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AFML-TR-65-2
PART I, VOLUME XII

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

PART I. BINARY SYSTEMS

VOLUME XII. REVISION OF THE VANADIUM-CARBON AND NIOBIUM-CARBON SYSTEMS

E. RUDY
ST. WINDISCH
C. E. BRUKL

AEROJET-GENERAL CORPORATION

TECHNICAL REPORT No. AFML-TR-65-2, PART I, VOLUME XII

SEPTEMBER 1967

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AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

NOTICE

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FOREWORD

The research described in this report was carried out 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, and was administered under the direction of the Air Force Materials Laboratory, Directorate of Laboratories with Lt. P.J. Marchiando acting as Project Engineer, and Dr. Erwin Rudy, Aerojet-General Corporation, as Principal Investigator. Professor Dr. Hans Nowotny, University of Vienna, served as consultant to the project.

The project, which includes the experimental and theoretical investigations of ternary and related binary 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, and was initiated on 1 January 1964. An extension effort to this contract commenced in January 1966.

The phase diagram work on the binary system described in this report was carried out by E. Rudy, St. Windisch, and C.E. Brukl. Assisting in the investigations were: J. Hoffman (metallographic preparations), J. Pomodoro (sample preparation), and R. Cobb (X-ray exposures and photographic work).

Chemical analysis of the alloys was performed under the supervision of Mr. W. E. Trahan, Quality Control Division of Aerojet-General Corporation. The authors wish to thank Mr. R. Cristoni for the preparation of the illustrations, and Mrs. J. Weidner, who typed the report.

The manuscript of this report was released by the authors May 1967 for publication.

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.	Systems Mo-B and W-B
Volume IV.	Hf-C System
Volume V.	Ta-C System. Partial Investigations in 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
Volume XI.	Final Report on the Mo-C System

Part II. Ternary Systems

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

FOREWORD (Cont'd)

Volume III.	Zr-Ta-C System
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
Volume VII.	Systems Ti-Si-C, Nb-Si-C, and W-Si-C
Volume VIII.	Ta-W-C System
Volume IX.	Zr-W-B System. Pseudo-Binary System TaB_2-HfB_2
Volume X.	Systems Zr-Si-C, Hf-Si-C, Zr-Si-B, and Hf-Si-B
Volume XI.	Systems Hf-Mo-B and Hf-W-B
Volume XII.	Ti-Zr-B System
Volume XIII.	Phase Diagrams of the Systems Ti-B-C, Zr-B-C, and Hf-B-C
Volume XIV.	The Hafnium-Iridium-Boron System
Volume XV.	Constitution of Niobium-Molybdenum-Carbon Alloys

Part III. Special Experimental Techniques

Volume I.	High Temperature Differential Thermal Analysis
Volume II.	A Pirani-Furnace for the Precision Determination of the Melting Temperatures of Refractory Metallic Substances

Part IV. Thermochemical Calculations

Volume I.	Thermodynamic Properties of Group IV, V, and VI Binary Transition Metal Carbides
Volume II.	Thermodynamic Interpretation of Ternary Phase Diagrams
Volume III.	Computational Approaches to the Calculation of Ternary Phase Diagrams.

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

The binary systems vanadium-carbon and niobium-carbon were reinvestigated by means of X-ray, melting point, DTA, and metallographic techniques on chemically and thermally characterized specimens; revised phase diagrams for both binary systems are given.

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I. INTRODUCTION AND SUMMARY

A. INTRODUCTION

Inspite of the considerable effort spent over the past few years on the elucidation of the high temperature phase relationships in binary and ternary systems of the refractory transition metals with carbon, many of these systems are still found to be incomplete; and some of the data presented by various authors are inconsistent. This pertains especially to the melting temperatures of these alloys, where their extreme refractoriness has resulted in considerable scatter in earlier measurements. In addition, recent investigations have also shown that some of the intermediate phases exhibit a more complex thermal behavior than previously anticipated. Thus, for example, the thermodynamic evaluation of the equilibria in ternary metal-carbon systems pointed to the existence of sublattice order-disorder transformations in the Me_2C phases(1). These indications have, in the meantime, been confirmed experimentally by X ray and differential-thermoanalytical means(2, 3, 4).

As a result of these findings, and since the observed phase changes will modify the high temperature phase relationships in the ternary metal-carbon systems presently under investigation(5, 6), the binary metal-carbon systems were very carefully re-examined anew.

B. SUMMARY

1. Vanadium-Carbon

The system contains two phases, V_2C and VC, of which V_2C exists in two different modifications and melts under decomposition, and the fcc. cubic (B1) monocarbide melts congruently. The revised phase diagram is shown in Figure 1.

The orthorhombic, low temperature modification of V_2C transforms in a homogeneous reaction at approximately 800°C into the disordered hexagonal high temperature form. The phase, which has a homogeneity

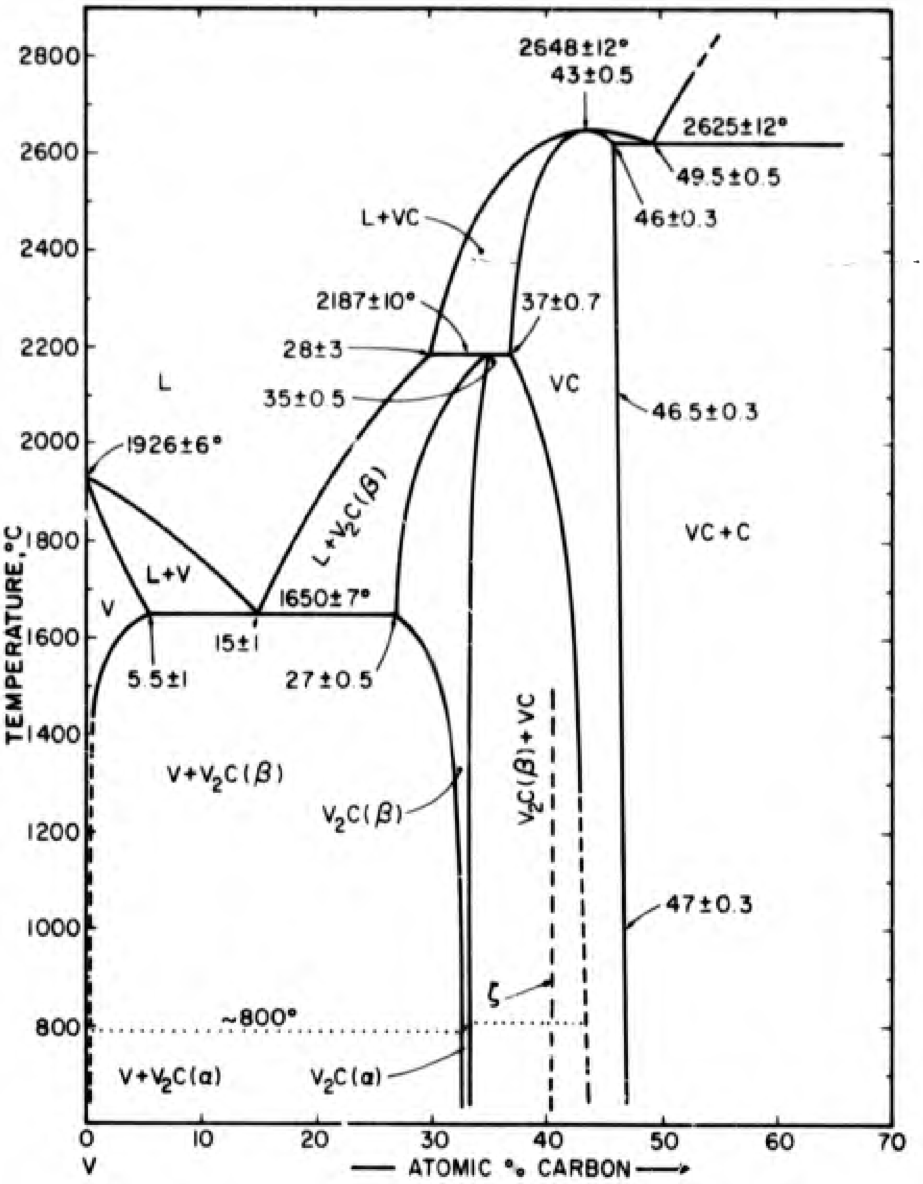

Figure 1. Constitution Diagram Proposed for the Vanadium-Carbon System.

(Error Figures are Based on Estimated Overall Temperature Uncertainties).

range of less than 1 At.% below 1000°C and extends from 27 to ~33 At.% C at 1650°C, melts peritectically at 2187°C.

The cubic (B1) monocarbide, VC, melts congruently at 2648°C at 43 At.% C. The high-carbon boundary of the phase decreases from 47 At.% C at 1000°C (a = 4.172 Å) to 46 At.% at 2625°C (a = 4.164 Å). The low-carbon boundary is strongly temperature dependent, and varies from 37 At.% C at 2200°C, 40.4 At.% C at 1800°C (a = 4.131 Å), to ~43 At.% C at temperatures below 1500°C. The presence of the ζ-phase was observed at temperatures below ~1500°C.

The following reaction isotherms were found (concentrations in At.% carbon):

a. $L\ (49.5) \rightleftharpoons VC\ (46) + C\ (>98)$ at 2625 ± 12°C

b. $L\ (28) + VC\ (37) \rightleftharpoons V_2C\ (\beta)\ (35)$ at 2187 ± 10°C

c. $L\ (15) \rightleftharpoons V\ (5.5) + V_2C\ (\beta)\ (27)$ at 1650 ± 7°C

2. Niobium-Carbon

Two intermediate phases, a peritectically melting subcarbide, which exists in several states of sublattice order, and a very refractory, congruently melting monocarbide, occur in the system. A revised constitution diagram for the system is shown in Figure 2.

Di-niobium carbide exists in three different modifications: an orthorhombic, ordered form, stable between room temperature and 1230°C; an hexagonal, ordered modification, presumably of the ϵ-Fe_2N-type described earlier by N. Terao, between 1230°C and approximately 2500°C; and an hexagonal modification (disordered, L'3-type) between 2500°C; and the melting temperature (3035°C). The phase extends from 28 to ~33 At.% C at 2353°C and has a homogeneity range of less than 1 At.% C at temperatures below 1200°C.

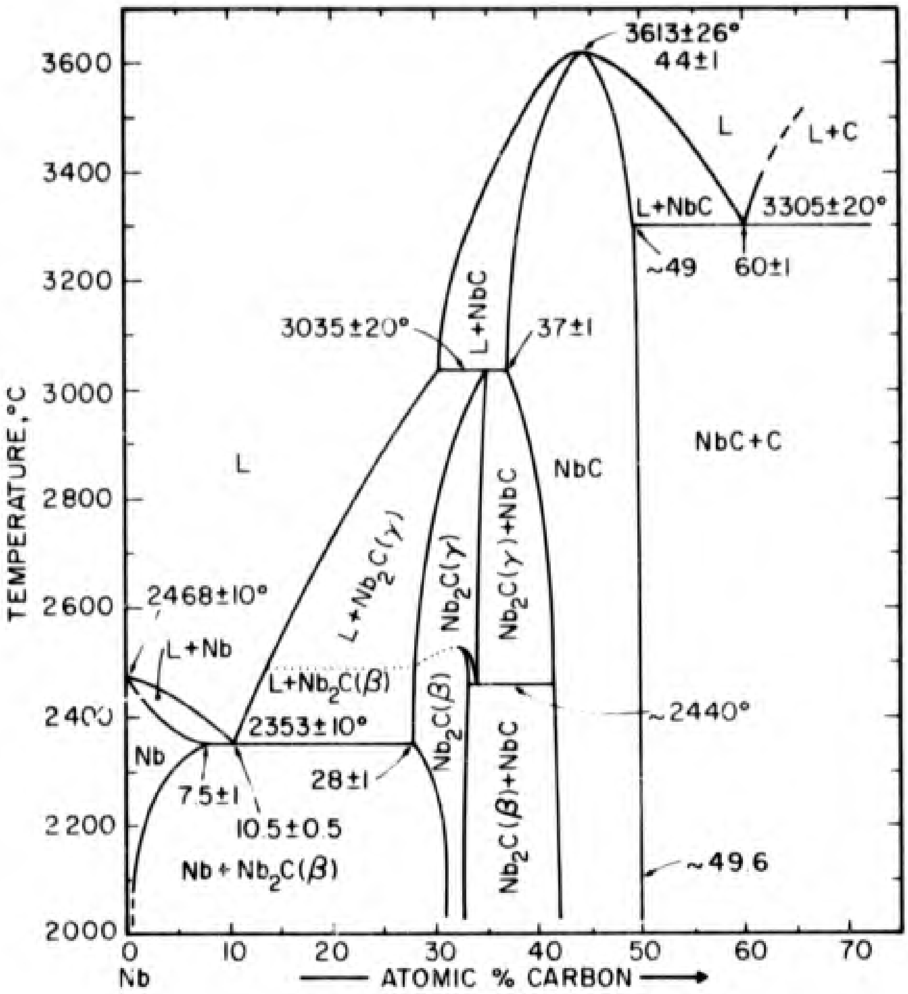

Figure 2. Revised Constitution Diagram for the Niobium-Carbon System.

(Additional Single-Phased Transformation of Nb_2C at 1230°C not Shown. Error Figures are Based on Estimated Overall Uncertainties.)

The cubic (B1) monocarbide, NbC, melts congruently at 3613°C at 44 At.% C. The phase extends from 37 to ~49 At.% C at 3000°C and from 41.3 At.% C (4.431 Å) to ~49.5 At.% C (a = 4.470 Å) at 2200°C. The lattice parameters found for the defect monocarbide are in good agreement with the values determined earlier by G. Brauer and co-workers.

Diffusion experiments indicate the ζ-phase to be metastable and its appearance to result from a non-equilibrium precipitation from the cubic monocarbide during cooling.

The following reaction isotherms were found (concentrations in At.% C):

a. $L\ (60) \rightleftarrows NbC\ (\sim 49) + C\ (>98)$ at 3305 ± 20°C

b. $L\ (30) + NbC\ (37) \rightleftarrows Nb_2C\ (\gamma)\ (\sim 34.5)$ at 3035 ± 20°C

c. $Nb_2C\ (\gamma)\ (\sim 33.5) \rightleftarrows Nb_2C\ (\beta)\ (\sim 33) + NbC\ (\sim 41)$ at ~2440°C

d. $L (10.5) \rightleftarrows Nb\ (7.5) + Nb_2C\ (\beta)\ (28)$ at 2353 ± 10°C

II. LITERATURE REVIEW

Apart from earlier work which has been summarized by R. Kieffer and F. Benesovsky(7), the most extensive, recent investigation of the vanadium-carbon system is by E.K. Storms and R.J. McNeal(8), and of the niobium-carbon system by E.K. Storms and N.H. Krikorian(9) and by H. Kimura and Y. Sasaki(10). Essential phase diagram features proposed by these as well as other authors are summarized in Tables 1 and 2.

Concerning the phase-relationships in the vanadium-carbon system, there appear to be several discpreancies, both in respect to the phase relationships, and to the structure of the intermediate phase V_2C. According to E.K. Storms and R.J. McNeal(8), the monocarbide melts peritectically, whereas previous work(13, 14, 15), as well as more recent measurements by E. Rudy and G. Profulski(12) indicate a congruent melting point and, consequently, the formation of a eutectic between the monocarbide and graphite. Di-vanadium carbide was reported to have a hexagonal L'3-type of structure (disordered carbon sublattice)(8, 35, 36). Recent work, however, has shown that the phase undergoes a displacive transformation in the vicinity of 800°C(23, 24) which is associated with ordering in the carbon sublattice(25). The resulting structure is orthorhombic (Table 3).

