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Part VII

EXPERIMENTAL PHASE EQUILIBRIA OF SELECTED BINARY, TERNARY, AND HIGHER ORDER SYSTEMS

Part VII. The Phase Diagram Ti-V-C

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FOREWORD

The research described in this technical report was carried out under USAF Contract F 33 615-67-C-1513 by the Materials Research Laboratory, Aerojet-General Corporation, Sacramento, California. The contract was initiated under Project No. 7350, Task No. 735001 and administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, with Captain P. J. Marchiando (MAMC) as Project Engineer. Dr.E. Rudy (now at the Oregon Graduate Center, Portland, Oregon) was the Principal Investigator.

This report covers work conducted during the period April 1967 through May 1969. It was submitted by the author February 1970.

Other reports issued, or in preparation, under USAF Contract AF 33 615-67-C-1513, are:

Part I.	The Phase Diagrams of the Systems Ti-Nb-C, Ti-Ta-C, and Ti-Mo-C.
Part II.	Effect of Re and Al Additions on the Metal-Rich Phase Equilibria in the Ti-Mo-C and Ti-Nb-C Systems.
Part III.	Phase Studies in the V-Ta-C and Nb-Ta-C Systems.
Part IV.	Effect of Mo and W Additions on the Subcarbide Solid Solutions in the V-Ta-C and Nb-Ta-C Systems.
Part V.	The Phase Diagram of the W-B-C System.
Part VI.	The Phase Equilibria in the Metal-Rich Region of the Hafnium-Tantalum-Nitrogen System.

This technical report has been reviewed and is approved.

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ABSTRACT

The phase relationships in the Ti-V-C system were experimentally investigated by means of X-ray, melting point, DTA, and metallographic methods on heat-treated and melted specimens, and a phase from 1400° C through the melting range established. The solid state equilibria are characterized by complete solid solution formation between the metals as well as the monocarbide phases, and a limited Ti-exchange in V_2C (15 At.% at 1400° C); a wide two-phase equilibrium is formed between the carbon-deficient monocarbide solid solution and the metal phase. The V_2C-solid solution is terminated by a three-phase equilibrium, $V_2C + (V,Ti)C_{1-x} + (V,Ti)$-ss, in the ternary. Four isothermal reactions occur in the system, of which three correspond to pseudobinary eutectic reactions, and the fourth to a ternary eutectic between metal, subcarbide, and monocarbide. The monocarbide solid solution has a minimum melting point of 2625° C at a composition Ti-V-C (6-50-44 At.%).

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I. INTRODUCTION AND SUMMARY

A. INTRODUCTION

In addition to the traditional application of vanadium as alloying additive in tool and die materials, titanium-vanadium based alloys find increasing applications as fuel cladding materials in nuclear power reactors. In spite of the large commercial interest, however, little work has been done to study the behavior of these alloys under the influence of other alloy components, notably the interstitial elements, and thus gain a better understanding of the complex metallurgical reactions occurring in these alloys during fabrication and heat treatment.

Studies of the phase relationships in ternary transition metal-carbon systems, such as Ta-W-C(1) and Ti-W-C(2), for example, have led to interesting alloys for tool and wear applications(2); and high strength castable boride alloys, using solid state decomposition reactions for microstructure control, are currently being investigated for hard-facing and high temperature bearing applications.

The experimental work in the Ti-V-C system was carried out to provide basic support data for Air Force sponsored development programs on improved cutting tool materials. Of principal interest in the studies were the range of coexistence of metal and monocarbide phase, the solidus temperatures of two-phased metal + monocarbide alloys and the tie line distribution within this two-phase field.

B. SUMMARY

The phase relationships in the Ti-V-C system were experimentally investigated and a phase diagram from 1400°C through the melting range established (Figure 1).

The solid state equilibria in the system are characterized by the occurrence of a wide two-phase equilibrium between the metal and monocarbide phase, a limited titanium exchange in V_2C, and complete miscibility of the cubic monocarbides VC and TiC. The V_2C phase is restricted by a three-phase equilibrium metal + subcarbide + monocarbide towards the titanium side of the system. The three partition equilibria, metal + monocarbide, metal + subcarbide, and subcarbide + monocarbide solid solution, show a strong enrichment of titanium in the carbon-richer phases, signifying the much higher stability of the titanium carbide in comparison to the vanadium-carbon phases.

Four isothermal reactions occur in the system (Figures 2 and 3) of which three correspond to pseudobinary eutectic reactions and the fourth to a ternary eutectic between metal, subcarbide (Me_2C), and monocarbide phase. The monocarbide solid solution has a minimum melting point of 2625°C at a composition Ti-V-C (6-50-44 At.%).

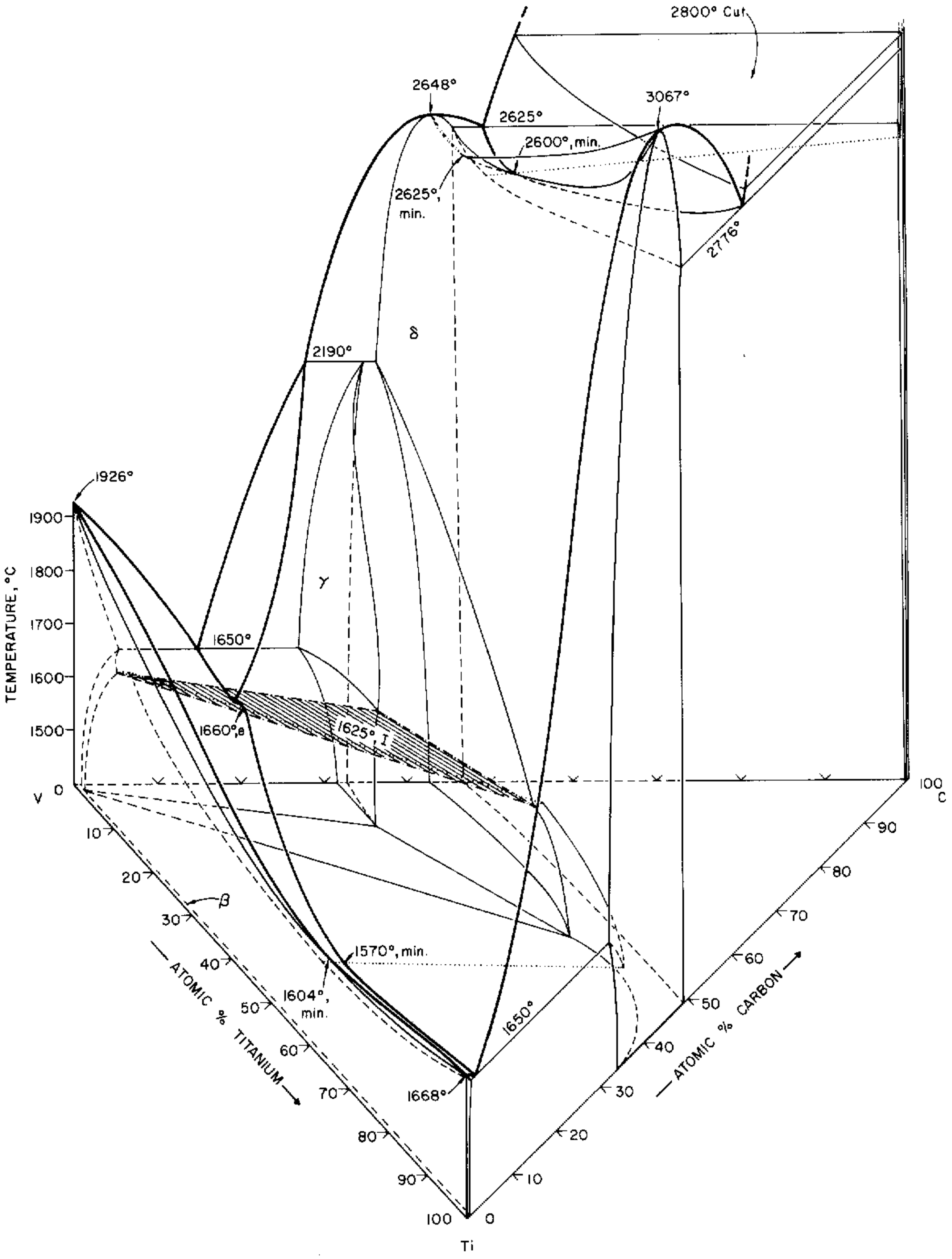

Figure 1. Isometric View of the Titanium-Vanadium-Carbon Phase Diagram

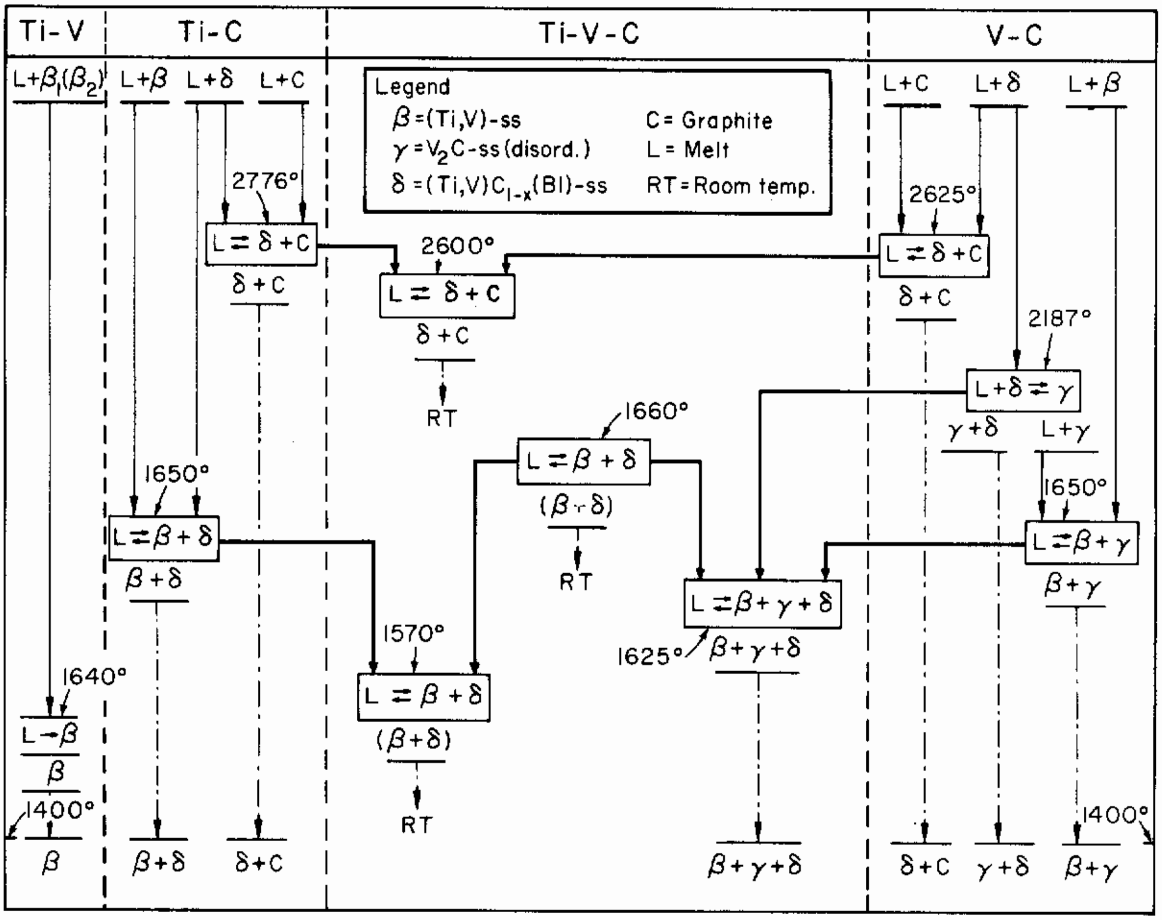

Figure 2. Reaction Diagram for the Ti-V-C System

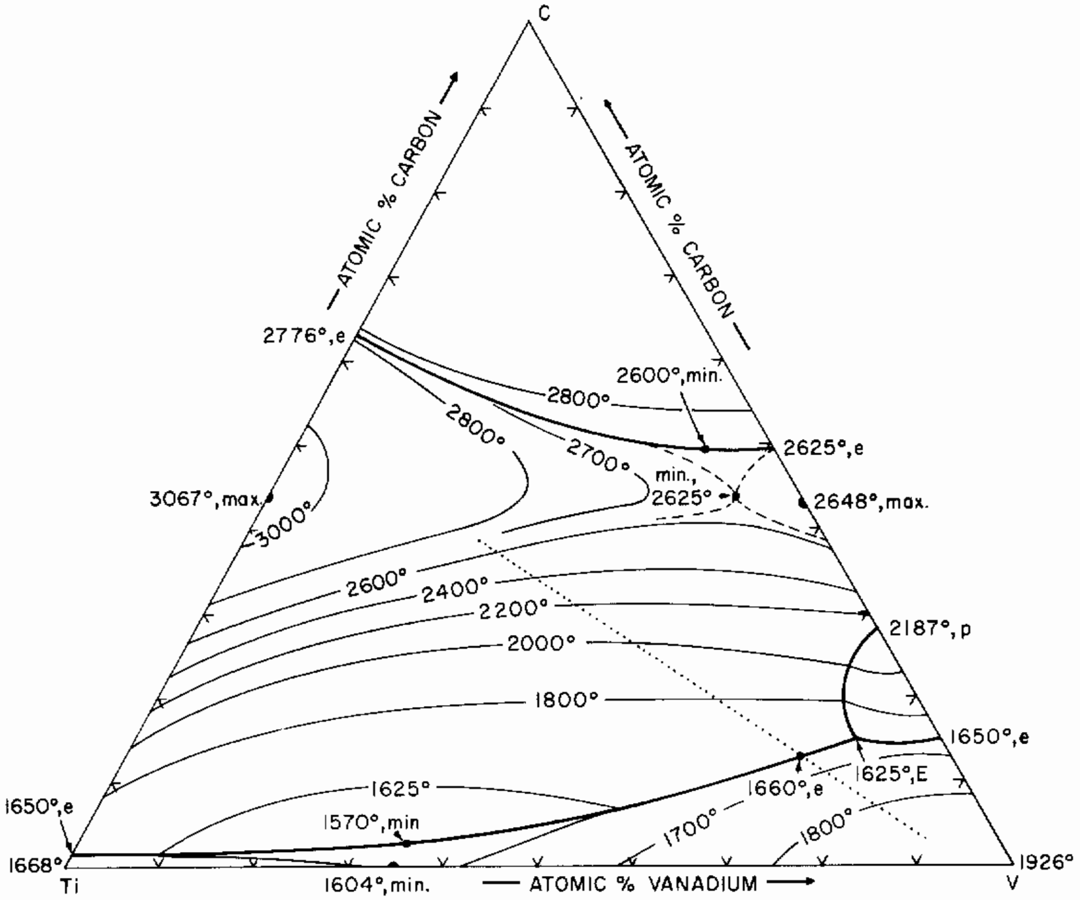

Figure 3. Liquidus Projections in the Ti-V-C System

II. LITERATURE REVIEW

A. THE EDGE BINARIES

The significant features of the boundary systems are well known from previous work(3,4,5).

Titanium and Vanadium are completely miscible above the α-β transition temperature of titanium(6,7). Below the transition temperature (882°C), the boundary of the body centered cubic β-solution becomes temperature dependent and is located at approximately 80 At.% Ti at 650°C(6,7,8). The solubility of vanadium in α-Ti is small, amounting to about 2.8 to 3.3 At.%(6) (0.9 and 1.9 At.%(7)) at 650°C. The investigations by H.K. Adenstedt et al.,(6) also indicate the occurrence of a minimum melting point at approximately 1620°C and 30 At.% vanadium.

The titanium-carbon(9,10) system (Figure 4) contains a refractory cubic monocarbide (Table 1) which forms eutectic equilibria with β-titanium and graphite.

The Vanadium-Carbon system(10) (Figure 5) contains three intermediate phases. A subcarbide, V_2C, with a hexagonal close-packed arrangement of metal atoms and a disordered carbon sublattice at high temperatures, undergoes a sublattice ordering transient below approximately 800°C (Table 1). The ζ-phase, which occurs at approximately 41 At.% C, has trigonal symmetry, with a metal layer stacking sequence of $(hhcc)_3$(*) (12). The congruently melting monocarbide has a face-centered cubic (B1) structure at high temperatures and exists only with a carbon defect. Modifications

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(*) h = stacked as in hexagonal close packing
c = stacked as in cubic close packing

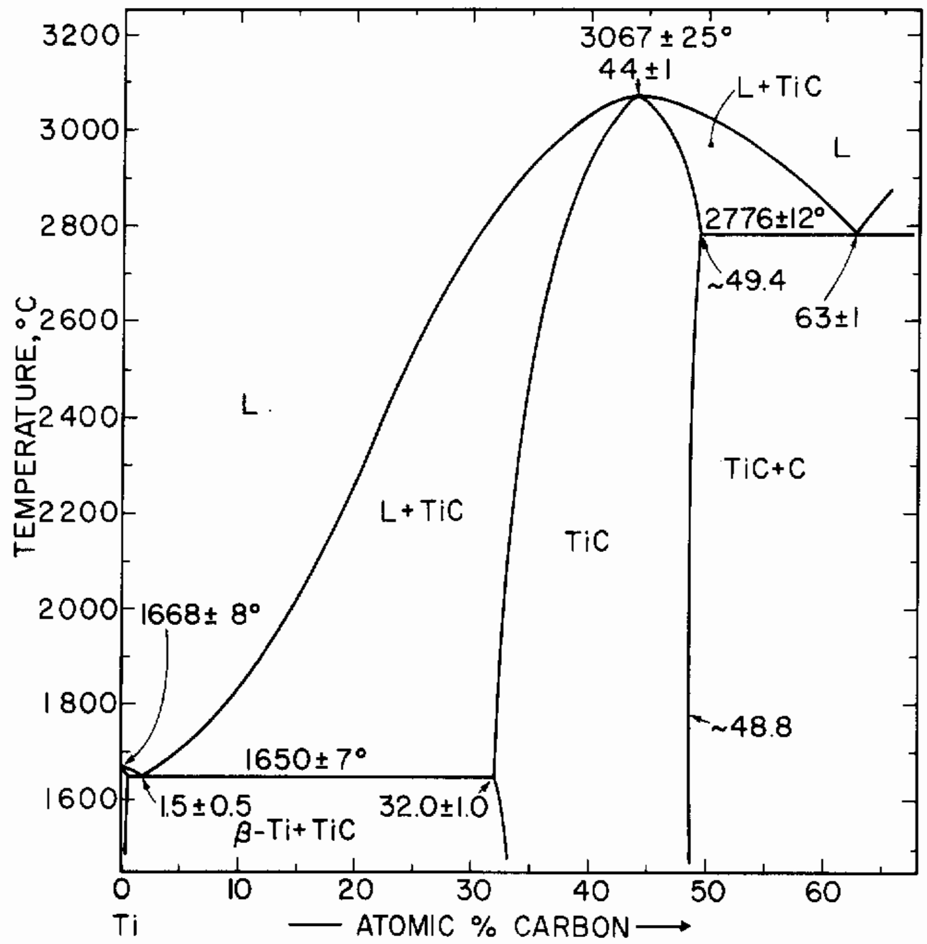

Figure 4. The Titanium-Carbon System.
(After E. Rudy et al., 1965)

with ordered carbon sublattices have recently been reported by deNovion et al.(13) and J.D. Venables et al.(14) (Table 2). Eutectic equilibria are formed at 1650° C and 15 At.% C between the metal and the subcarbide, and at 2625° C and 49.5 At.% C between the monocarbide and graphite(11). The subcarbide forms in a peritectic reaction at 2187° C.

