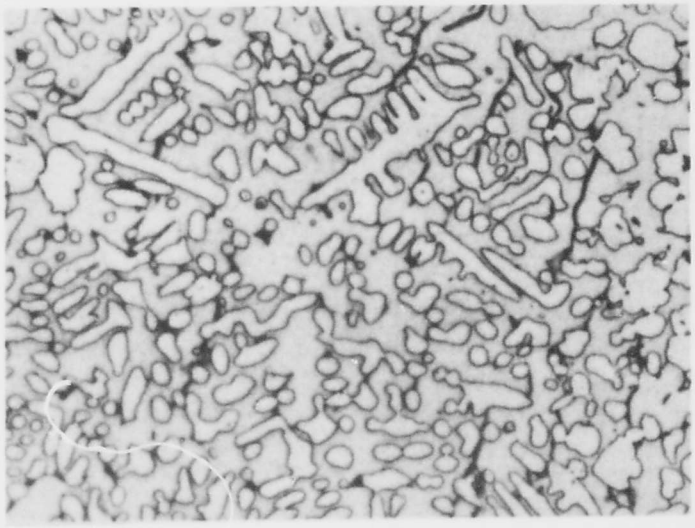


Figure 17. W-Si: 75/25. Primary Tungsten in W_5Si_3 Matrix. X1000

A roentgenogram of this melted alloy showed only the patterns of tungsten and W_5Si_3.

In view of these findings it may be said that no "W_3Si" phase exists — at least not at temperatures near the solidus line — and the interpretations of R. Kieffer[70, 72] as well as L. Brewer[68] on the constitution of the W-Si diagram in this region are correct. The approximate isothermal eutectic temperature (2250°C), of the W-W_5Si_3 mixture, as reported by R. Kieffer[72] appears to be somewhat high (as also stated by this author), and a more thorough investigation into the melting behavior of the more tungsten-rich portion of the W-Si system will certainly show the melting point of the W-W_5Si_3 eutectic to be in the close vicinity of 2065°C.

4. The Tungsten-Silicon-Carbon System

Twenty-eight ternary and binary samples were made for the solid-state investigation of the W-Si-C system at 1800°C.

Figure 18 shows the compositional location of the samples as well as the qualitative X-ray analysis.

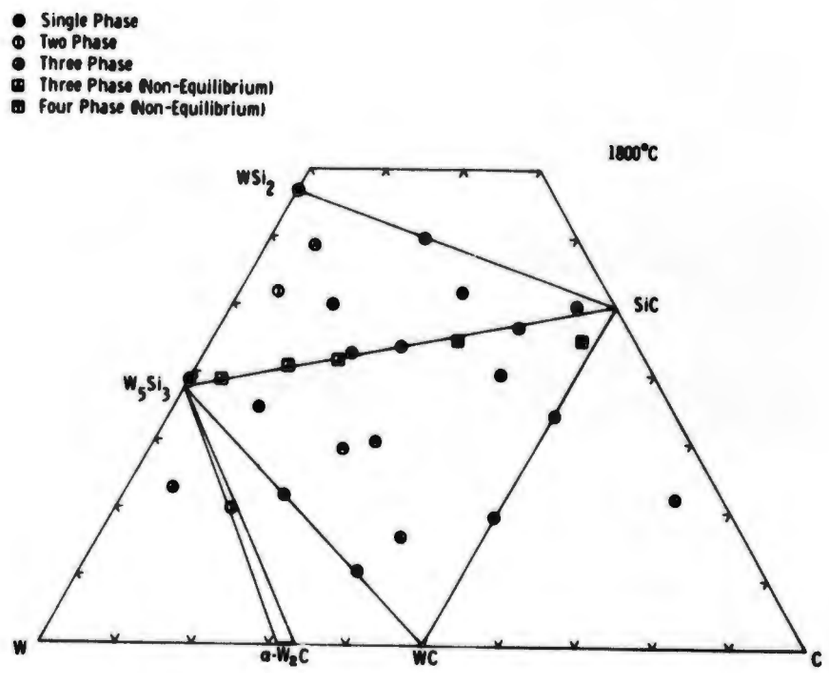


Figure 18. W-Si-C: Location and Qualitative X-ray Analysis of 1800°C Samples.