The solubility of carbon in vanadium was determined by E.K. Storms and R.J. McNeal(8) to be 8.8 At.% C at the eutectic temperature, whereas

Table 1. Phase Diagram Data for the Vanadium-Carbon System

Reaction	Temperature, °C	Investigator	Ref
$V + V_2C$ Eutectic	1650° at 13 At.% C	W. Rostoker and A. Yamamato, 1954	11
	1630 ± 20° at 16.7 At.% C	E.K. Storms and R.J. McNeal, 1962	8
	1650 ± 7° at 15 At.% C	E. Rudy and G. Progulski, 1967	12
Peritectic decompo. of V_2C	2165 ± 25°	E.K. Storms and R.J. McNeal, 1962	8
	2187 ± 10°	E. Rudy and G. Progulski, 1967	12
Melting Point of VC	2750°	O. Ruff and W. Martin, 1912	13
	2830°	E. Friedrich and L. Sittig, 1925	14
	2780°	J.L. Engelke et al., 1960	15
	2650° (peritectic decompo. at 46 At.% C)	E.K. Storms and R.J. McNeal, 1962	8
	2648 ± 12° at 43 At.% C	E. Rudy and G. Progulski, 1967	12
VC + C Eutectic	2625 ± 12° at 49.5 At.% C	E. Rudy and G. Progulski, 1967	12

Table 2. Phase Diagram Data for the Niobium-Carbon System

Reaction	Temperature, °C	Investigator	Ref
$Nb + Nb_2C$ Eutectic	2335° at 10.5 At.% C	M.L. Pochon et al., 1959	16
	2335° ± 20°	E.K.Storms and N.H.Krikorian, 1960	9
	2328° ± 17°	M.R.Nadler and C.P.Kempter, 1960	17
	2340° ± 20° at 13.5 At.% C	H.Kimura and Y.Sasaki, 1961	10
	2230° at 10.5 At.% C	R.P. Elliott, 1961	18
	2353° ± 10° at 10.5 At.% C	E.Rudy and G.Progulski, 1967	12
Peritectic decomp. of Nb_2C	3265°	M.L. Pochon et al., 1959	16
	3080° ± 35°	M.R. Nadler and C.P.Kempter, 1960	17
	3080° ± 50°	E.K.Storms and N.H.Krikorian, 1960	9
	3080° ± 50°	H.Kimura and Y.Sasaki, 1961	10
	3035° ± 20° at ~35 At.% C	E. Rudy and G.Progulski, 1967	12
Melting Point of NbC	3700° - 3800°	E.Friedrich and L.Sittig, 19~5	19
	3500° ± 125°	C. Agte and H.Alterthum, 1930	20
	3490°	L.F. Brownlee, 1958	21
	3500° ± 75° at 46 At.% C	E.K.Storms and N.H. Krikorian, 1960	9
	3480° ± 50°	M.R.Nadler and C.P.Kempter, 1960	17
	3600° ± 50°	H.Kimura and Y.Sasaki, 1961	10
	3613° ± 26°	E. Rudy and G. Progulski, 1967	12
NbC + C Eutectic	~3250°	E.K. Storms and N.H.Krikorian, 1960	9
	3220° ± 40° at 49 At.% C	M.R.Nadler and C.P.Kempter, 1960	17
	3150°	K.I. Portnoi et al., 1961	22
	3300° ± 50° at 60.5 At.% C	H.Kimura and Y.Sasaki, 1961	10
	3305° ± 20° at 60 At.% C	E. Rudy and G. Progulski, 1967	12

Table 3. Structure and Lattice Parameters of Vanadium and Niobium Carbides

Phase	Structure	Lattice Parameters
V_2C	T<~800°C: Orthorh., Carbon Sublattice Ordered	a=11.49Å ; b=10.06Å ; c=4.55Å (23, 24)(*) a=4.58_6Å ; b=5.75_3Å ; c=5.04_7Å (25)(**)
	T>~800°C: Hexag., L'3-type	a=2.885Å ; c=4.570Å at $VC_{0.47}$ a=2.902Å ; c=4.577Å at $VC_{0.50}$
ζ-VC_{1-x} (8) (at~40At% C)	Unknown	- - -
VC	Cubic, B1-type	a=4.131Å at $VC_{0.73}$ a=4.1655Å at $VC_{0.87}$ a=4.173Å at $VC_{0.88}$
Nb_2C	1. T<1230°C: Orthor., Carbon Sublattice Ordered	a=12.36Å ; b=10.85_5Å ; c=4.968Å (23, 24)(*) a=10.92Å ; b=4.974Å ; c=3.090Å (26)(***)
	2. 1230°C<T<~2500°C, Hexag., Probably ϵ-Fe_2N-type (28)	a=5.40_7Å ; c=4.96_0Å (28) (****)
	3. T>~2500°C: Hexag., L'3-type	a=3.127Å a=4.972Å at 33 At.% C (9)
ζ-NbC_{1-x} (29) (at~40At.% C	Unknown	- - -
NbC	Cubic, B1-type	a=4.431Å at 41.5 At.% C a = 4.469_0Å at~47.6 At.% C (29)

(*) The orthorhombic axes are related to the distorted hexagonal subcell approximately by:

$$a_{o.r.} \approx 4a_{hex};\ b_{o.r.} \approx 2a_{hex}\sqrt{3};\ c_{o.r.} = c_{hex}$$

(**) $a_{o.r.} \approx c_{hex};\ b_{o.r.} \approx 2a_{hex};\ c_{o.r.} \approx a_{hex.}\sqrt{3}$

(***) $a_{o.r.} \approx 2a_{hex.}\sqrt{3};\ b_{o.r.} \approx c_{hex};\ c_{o.r.} \approx a_{hex}$

(****) $a_{hex} = a_{hex.\,subcell.}\sqrt{3};\ c_{hex} = c_{hex.\,subcell.}$

E. Gebhardt et al.(30), in a recent investigation, proposed a maximum solid solubility of 5 At.% C. The carbon-solubility decreases rapidly with decreasing temperature(30) and amounts to less than 2000 ppm at 1000°C(31, 32). According to G. Thomas and R.E. Villagrana(33), a compound, $V_{64}C$, is formed by an ordered distribution of the interstitial atoms in the < 0, 1/2, 0 > octahedral positions in the metal lattice.

The homogeneity range of the V_2C-phase was said to extend from 27 to 33.3 At.% C (a = 2.881 Å, c = 4.547 Å to a = 2.906 Å, c = 4.597 Å (31)), from 29.1 to 37.1 At.% C(32), and from 31.5 to 32 At.% C(34). As pointed by E.K. Storms and R.J. McNeal(8), precipitation of vanadium metal from the subcarbide phase occurs rather rapidly below the V + V_2C eutectic temperature, and alloys below 30.5 At.% C usually cannot be retained single-phased by quenching.

The monocarbide, VC, has a face-centered cubic, B1-type, structure which exists over a wide range of defect compositions(8, 27, 31, 34, 37, 38). It appears well established now that the carbon-rich boundary is located at 46 to 47 At.% C, and that earlier claims of other compounds in the concentration domain of the monocarbide probably referred to substoichiometric compositions, or to impurity phases(7, 39).

A ζ-phase, analogous to the intermediate compounds observed by G. Brauer and co-workers in the Nb-C and Ta-C systems(29, 40), was also reported in the V-C system(8), but its structure was not clarified.

With the exception of the transformations of the Nb_2C-phase, which had been found only recently(2, 24), the gross features of the phase diagram Nb-C appear well established through the investigations by E.K. Storms and N.H. Krikorian(9) and by H. Kimura and Y. Sasaki(10). Preliminary measurements in this laboratory(3, 12) indicated that the generally higher melting temperatures reported by the latter authors seem to deserve preference with respect to the data by E. K. Storms and N.H. Krikorian(9).

According to R. Elliott(41), the solid solubility of carbon in niobium at the eutectic temperature (2230°C) is 5.9 At.% C and decreases rapidly to approximately 0.77 At.% C at 1800°C. Using metallographic techniques, H. Kimura and Y. Sasaki(10) place the solubility limits at 1.8 At.% C at 1900°C, 0.4 At.% C at 1500°C, and 0.2 At.% C at 1200°C. Recent data by E.Gebhardt and co-workers(30) are in good agreement with the above values.

The homogeneity range of Nb_2C extends from 28 to 33.3 At.% C(9, 10) at the Nb + Nb_2C eutectic temperature and decreases to less than 2 atomic percent in width below 1800°C. Using thermal analytical techniques, E.K.Storms and N.H. Krikorian(9), showed that precipitation of niobium from the substoichiometric carbide occurs extremely fast, and that the terminal composition at 28 At.% C cannot be retained by rapid cooling.

Whereas in previous work Nb_2C was assumed to be of the L'3-type, which is characterized by a statistical distribution of the carbon atoms among the two octahedral interstitial lattice sites(9, 35), more recent work showed a fairly complex phase behavior, and, dependent upon the temperature, the formation of at least three different states of sublattice order. Using electron diffraction techniques, N. Terao(28) derived a hexagonal superstructure which is ordered according to the ϵ-Fe_2N type (Table 3). An orthorhombic subcarbide of the approximately composition $NbC_{0.4}$, having parameters of a = 5.371 kX, b = 4.95_6 kX, and c = 3.12_9 kX was obtained by Russian investigators(42, 43) by partial oxidation of niobium carbide. More recently, orthorhombic modifications were also found by H. Nowotny and co-workers(26) and by E. Rudy and C. E. Brukl(23, 24) in heat treated material (Table 3). The transformation behavior is quite complex and, in addition, seems to be strongly dependent upon the stoichiometry of the alloys(26). Based on DTA-studies, the latter authors conclude that the orthorhombic, room temperature-stable modification is formed in a displacive-type of transformation from the already preordered (presumably the ϵ-Fe_2N-type) structure at temperatures around 1200°C. Sublattice order is finally destroyed in a second transformation at ~2450°C, above which the structure is assumed to correspond to the L'3-type.

The face-centered cubic monocarbide, NbC, exists between approximately 41.1 At.% C (a = 4.431 Å) and 47.6 At.% C (a = 4.469_0 Å)(29) at 2000°C. The variation of the lattice parameters with the carbon content, which has been studied in detail by G. Brauer and R. Lesser(29) on pure and well-characterized alloys(29), has since then been confirmed numerous times (9, 10, 44, 45). Another phase, ζ, occurring in the concentration range around 40 At.% C, which is identical to the phase found in tantalum-carbon alloys(40), has been observed by G. Brauer and R. Lesser(29); its structure, however, remains unclarified.

According to Yu. G. Godin(46), the solid solubility of niobium in carbon is less than 0.01%.

III. EXPERIMENTAL

A. STARTING MATERIALS AND ALLOY PREPARATION

The elemental powders, as well as specially prepared master alloys consisting of V_2C, VC, Nb_2C, and NbC, served as the starting materials for the preparation of the experimental alloys. The vanadium powder, as purchased, had an overall purity of better than 99.65%; the supplier was Oregon Metallurgical Corporation, Albany, Oregon. The major impurities were oxygen (420 ppm), nitrogen (180 ppm) and iron (600 ppm). The lattice parameter of this starting material was a = 3.031 Å.

The impurities in the niobium powder (>99.8% Nb, Wah-Chang Corporation, Albany Oregon) were as follows (in ppm): O-<420, N-<90, C-30, Ta-400, Zr-200, and the sum of other metallic impurities-<400. A lattice parameter of a = 3.3006 ± 0.0007 Å, obtained for this niobium powder, is consistent with parameters given in the literature for high purity niobium(35).

The spectrographic-grade graphite powder was purchased from Union Carbide Corporation, Carbon Products Division. The total impurity content was below 2 ppm.

The carbide master alloys were prepared by reacting the carefully blended and cold-compacted mixtures of the metal powders and carbon in a graphite-element furnace. The niobium carbides were made under vacuum (1900°C, $< 5 \times 10^{-5}$ Torr), while the vanadium carbides were first heated under vacuum (< 1300°C), and the reaction then completed at 1750°C under a high purity helium atmosphere. The resulting reaction cakes of the carbides were crushed and ball milled under helium to a grain size smaller than 60 microns. The powders were leached in a hot 2N mixture of hydrochloric and sulfuric acid, the slurry centrifuged, washed with ether, and then dried in vacuum. The chemical and X-ray analyses of the carbide powders are listed in Table 4.

Table 4: Chemical Analysis and Lattice Parameters of Carbide Starting Materials

Carbide	Carbon Content At.% C	O + N ppm	Phases Present	Lattice Parameters, Å
V_2C	32.4 ± 0.02	290	V_2C	a = 2.900; c = 4.574
VC	$C_{bound} = 46.9$ $C_{free} = 1.7$	160	VC	a = 4.172
Nb_2C	33.2 ± 0.2	<160	Nb_2C + trace NbC	a = 3.125; c = 4.963
NbC	49.2 ± 0.2	<100	NbC	a = 4.470

The experimental alloys were prepared by cold-pressing and sintering, as well as by short duration hot pressing of the hand-mixed powders in graphite dies. The homogenization treatments were carried out either under vacuum ($< 10^{-5}$ Torr) or under high purity helium in a tungsten mesh element furnace manufactured by the R. Brew Company. Selected equilibration treatments at subsolidus temperatures, followed by rapid cooling or quenching in tin, were carried out in the Pirani-furnace(12) or in the DTA-apparatus(2). A few alloys, primarily for metallographic purposes, were also prepared by arc melting under helium using a nonconsumable tungsten electrode.

B. DETERMINATION OF MELTING TEMPERATURES AND DIFFERENTIAL THERMAL ANALYSIS

The melting temperatures of the alloys were measured using the method of M. Pirani and H. Alterthum. The apparatus used in this laboratory and the temperature calibration and correction procedures have been described previously(12) and need not be repeated in detail here.

Differential-thermoanalytical studies(2) were carried out on approximately 40 different alloy compositions in both systems. The sample containers were graphite, and annealed graphite also served as comparison standards for the experimental alloys.

C. METALLOGRAPHIC, X-RAY AND CHEMICAL ANALYSES

For the metallographic studies, the specimens were mounted in a mixture of diallylphtalate and lucite-coated copper powder and preground on silicon-carbide papers of various degrees of coarseness. They were polished on microcloth using a slurry of Linde "B" alumina (0.3μ) in a 5% chromic acid solution. The etching procedures are described in Table 5.

Carbon in the alloys was determined in the well-known manner by combustion and conductometric analysis of the gas mixture. For the determination of unbound graphite, the powdered samples were dissolved in a mixture of nitric and hydrofluoric acid. The residual graphite flates were then filtered off, washed with methanol and warm heptane to remove the paraffins formed in the dissolution process, and dried for 24 hrs at 105°C in a vacuum oven. The graphite remaining was then determined by combustion.

Approximately one-quarter of the experimental alloy material was analyzed for oxygen and nitrogen by the gas-fusion technique, and low level metallic impurities were, on a random selection basis, determined spectrographically in a semi-quantitative manner.

Table 5. Etching Procedures for Vanadium-Carbon and Niobium-Carbon Alloys

Alloys	Etching Procedure
V-C (0-35 At.% C)	Electroetched in 5% sulfuric acid solution
V-C (35-46 At.% C)	Electroetched in concentrated ammonia solution
V-C (46-60 At.% C)	Used as-polished, phase-contrast improved by short dipping in concentrated ammonia
Nb-C (0-16 At.% C)	Anodized in 0.5% oxalic acid solution
Nb-C (16-39 At.% C)	First anodized in 0.5% oxalic acid solution, followed by dip-etching in a 10% acid (2 parts HCl, 2 parts HNO_3, 1 part HF) solution and further dip-etching in 20% Murakami's solution
Nb-C (39-62 At.% C)	Dip-etched in 20% Murakami's solution
Nb-C (>62 At.% C)	Used in the as-polished state

In general, it was found that the analyzed carbon contents in the processed alloys agreed very closely (~ 1 At%) with the weighed-in compositions. Also, after melting, the combined contents of oxygen and nitrogen was in each instance below 100 ppm, so that the effect of these impurities upon the measured phase equilibrium data may be disregarded.

Powder patterns, using Cu-Kα radiation, were prepared from all experimental alloys. The film strips were measured on a Siemens-Kirem coincidence scale with micrometer attachment (0.01 mm scale divisions).