Table 1. Structure and Lattice Parameters of Titanium and Vanadium Carbides.

Phase	Structure	Lattice Parameters, Å
V_3C	T<~800°C: Orthorh. Carbon Sublattice Ord.	a=11.49; b=10.06; c=4.55 (15)(*) a=4.58_6; b=5.75_3; c=5.04_7 (16)(**)
	T>~800°C: Hex., L'3-Type	a=2.885; c=4.570 at $VC_{0.47}$ (17) a=2.902; c=4.577 at $VC_{0.50}$
VC	Cubic, B1-type	a=4.131 at $VC_{0.73}$ (17) a=4.1655 at $VC_{0.87}$ a=4.124 at $VC_{0.64}$ a=4.172 at $VC_{\sim 0.89}$ (15)
TiC	fcc, B1-type	a=4.3305 at $TiC_{0.86}$ (18) a=4.305 at $TiC_{0.5}$ a=4.328 at $TiC_{\sim 1.0}$ (10)
	fcc, O_h^7-Fd3m (32 to 40 At.%, T < 1900°C)	a=8.606 at $TiC_{\sim 0.5}$ (19)

(*) $a_{o.r.} \approx 4\, a_{hex}$; $b_{o.r.} \approx 2\, a_{hex} \cdot \sqrt{3}$; $c_{o.r.} = c_{hex}$

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

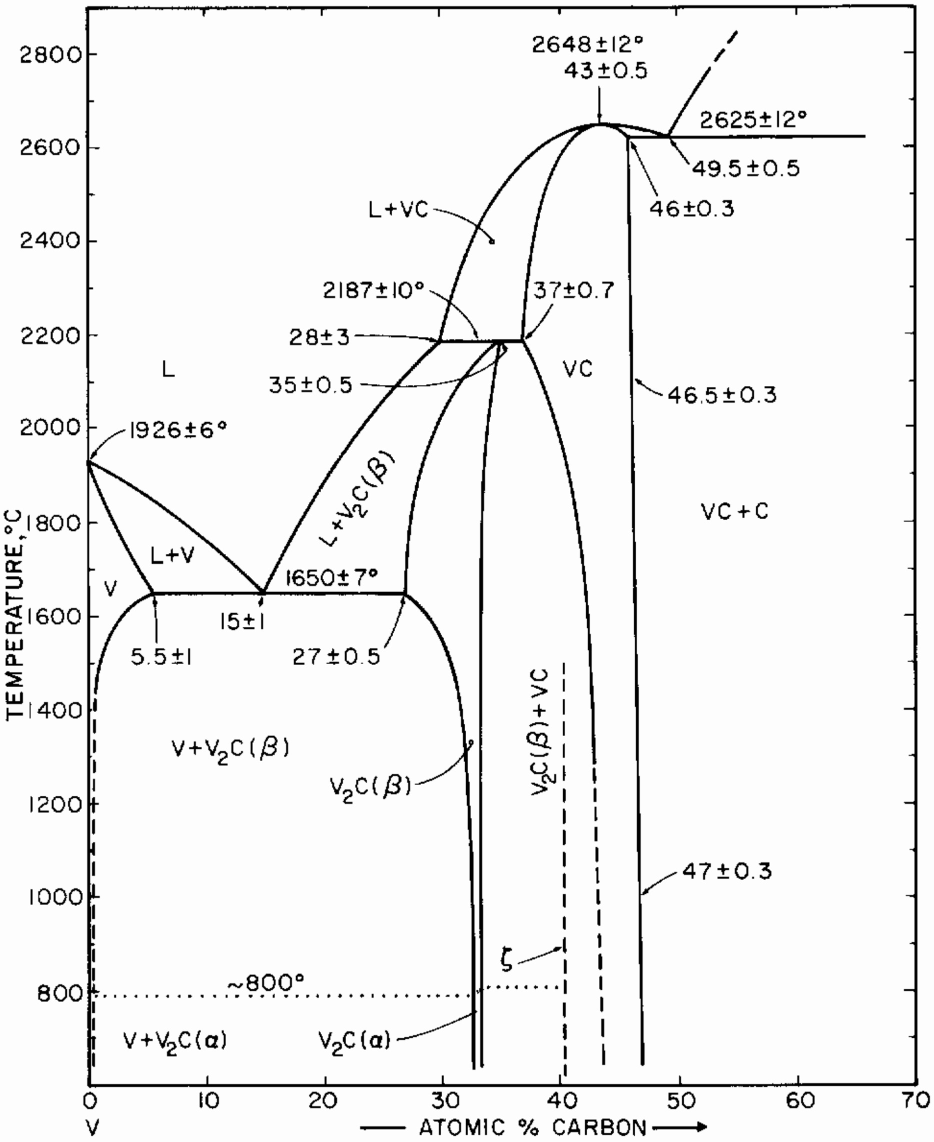

Figure 5. The Vanadium-Carbon System. (After E. Rudy, 1967 (11))

B. PREVIOUS WORK ON THE Ti-V-C SYSTEM

The complete solid solubility of the isomorphous monocarbides has been established by H. Nowotny and R. Kieffer and H. Kraimer and K. Konopicky(20). Lower temperature sections of the phase diagram were established by W.N. Eremenko et al.,(21) and T.F. Fedorov et al.(22) (Figures 6 and 7). Although somewhat at variance in respect to the location

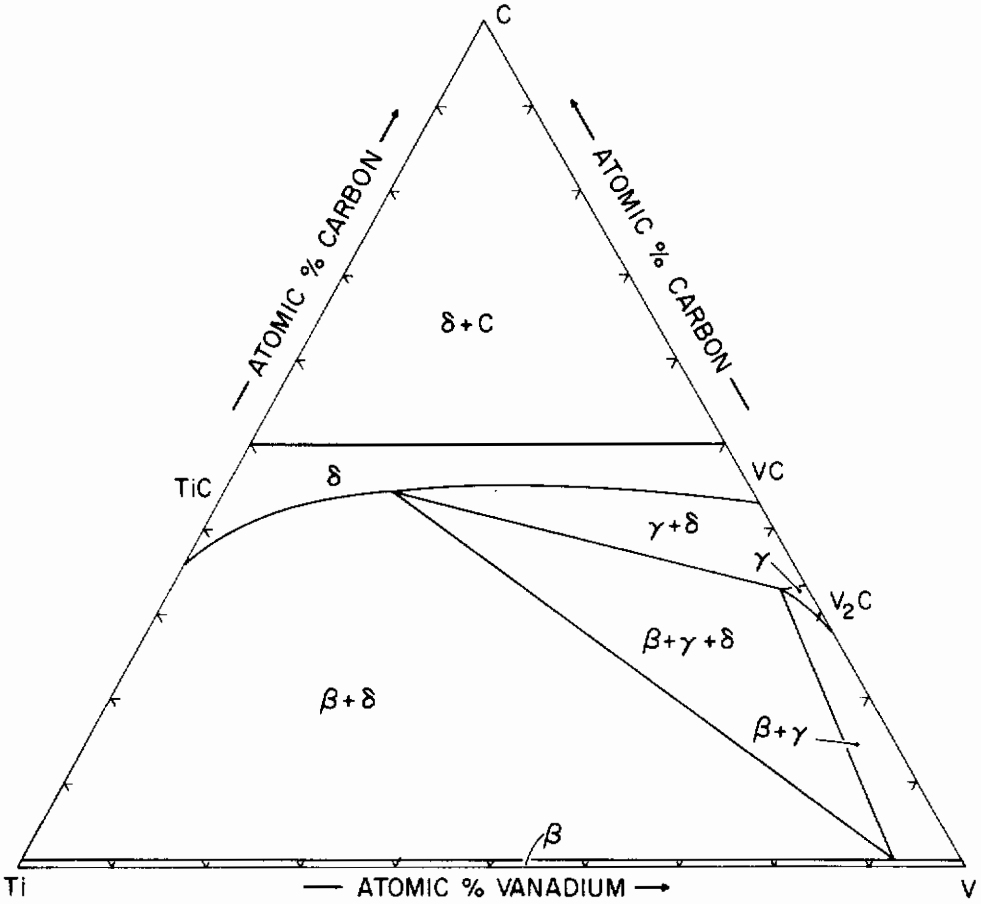

Figure 6. Isothermal Section of the Ti-V-C System at 1450°C.

(After Eremenko et al., 1964)

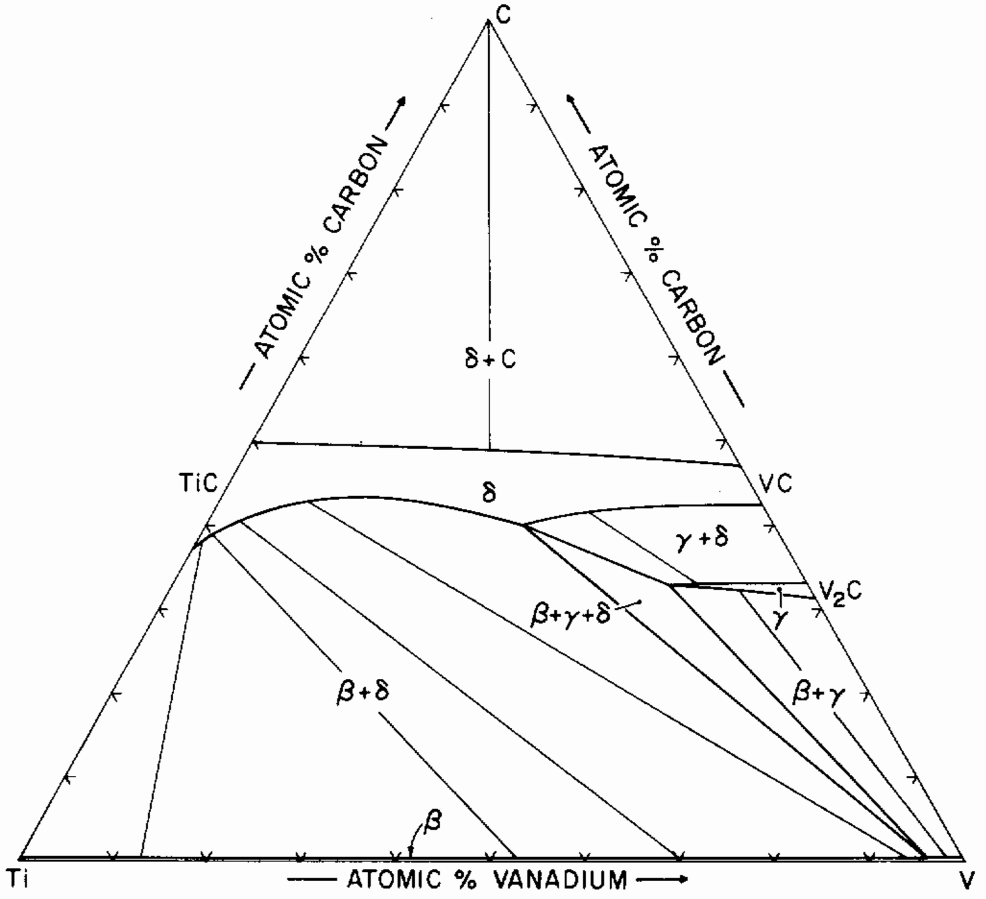

Figure 7. Isothermal Section of the Ti-V-C System at 1000°C.

(After Fedorov et al., 1966)

of vertices of the three-phase equilibrium metal + subcarbide + monocarbide and the titanium exchange in V$_2$C, the gross features of the system are the same in the two investigations. The low temperature phase equilibrium were later supplemented by additional investigations of the alloy structures along selected concentration sections by the cited russian authors(23, 24).

III. EXPERIMENTAL

A. STARTING MATERIALS AND ALLOY PREPARATION

The elemental powders, as well as prepared master alloys consisting of V_2C, VC, and TiC served as the starting materials for the fabrication of the alloy specimens.

The vanadium powder, purchased from Oregon Metallurgical Corporation, Albany, Oregon, had an overall purity of better than 99.65%. 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.

Titanium powder of 99.8% overall purity was purchased from Varlacoid Chemical Company. The main contaminants included 800 ppm oxygen, and 1100 ppm carbon. Measured lattice parameters of a=2.949 Å and c = 4.687 Å are in reasonable agreement with values of a=2.950 Å and c=4.6833 Å reported in the literature for iodide titanium(25).

The spectrographic grade graphite powder (National Carbon Company) contained the following impurities (in ppm): Al-0.3; Cu-0.1; Fe-0.2; Mg-0.1; and Si-0.2.

The vanadium carbide master alloys were prepared by reacting the carefully blended and cold-compacted mixtures of the vanadium metal powder and carbon in a graphite element furnace. The reaction to form the carbides was initiated under vacuum (2×10^{-6} Torr) at temperatures around 1000°C, and brought to completion by a homogenization treatment for 2 hrs at 1750°C after admitting helium to the furnace chamber. The resulting reaction lumps were crushed and ball-milled under helium to a grain size smaller than 60 microns. The powders were then leached in a mixture of hydrochloric and sulfuric acid, the wet cake centrifuged, washed with ether, and then dried in vacuum. Previous experience has shown that the subcarbide, V_2C, was slowly oxidized upon prolonged exposure to air and therefore the powder was stored in helium-filled sealed bottles until used.

The chemical and X-ray analysis of the two carbides are listed in Table 2.

Table 2. Chemical Analyses and Lattice Parameters of Carbide Starting Materials

Carbide	Carbon Content At% C	0 + N, ppm	Phases Present	Lattice Parameters Angstrom
V_2C	32.4 ± 0.02	290	V_2C	a=2.900; c-4.574
VC	C_{bound}=46.0 C_{free}= 1.7	160	VC	a=4.172
TiC	C_{bound}= 49.1 C_{free}= 1.1	1300	TiC	a=4.329

The titanium monocarbide powder (Table 2) was purchased as a < 80 micron powder from Varlacoid Chemical Company. After a degassing treatment for 3 hrs at 2200° C under a vacuum of 5×10^{-6} Torr, the carbide had a total carbon content of 50.2 At.%, of which 1.1 At.% were present as elemental graphite. The combined contents of oxygen and nitrogen, as determined by hot-extraction, were 1300 ppm, and the sum of metallic impurities, determined by a semiquantitative spectrographic method, was less than 700 ppm.

The majority of experimental ternary alloys were prepared by short-duration (2-5 min) hot pressing of the powder mixtures in graphite dies. After hot pressing, the carbon-contaminated surface zones were removed by grinding and the samples then homogenized in a tungsten-mesh element high temperature furnace under a vacuum better than 10^{-5} Torr.

All alloys prepared for the investigation of the solid state phase equilibria received an 80 hr heat treatment at 1400° C. Selected sample batches received additional heat treatments at 1300° C (130 hrs) and 1500° C (60 hrs). Equilibration treatments of excess metal containing alloys at temperatures near the solidus, and of high melting, single-phased monocarbide alloys, were carried out in the melting point furnace and the DTA-apparatus.

Binary Ti-V and metal-rich ternary Ti-V-C melting point samples were prepared by cold pressing the metal powder mixture and were used without prior homogenization. Carbon-richer (> 20 At.% C) ternary melting point and DTA-samples were hot pressed, shaped to the desired configuration by grinding, and equilibrated directly in the melting point furnace or the DTA-apparatus prior to the runs. Mainly for metallographic purposes, selected alloy samples were melted under helium in a non-consumable (tungsten) electrode arc-furnace.

B. DETERMINATION OF MELTING TEMPERATURES AND DIFFERENTIAL-THERMOANALYTICAL STUDIES

Melting temperatures of 12 binary Ti-V, and approximately 140 ternary Ti-V-C alloys, were measured using the method devised by Pirani and Alterthum. Design details of the furnace used in this laboratory, as well as temperature calibration and correction procedures, were described earlier.(26) The measurements were carried out under vacuum (binary

Ti-V and metal-rich Ti-V-C alloys), or under helium of ambient pressure after the samples were degassed under vacuum and preequilibrated at slightly subsolidus temperatures. Traces of objectionable impurities in the helium were continuously gettered by a strip of titanium heated by a separate power supply.

Using tantalum carbide as well as annealed graphite as reference standards, the thermal behavior of 41 ternary alloys were studied in the DTA-apparatus described in an earlier publication(27). The furnace atmosphere was helium (1 atm) and the container material high purity graphite. Carburization of excess metal containing alloys appeared slow under the chosen experimental conditions, apparently as a result of a thin layer of Ti-rich monocarbide solution formed between the metal alloy and the graphite container wall. To avoid rapid and excessive interaction with the sample container, the temperatures in DTA-runs on single-phased monocarbide alloys were kept below those of monocarbide + graphite eutectic trough.

C. METALLOGRAPHIC, X-RAY, AND CHEMICAL ANALYSIS

For the microscopic studies, the specimens were mounted in a mixture of diallylphthalate and lucite-coated copper powder and preground on silicon carbide paper. The ground surfaces were polished on nylon cloth using a slurry on Linde B alumina (0.3 microns) in a 5% chromic acid solution. The etching conditions are given in Table 3.