In accord with other findings, there is no ternary phase in the W-Si-C system; only the binary constituents partake of the equilibria. None of the binary phases show any mutual solubility whatsoever.

WSi_2 is in equilibrium with β-SiC as well as with its binary neighbors Si and W_5Si_3. The lattice parameters of a binary sample of this phase were a = 3.21$_2$ Å and c = 7.82$_7$ Å; there was no change in the cell

dimensions of the WSi_2 phase as measured in ternary carbon containing specimens. The lattice parameters of the W_5Si_3 phase as taken from ternary samples were unchanged compared with the binary values of a = 9.61_4 Å and c = 4.94_8 Å. W_5Si_3 is in equilibrium with β-SiC, WC, and α-W_2C.

Tungsten monocarbide, WC, is in equilibrium with W_5Si_3 and β-SiC; the lattice parameters of this phase in ternary silicide containing samples were a = 2.90_5 Å and c = 2.83_6 Å. These values are practically identical with those[2] taken from binary samples.

The subcarbide, α-W_2C, the low temperature form[2] has a slight homogeneous range[2] from about 30 to 33.3 At.% C at 1800°C; the lattice constants vary in the single phase region: a = 2.98_5 - 3.00 Å, c = 4.71_7 - 4.72_8 Å (taken from samples quenched from 2200°C[2]). Tne unit cell measurements of the α-W_2C phase present in ternary alloys in the W-Si-C system also reflect this variation. The α-W_2C phase in samples in equilibrium with the carbon-poor end of the α-W_2C homogeneous range had lattice parameters of a = 2.99_0 Å and c = 4.72_2 Å where as those phases in ternary samples in equilibrium with the carbon-rich end of the α-W_2C single phase region had a = 2.99_5Å and c = 4.72_3Å. Since those values fall within the range indicated by investigations[2] on the W_2C homogeneous region, and, not forgetting that the binary literature values were obtained from samples quenched from 2200°C[2] (the homogeneous range as well as the spread in lattice parameters is somewhat larger than at 1800°C), it was concluded that there is no solubility into the ternary W-Si-C system shown by the α-W_2C phase at 1800°C.

The β-SiC shows no solid solution into the ternary W-Si-C region; the lattice parameter of this phase in ternary samples carries the same value as in the pure binary sample: 4.35_8Å.

Preliminary hot pressed and heat treated samples from the middle portion of the W-Si-C system led initially to an erroneous conclusion. The roentgenograms of these samples showed the four phases W_5Si_3, SiC, WSi_2, and WC present in many cases (see Figure 18). In the silicon

richer region a considerable amount of WC was present indicating a WSi_2-WC equilibrium. The X-ray analysis of additional samples in this region showed quite a bit less of the WC phase and cast doubt on the original conclusion; in fact the equilibrium W_5Si_3-SiC was strongly indicated. The possibility of a four phase reaction: $WSi_2 + WC \longrightarrow W_5Si_3 + SiC$ at a temperature near 1800°C was also considered.

To clarify this situation a special DTA experiment was made.

Prepared WSi_2 and WC powders were mixed to yield an overall composition of W-Si-C: 40/42/18; the loose powder was tampered into a graphite DTA holder and covered with a graphite plug having a black body hole. Two consecutive runs were made with the same sample. Figure 19 shows the results of this experiment.

The first run showed a strong exothermic reaction initiating at about 1500°C and carrying up to approximately 1850°C; subsequent to this exothermic reaction, the start of the melting isotherm was observed at about 1925°C. After cooling, the sample was reheated and gave no evidence of any reaction other than incipient melting. During the first run the WSi_2-WC mixture reacted irreversibly to the correct conjugate compounds, W_5Si_3 and SiC. An X-ray powder diagram of the starting mixture, showing the patterns of WSi_2 and WC, was compared with a roentgenogram of the DTA sample after heating. The post experimental X-ray film showed an overwhelming quantity of W_5Si_3 along with SiC and small quantities of WC. The correct equilibrium: W_5Si_3 -SiC was established, and no evidence of a possible four-phase reaction was detected in the temperature range 1400° - 1925°C. It is conceivable that during the hot pressing of the solid-state samples small quantities of WC, whose presence is not consistent with the correct equilibrium, were formed. Even at the heat treating temperature of 1800°C, the WC did not react completely to form the correct conjugate compounds.