IV. RESULTS

A. VANADIUM-CARBON

The melting temperatures of approximately 25 different alloy compositions, of which most were run in duplicate (Figure 3), confirm a metal-rich eutectic temperature of 1650°C and a peritectic isotherm involving subcarbide, monocarbide, and melt, at a temperature close to 2200°C. The monocarbide melts with a maximum of 2648 °C and forms a eutectic with graphite at 2625°C.

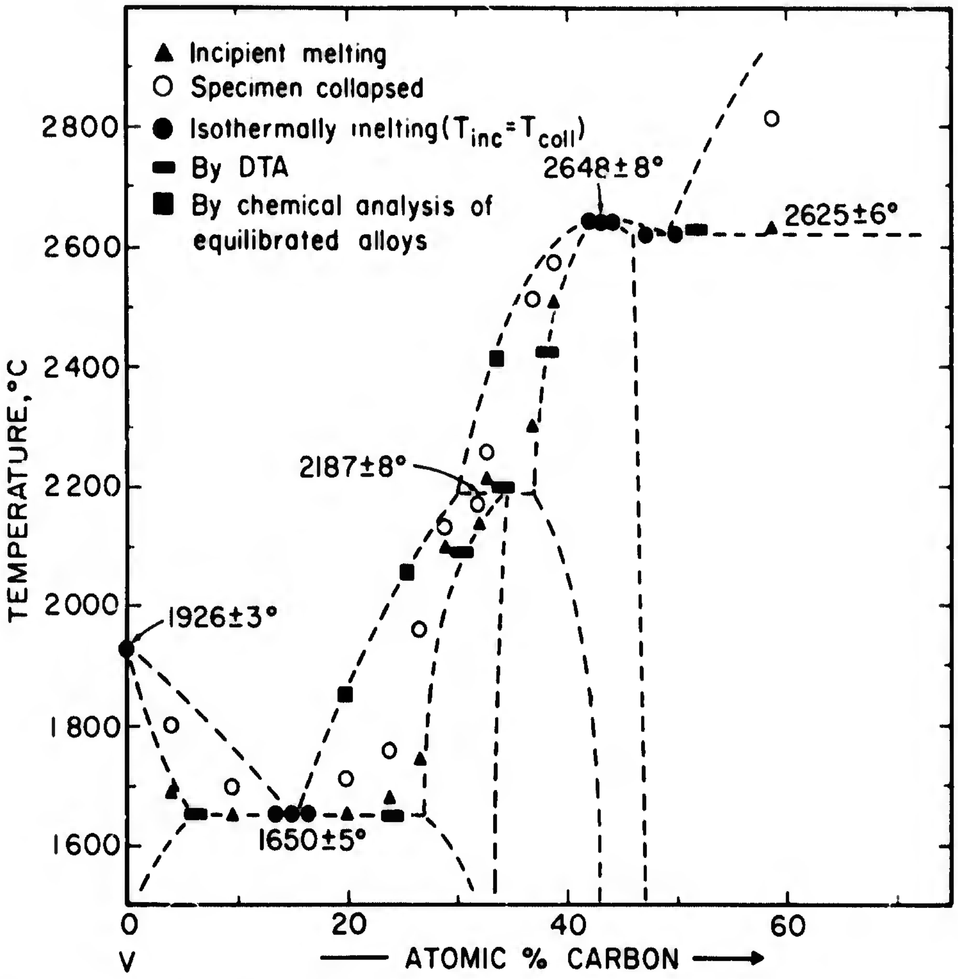

Figure 3. Melting Temperatures of Vanadium-Carbon Alloys. (Temperature Error Figures Based on Reproducibility in the Measurements).

A few liquidus data for the metal-rich portion of the system were obtained by allowing vanadium plugs, which were placed inside graphite containers and allowed to react with the surrounding graphite at a series of preselected temperatures. After establishing equilibrium between the melt and the outer core of solid crabide phases, the samples were rapidly cooled, and the molten center chemically analyzed.

Metallographic analysis showed melted vanadium-carbon alloys containing up to 5.5 At.% C to be single-phased at the eutectic temperature, although rapid precipitation of the subcarbide from the metal-solution prevented retainkent of the high temperature equilibrium states (Figures 4 and 5). As was found for tantalum-carbon(3) and also for niobium-carbon alloys which will be discussed in the following section, the carbide precipitates agglomerate rather rapidly and have the tendency to segregate to the boundaries of the metal grains.

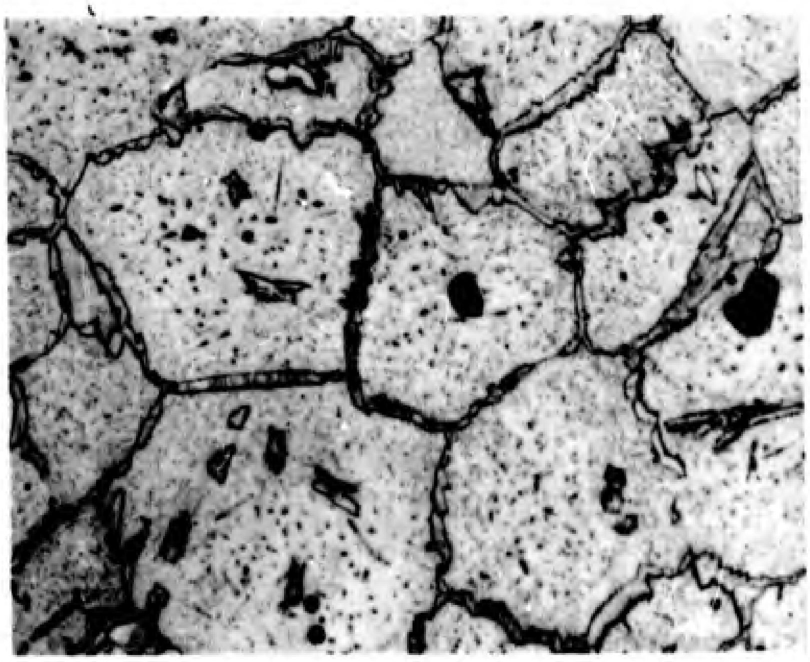

Figure 4. V-C (5.2 At.% C), Equilibrated at 1600°C and Cooled at ~ 30°C per Second. X375

Vanadium with Intragranular Carbide Precipitations and V_2C Agglomerated at the Grain Boundaries.

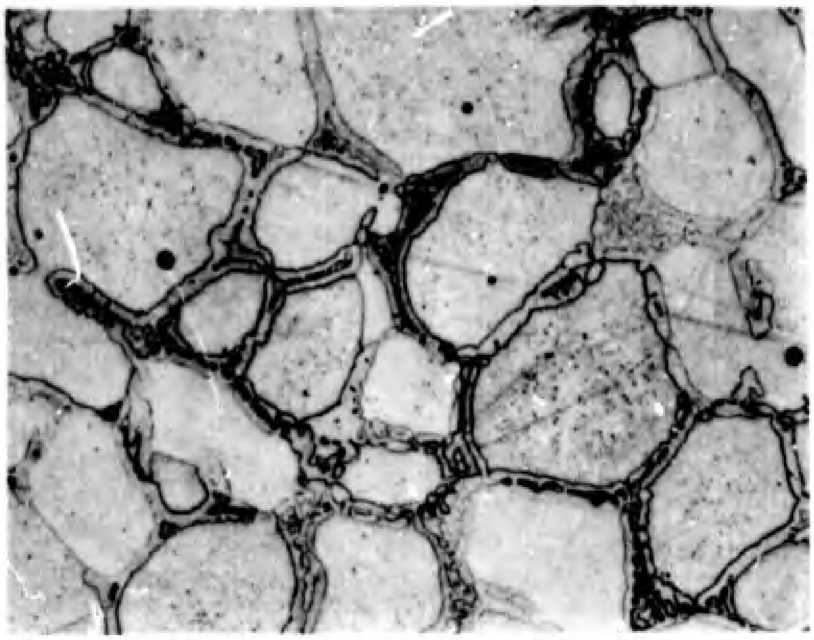

Figure 5. V-C (6.3 At.% C), Equilibrated at 1655°C and Cooled at ~40°C per Second. X375

Primary Vanadium Grains Surrounded by Agglomerated V_2C Precipitates and V + V_2C Eutectic.

Melted alloys containing between 5.5 to ~15 At.% C showed primary crystallized metal in a eutectic matrix. The alloy at 15 At.% C consisted of pure eutectic (Figure 6), whereas samples higher in carbon contained primary crystallized V_2C (Figure 7). At 1650°C, V_2C extends between 27 and ~33 At.% C, as verified by metallographic inspection, although rapid metal-precipitation in samples containing less than 30 At.% C did not allow the alloys to be retained single-phased.

The melting equilibria in the metal-rich region of the system, as well as the peritectic decomposition of the V_2C-phase were independently verified by DTA (Figures 8 and 9), as well as X-ray studies. The X-ray films and metallographic analysis specifically showed that specimens in the concentration region from 30 to 37 At.% consisted of a non-equilibrium mixture of $V + V_2C + VC_{1-x}$ when quenched from temperatures above 2190°C (Figure 10).

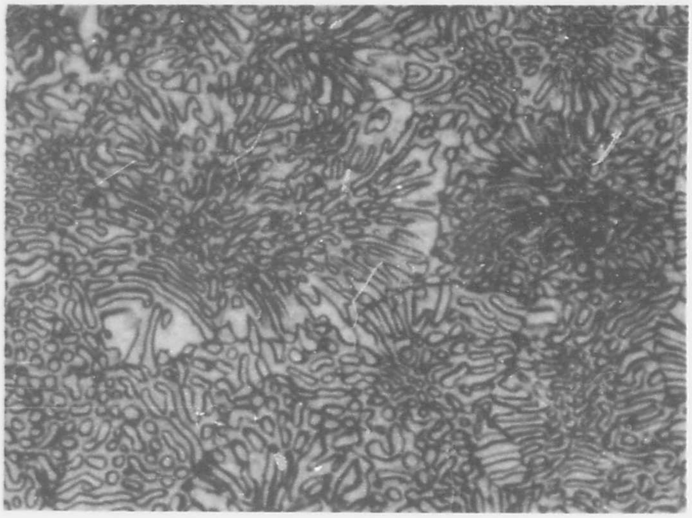

Figure 6. V-C (15 At.% C), Cooled at ~60°C per Second from 1650°C. X1000

$V + V_2C$ Eutectic

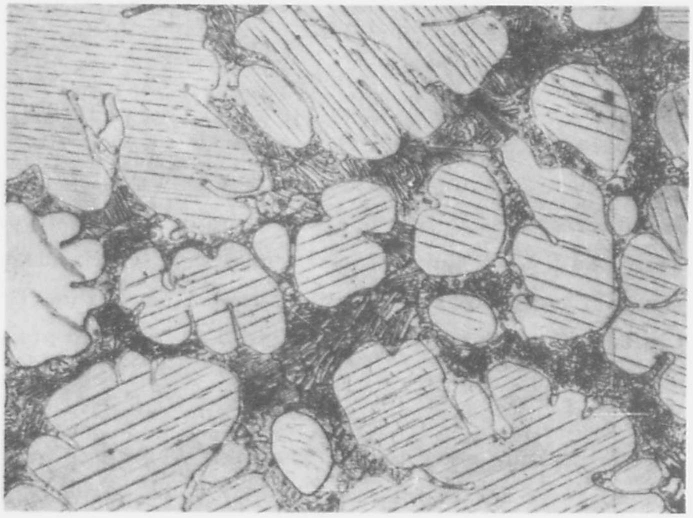

Figure 7. V-C (22 At.% C), Cooled at ~60°C per Second from 1750°C. X325

Primary Crystallized V_2C with Unidirectional Vanadium Precipitates in a Matrix of $V + V_2C$ Eutectic.

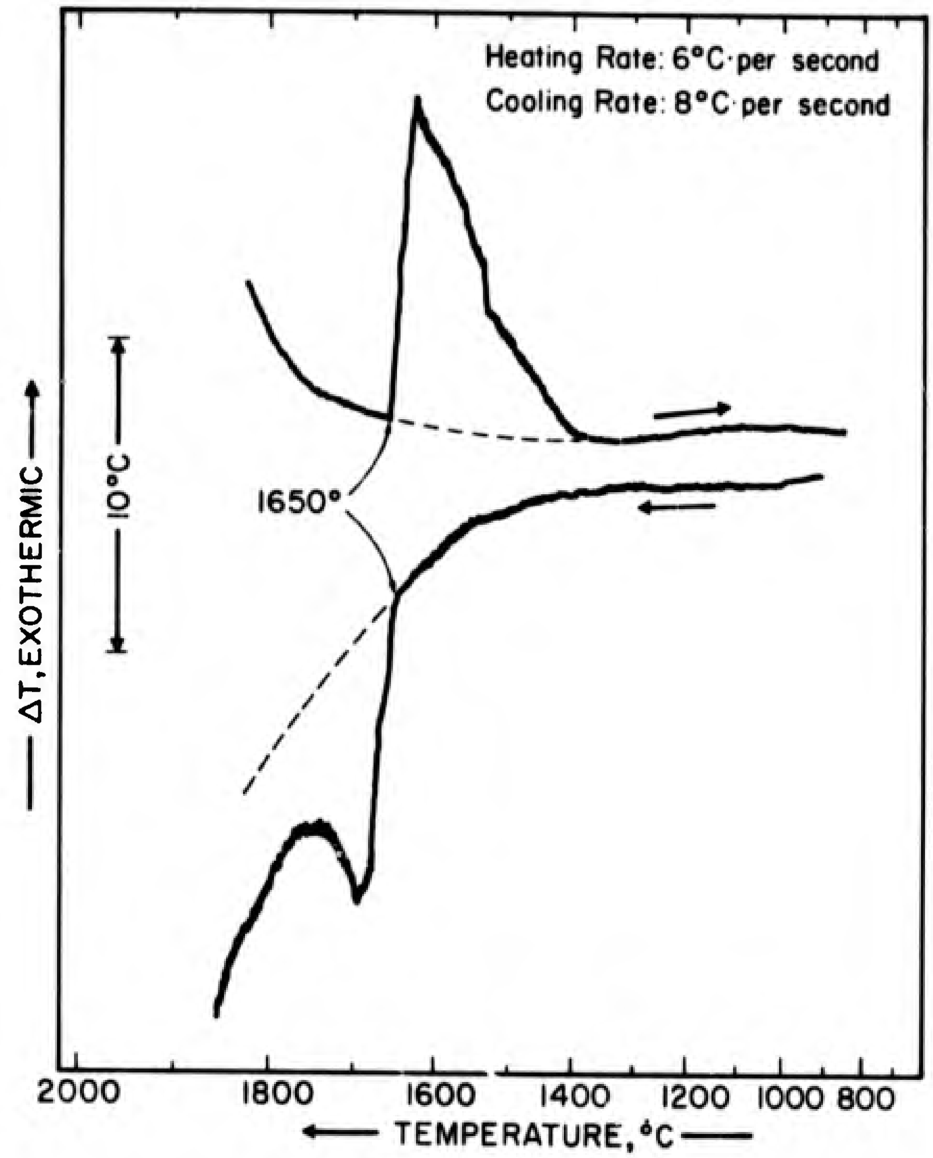

Figure 8. DTA-Thermogram of a Vanadium-Carbon Alloy Containing 24 Atomic Percent Carbon.

(Indicated Temperature for Thermal Arrest Refers to Independent Pyrometric Reading).