Carbon in the alloys was determined by combustion of the powdered specimens in oxygen and by conductrometric analysis of the resulting gas mixture in a Leco Carbon Analyzer. For the determination of free graphite, the powdered samples were first dissolved in a mixture of nitric and hydrofluoric acid, the residual graphite filtered off and determined by combustion as described above.

Table 3. Etching Conditions for Ti-V-C Alloys

Composition Range	Etching Procedure
$Ti-Ti_{0.30}V_{0.70}-Ti_{0.30}V_{0.33}C_{0.37}-Ti_{0.63}C_{0.37}$	Anodized in 0.5% oxalic acid solution.
$Ti_{0.30}V_{0.70}-Ti_{0.30}V_{0.45}C_{0.25}-V_{0.75}C_{0.25}-V$	Electroetched in 0.5% oxalic acid solution
$V_{0.75}C_{0.25}-Ti_{0.30}V_{0.45}C_{0.25}-Ti_{0.30}V_{0.22}C_{0.48}-V_{0.52}C_{9.48}$	Electroetched in 5% sulfuric acid
$Ti_{0.63}C_{0.37}-Ti_{0.30}V_{0.33}C_{0.37}-Ti_{0.30}V_{0.22}C_{0.48}-Ti_{0.52}C_{0.48}$	Dip-etched in a 10% solution of 6 parts HNO_3, 2 parts HCl and 2 parts HF
$Ti_{0.52}C_{0.48}-V_{0.52}C_{0.48}-C$	Examined in the as-polished state

Oxygen and nitrogen were hot-extracted in a gas fusion analyzer. The contents of these impurities, determined on a random selection basis on about 15 specimens, were on the order of 1200 ppm in the excess metal containing, hot pressed and sintered specimens, on the order of 300 ppm in the arc melted samples, and 600 ppm in the monocarbide alloys.

Powder diffraction patterns were prepared from all experimental alloys and the film strips evaluated with respect to number, structure, and lattice parameters of the phases present. The lattice parameter technique was also used to locate the vertices of the three-phase equilibria and to determine the conjugation lines in the two-phase fields.

IV. RESULTS

A. THE Ti-V SYSTEM

Melting point measurements on 12 alloys substantially confirmed the high temperature phase diagram features as proposed by Adenstedt et al.(6) (Figure 8). Our measurements place the minimum melting point at 35 At.% V and 1604° C. The measured lattice parameters of the metal solid solution were also in good agreement with literature data(6, 7, 28) (Figure 9). A slightly revised phase diagram of the Ti-V system, based on previous work and also including our measurements, is shown in Figure 10.

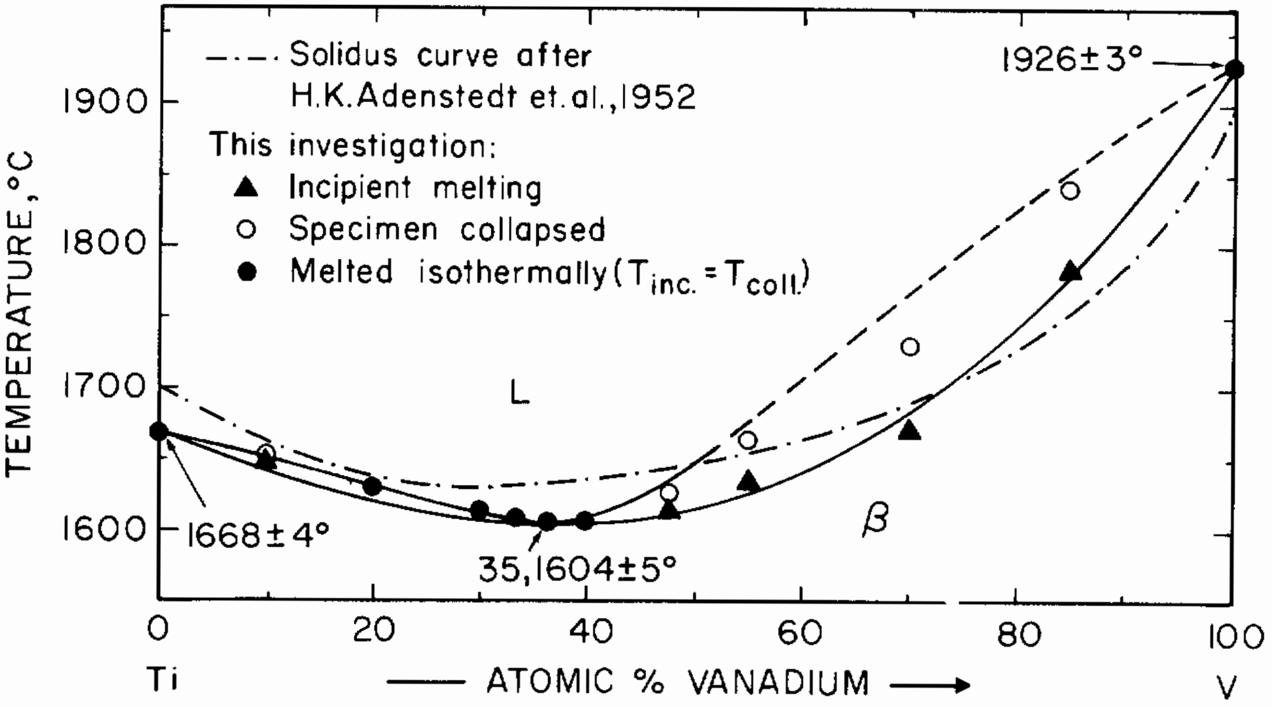

Figure 8. Melting Temperatures of Titanium-Vanadium Alloys.

(Temperature Error Figures Based on Reproducibility).

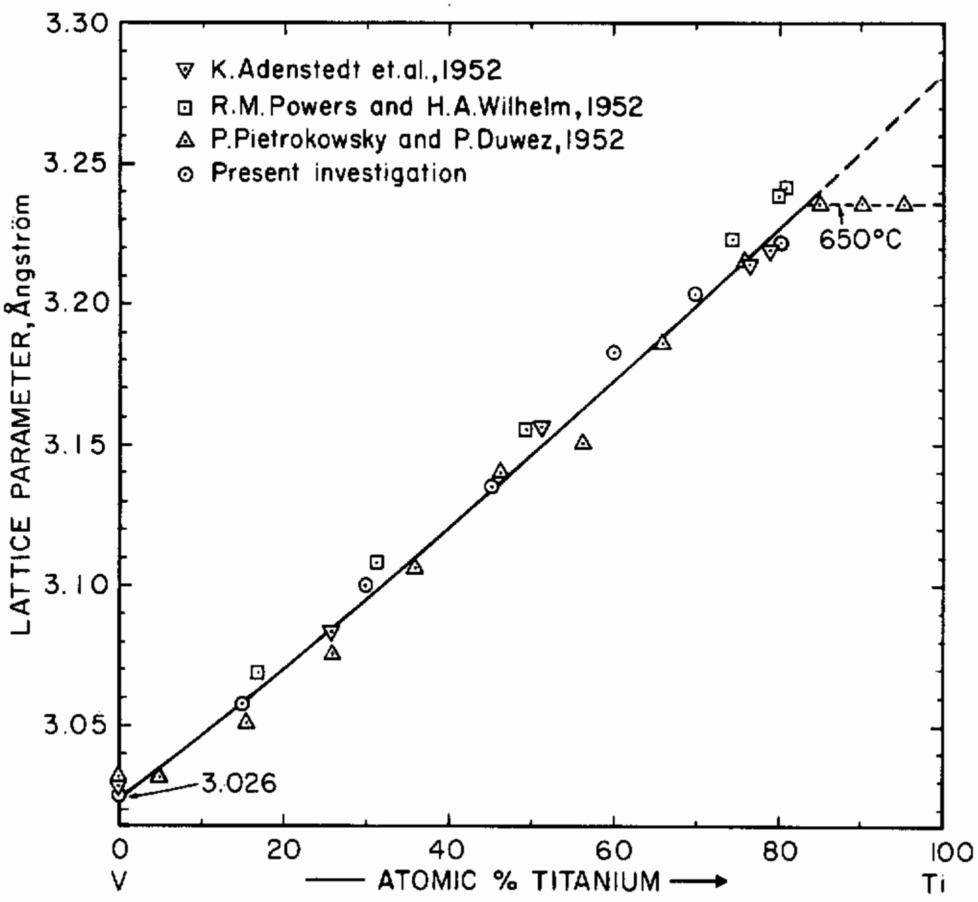

Figure 9. Lattice Parameters of the bcc (A2) Metal Solid Solution.

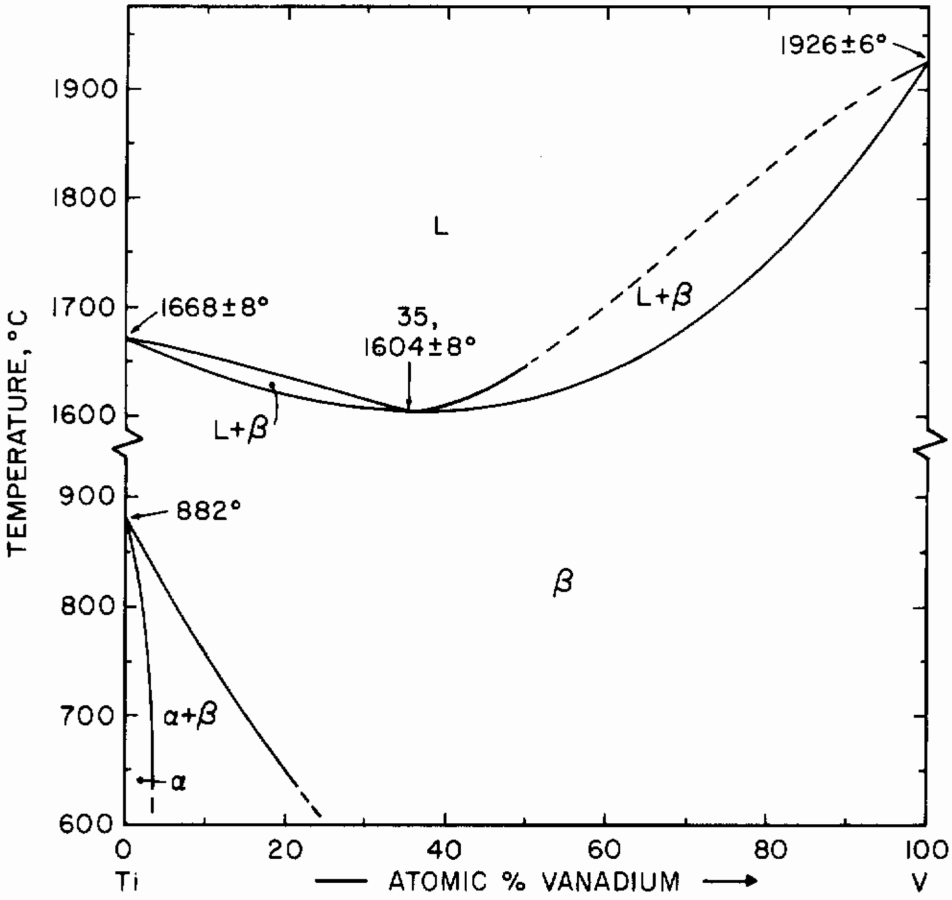

Figure 10. Accepted Phase Diagram for the Titanium-Vanadium System.

(Temperature Error Figures Based on Estimated Overall Uncertainty)

B. THE Ti-V-C SYSTEM

1. Phase Equilibria in the Solidus Range

Qualitative X-ray evaluation of the sample series equilibrated at 1400° C yielded the isothermal section shown in Figure 11. At this temperature the component metals as well as the monocarbide phases are completely miscible, while V_2C (a=2.902 Å, c=4.577 Å) substitutes

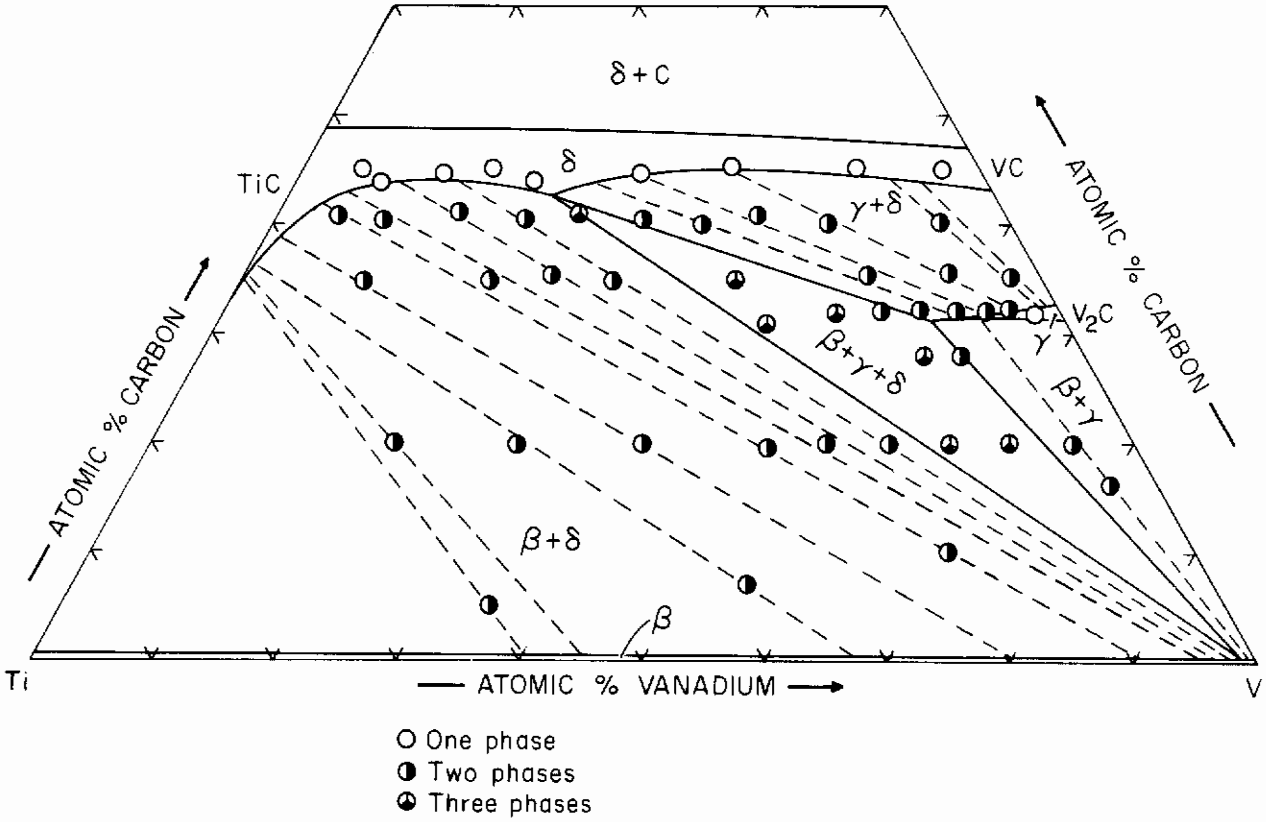

Figure 11. Sample Location and Qualitative Phase Evaluation of the Alloy Series Equilibrated at 1400° C.

approximately 15 At.% titanium (a= 2.916 Å, c= 4.622 Å). The metal-rich boundary of titanium monocarbide at this temperature changes from about 33 At.% C in the binary, to about 44 At.% upon substitution of less than 10 At.% vanadium. The B1-vertex of the three-phase equilibrium (Ti, V) + + V_2C-ss + (Ti, V)C_{1-x}(B1) found in our work corresponds closely to that reported by Eremenko et al.(1), while our data concerning the titanium exchange in the V_2C phase are more in favor of those given by Fedorov et al.(22). The two-phase equilibrium metal + monocarbide, bounded by the three-phase

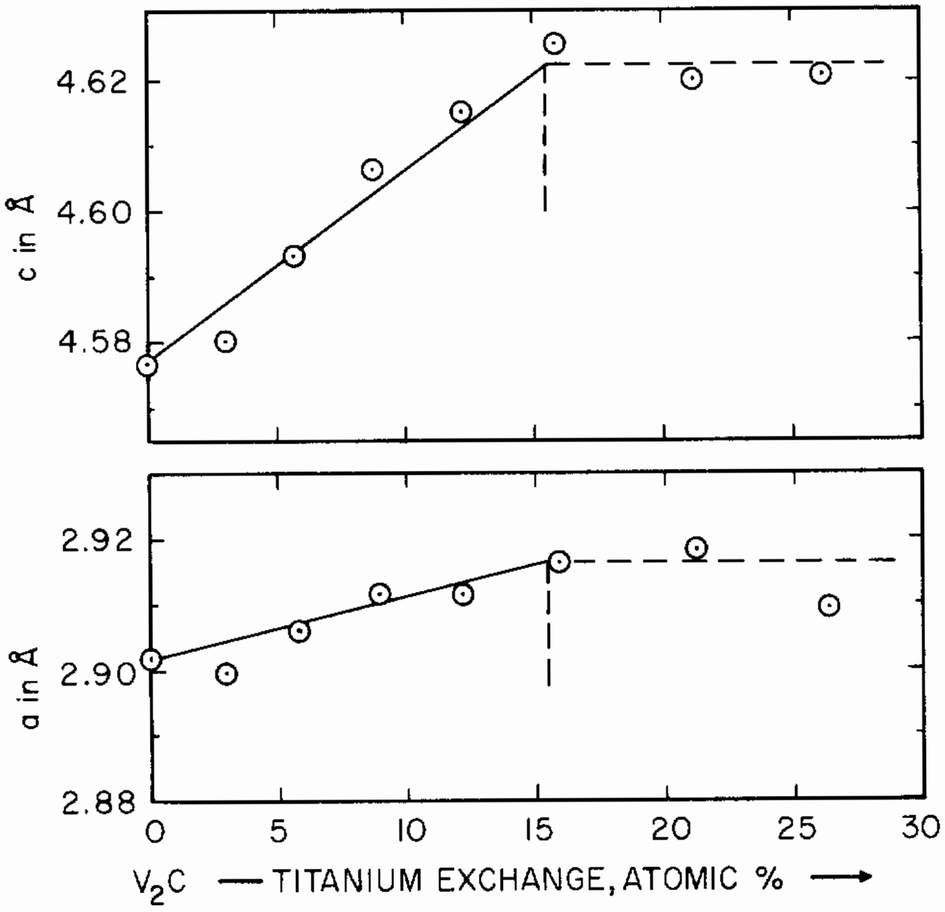

Figure 12. Lattice Parameters of the (Ti, V)$_2$C Solid Solution.