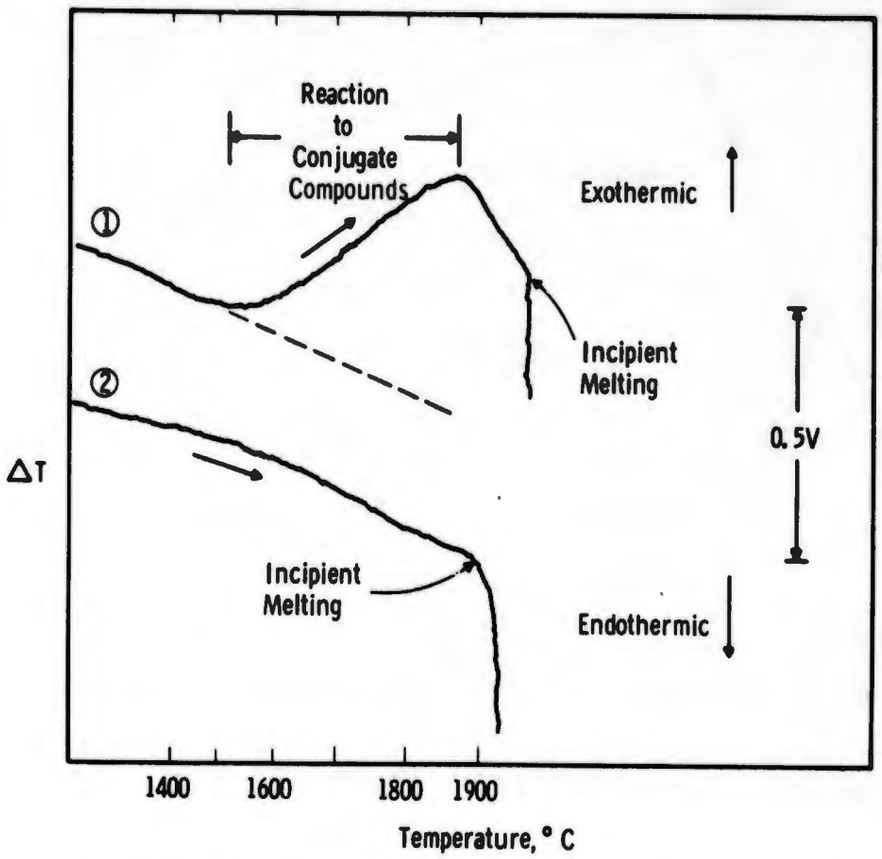


Figure 19. W-Si-C: DTA Heating Curves of a 40/42/18 Alloy Prepared with WSi_2 and WC.

Figure 20 portrays the solid-state portion of the W-Si-C 1800°C isotherm. Three random solid state samples were analyzed post experimentally for their carbon and silicon contents to check the nominal compositions. The results of these analyses are compiled in Table 16.