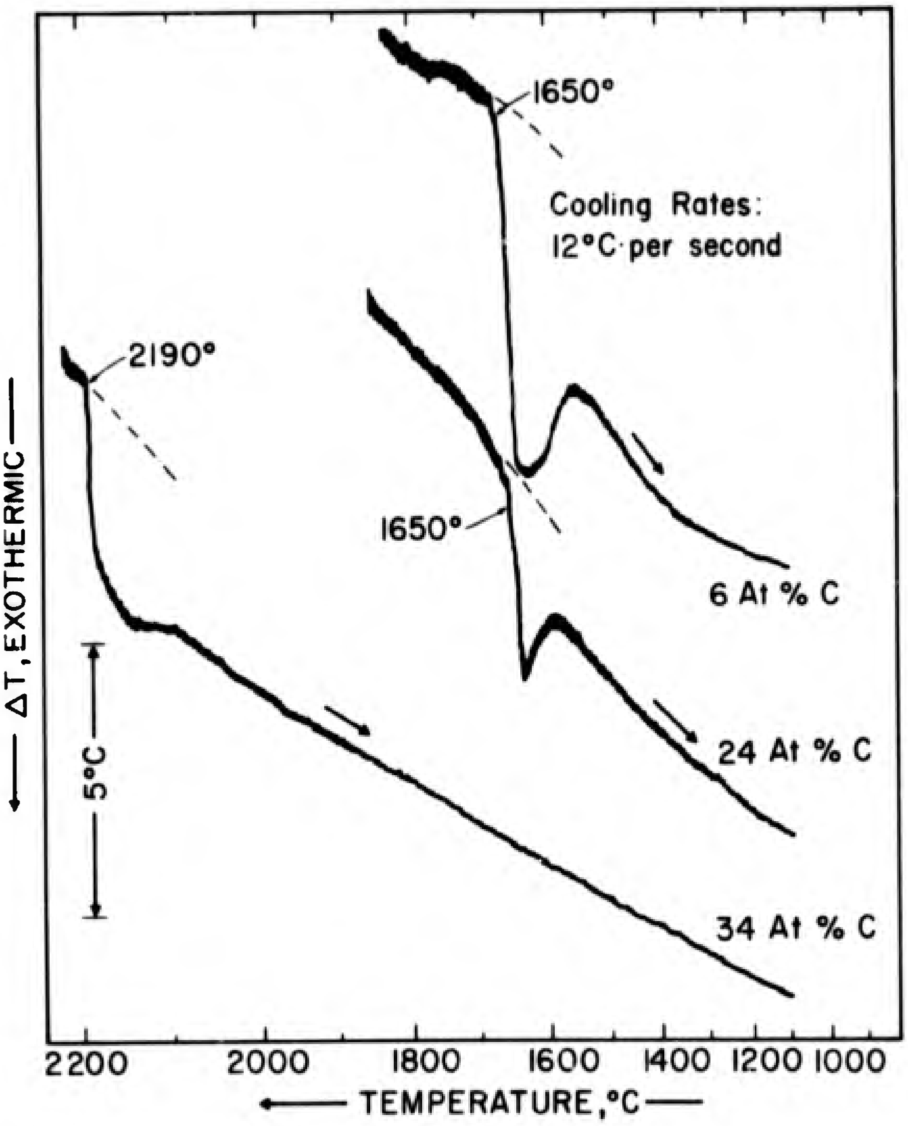

Figure 9. DTA-Thermograms (Cooling) of Metal-Rich Vanadium-Carbon Alloys.

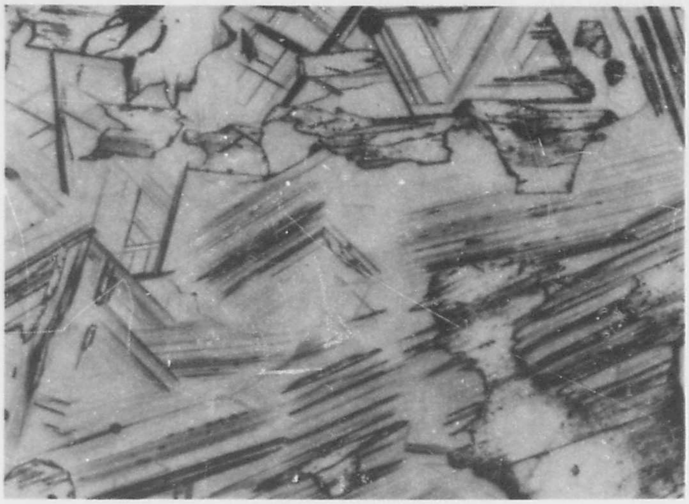

Figure 10. V-C (35.5 At.% C), Rapidly Cooled from 2250°C. X475

Nonequilibrium Mixture V_2C + VC + traces of V.

Precipitation of V_2C from the substoichiometric (< 40 At.% C) monocarbide also occurs extremely fast; but, unlike the behavior of the other group V transition metal monocarbides, it proved in this case to be possible, by tin-quenching, to retain alloys single-phased down to 38 At.% C. The series of photomicrographs shown in Figures 11a through 11f, taken from samples quenched at various rates, show in somewhat greater detail the nucleation and growth stages of the orientated V_2C and ζ-VC_{1-x} precipitates in the monocarbide. From crystallographic considerations, it is to be assumed that the planes of coherence are the close-packed plane (111) in the face-centered cubic matrix and the (0001) plane in the hexagonal V_2C, both of which have nearly identical occupational characteristics.

Microscopic inspection of a number of specimens quenched from temperatures ranging between 2200 and 2600°C indicated the phase boundaries of the monocarbide to be between 37 and ~46.5 At.% C and ~2200°C, and the high carbon boundary at 2625°C at 46 At.% C. The existence of a eutectic

Figures 11a through 11f: Precipitation of V_2C from Substoichiometric Vanadium Monocarbide as a Function of the Cooling Conditions, (Alloys Preequilibrated at 2400°C).

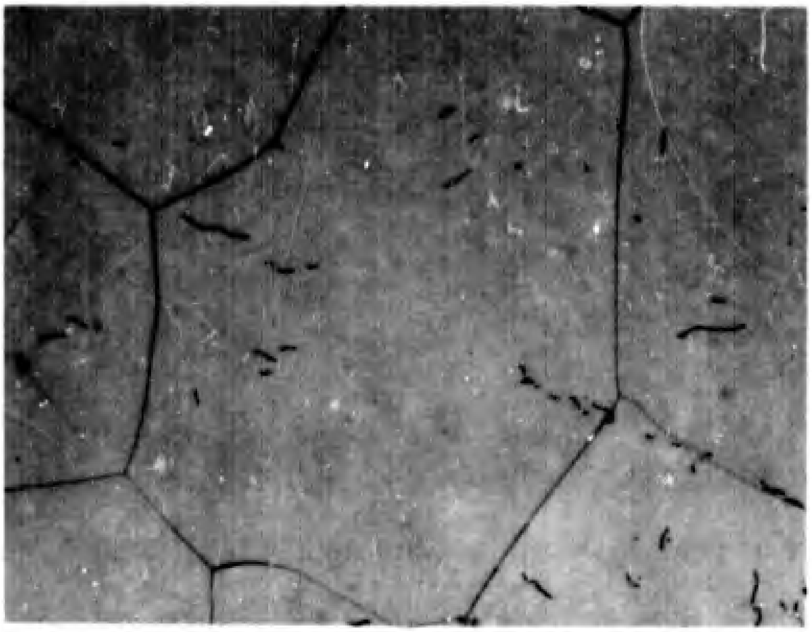

Figure 11a. V-C (38 At.% C), Cooled at >250°C per Second. X550

Practically Single Phase Monocarbide, a = 4.116 Å.

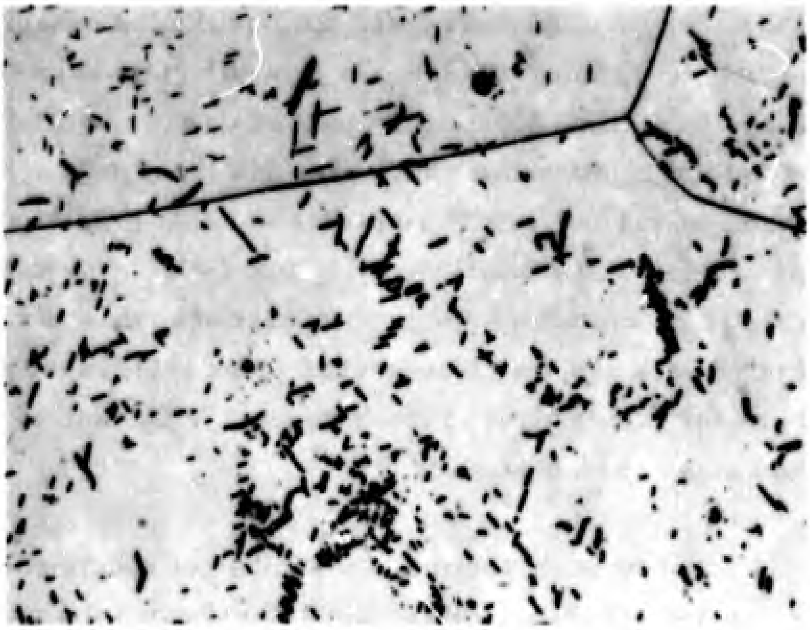

Figure 11b. V-C (38 At.% C), Average Cooling Rate Approximately 150°C per Second. X550

Intragranular Nucleation of V_2C in the Substoichiometric Monocarbide.

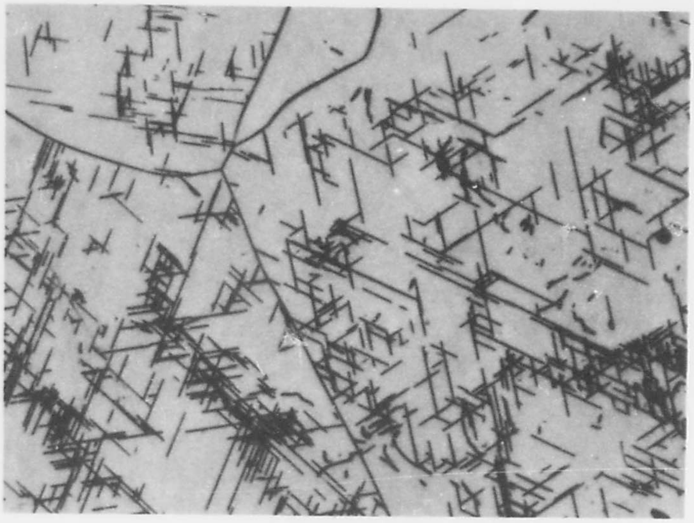

Figure 11c. V-C (38 At.% C), Cooled at Approximately 100°C per Second. X600

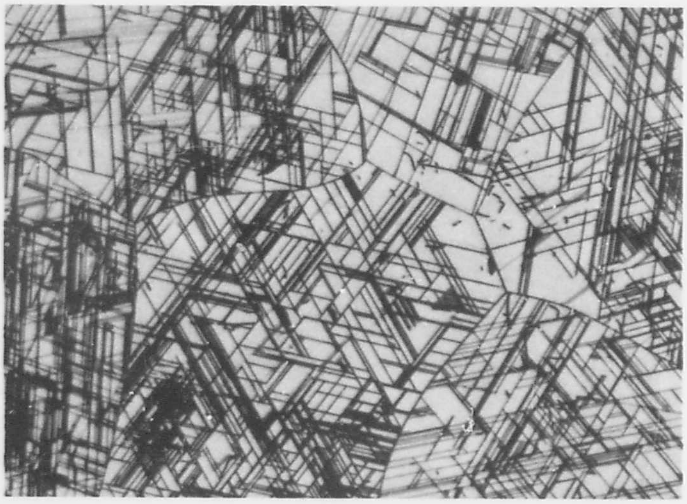

Figure 11d. V-C (38 At.% C), Cooled at ~40°C per Second. X550

Lattice Parameter of Matrix: a = 4.123 Å.

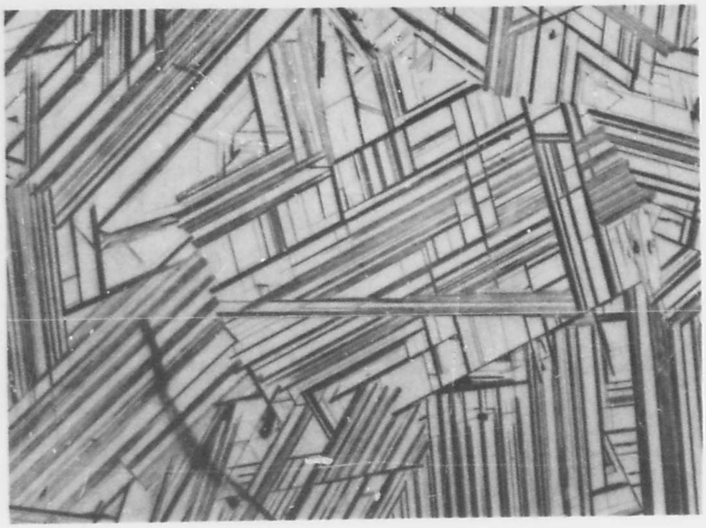

Figure 11e. V-C (38 At.% C), Cooled at ~10°C per Second. X440
Lattice Parameter of Matrix: a = 4.12$_5$

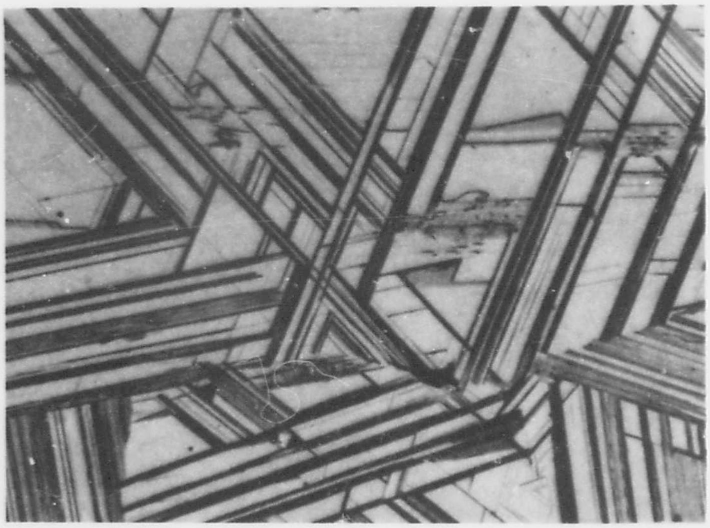

Figure 11f. V-C (38 At.% C), Cooled at 0.2°C per Second. X720
Note Growth of Precipitate Phases.

between the monocarbide and graphite at 49.5 ± 0.5 At.% C is unequivocally verified by the microstructures of melted alloys (Figures 12 through 14), thus ruling out the possibility of peritectic melting of the monocarbide as proposed by E. K. Storms and R. J. McNeal(8). A eutectic temperature of 2625°C was independently verified by differential thermoanalysis (Figure 15). It is interesting to note, that among the monocarbide + graphite eutectics found in the refractory transition metal-carbon systems, the vanadium system is the only one where the occasional occurrence of spherical graphite was observed in hypereutectic alloys (Figure 16).

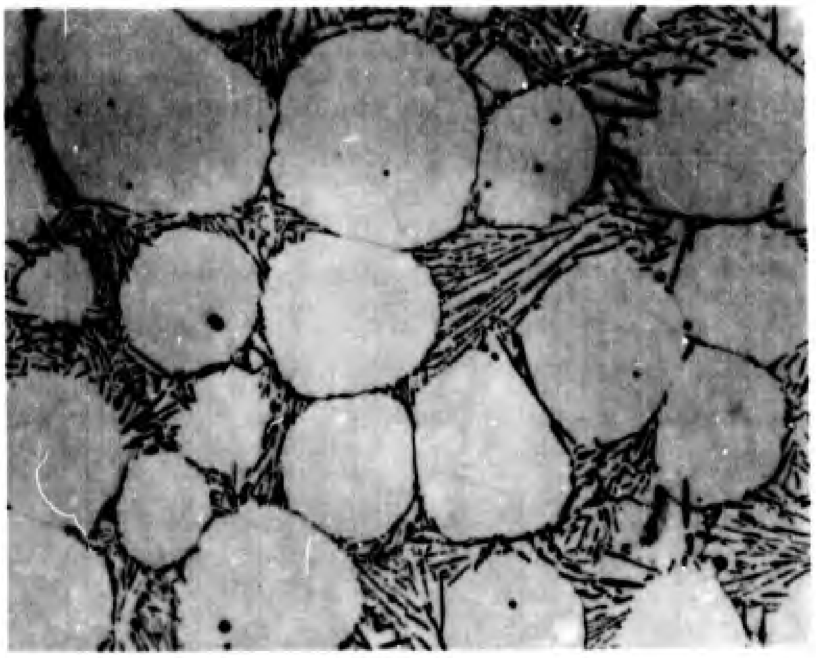

Figure 12. V-C (48.1 ± 0.05 At.% C), Rapidly Cooled from 2630°C. X400
Primary Monocarbide in a VC + C Eutectic Matrix.