(Alloys Equilibrated at 1400° C)

equilibrium metal + subcarbide + monocarbide in the ternary, extends from the binary Ti-C system to 98 At.% V at the Ti-V edge binary, and to a vanadium exchange of approximately 38 At.% at the monocarbide phase.

The tie line distribution in the three two-phase fields $\beta + \delta$, $\beta + \gamma$, and $\gamma + \delta$ were determined from lattice parameter-concentration plots such as shown for the $\beta + \delta$ partition equilibrium in Figure 13. All three partition equilibria show a strong relative enrichment of titanium in the higher carbon phases which is indicative of the higher stability of the titanium carbides as compared to the vanadium carbides.

The lattice parameters of the carbon-saturated monocarbide solid solution, determined on a sample series equilibrated at 2000° C, are in good agreement with data reported in the literature(22, 23, 24, 29, 30) (Figure 14 and 15). The linearity of the lattice parameter-concentration relationships is preserved in carbon-deficient alloys (Figure 16).

2. Phase Equilibria at High Temperatures

According to the melting point data obtained on alloys located along the eutectic trough in the metal-rich region of the system (Figure 17), the minimum melting point in the Ti-V system results in the formation of a pseudobinary (minimum) eutectic at 1570° C at a titanium exchange of approximately 35 At.% C. Two three-phase equilibria, $L_{(1)} + Me_{(1)} + MeC_{1-x(1)}$, and $L_{(2)} + Me_{(2)} + MeC_{1-x(2)}$, originate at this eutectic isotherm: One of the two equilibria advances towards the Ti-C edge binary as the temperature is increased and finally degenerates into the β-Ti + TiC eutectic isotherm at 1650° C. The second equilibrium, whose liquidus vertex forms the locus of concentration points constituting the eutectic trough, shifts towards the vanadium side and degenerates, in combination with

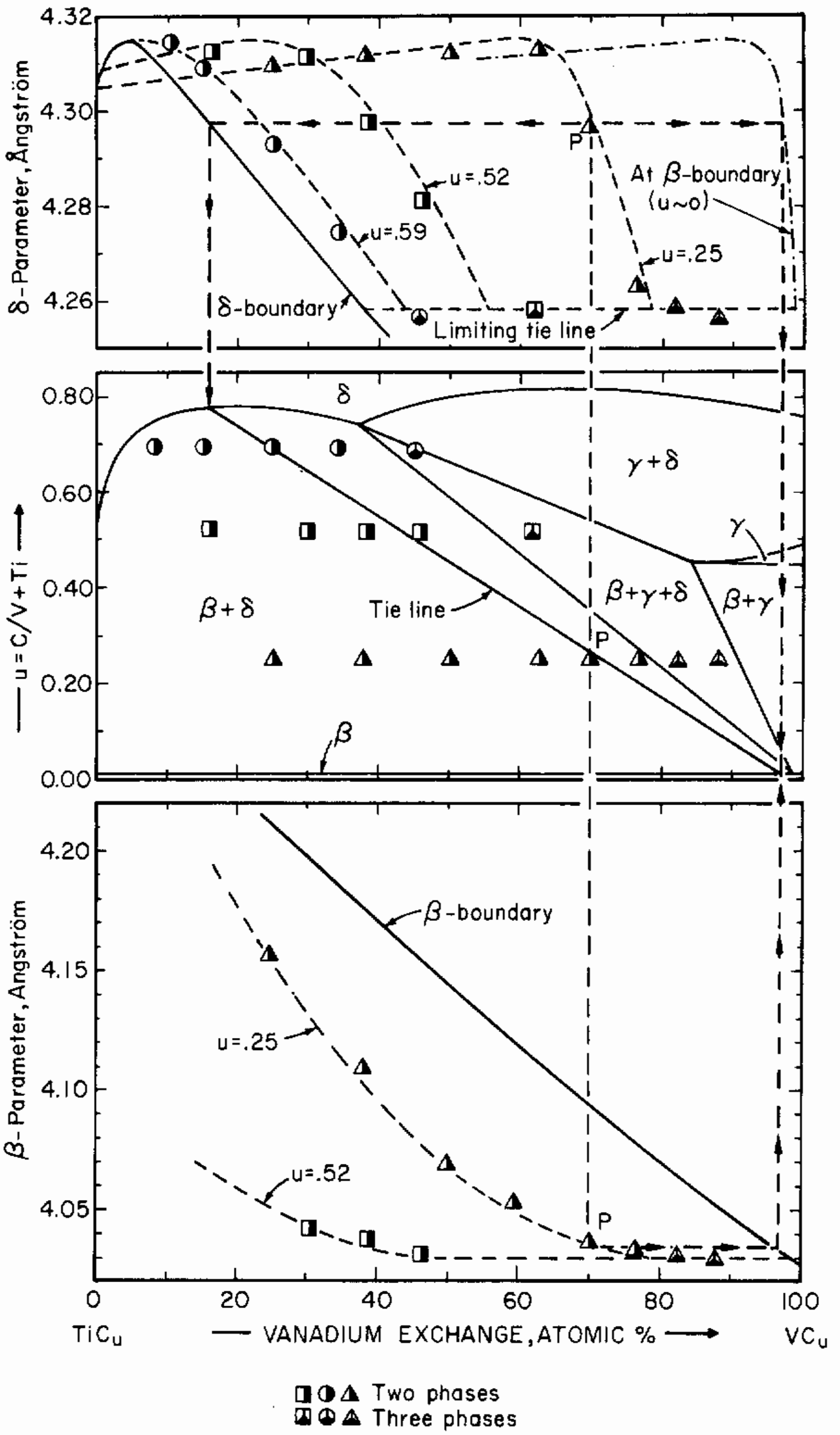

Figure 13. Determination of the Tie Line Distribution in the Two-Phase Field β + δ by Lattice Parameter Measurements on Two-Phased, β + δ, and Three-Phased, β + γ + δ, Alloys. (Samples Equilibrated at 1400° C).

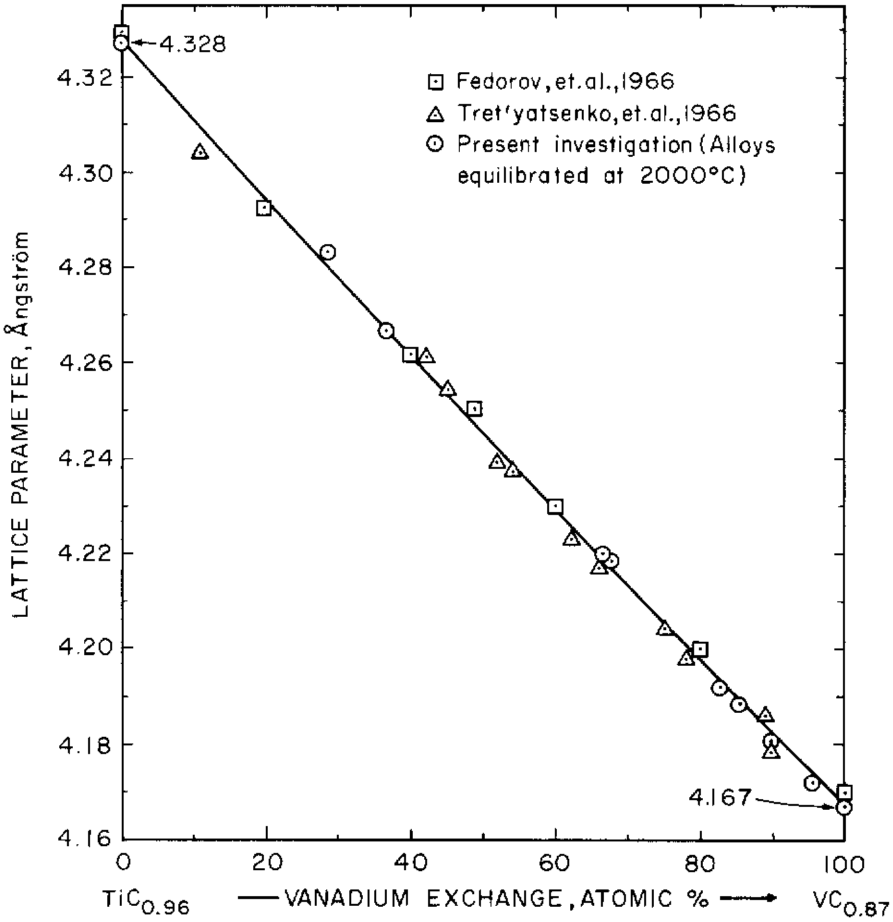

Figure 14. Lattice Parameters of the Carbon-Saturated Monocarbide Solution.

(Literature and Own Data).

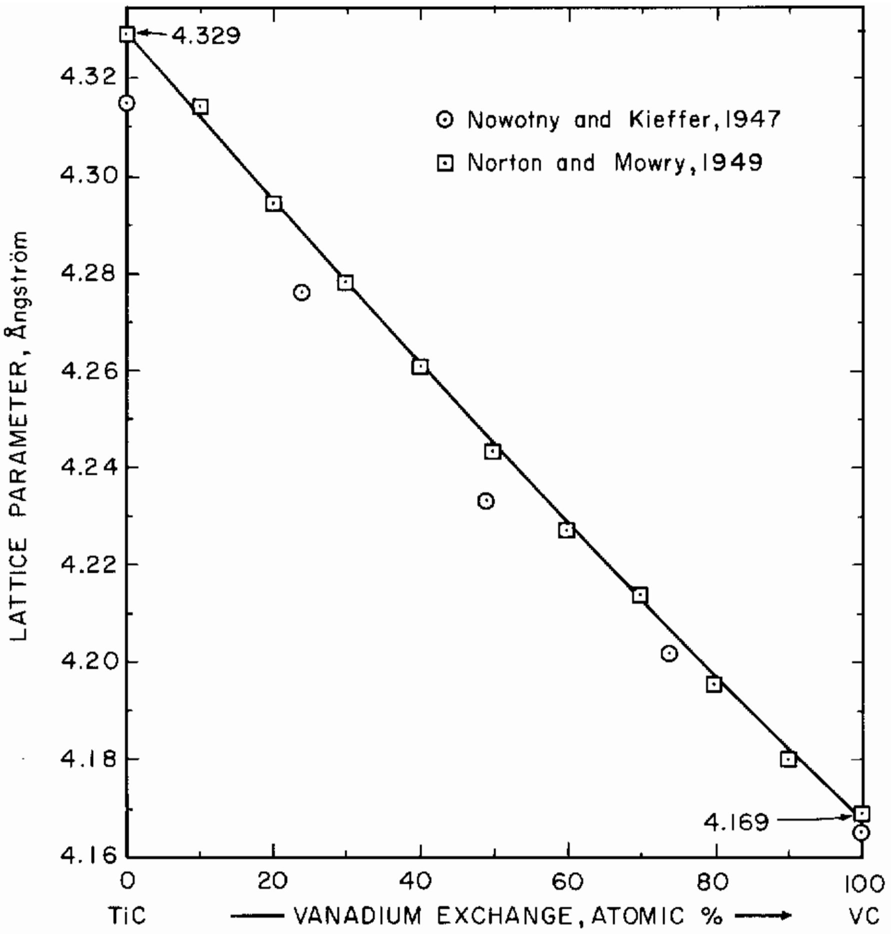

Figure 15. Lattice Parameters of the Titanium-Vanadium Monocarbide Solid Solution.

(Literature Data).

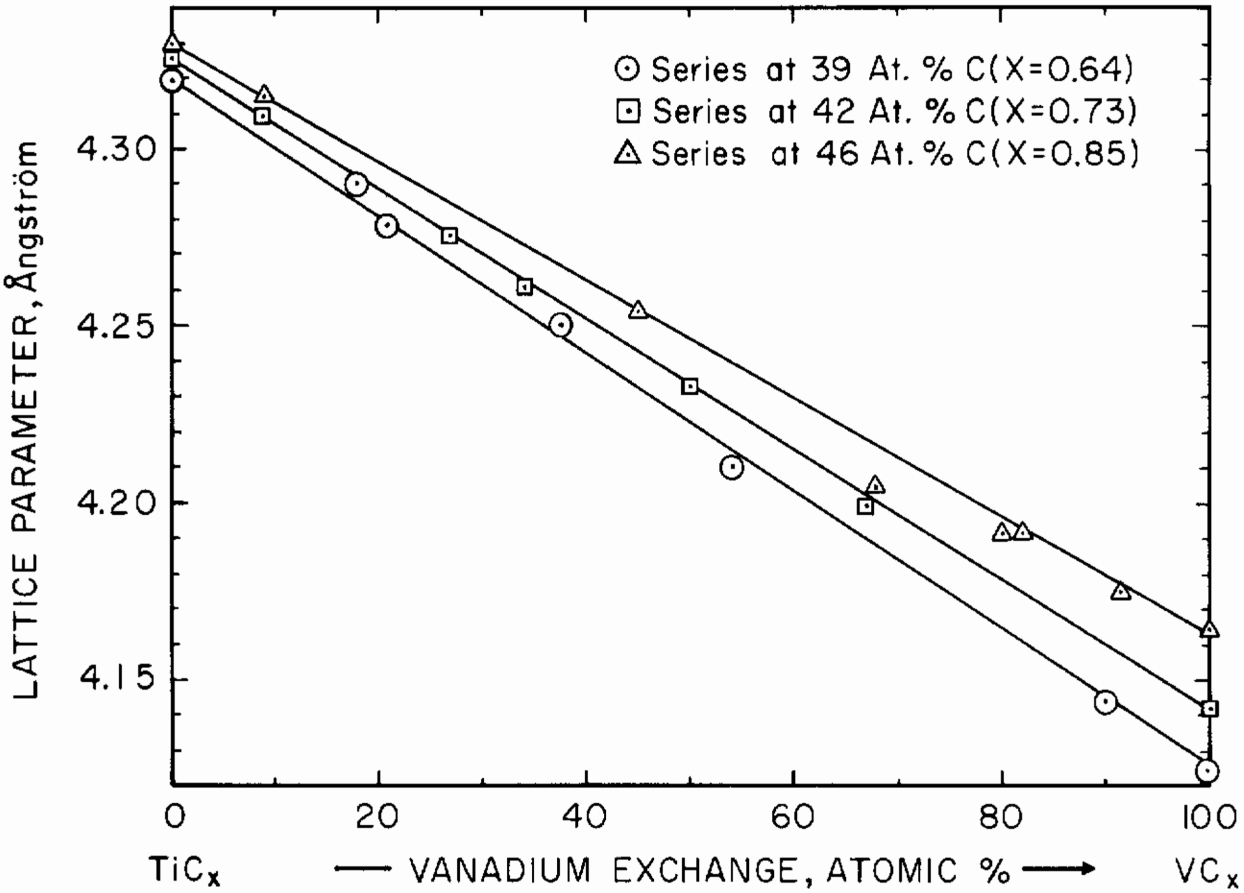

Figure 16. Lattice Parameters of the Cubic Monocarbide Solution at Various Carbon Defect Concentrations.

(Alloys equilibrated at 2000° C and quenched)

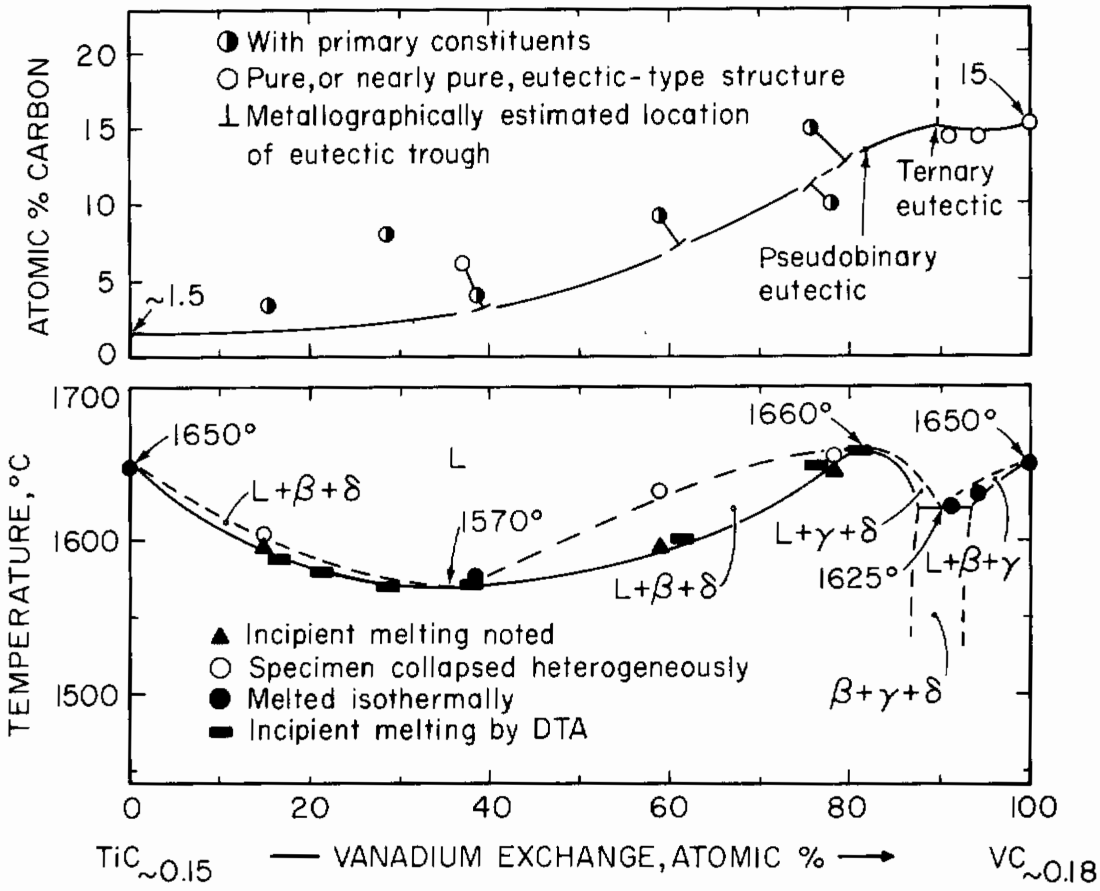

Figure 17. Experimental Melting Temperatures in Alloys Located Along the Metal-Rich Eutectic Trough.