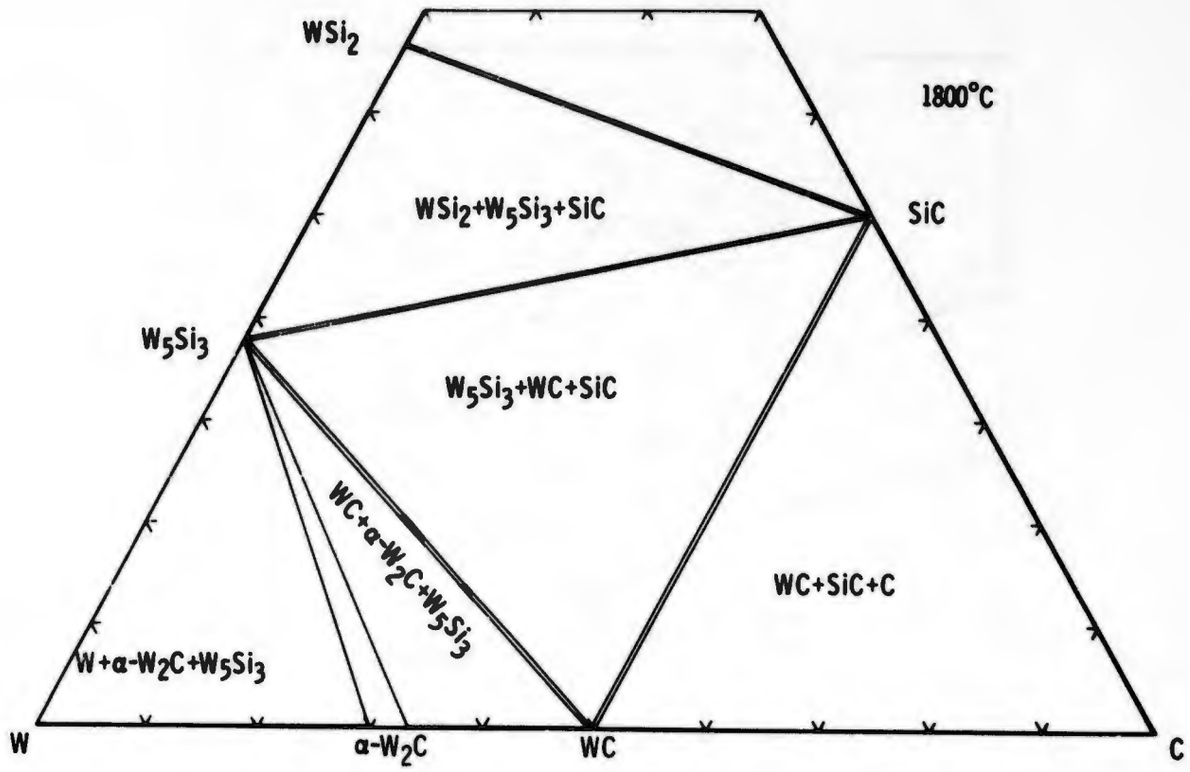


Figure 20. W-Si-C: Isothermal Section at 1800°C.

Table 16. Chemical Analysis Value of Some W-Si-C Samples

Atomic Percent

Nominal				Analyzed		
W	Si	C		W*	Si	C
20	60	20		20.5	61.0	18.5
57	22	21		56.1	21.4	22.5
65	20	15		65.8	20.2	14.0

*by difference

IV. DISCUSSION

The only published phase equilibria diagram of the Ti-Si-C system is the schematic diagram by L. Brewer[49] (Figure 9). In the majority of points this schematic is in accord with the findings disclosed herein. The present investigations have shown the existence of a ternary phase near the composition "Ti_2SiC", and the more complete phase diagram presented here includes the equilibria involving this ternary phase as well as the more accurate determinations of the homogeneous ranges of both the $Ti_5Si_3(C)$ and TiC_{1-x} phases.

L. Brewer[49], in the publication from 1954, has compiled a list giving limits for the heats of formation of many of the refractory silicides; there is still, however, a dearth on other independent calorimetric data concerning these silicides which might be used for confirmation. No attempt will be made, therefore, to elaborate on the findings of L. Brewer[49]. However, a simple evaluation showing the heat of formation of the new ternary phase will be shown.

From the isothermal section of the Ti-Si-C System (Figure 9), the following reaction equation may be written:

$$C_{graphite} + Ti_{48}Si_{21}C_{31} \text{ (ternary phase)} \rightarrow SiC + TiC_{\sim 1}$$

with a most recent value[80] for the heat of formation of $TiC_{\sim 1}$ of -43.1 kcal* and the value[81] of -20.6 kcal* for the heat of formation of SiC, the standard state heat of formation of the ternary phase is calculated to

-52.1 kcal/gram atom Ti.

The schematic diagram of the Nb-Si-C system presented by L. Brewer (Figure 10) is basically correct with the exception of a few minor modifications. At the time of Brewer's publication, the correct constitution of the

*Standard state for convenience.

Nb-Si binary diagram was not known, and the phase designated in the schematic drawing as Nb_5Si_3 is not the $D8_8$ phase in the binary, but rather the ternary stabilized structure. The phase labeled $NbSi_{.55}$ is in reality the binary α-Nb_5Si_3 or α-$NbSi_{.6}$ phase.