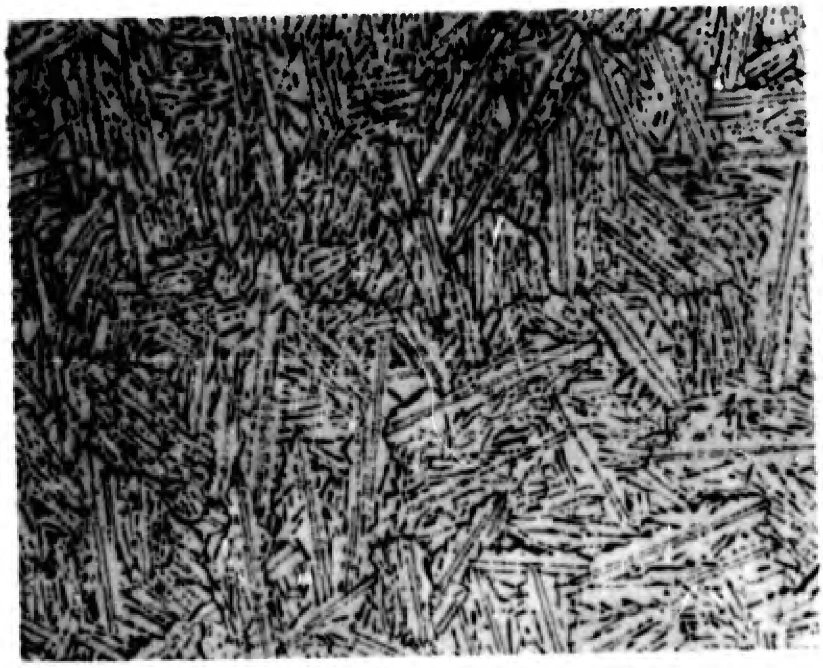

Figure 13. V-C (49.5 ± 0.05 At.% C), Rapidly Cooled from 2630°C. X500
VC + C Eutectic.

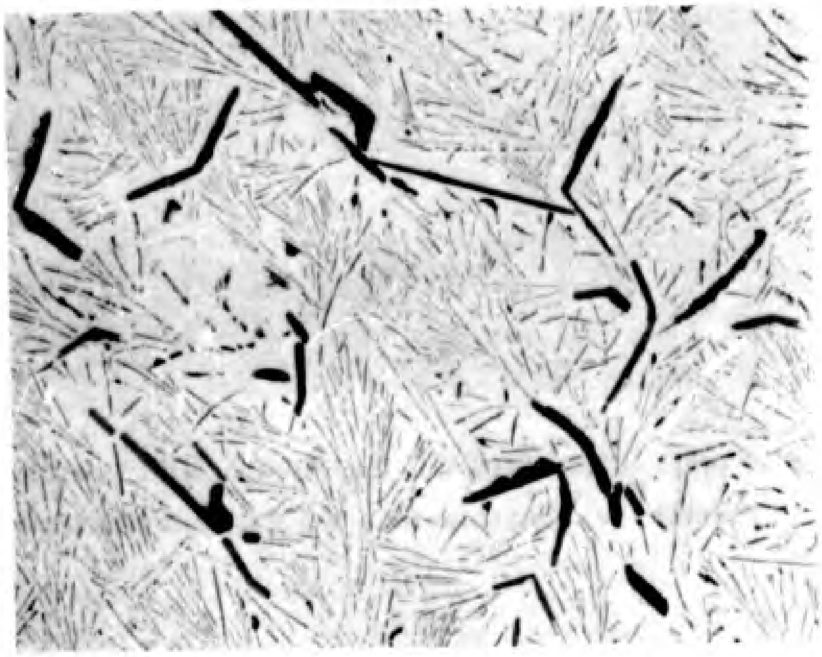

Figure 14. V-C (49.8 ± 0.05 At.% C), Rapidly Cooled from 2635°C. X120
Small Amounts of Primary Graphite in a VC + C Eutectic Matrix.

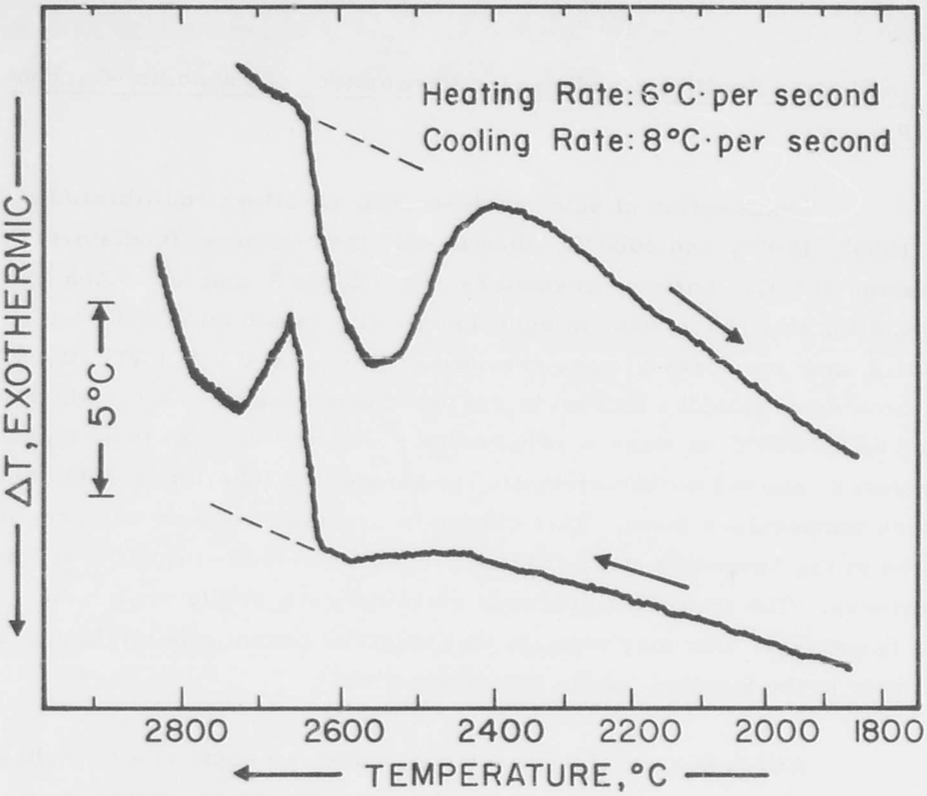

Figure 15. DTA-Thermogram of a Vanadium-Carbon Alloy Containing 62 Atomic Percent Carbon.

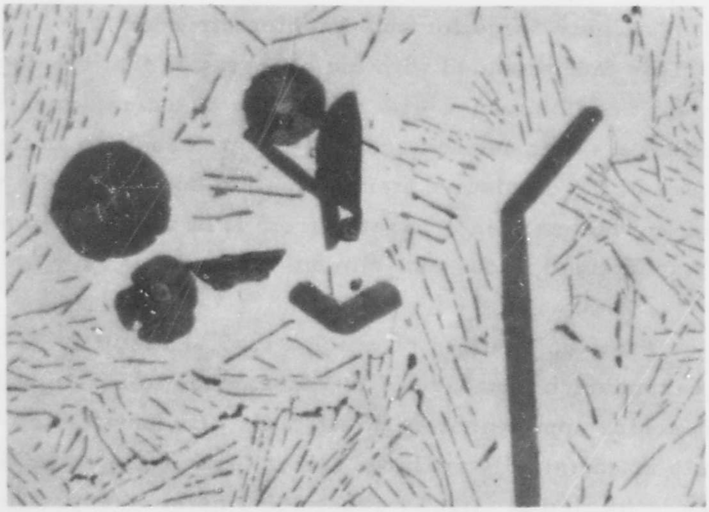

Figure 16. Spherical and Platelet-Shaped Graphite in a Hypereutectic VC + C (50 At.% C). X640

Solid State Equilibria and Lattice Parameters of Vanadium-Carbon Phases

Examination of subcarbide-containing alloys equilibrated at 1000°, 1500°, 1800°, and 2000°C, showed only the hexagonal (undistorted) modification of V_2C. Lattice parameters of a = 2.884 Å and c = 4.565 Å were found for this phase when in equilibrium with vanadium at 1500°C; a = 2.901 Å and c = 4.575 Å were obtained in two-phased V_2C + VC alloys. X-ray patterns of samples located in the two-phase range V + V_2C, which were annealed below 800°C or were slowly cooled (2°C per second) from higher temperatures, showed a characteristic splitting of the (hko) lines of the hexagonal high temperature form. This change in crystal structure was previously(23,24,25) attributed to the formation of an ordered, orthorhombic modification at lower temperatures. The transition proceeds extremely sluggishly when monocarbide is present; this may indicate that epitaxial phenomena might play a certain role in the kinetics of the transformation.

Although a careful search was made, no signs of a two-phased transformation process, such as found in Mo_2C at the stoichiometric composition(47) could be detected. Instead, only the characteristic rippling of the grains, which probably is due to heavy slippage in the transformation process and which also has been found for substoichiometric Mo_2C(47), was noticed (Figure 17). This fact, coupled with the observation that the degree to which the lines are split can be varied with the choice of thermal treatment, leads us to believe that a single-phased, second-order transition is involved. Whether the temperature of the displacive transformation coincides with the ordering temperature, or whether it is separated from it by a small temperature gap could not be ascertained in our experiments.

Diffusion studies, of which a typical result is shown in Figure 18, indicate the carbon-rich boundary of the subcarbide to be slightly temperature-dependent, reaching approximately 35 At.% C at the peritectic temperature. X-ray analysis of chemically analyzed alloys further indicates that the carbon-rich boundary is located at slightly substoichiometric compositions 32.9 ± 0.2 At.% C) at temperatures below 1200°C.

Figure 17. Diffusion Couple L (V,C) + C, V_2C-Zone X500
Diffusion Couple Reacted at 1800°C, Then Reannealed for 15 Minutes at 8000°C.

Slip Lines in V_2C Due to the Order-Disorder Transformation Irregular Dark Lines and Spots are Cracks and Voids.

(Vertical Illumination for Improved Contrast)

The ζ-phase, previously described by E.K. Storms and R.J. McNeal(8), and presumed to be of the same structure as the phases in the Nb-C and Ta-C systems described by G. Brauer and co-workers(29, 40), was observed as a distinct zone in diffusion samples treated at temperatures below 1500°C (Figure 19). No attempt, however, was made to determine whether the phase remains stable or disappears upon prolonged heat-treatment at this or lower temperatures. No conclusion can therefore be reached as to whether the phase is stable or has metastable characteristics as the analogous phases in the Ta-C(3) and Nb-C systems.

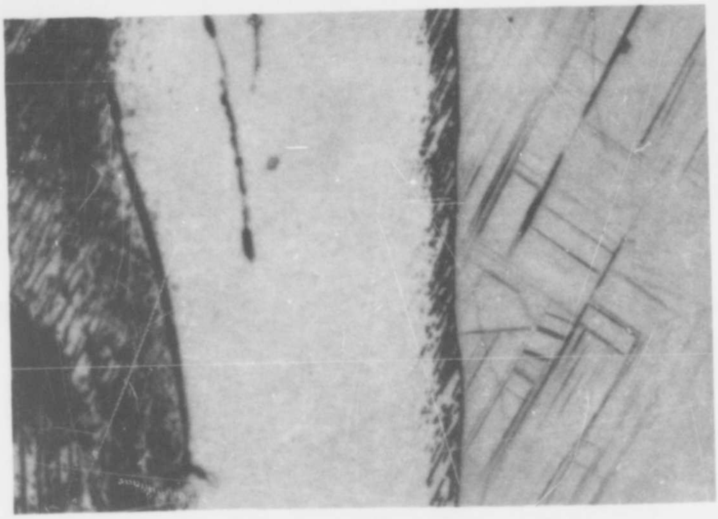

Figure 18. Diffusion Couple V-C (29 At.% C)-Graphite, Held 15 Minutes at 2000°C, and Rapidly Cooled. X750

Note Unidirectional Monocarbide Precipitations in V_2C at the $V_2C + C$ Interface.

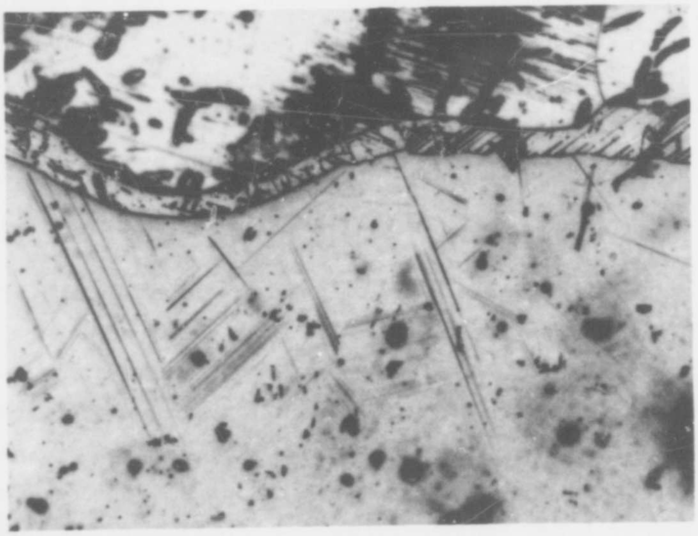

Figure 19. Diffusion Couple V_2C (30 At.% C)-C. X500

Reacted for 10 min. at 2000°C, and Heated for 62 hrs at 1500°C.

Note Distinct Layer of ζ-VC_{1-x} Between the Sub- and the Monocarbide.

The variation of the lattice parameters of the monocarbide with the carbon content exhibits a nearly linear relationship. The data points shown in Figure 20 were obtained from alloys which were first melted in the Pirani-furnace and then equilibrated for 2 min at 2600°C, 1 hr at 2000°C, 4 hrs at 1800° to 1850°C, and 200 hrs at 1000°C; these alloys were subsequently analyzed chemically for bound and free carbon, and studied by X-ray diffraction.