Top: Microscopically Evaluated Alloys and Estimated Location of Eutectic Trough.

another three-phase equilibrium, $L_{(3)} + Me_{(3)} + MeC_{1-x(3)}$, into a pseudobinary (maximum type) eutectic at 1650° C (Figure 17). The latter three-phase equilibrium, along with two other three-phase equilibria, $L + Me_2C +$ $+ Me$, and $L + Me_2C + MeC_{1-x}$, originate at a ternary eutectic formed between a vanadium-rich metal alloy, V_2C-solid solution, and the monocarbide phase at 1625° C. Melting point data along the pseudobinary section metal + + monocarbide are shown in Figure 18.

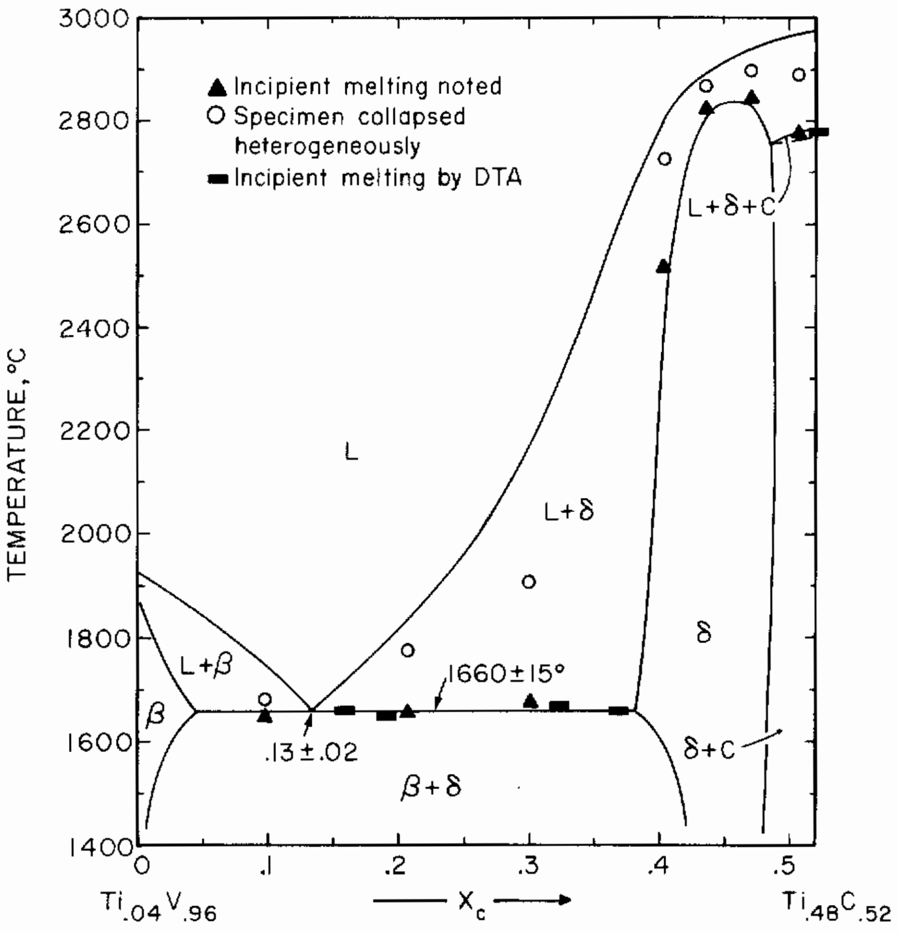

Figure 18. Experimental Melting Temperatures at the Pseudobinary Section Metal + Monocarbide.

The location of the eutectic trough near the Ti-V binary was determined mainly by metallographic inspection of the as-melted specimens (Figures 17, 19 through 23).

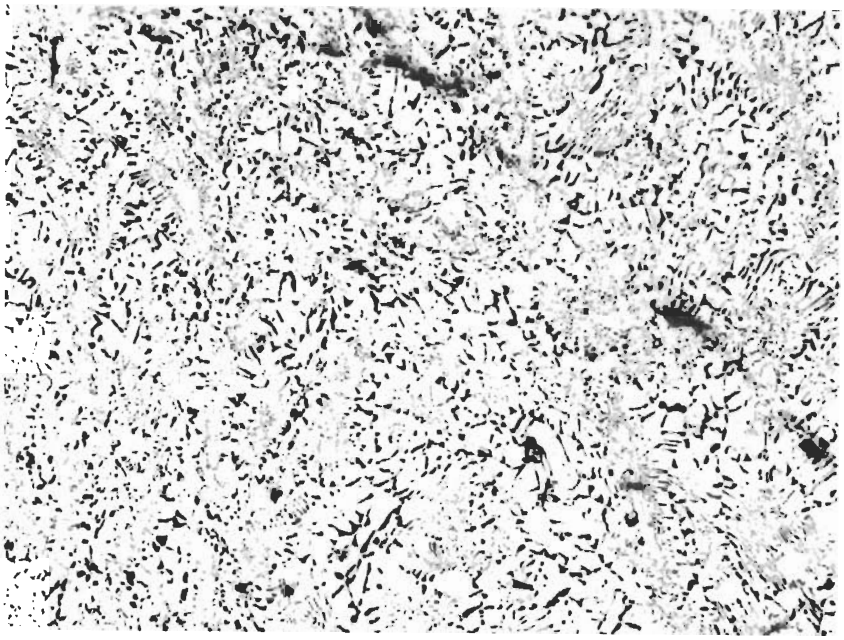

Figure 19. Ti-V-C (38-55-7 At.%), Arc Melted. X375
Bivariant Metal + Monocarbide Eutectic Structure

Melting near the metal-rich boundary of the monocarbide phase occurred extremely heterogeneously and incipient melting difficult to detect by the Pirani-technique. The data collected by differential thermal analysis, which responded very sensitively to the formation of even small amounts of melt, were therefore given preference in the evaluation of the experimental results. DTA-runs on titanium-rich alloys located very near the monocarbide boundary showed two distinct thermal arrests (Figure 24). The higher temperature peak was readily identified by metallographic inspection to correspond to melting of the metal-rich eutectic alloys.

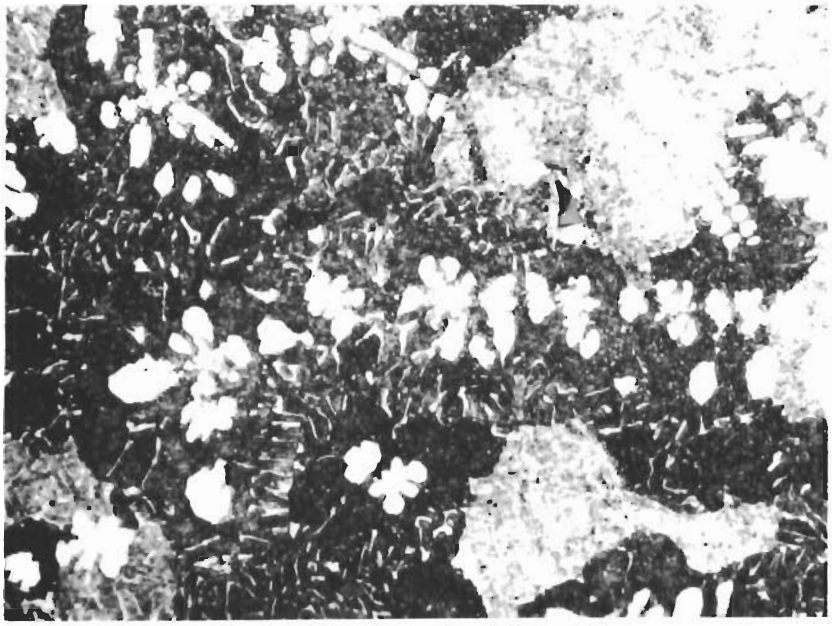

Figure 20. Ti-V-C (20-70-10 At.%), Melted and Quenched. X600

Isolated Grains of Binary Metal in a Largely Unresolved Eutectic ($\beta + \alpha$) Matrix.

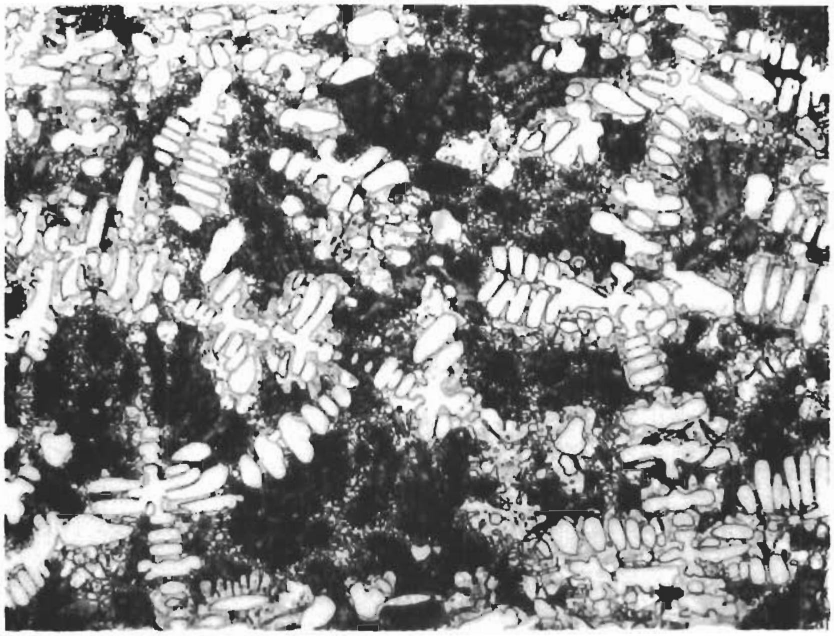

Figure 21. Ti-V-C (20-60-20 At.%), Melted and Rapidly Cooled. X375

Primary Monocarbide (δ) in a Pseudobinary Eutectic Matrix $\beta + \delta$.

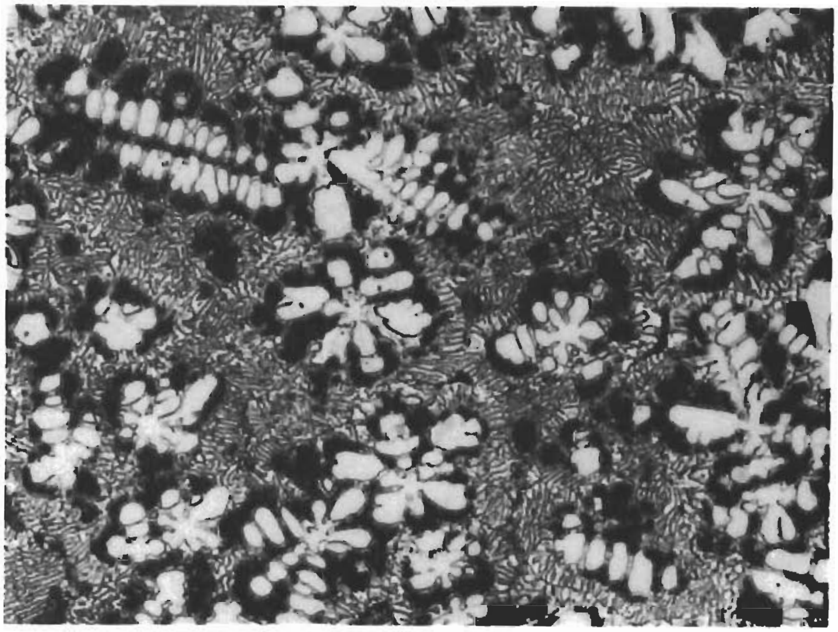

Figure 22. Ti-V-C (19-65-16 At.%), Melted and Quenched X275

Primary Monocarbide in a Predominately Eutectic Structure.

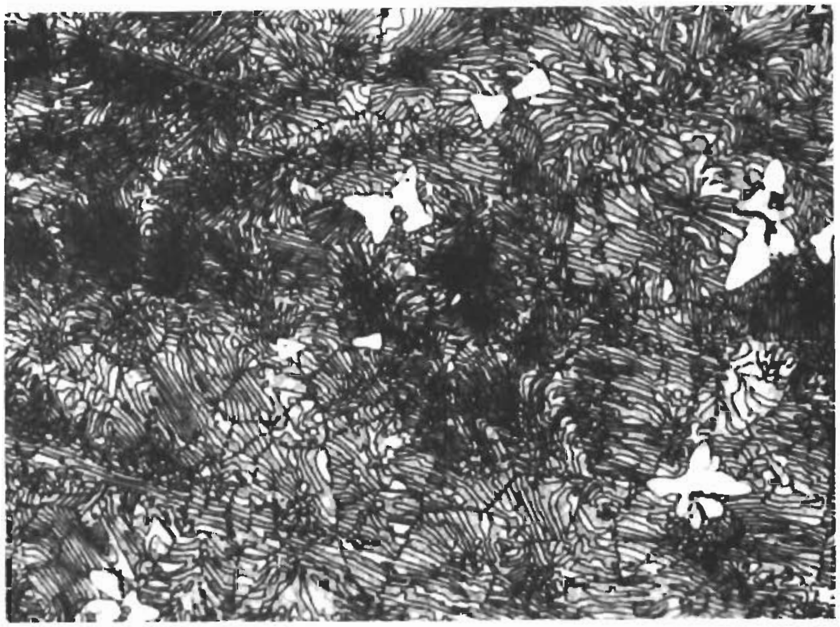

Figure 23. Ti-V-C (5-81-14 At.%), Melted and Rapidly Cooled. X600

Eutectic Solidifcation Structure at the Three-Phase Boundary $\beta + \gamma + \delta$, with Traces of Binary Metal Phase.

X-Ray: β, γ, and traces of δ.

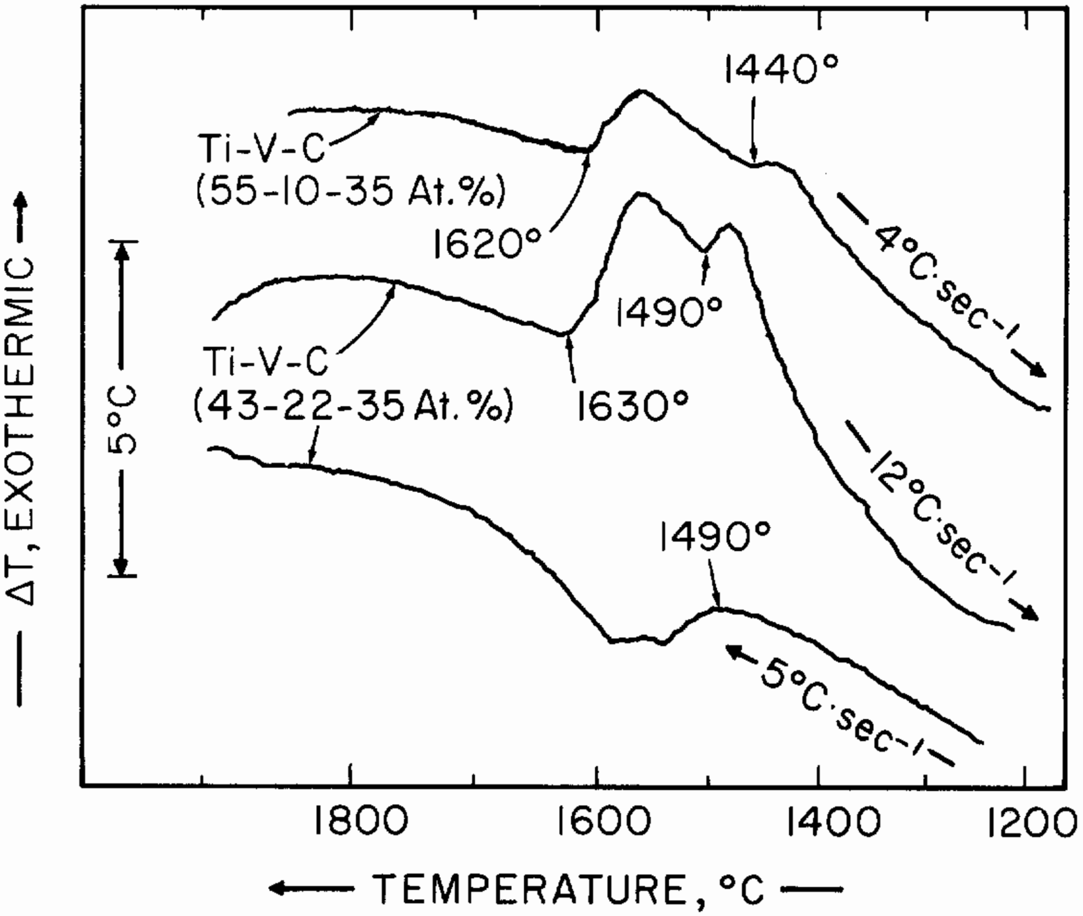

Figure 24. DTA-Thermograms of Two Ti-V-C Alloys Located Near the Metal-Rich Monocarbide Boundary.

The peaks in the vicinity of 1600° C are due to bivariant solidification (melting) of the metal-rich eutectic, whereas the peaks in the range from 1440 to 1500° C are believed to be due to precipitation of metal alloy from the monocarbide.

The cause for the second peak at somewhat lower temperatures, however, is not as clearly defined. Work by H. Goretzki(19) has indicated a sublattice order-disorder transition of 1900°C. Although the interpretation of our DTA-data in terms of such a transition in the ternary solid solution cannot be rejected entirely, the observed independence of the temperatures of the thermal arrests upon the vanadium exchange and the much lower temperatures at which the peaks occurred in the ternary alloys, led us to search for another explanation. Occurrence and magnitude of the peaks obtained at various cooling speeds correlated closely with the formation of precipitation structures in the carbon-deficient monocarbide at temperatures somewhat below the metal-rich eutectic trough (Figures 25 and 26).