The other change involves the equilibrium Nb_2C-$D8_8$(ternary phase). It was found in this investigation that the equilibrium NbC_{1-x}-α-Nb_5Si_3 is present instead of Nb_2C-$D8_8$ (ternary) at 1300°C, although signs were present indicating the possibility of a four-phase reaction plane: $D8_8$-α-Nb_5Si_3-Nb_2C-NbC_{1-x} near this temperature.

An evaluation similar to the one employed for the Ti-Si-C ternary phase was also performed for the $D8_8$ ternary phase in the Nb-Si-C system using a reaction equation to calculate the standard heat of formation:

$$Nb_2C + Si \longrightarrow NbC + Nb_{51}Si_{39}C_{10} \text{ (ternary } D8_8 \text{ phase)}$$

The values used for Nb_2C and NbC are -45.0 and -32.8 kcal taken from a recent compilation[80]. The value obtained for the standard state heat of formation of the ternary Nb-Si-C phase was <-21.2 kcal/gram-atom Si.

The results of the present investigations on the W-Si-C 1800°C isothermal section are in perfect accord with those presented by L. Brewer in a schematic diagram (Figure 11). The minor exception is that in the present work the small homogeneous region of α-W_2C is depicted. Furthermore, the absence of any mutual solubility has been ascertained.

Of all the silicocarbide systems investigated, or presently under investigation, (V-Si-C and Cr-Si-C have not been studied), it is seen that in none of the systems does an equilibrium silicide — graphite exist. The closest approach occurs in the Mo-Si-C system[40] where a ternary $D8_8$ phase forms a two phase field with graphite. This unfortunate fact limits the choice of silicide materials which could conceivably be used as possible oxidation protection for, or composites with, graphite. Some of the disilicides are in equilibrium with the monocarbides ($ZrSi_2$-ZrC, $NbSi_2$-NbC, $TaSi_2$-TaC)[49], and although

these particular disilicides do not belong to the group of disilicides associated with good oxidation protection behavior, it is possible that with refractory metal substitutions in the silicide, a sufficient amount of silicide oxidation protection might be achieved.

REFERENCES

1. E. Rudy, D.P. Harmon, and C.E. Brukl: AFML-TR-65-2, Part I, Vol. II.
2. E. Rudy, St. Windisch, and J. R. Hoffman: AFML-TR-65-2, Part I, Vol. VI.
3. E. Rudy and D.P. Harmon: AFML-TR-65-2, Part I, Vol. V.
4. G. Brauer, H. Renner, and J. Wernet: Z. anorg.allg.Chem., 277 (1954)249.
5. G. Brauer and R.Lesser: Z. Metallkunde 50 (1959), 8.
6. G. Brauer and R. Lesser: Z.Metallkunde 50 (1959), 487.
7. E.K. Storms and N.G. Krikorian: J.Chem.Phys., 64 (1960), 1411.
8. E.K. Storms and N.G. Krikorian: J.Chem.Phys., 63 (1959), 1747.
9. R. Elliott: Armor Res.Found.Rept. 2120-4 (1959).
10. H. Kimura and Y.Sasaki: Trans.Jap. Inst. Met. 2 (1961), 98.
11. K. Schubert, A. Ramon, and W. Rossteutscher: Naturwiss. 21 (1964), 506.
12. N. Mateuschenko, L. Efimenko, and D.Solonichin: Fiz.Metallov Metalloved. 8 (1959), 878.
13. M. Hansen: Constitution of Binary Alloys (McGraw-Hill, 1958).
14. R. Kieffer and F. Benesovsky: Hartstoffe (Springer-Wien, 1963).
15. E.K. Storms: A Critical Review of Refractories, Los Alamos Report, 2942, August 1964.
16. K. Becker and F. Ebert: Z. Physik, 31 (1925), 268.
17. C. Agte and H. Alterthum: Z.techn. Physik, 11 (1930) 182.
18. G. Brauer: Z. Elektrochem. 46 (1940) 397.
19. C.P. Kempter and M.R. Nadler: J.Chem.Phys. 32 (1960), 1477.
20. M. Pochon, C. McKensey, R. Perkins, and W. Forgeng: In: Reactive Metals, Intersci. Publ.New York 1959, Vol 2, pg 327.
21. R. Begley and A. Lewis: In: Colombium Symposium, Met.Soc.Conf. Vol. 10, Intersci. Publ. New York 1961, pg 53.