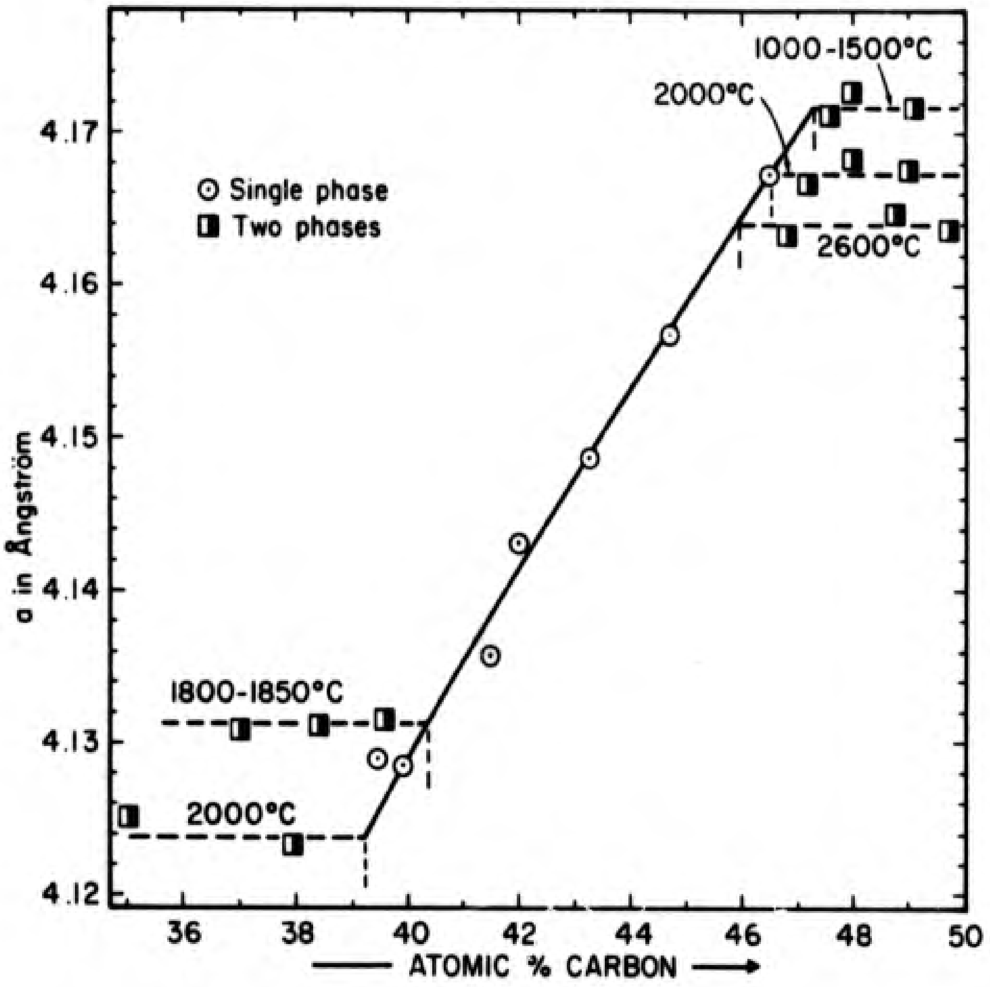

Figure 20. Lattice Parameters of Vanadium Monocarbide.

All experimental results have been combined to construct the phase diagram shown in Figure 1. The dotted line at approximately 800°C in the diagram is used to indicate the temperature of the order-disorder transition in V_2C; however, since the reaction is homogeneous and is regarded as being of higher order, these lines are not to be understood as reaction isotherms in the usual sense. The presence of the ζ-phase is indicated as a dashed line, since its exact temperature and concentration domain, as well as its mode of formation, were not delineated in our experiments.

B. NIOBIUM-CARBON

The melting behavior of approximately 5- different alloy compositions was studied and the results, shown in Figure 21, are in close agreement with the data by H. Kimura and Y. Sasaki(10).

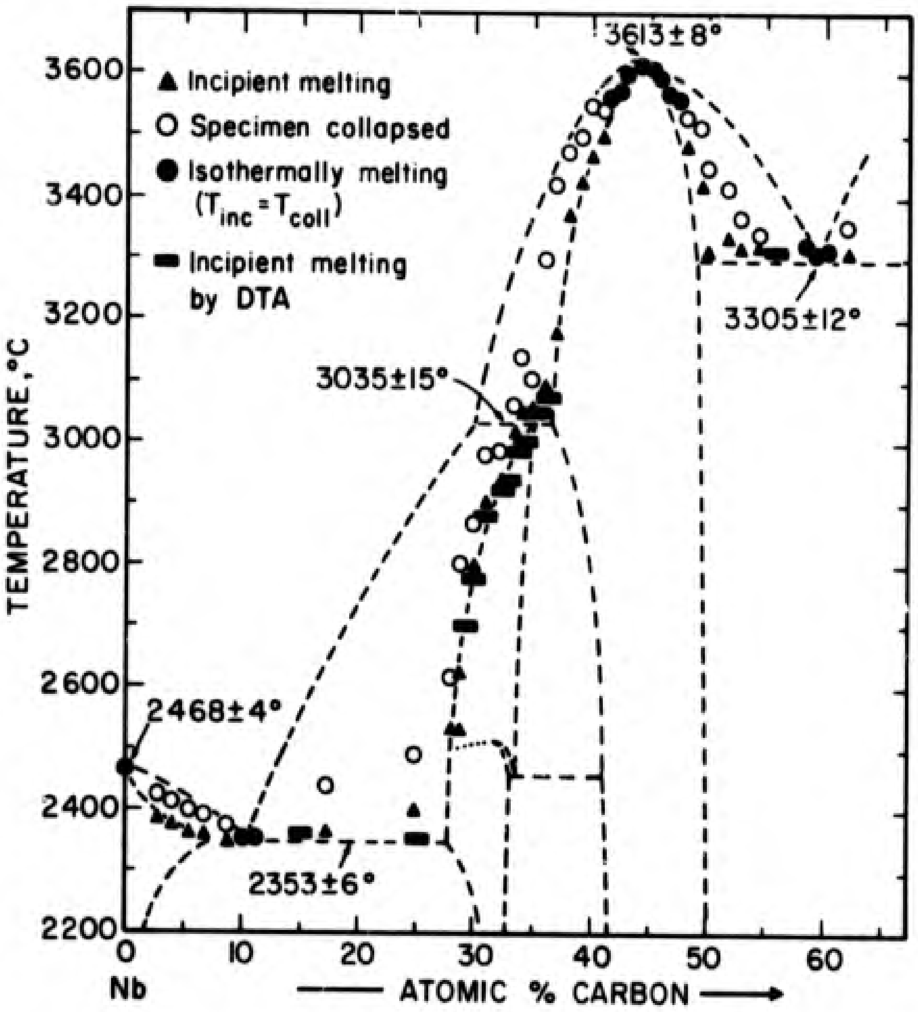

Figure 21. Melting Temperatures of Niobium-Carbon Alloys. (Error Figures Based on Reproducibility)

The nonvariant melting equilibria (p = const), as determined from these melting studies, were independently confirmed by DTA-techniques (Figure 22). The respective isothermal points and phase boundaries were located mainly by metallographic techniques (Figures 23 through 35). The lattice parameters of the monocarbide phase, determined on three sample series equilibrated and quenched from 2200, 2600, and 3300°C, closely follow the data given by G. Brauer and R. Lesser(29) (Figure 36).

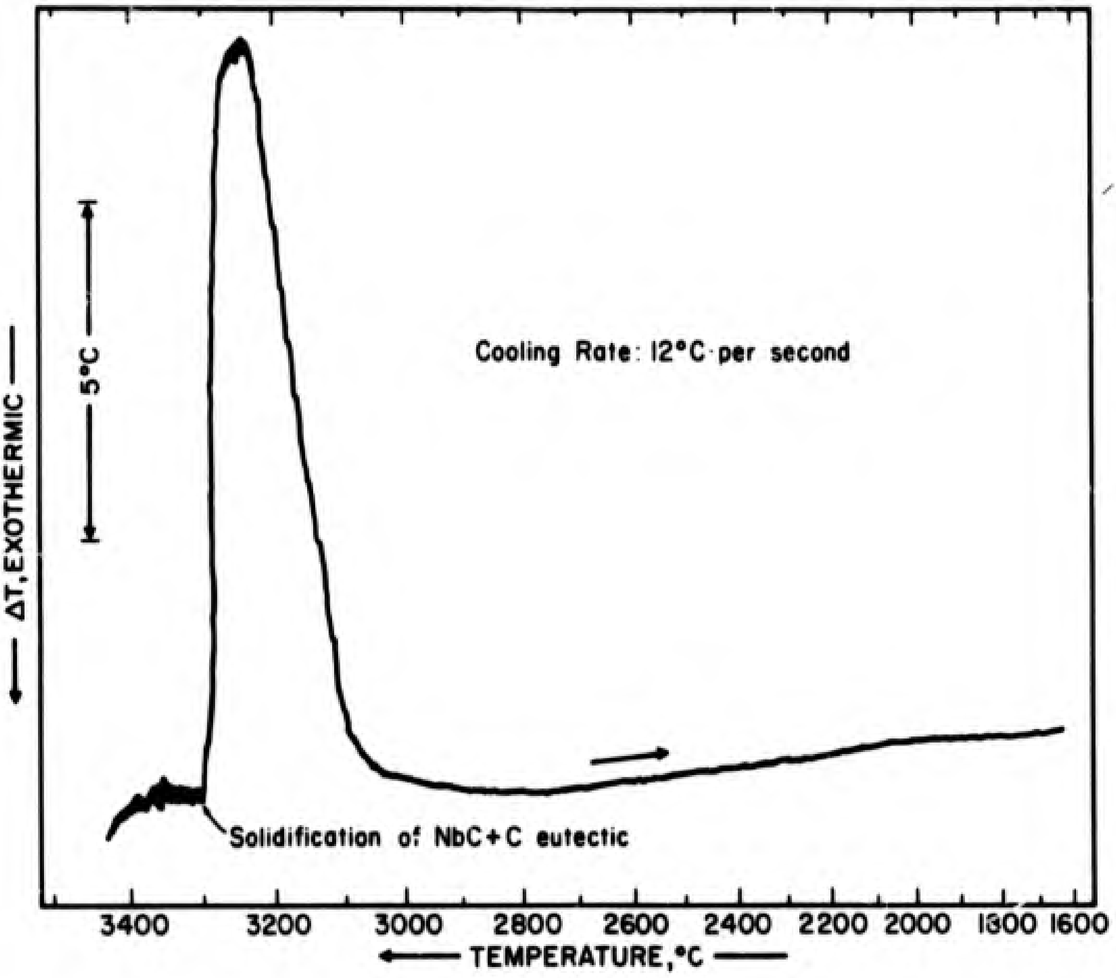

Figure 22. Reproduction of a DTA-Recorder Trace Showing Eutectic Solidification in a Niobium Carbide + Carbon Alloy (59 At.% C).

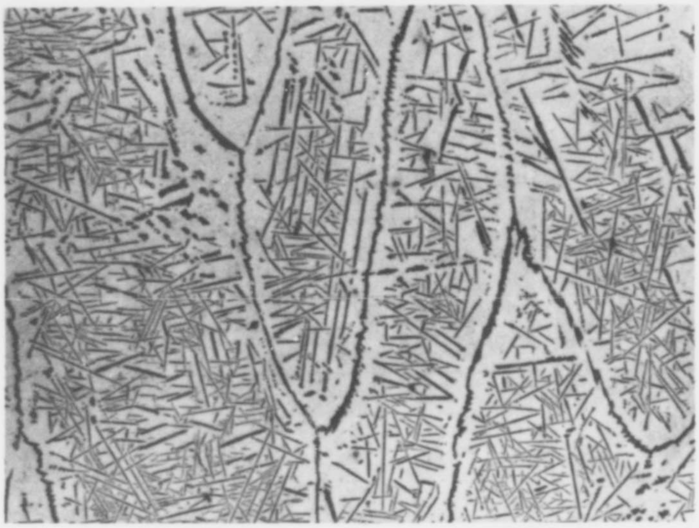

Figure 23. Nb-C (4.2 At.% C), Cooled at ~50°C per Second from 2400°C. X150

Niobium Phase with Localized Nb_2C Precipitations. Note Segregation of Precipitate Phase to the Grain Boundaries.

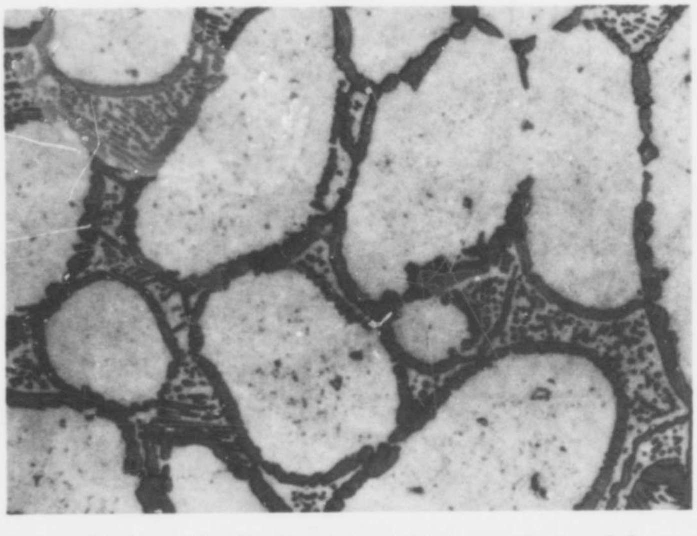

Figure 24. Nb-C (8.4 At.% C), Cooled at 5°C per Second from 2360°C. X625

Primary Niobium in a Matrix of Nb + Nb_2C Eutectic. Nb_2C-Precipitates Completely Segregated to Grain Boundaries.

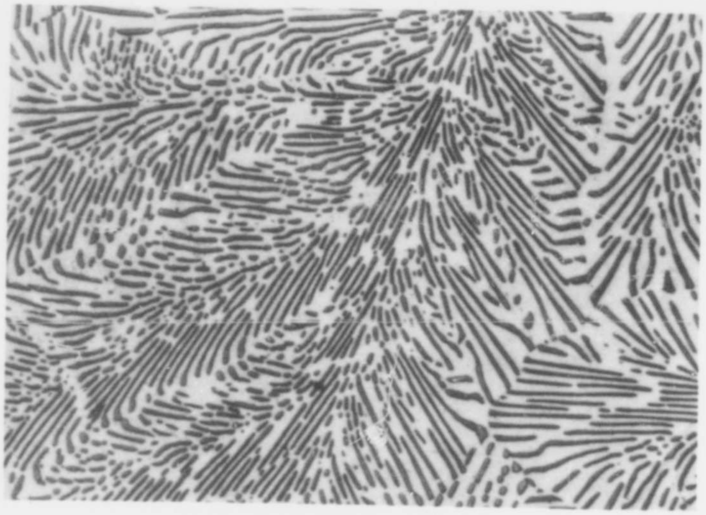

Figure 25. Nb-C (10.5 At.% C), Cooled at ~ 40°C per Second from 2355°C. X1000

$Nb + Nb_2C$ Eutectic.

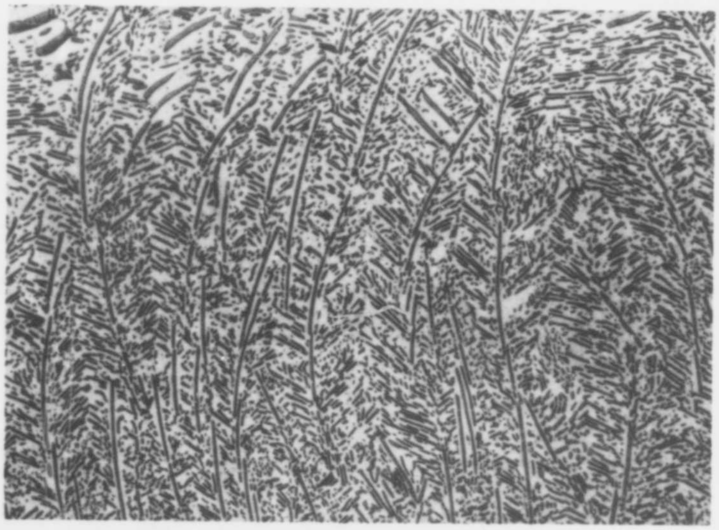

Figure 26. Nb-C (10.9 At. % C), Cooled at ~ 40°C per Second from 2360°C. X500

Traces of Primary Nb_2C in a $Nb + Nb_2C$ Eutectic Matrix.

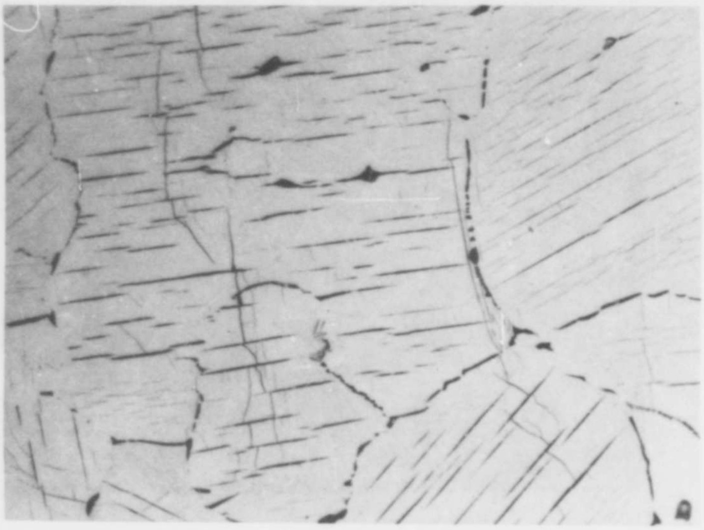

Figure 27. Nb-C (28 At. %C), Cooled at ~60°C per Second from 2450°C. X500

Nb_2C with Unidirectional Metal Precipitations and Small Amounts of Excess Niobium at the Grain Boundaries.