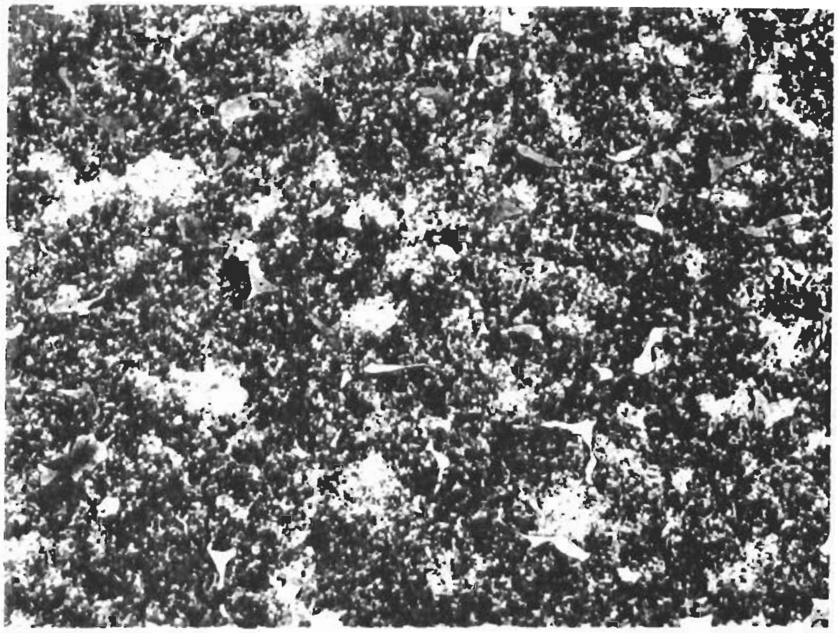

Figure 25. Ti-V-C (55-10-35 At.%), Melted, Reequilibrated at 1800°C, and Cooled at ~40°C per Second. X425

Heavy, Intragranular Metal Precipitates in the Ti-Rich Monocarbide Formed During Cooling, and Small Amounts of Excess Metal at the Original Monocarbide Grain Boundaries.

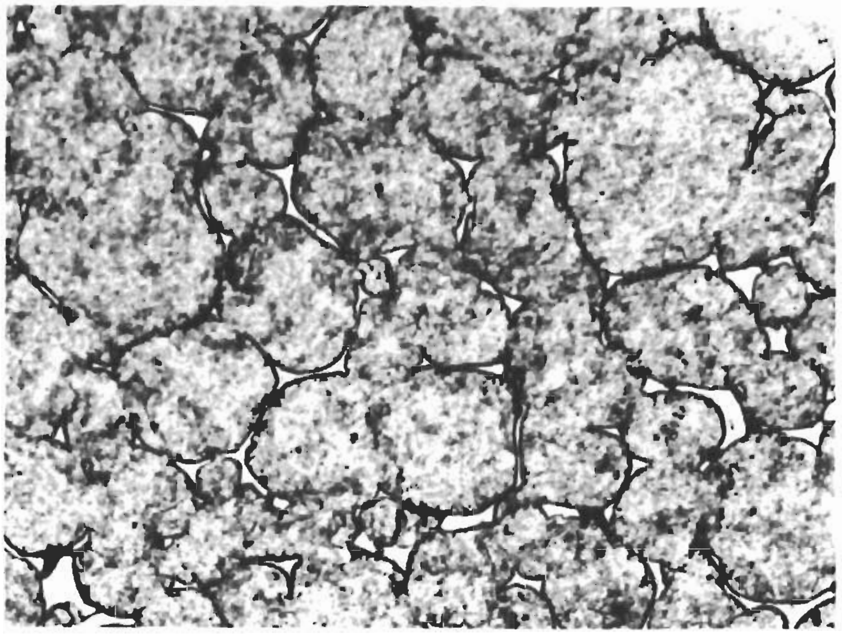

Figure 26. Ti-V-C (42-22-36 At.%), Melted Reequilibrated at 1750° C, and Rapidly Cooled. X425

Metal Precipitates (Unresolved) in the Monocarbide Grains, and Small Amounts of Excess Metal at Grain Boundaries.

These indications received support from additional DTA-experiments which showed a gradual disappearance of the lower temperature peaks as the carbon contents of the alloys were raised to about 43 At.%; metal precipitation at these carbon levels was shown to be negligible by microscopic inspection of the alloys. From the DTA-experiments, coupled with the metallographic findings, it was then concluded that the observed lower temperature peaks were most likely attributable to metal-precipitation phenomena in the titanium-rich monocarbide solid solution. Solid state reaction in addition to those attributable to precipitation (Figures 27 and 28), and which may be related to order-disorder phase transitions in the monocarbide, have been formed in vanadium-rich alloys (Figure 28 and 29). A detailed analysis and investigation, however, is still missing.

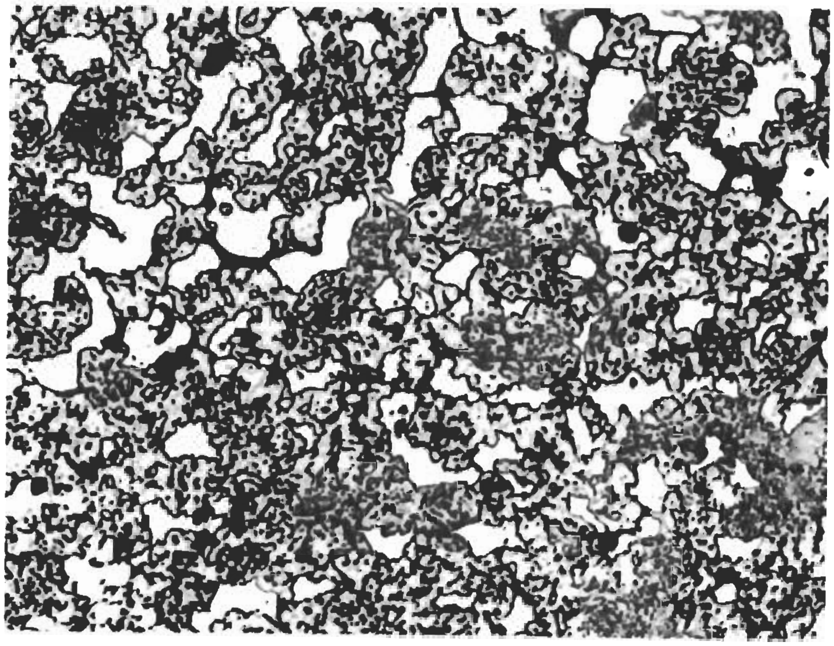

Figure 27. Ti-V-C (25-45-30 At.%), Melted, Rehomogenized for 15 Minutes at 1700°C, and Cooled at 3°C per Second. X600

Monocarbide with Intragranular Metal Precipitates and Excess Metal. Note the Agglomeration and Growth of the Precipitate Phase as a Result of the Low Cooling Rate.

Melting point measurements on the (Ti,C)C_{1-x} solid solution alloys showed the occurrence of a congruent (minimum) melting point of 2625°C at a titanium carbide content of approximately 10 mole% and a carbon concentration of ~44 At.% (Figures 30 and 31). Melting point data collected on about 60 alloys, spread across the range of homogeneous monocarbide alloys, were combined to yield the solidus isotherms of the monocarbide phase plotted in Figure 32. Figure 33 shows a micrograph of a slightly cored monocarbide alloy located close to the congruently melting composition.

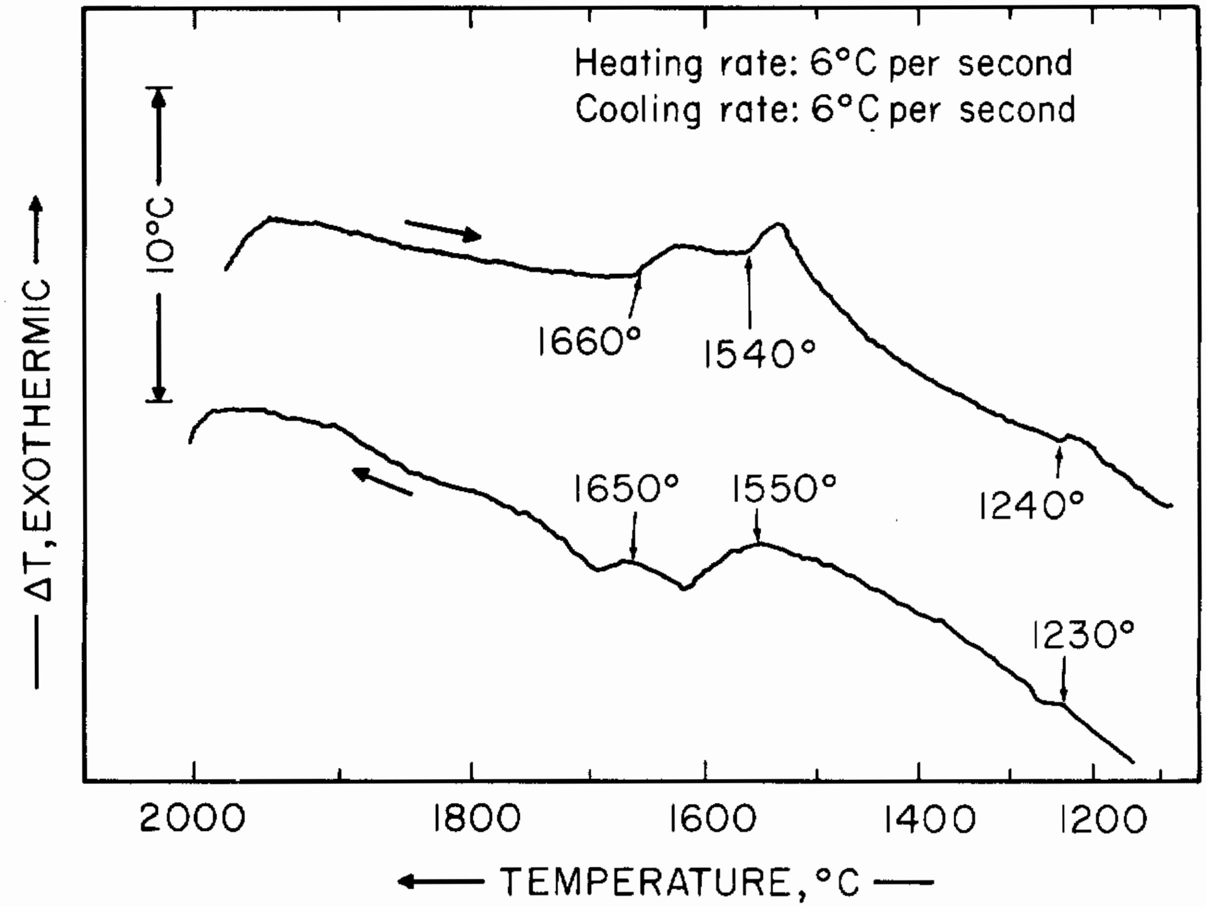

Figure 28. DTA-Thermogram of a Ti-V-C (25-45-30 At.%) Sample.

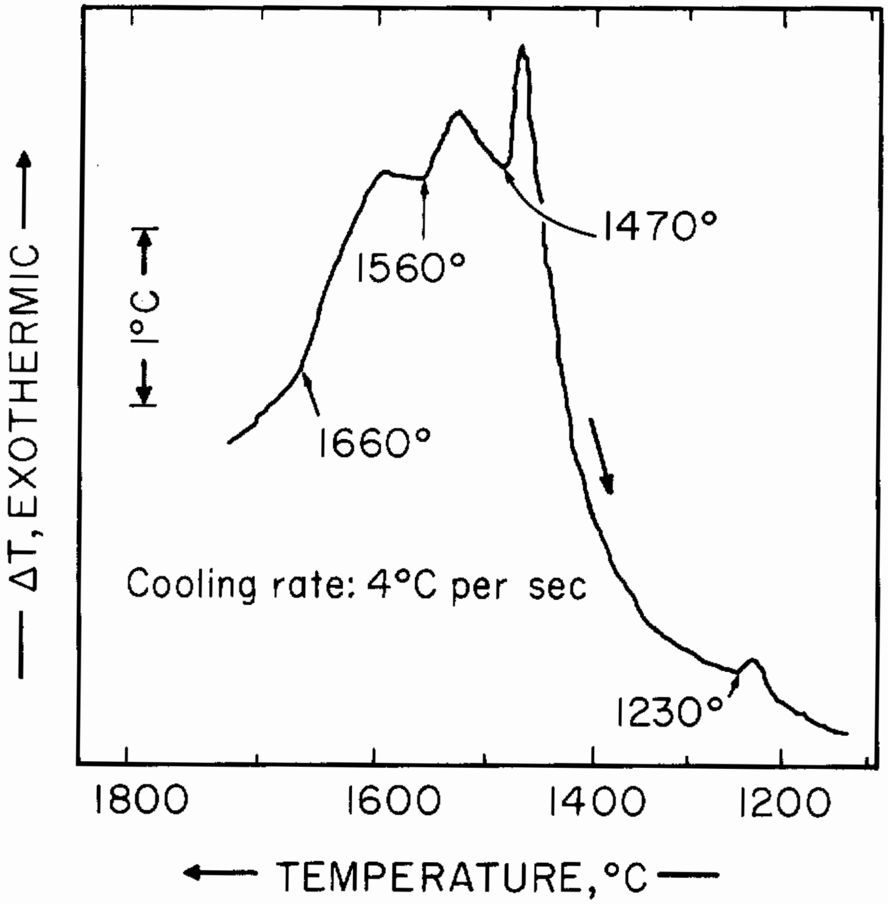

Figure 29. DTA-Thermogram of a Ti-V-C (30-35-35 At.% Alloy.

The origin of the slight thermal arrest at 1230°C is uncertain, but is probably related to a sublattice ordering reaction in the substoichiometric monocarbide solution.

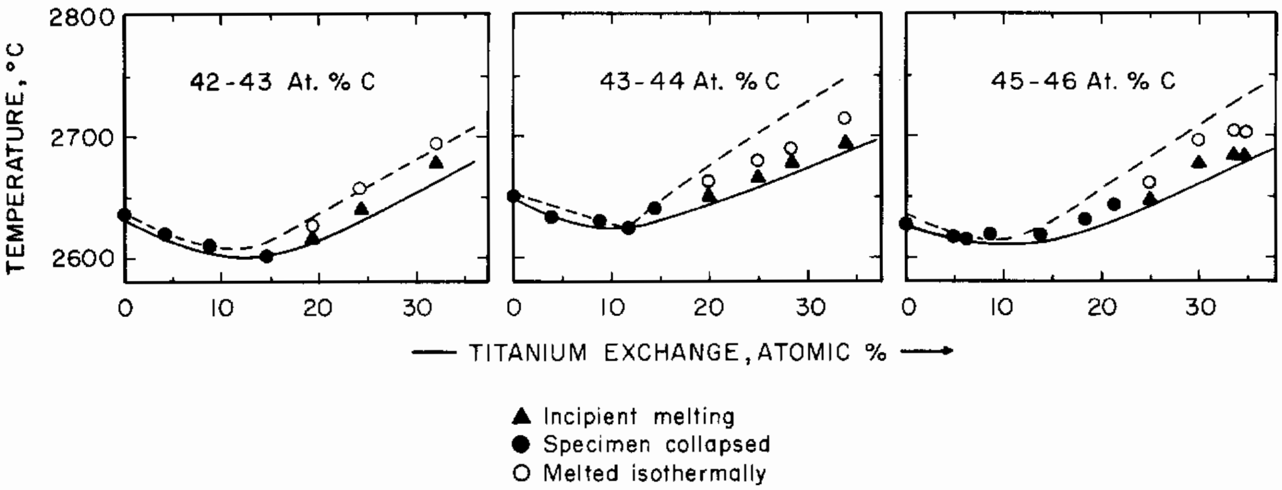

Figure 30. Melting Temperatures of the Monocarbide Solution Near the Vanadium-Carbon Binary.

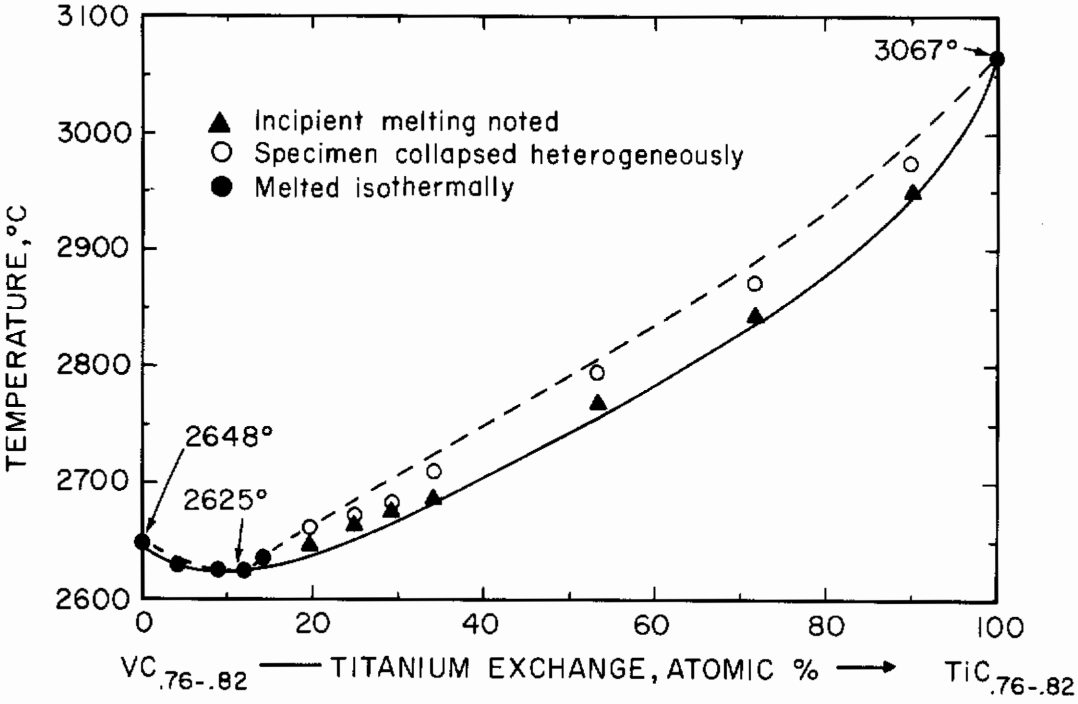

Figure 31. Maximum Solidus Temperatures of the $(Ti,V)C_{1-x}(B1)$ Solid Solution.