REFERENCES (Continued)

22. M. Nadler and C. Kempter: J. Phys. Chem. 64 (1964), 1468.

23. G. Santoro and H.B. Probst: NASA Lewis Laboratory, Private Communication to E. Rudy.

24. W. Sykes: Trans. Am.Soc. Steel Treat. 18 (1930), 968.

25. F. Skaupy: Z. Elektrochem. 33 (1927), 487.

26. K. Becker: Z. Elektrochem. 34 (1938) 640.

27. K. Becker: Z. Physik. 51 (1928), 481.

28. K. Becker: Z. Metallkunde 20 (1928), 437.

29. K. Kimer: 1957 (Work quoted in R. Kieffer and F. Benesovsky, Hartstoffe, Springer-Wien.

30. G. Lantz and D. Schneider: Z. Naturforschung 16a (1961) 1368.

31. H.J. Goldschmidt and J.A. Brant: J.Less Com.Met. 5 (1962) 181.

32. R. Doloff and R. Sara: WADD-TR-60-143 (1961), Part II.

33. R. Sara: J.Am.Ceram.Soc. 48 (1965), 251.

34. L.Butorina and Z.G. Pinsker: Soviet Physics, Crystallography, 5 (1960), 560.

35. E. Rudy, F. Benesovsky, and L. Toth: Z.Metallkunde, 54 (1963), 345.

36. H.Krainer: Arch.Eisenhüttenwesen, 21 (1950), 119.

37. A.Metcalfe: Met. Treat. 13 (1946), 127.

38. Opt. cit. ref. #13, pg. 378.

39. N.W. Thibault: Amer. Min. 29 (1944) 249 and 327.

40. H. Nowotny, E. Parthé, R. Kieffer, and F. Benesovsky: Mh.Chem. 85 (1954), 255.

41. O. Ruff: Trans. Elektrochem. Soc. 68 (1935) 87

42. H. Baumann: J. Electrochem. Soc. 99 (1952), 109.

43. F. Laves and H. Wallbaum, Z. Krist A101 (1939) 78.

REFERENCES (Continued)

44. H. Nowotny, H. Schroth, R. Kieffer, and F. Benesovsky: Mh.Chem. 84 (1953), 582.

45. P. Cotter, P. Kohn, and R. Potter: J. Am.Ceram.Soc: 39 (1956), 11.

46. M. Hansen, H. Kessler, and D. McPherson: Trans.Amer.Soc. Met. 44 (1952), 518.

47. C. Brukl, H. Nowotny, O. Schob, and F. Benesovsky: Mh.Chem. 92 (1961), 781.

48. P. Pietrokowsky and P. Duwez: J.Metals 3 (1951), 772.

49. L. Brewer and O.Krikorian, U.S., - AEC Publ.UCRL - 2544 (1954).

50. W. Freundlich, A.Chretien, and M.Bichara: Compt.Rend. 239 (1954), 1141.

51. O. Schob, H. Nowotny, and F. Benesovsky: Plansee Ber. 10 (1962), 65.

52. N.V. Ageev and G.V. Samsonov: J.Neorg.Chim. 4 (1950), 950.

53. H. Schachner, E.Cerwenka, and H. Nowotny: Mh.Chem. 85 (1954), 245.

54. E. Parthe, H. Nowotny, and H. Schmid : Mh.Chem. 86 (1955), 385.

55. E. Parthe, B. Lux and H. Nowotny: Mh.Chem. 86 (1955), 859.

56. L. Brewer and O. Krikorian: J.Electrochem.Soc. 103 (1956), 38.

57. R. Kieffer, F. Benesovsky, and H. Schmid: Mh.Chem. Z.Metallkde, 47 (1956), 247.

58. G. Geach and A. Knapton: As quoted in Hartstoffe by R. Kieffer and F. Benesovsky, Springer Pub. (1963).

59. G. Samsonov, V. Neschpor, and V. Ermakova: Zur. Neorg. Chim. 3 (1958).

60. H. Goldschmidt: J. Iron and Steel Inst. 194 (1960), 169.

61. E. Rudy: Dissertation Techn. Hochschule, Vienna (1960).

62. P. Arschani, R. Volkova, and D. Prokoschkin: Izv. Akad.Nauk. SSSR Met. Topl. (1959), 127 and (1960), 156.

63. H. Wallbaum: Z. Metallkde 33 (1941), 378.

64. G. Brauer and W. Scheele in W. Klemm: Anorganische Chemie 24, Part II, Dietrech's Publishing House, Wiesbaden (1948), 103.