Figure 28. Nb-C (33.2 At.% C), Cooled at ~60°C per Second from 3100°C. X300

Peritectic Reaction Mixture $Nb + Nb_2C + NbC_{1-x}$.

Center of Grains	:	Monocarbide with ζ and Nb_2C Precipitations.
Light Seam	:	Nb_2C, Crystallized between 3035° and 2353°C.
Matrix	:	Rest of Eutectic $Nb + Nb_2C$.

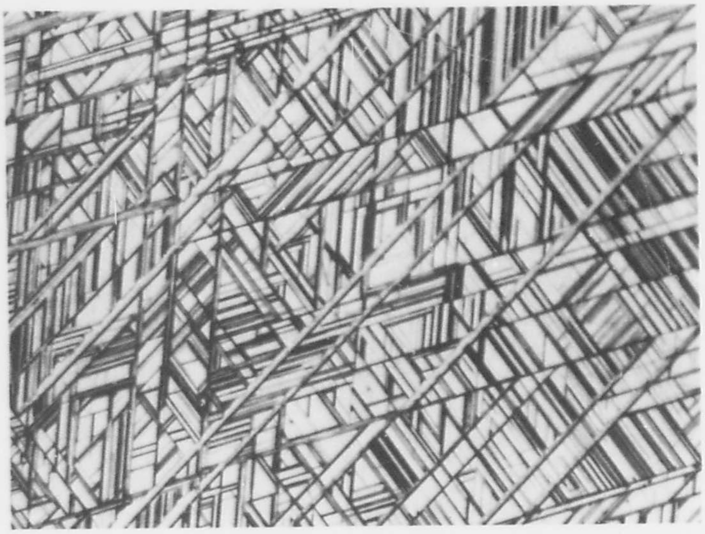

Figure 29. Nb-C (37.3 At.% C), Cooled at ~20°C per Second from 3090°C. X600

Single Phase NbC_{1-x} at the Equilibrium Temperature, Disproportionated During Cooling.

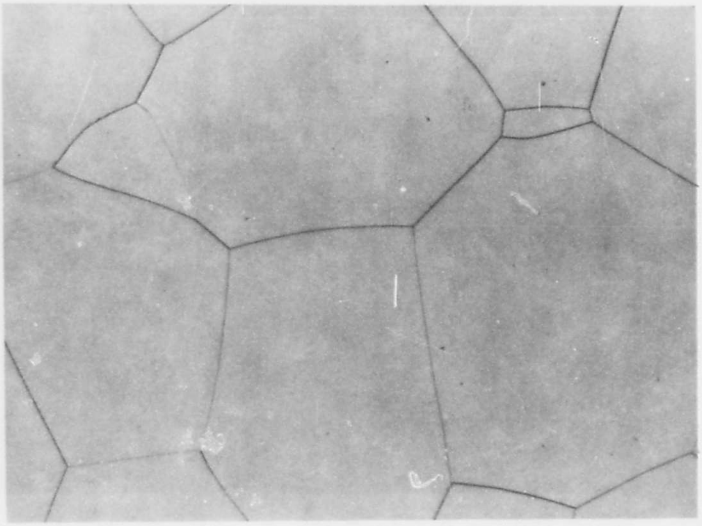

Figure 30. Nb-C (48.8 $\pm$ 0.3 At.% C), Equilibrated at 3300°C, and Quenched. X175

Single Phase Niobium Monocarbide.

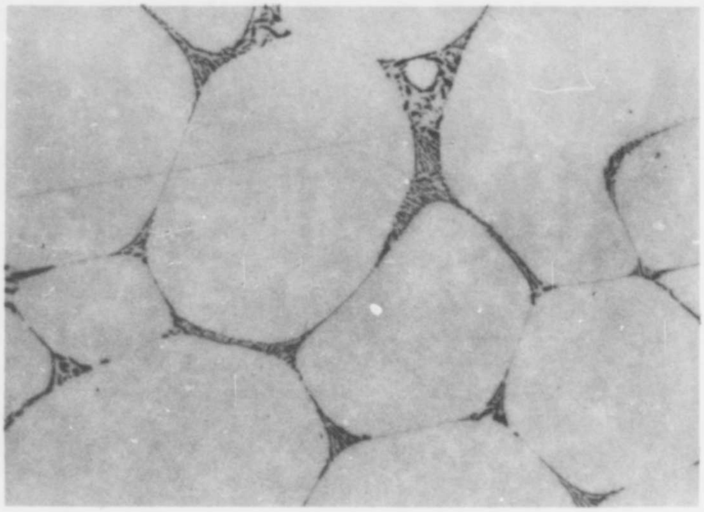

Figure 31. Nb-C (50.1 At.% C), Quenched from 3350°C. X550

Primary Monocarbide with Small Amounts of NbC + C Eutectic at the Grain Boundaries.

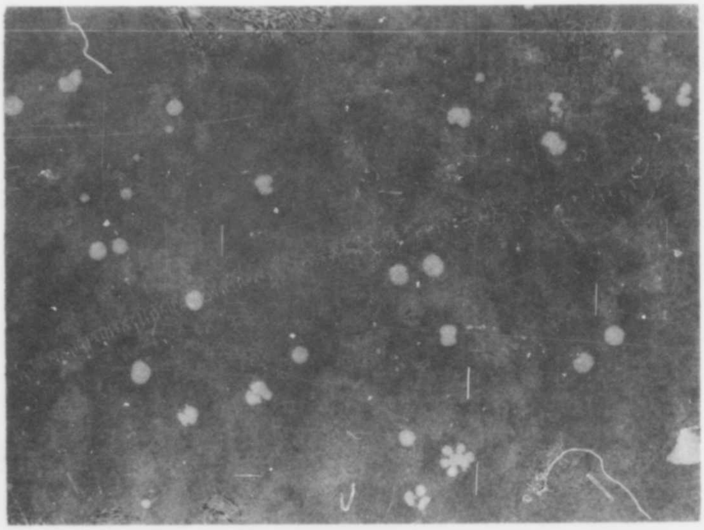

Figure 32. Nb-C (50.8 ± 0.4 At.% C), Rapidly Cooled from 3310°C. X100

Small Amounts of Primary NbC in a NbC + C Eutectic Matrix. Eutectic Not Resolved.

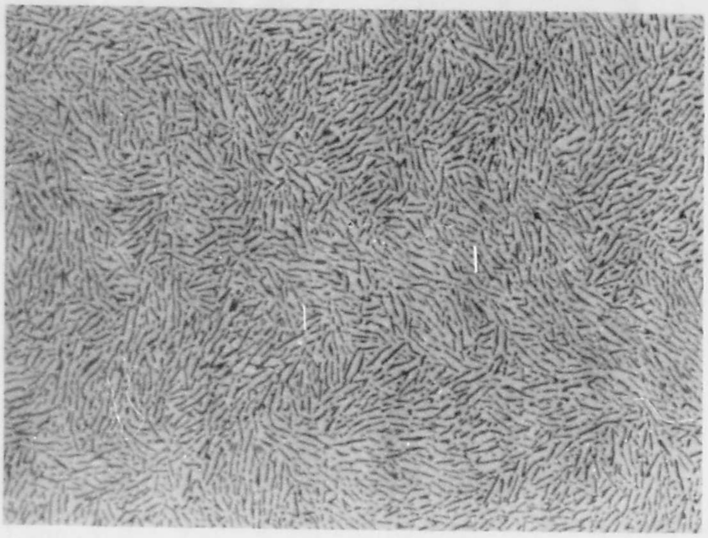

Figure 33. Nb-C (60 ± 0.5 At.% C), Cooled at ~40°C from 3310°C. X640
NbC + C Eutectic.

Figure 34. Nb-C (60.5 + 0.5 At.% C), Cooled at ~50°C per Second X600 from 3310°C.

Traces of Primary Graphite and NbC + C Eutectic.

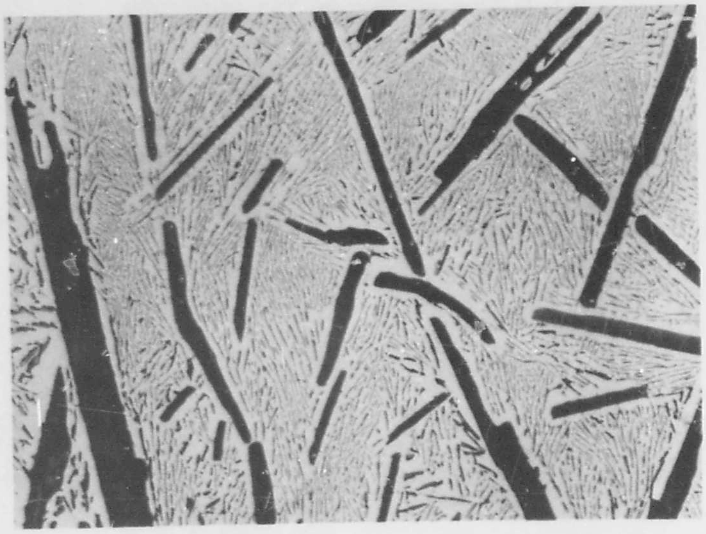

Figure 35. Nb-C (63.4 ± 0.5 At.% C), Cooled at ~50°C per Second from 3330°C. X600
Plate Shapted, Primary Graphite in a NbC + C Eutectic Matrix.

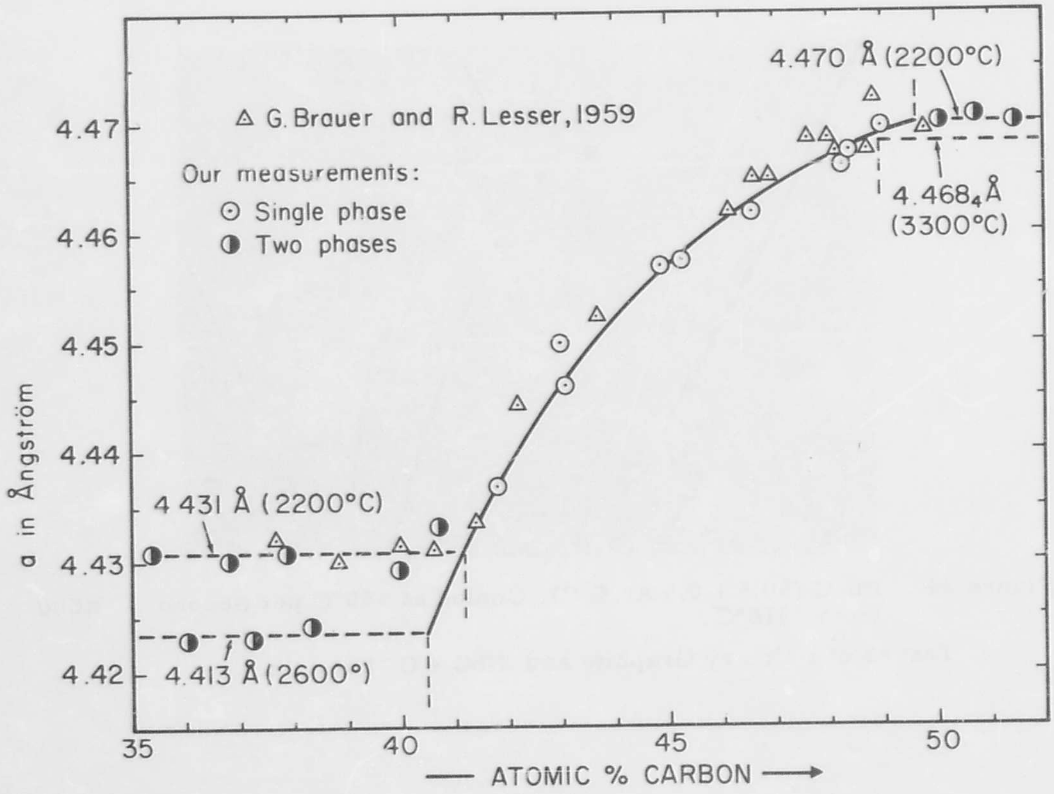

Figure 36. Lattice Parameters of Niobium Monocarbide.

A rather interesting thermal behavior was exhibited by niobium subcarbide: In the DTA-heating curves of an alloy containing 25 atomic percent carbon, a sharp thermal arrest is observed at 1230°C (Figure 37). At approximately 2200°C, a gradual thermal arrest, attributed to the solutioning of niobium in the subcarbide, begins; this break is then followed by sharp arrest due to melting of the Nb + Nb_2C eutectic. Finally, at about 2450°C, a third arrest indicates a second transition in the solid phase.

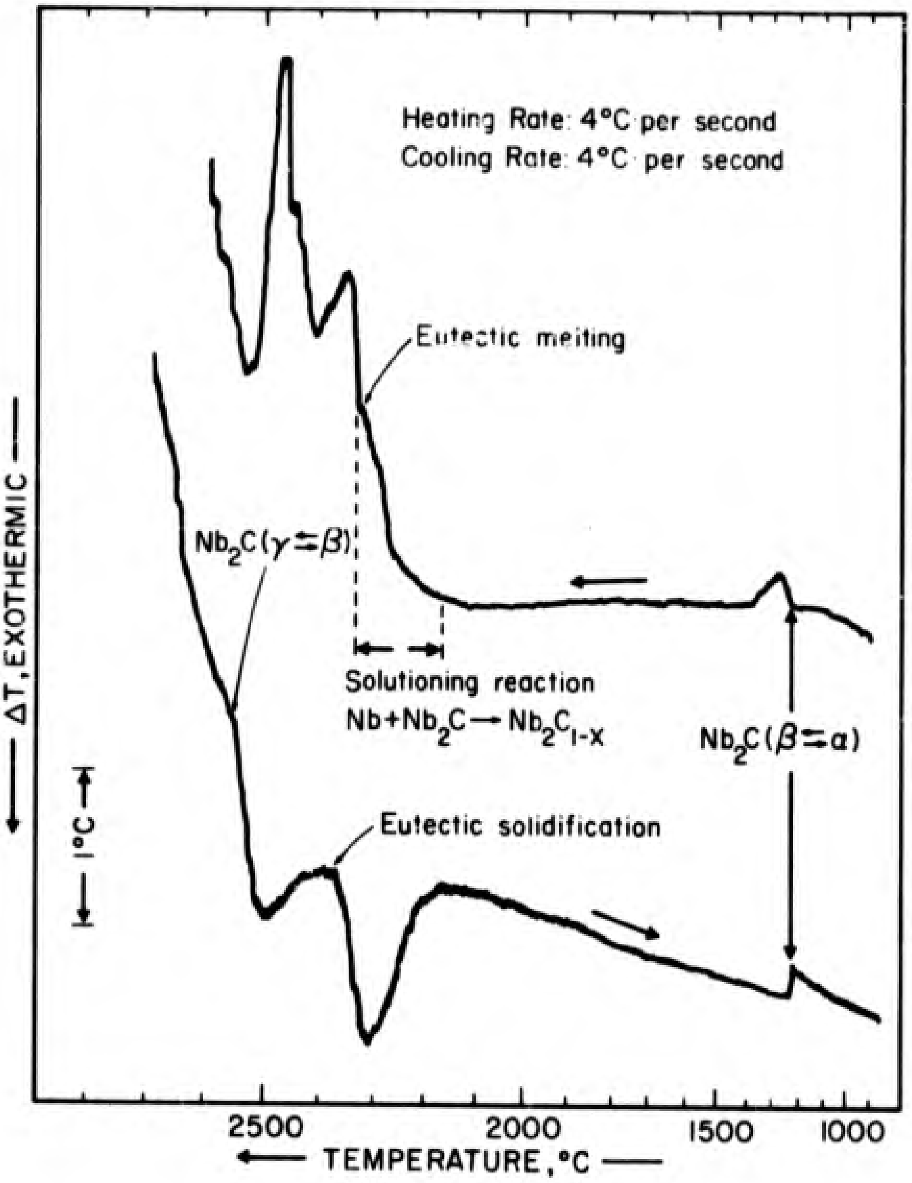

Figure 37. DTA-Thermogram of a Niobium-Carbon Alloy Containing 25 Atomic Percent Carbon.