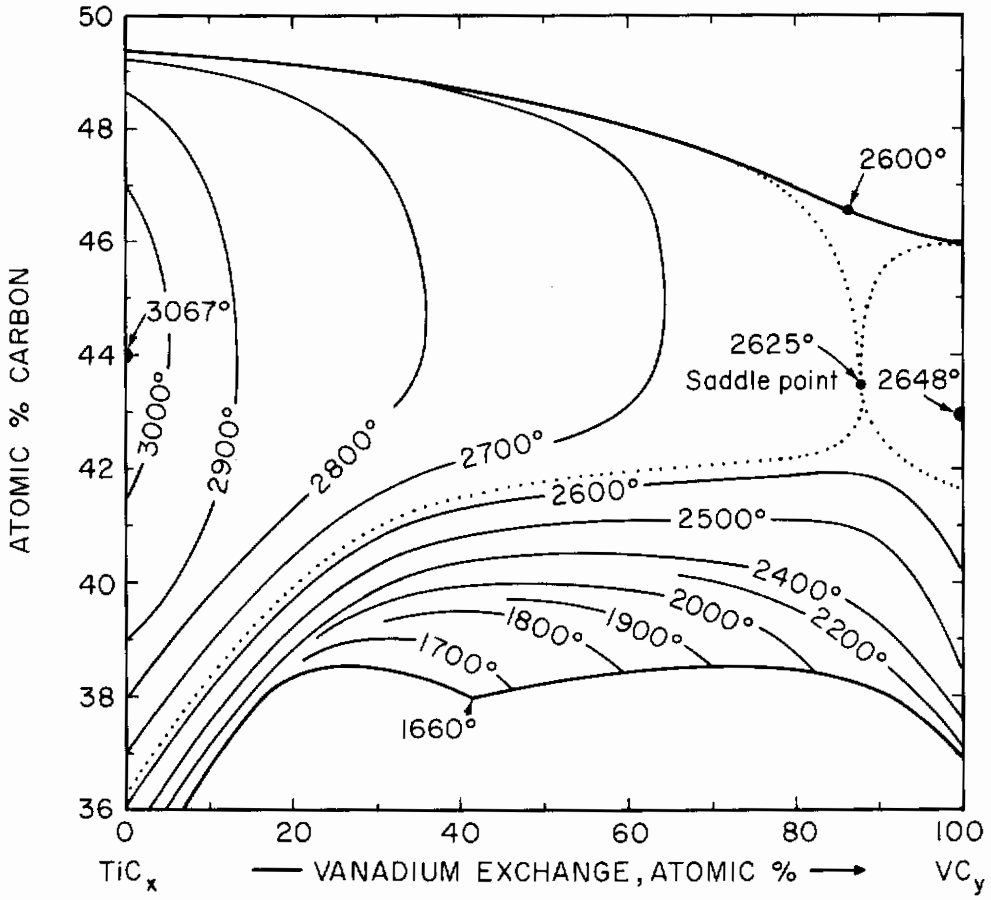

Figure 32. Solidus Isotherms for the (Ti,V)C_{1-x} Solid Solution.

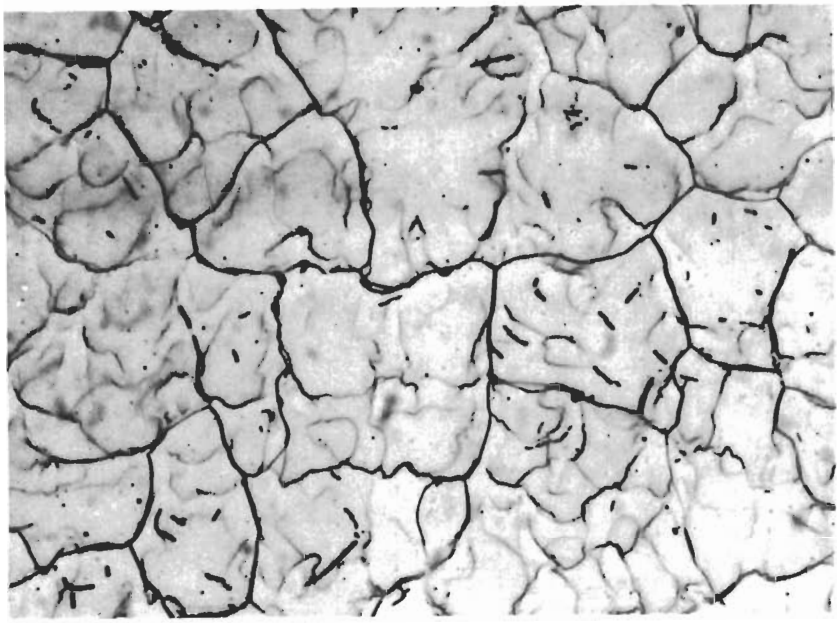

Figure 33. Ti-V-C (8-40-42 At.%), Melted and Rapidly Cooled. X425

Slightly Cored, Vanadium-Rich Monocarbide Solution.

The monocarbide + graphite eutectic trough also has a minimum melting point (pseudobinary eutectic) in the ternary (Figure 34). The microstructures of melted and then rapidly cooled specimens located at, or near, the eutectic trough are eutectic-like across the entire range of metal exchanges (Figures 35, 36, and 37).

3. Assembly of the Phase Diagram

The experimental data were combined to yield the proposed phase diagram shown in Figure 1. The diagram is supplemented by the flow diagram of non-variant (p = const) binary and ternary reactions (Figure 2) and a plot of the liquidus isotherms (Figure 3).

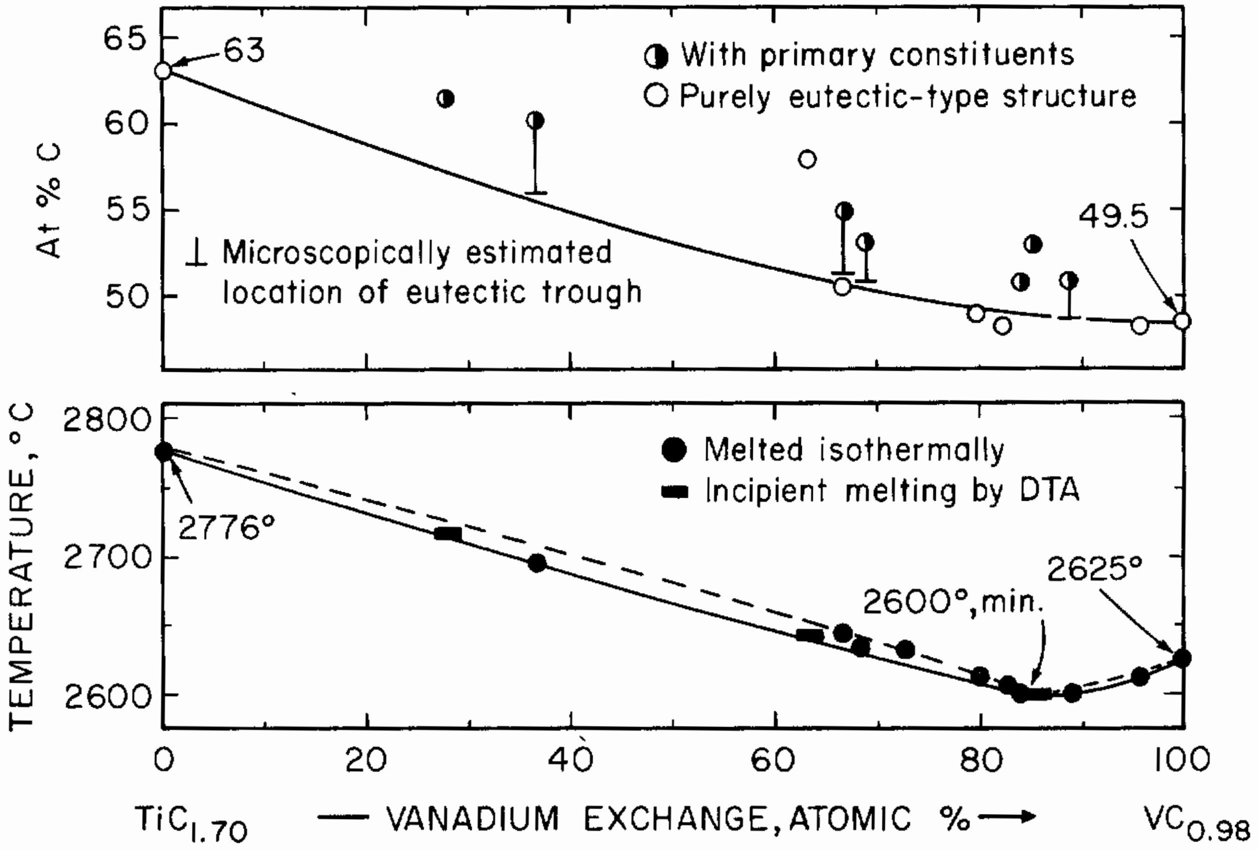

Figure 34. Metallographically Examined Alloys (Top Section) and Melting Temperatures in Samples Located Along the Monocarbide + Graphite Boundary Line.

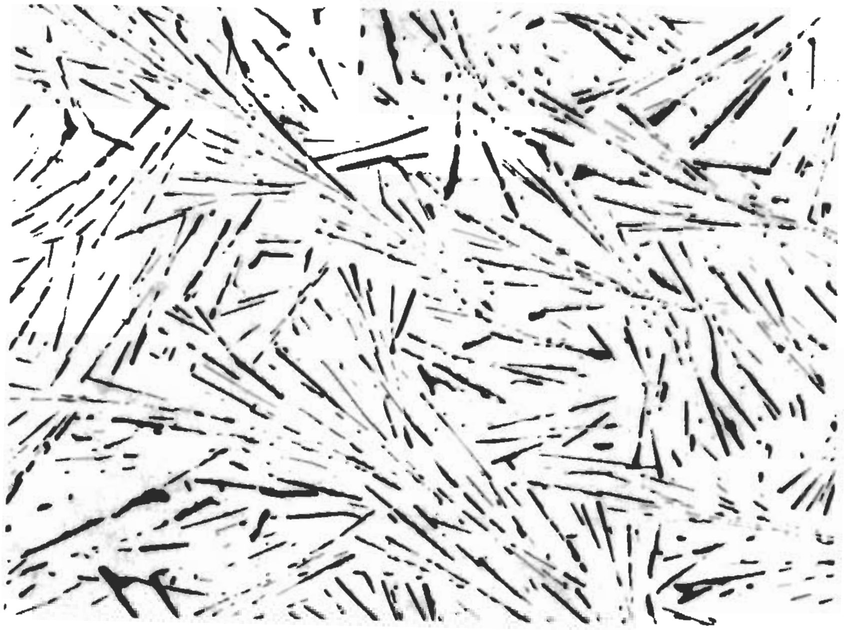

Figure 35. Ti-V-C (8-41-51 At.%), Melted and Rapidly Cooled. X375

Pseudobinary Eutectic Structure at the Congruent (Minimum) Melting Point. Selected Areas of this Sample Contained Some Primary Graphite.

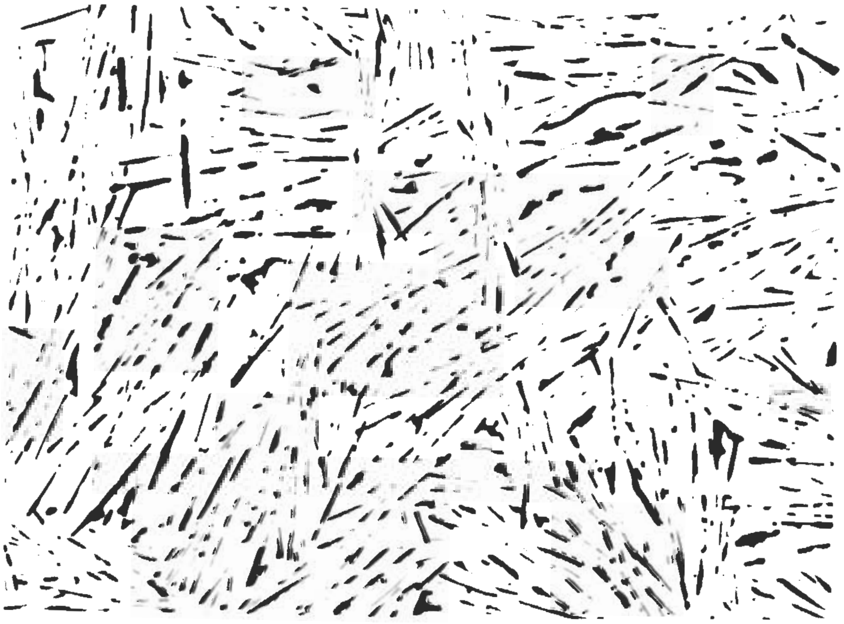

Figure 36. Ti-V-C (15-33-51 At.%), Melted and Rapidly Cooled. X475

Eutectic-Like Structure at the Monocarbide + Graphite Eutectic Trough.

Figure 37. Ti-V-C (25-15-60 At.%), Melted and Rapidly Cooled. X150

Primary Graphite and Eutectic-Like Structure at the Boundary Line Monocarbide + Graphite.

Isometric views are inherently difficult to visualize and interpret and further have the disadvantage that certain information such as, for example, data concerning the compositions of coexisting phases within two-phase fields, becomes difficult to extract or is lost entirely. For this reason, and also for the convenience of use of the phase diagram data, a series of isothermal sections, depicting clearly the change of phase equilibria with temperature, have been assembled from the available experimental information and are shown in Figures 38 through 45. The isothermal sections are supplemented by a number of vertical sections along the most important concentration lines in the system (Figures 46 through 52).

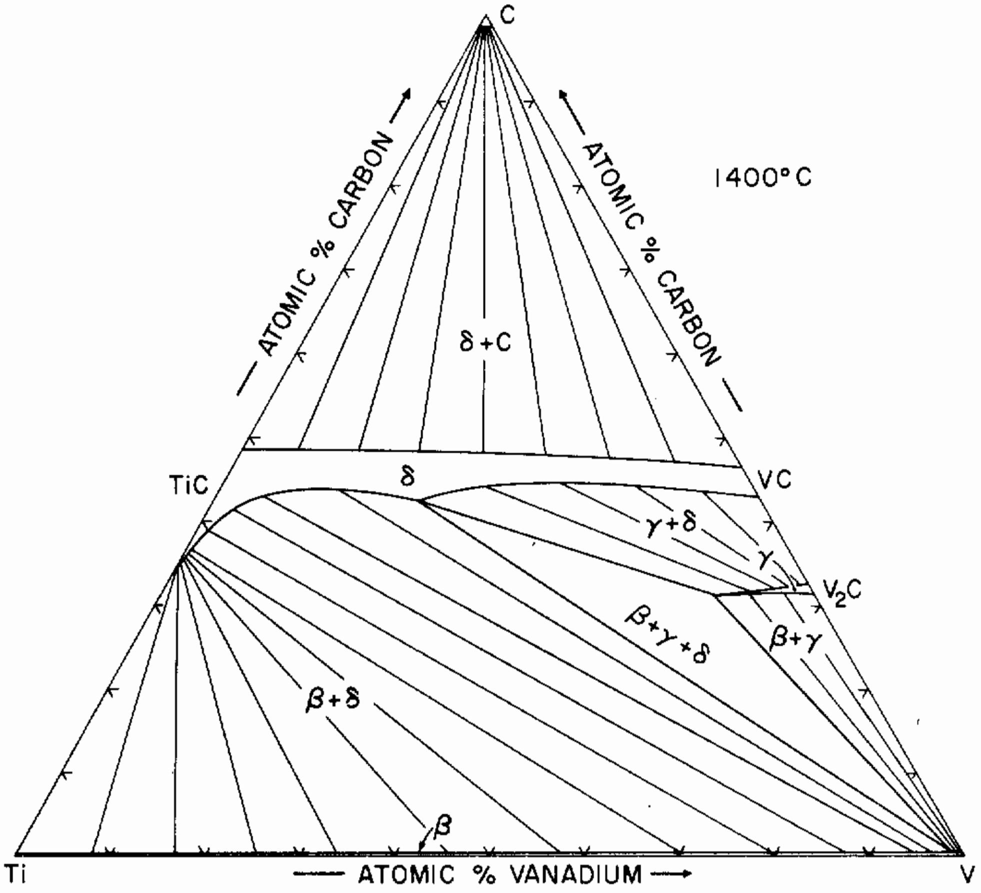

Figure 38. Isothermal Section of the Ti-V-C System at 1400° C.

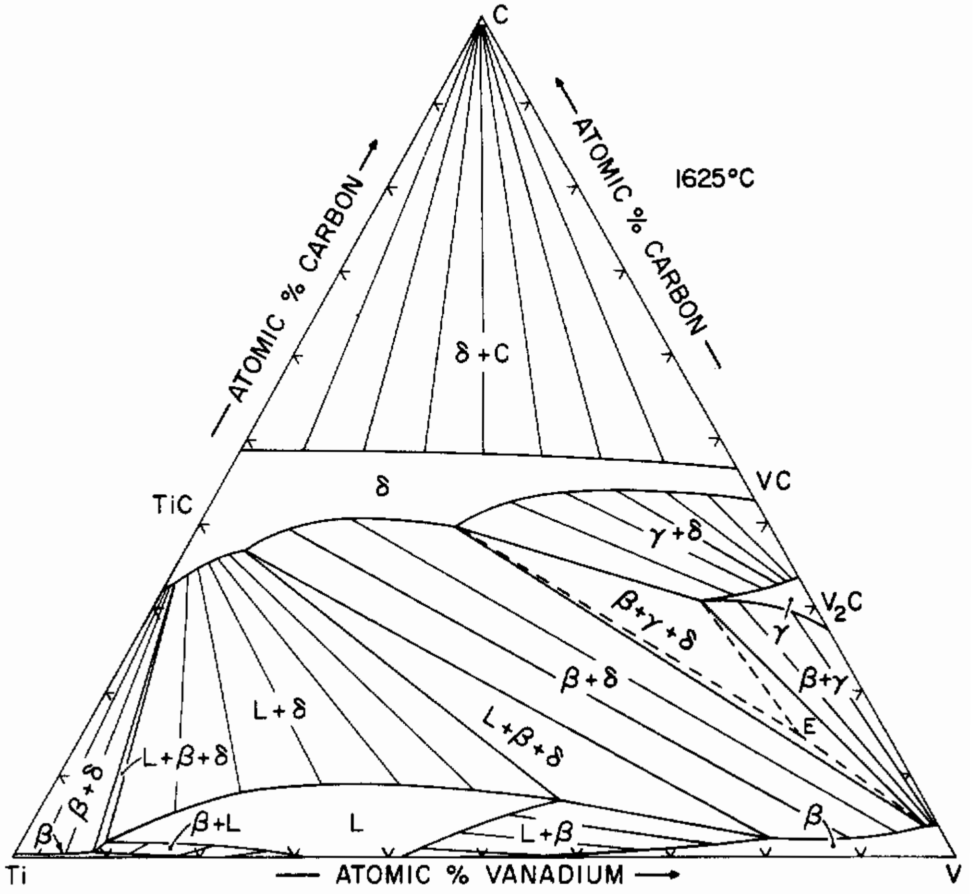

Figure 39. Isothermal Section of the Ti-V-C System at 1625° C.