65. A. Knapton: Nature, 175 (1955), 730.

66. R. Kieffer, F. Benesovsky and H. Schmid: in Hartstoffe by R.Kieffer and F. Benesovsky, Springer Pub. Vienna (1963).

67. P. Ewald and C. Hermann: Strukturber. (1913-1928), 219.

68. L. Brewer, A. Searcy, D. Templeton, and C. Dauben: J.Amer. Ceram.Soc. 33 (1950), 291.

69. R. Blanchard and J. Cueilteron: Compt.Rend. 244 (1957), 1782.

70. R. Kieffer, O. Schob, H. Nowotny, and F. Benesovsky: Mh.Chem. 93 (1962), 517.

71. B. Aronsson: Acta Chem. Scand. 9 (1955), 137.

72. R. Kieffer, F. Benesovsky and E. Gallistl: Z.Metall kde 43 (1952), 1243.

73. W. Obrowski: J. Inst.Met. 89 (1960), 79.

74. H. Nowotny, F. Benesovsky, and C. Brukl: Mh.Chem. 92 (1961), 365.

75. H. Nowotny, B. Lux, and H. Kudielka: Mh.Chem. 87 (1956), 447.

76. E. Parthé, H. Schachner, and H. Nowotny: Mh.Chem. 86 (1955), 182.

77. E. Rudy, St.Windisch, and Y.A. Chang: AFML-TR-65-2, Part I, Vol. I. (Jan. 1965).

78. H.D. Heetderks, E. Rudy, and T. Eckert: AFML-TR-65-2, Part III, Vol. I (April 1965).

79. W. Jeitschko, H. Nowotny, and F. Benesovsky: M.H. Chemie, 94 (1963) 1201.

80. Y.A. Chang: AFML-TR-65-2, Part IV, Vol. I. June 1965.

81. JANAF Thermochemical Tables - Dow Chemical Company, 31 Dec 1963.

82. W. Zachariasen: Z. Physik. Chem. 128 (1927), 39.

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Materials Research Laboratory Aerojet-General Corporation Sacramento, California	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP N.A.

3. REPORT TITLE

Ternary Phase Equilibria in Transition Metal-Boron-Carbon-Silicon Systems Part II. Ternary Systems; Volume VII. The Ti-Si-C, Nb-Si-C, and W-Si-C Systems

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

5. AUTHOR(S) (Last name, first name, initial)

Brukl, C. E.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
March 1966	57	82

8a. CONTRACT OR GRANT NO. AF 33(615)-1249 b. PROJECT NO. 7350 c. Task 735001 d.	9a. ORIGINATOR'S REPORT NUMBER(S) AFML TR 65-2 Part II. Vol. VII 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) N.A.

10. AVAILABILITY/LIMITATION NOTICES

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Air Force Materials Laboratory(MAM), Wright-Patterson Air Force Base, Ohio.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	AFML (MAMC) Wright-Patterson AFB, Ohio 45433

13. ABSTRACT

Phase equilibria in isothermal sections of the ternary Ti-Si-C, Nb-Si-C, and W-Si-C systems were established with X-ray films employing the Debye-Scherrer powder technique. The Ti-Si-C system contains a new ternary phase near the composition "Ti_2SiC"; the Nb-Si-C system also has a known ternary phase near the Nb-Si binary, whereas the W-Si-C system exhibits no ternary compounds.

With the exception of the Ti_5Si_3 phase, the mutual solubilities of the binary carbide and silicide phases are exceedingly small or nonexistent.

The results of these investigations are compared with other previous investigations.

DD FORM 1 JAN 64 1473

Unclassified
Security Classification

Unclassified

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Ternary Systems **Titanium-Silicon-Carbon** **Niobium-Silicon-Carbon** **Tungsten-Silicon-Carbon** **Ternary Equilibria** **High Temperature Equilibria**						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through

_____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through

_____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through

_____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS), (S), (C), or (U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.