The same reactions, but in reverse order, appear on the cooling cycle. In the runs, it should be especially noted that the upper temperature transition in the substoichiometric alloy appears at a higher temperature on the cooling than on the heating cycle; this behavior is typical for second order phase changes. The thermal arrests in the vicinity of 2500°C are also obtained in single-phased subcarbide alloys (Figure 38).

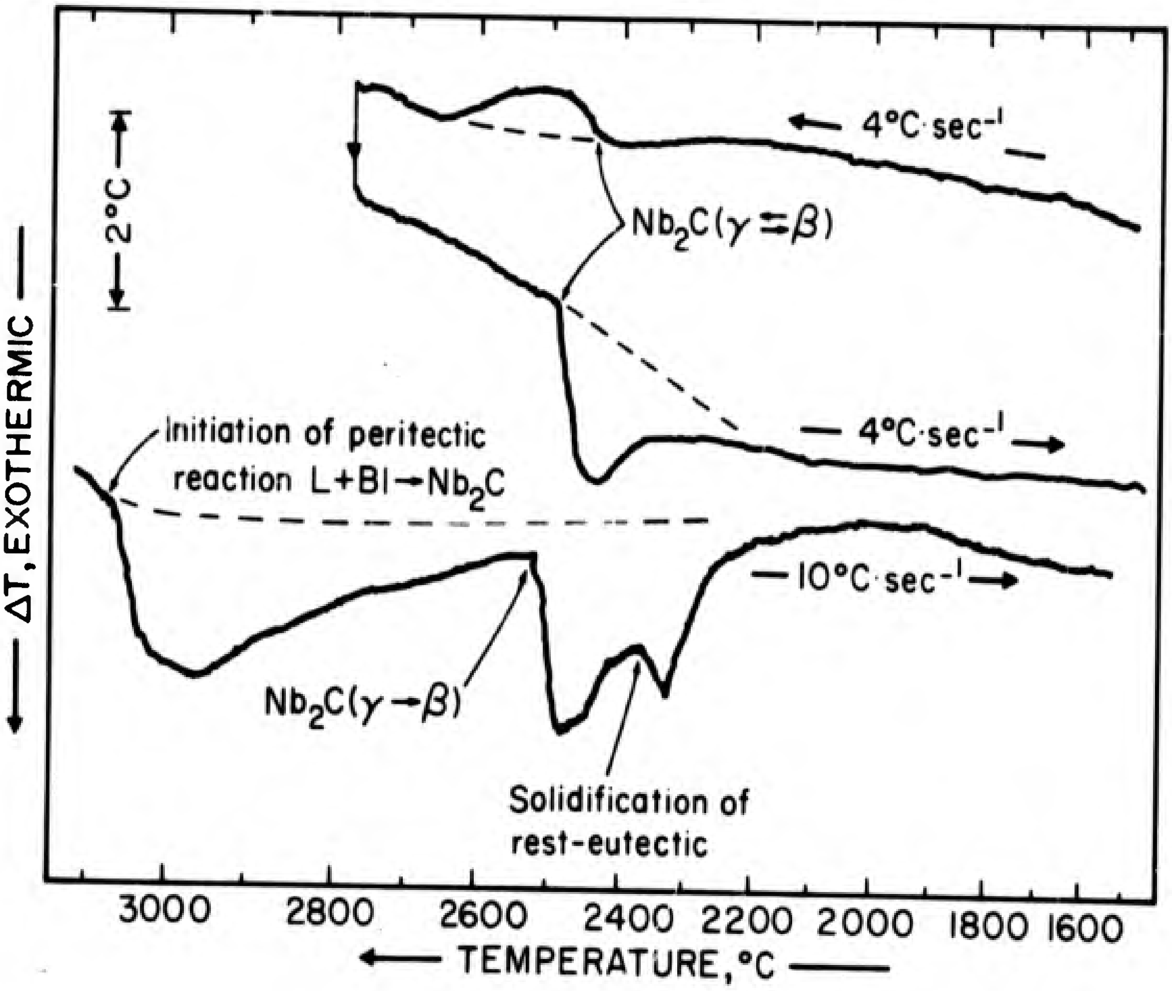

Figure 38. DTA-Thermogram of a Niobium-Carbon Alloy Containing 34 Atomic Percent Carbon.

The DTA-results, gained from studies on eleven alloys placed across the homogeneity range of the Nb_2C-phase, indicate a slight maximum in the transition temperature at about 2530°C and 32 At.% C (Figure 39); the transition temperatures drop to approximately 2440°C in excess monocarbide-containing alloys. The transformation proceeds with high speed, and it was not possible to retain the high temperature equilibrium states by quenching.

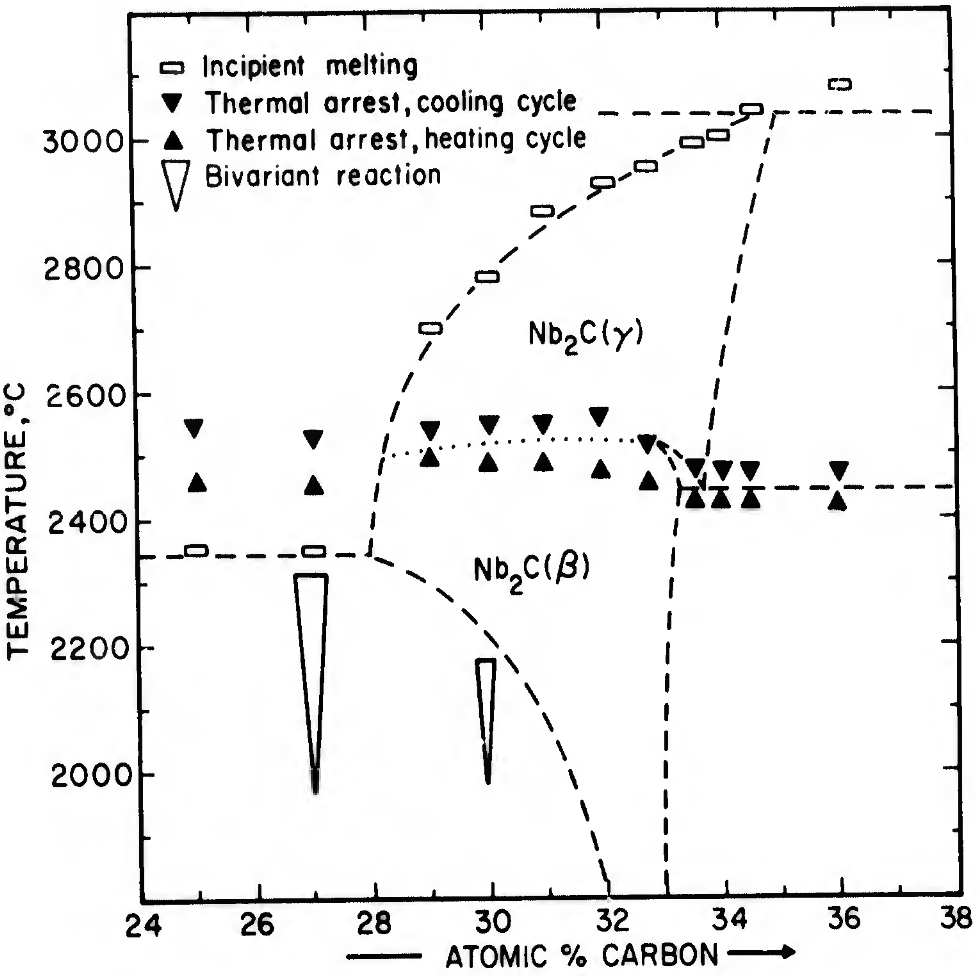

Figure 39. High Temperature Order-Disorder Transformation in Nb_2C. Dotted Line: Temperatures of Maximum Enthalpy Change.

A somewhat more detailed study concerning the type of transition involved revealed no signs of a two-phased transformation at compositions below 32 At.% C. In the range from 32.8 to 33.5 At.% C, a substructure, consisting of isolated veinlets, was observed in the Nb_2C-grains; it proved to be difficult to achieve sufficient phase contrast to obtain photomicrographs of sufficient quality to warrant reproduction. Nevertheless, these results, coupled with the data from the DTA-studies, as well as with the similarity of the transformations in the other carbides where the character of these transformations could be investigated in greater detail; strongly favor the assumption of a two-phased process in the vicinity of the stoichiometric composition of Nb_2C.

The lower temperature transition at 1230°C appears to be slow, especially at the carbon-rich end of the phase. While normal furnace-cooling or cooling rates up to approximately 10°C per second from high (>1250°C) temperatures will produce the distorted modification of Nb_2C in dense, substoichiometric alloys; annealing times of several hundred hours at substransition temperatures may sometimes be required to produce indications of the phase change in alloys located in the two-phase field Nb_2C + NbC. The displacive transformation is easily recognized by the rippled appearance of the grains (Figure 40).

Diffusion experiments at temperatures 1600° and 2500°C, of which a typical result is shown in the photomicrograph in Figure 41, did not indicate the ζ-NbC_{1-x}-phase to be stable in this temperature range. No distinct layer between the Nb_1C and the monocarbide was found, and the occasional appearance of ζ in the X-ray films of high-temperature (>1800°C) heat-treated alloys was therefore attributed to products formed by non-equilibrium precipitation from the monocarbide during cooling.

Lattice parameter measurements of Nb_2C (β), using the L'3-type indexing, yielded data in close agreement with the results by G. Brauer and co-workers$^{(29)}$. On the average, $a = 3.117$ Å and $c = 4.956$ Å were found for Nb_2C in equilibrium with the metal phase, and $a = 3.127$ Å and $c = 4.974$ Å in two-phased Nb_2C + NbC alloys; after equilibration at 2000°C.

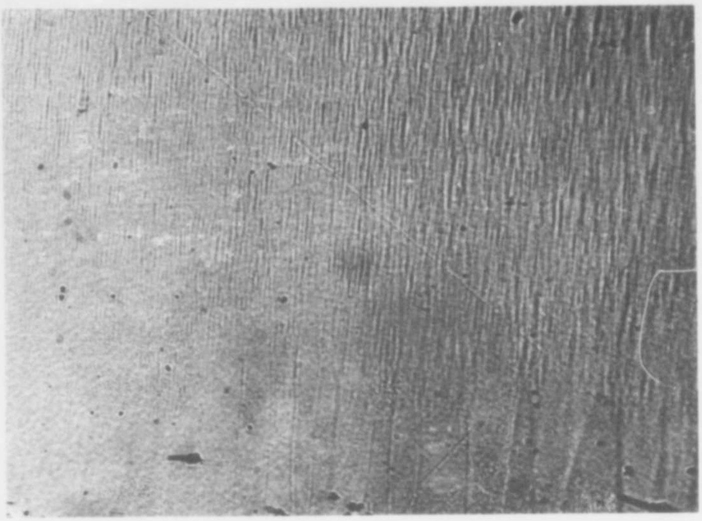

Figure 40. Diffusion Couple Nb + C, Treated for 3 hrs at 2200°C and Cooled at 1°C per Second. X680

Heavy Slip Lines in Nb_2C Resulting from the Displacive Transformation at ~ 1230°C.

(Vertical Illumination for Improved Phase Contrast).

Figure 41. Diffusion Couple Nb + C. X600

Sample Prepared by 3 hr Reaction at 2300°C, Followed by 30 hrs Annealing at 1800°C.

Interface Nb_2C-NbC: Note Continuity Between the Precipitates in NbC and the Nb_2C-Phase.

The smallest parameters for the subcarbide phase, a = 3.105 Å and c = 4.938 Å, were measured in an alloy containing 28 At.% C following rapidly quenching from 2300°C. Metallographic inspection of this alloys, however, revealed metal precipitations in the subcarbide, i.e. the alloy was heterogeneous. Further metallographic studies indicated very rapid metal precipitation from the subcarbide up to carbon contents of 30.5 At.%.

X-ray studies on alloys which were equilibrated at 2100°C and afterwards chemically analyzed, indicated that the upper homogeneity limit of the phase does not exceed ~33.1 At.% C, i.e. the single phase region does not include the stoichiometric composition at this temperature. Unidirectional monocarbide precipitations, identical to those noticed in V_2C (Figure 7), were also observed in Nb_2C in high temperature (2600 to 3000°C) equilibrated alloys and diffusion specimens. From these metallographic observations, a terminal composition of ~34.5 At.% C at the peritectic temperature was deduced.

The results of the experimental investigations have been combined to construct the phase diagram shown in Figure 2. According to our data, the high temperature transition in substoichiometric Nb_2C, which is due to the destruction of long range order in the carbon sublattice, proceeds single-phased and is of the second order type. The dotted line shown in Figure 2 is therefore not to be interpreted as a true reaction isotherm. On cooling through the transition temperature, alloys located in the immediate vicinity of the stoichiometric composition disproportionate into two separate phases, of which the hyperstoichiometric phase remains disordered and decomposes in a eutectoid reaction at somewhat lower temperatures into the ordered phase and monocarbide; and the hypostoichiometric phase transforms into the ordered state. The ordered, substoichiometric phase then undergoes a second transition at 1230°C (not shown in Figure 2), which also is believed to be single-phased and not of the first order. The change in the sublattice order in Nb_2C in this second transformation is accompanied by a distortion of the hexagonal subcell of the ordered, intermediate temperature form.

V. DISCUSSION

The most significant, new results obtained in both systems concern the establishment of the existence of sublattice order transformations in the subcarbide phases and their effect upon the phase diagram characteristics. Considering that the transformations in Nb_2C occur fairly rapidly and are associated with sizeable enthalpy changes, it is quite surprising that they have escaped previous observation; especially, since this phase has been studied in detail by thermoanalytical means by E.K. Storms and N.H. Krikorian(9).

In addition, the displacive transformation results in a pronounced distortion of the hexagonal close-packed cell, affecting the lengths of the base axes even in the second decimal place, as evidenced by a comparison of the hexagonal pseudoaxes of $a_{1H} = 3.092$ Å, $a_{2H} = 3.145$ Å in the orthorhombic structure, to a base-length of a = 3.118 Å in the hexagonal subcell of $Nb_2C(\beta)$. For the orthorhombic $V_2C(\alpha)$, the corresponding dimensions are $a_{1H} = 2.872$ Å, and $a_{2H} = 2.904$ Å, while the base length of the hexagonal form is a = 2.884 Å.

There are still some discrepancies, however, in respect to the exact structure of the ordered phases. According to the investigations by K. Yvon et al.(25), who used neutron diffraction techniques, the ordered structure of V_2C corresponds to the ζ-Fe_2N-type, a type which is also exhibited by the ordered modification of Mo_2C. A similar structure, but with the base plane axes doubled, was proposed by E. Rudy and C.E. Brukl(24) in order to account for extra reflections appearing at low angles in the X-ray powder patterns. Similar conditions exist for Nb_2C where, from neutron diffraction studies, the structure type C_{2v}^{9}-Pnma was derived by K. Yvon et al.(26); however, an orthorhombic cell analogous to that of V_2C was also proposed(24). A clear decision as to whether these planes, depending upon stoichiometry, thermal treatment, and presence of impurities, are capable of existing in several, energetically very similar, ordered states, and whether the presence of foreign phases, such as, for example, metal-precipitates in the substoichiometric subcarbides have an effect upon the order-disorder phenomena, cannot be made at the present time, and a final interpretation will have to await future work.

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The binary systems vanadium-carbon and niobium-carbon were re-investigated by means of X-ray, melting point, DTA, and metallographic techniques on chemically and thermally characterized specimens; revised phase diagrams for both binary systems are given.

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