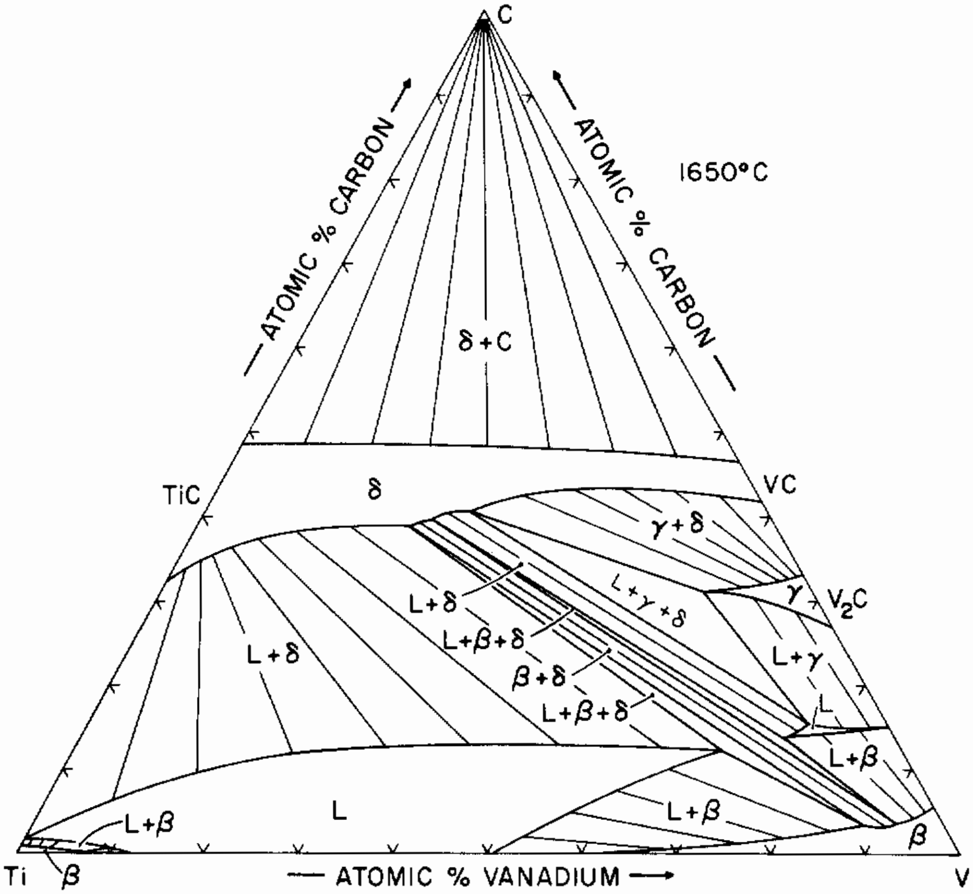

Figure 40. Isothermal Section of the Ti-V-C System at 1650° C.

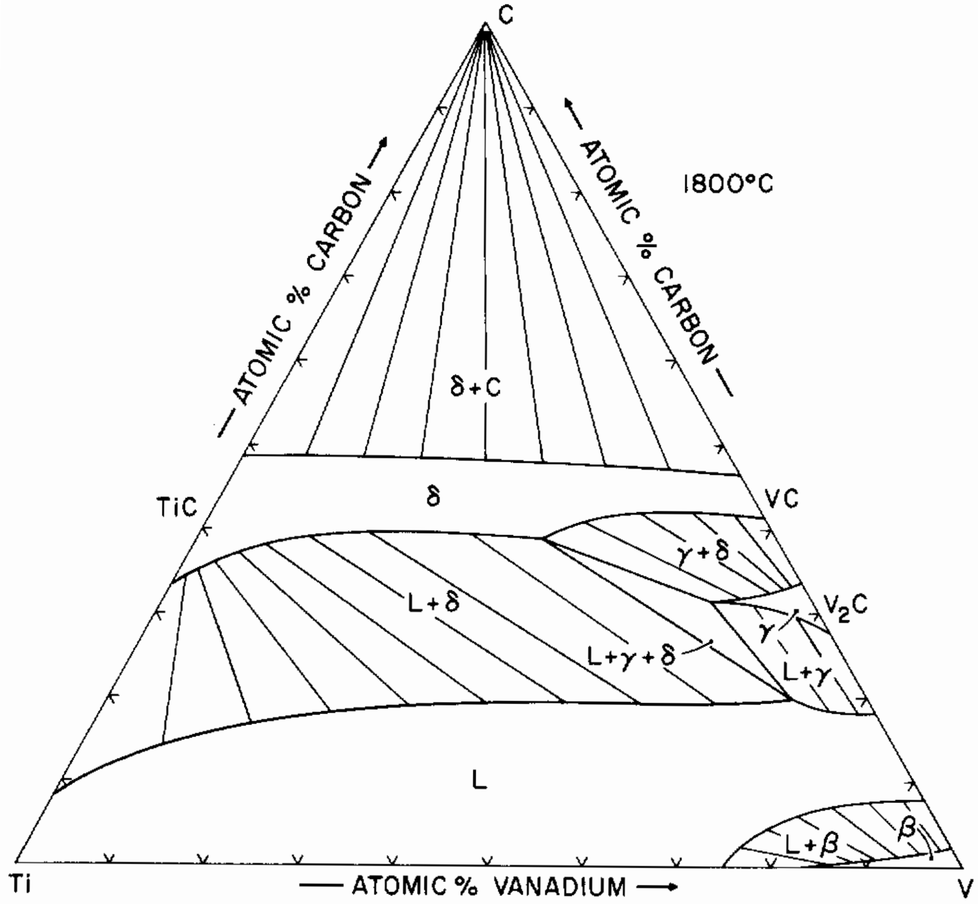

Figure 41. Isothermal Section of the Ti-V-C System at 1800°C.

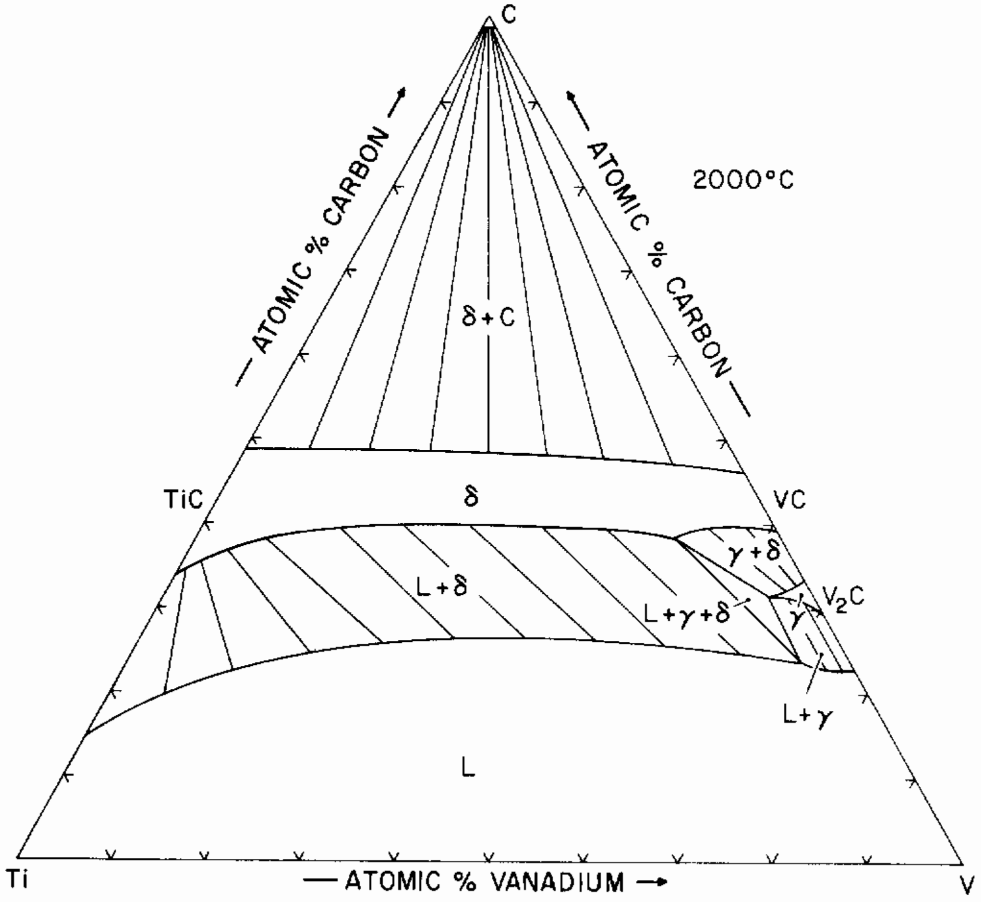

Figure 42. Isothermal Section of the Ti-V-C System at 2000° C.

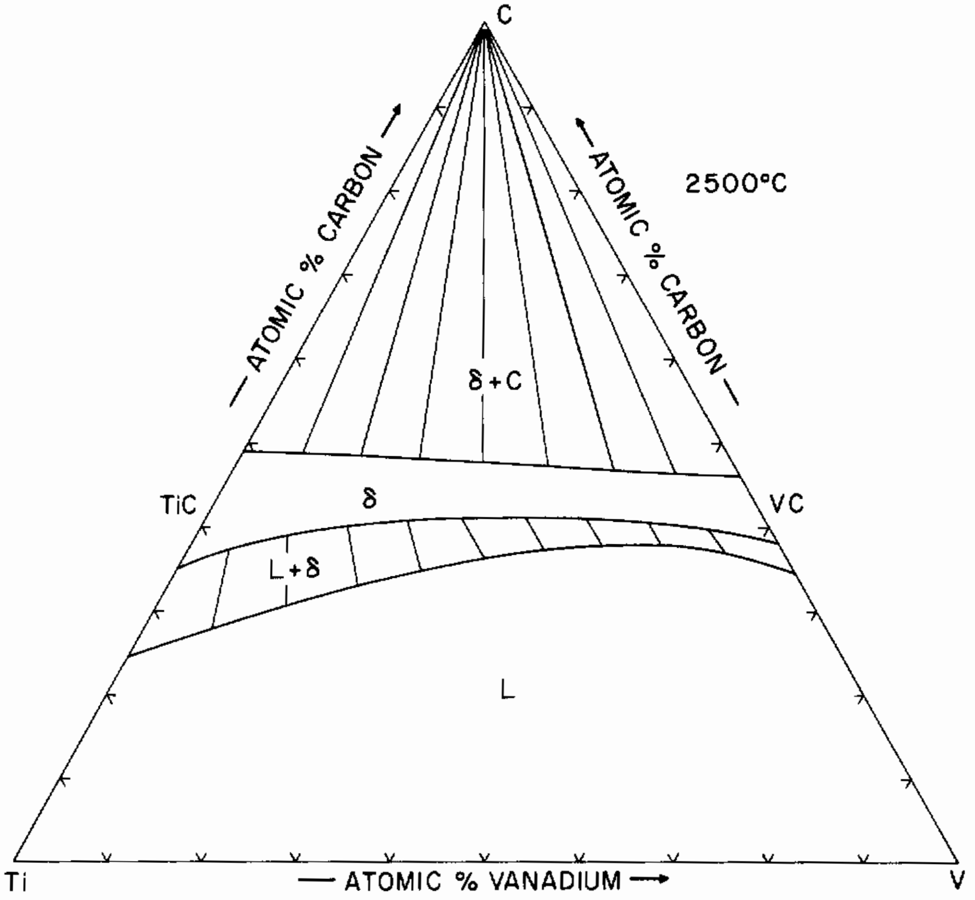

Figure 43. Isothermal Section of the Ti-V-C System at 2500° C.

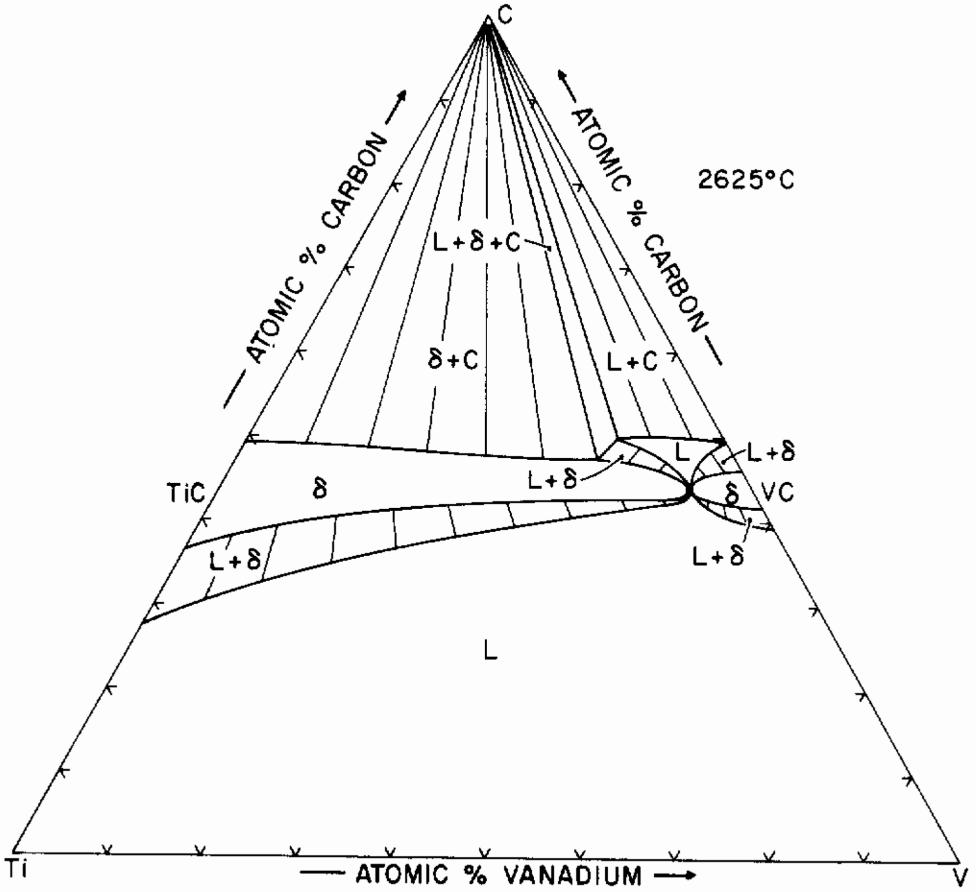

Figure 44. Isothermal Section of the Ti-V-C System at 2625° C.

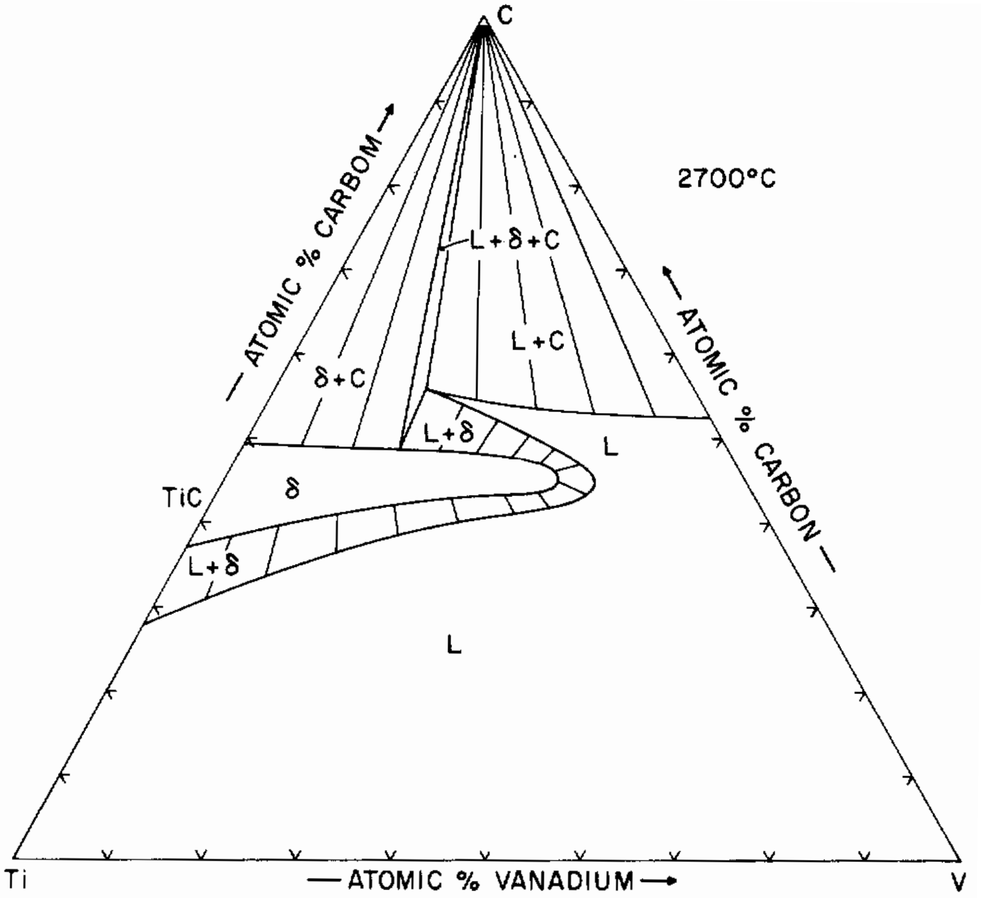

Figure 45. Isothermal Section of the Ti-V-C System at 2700° C.

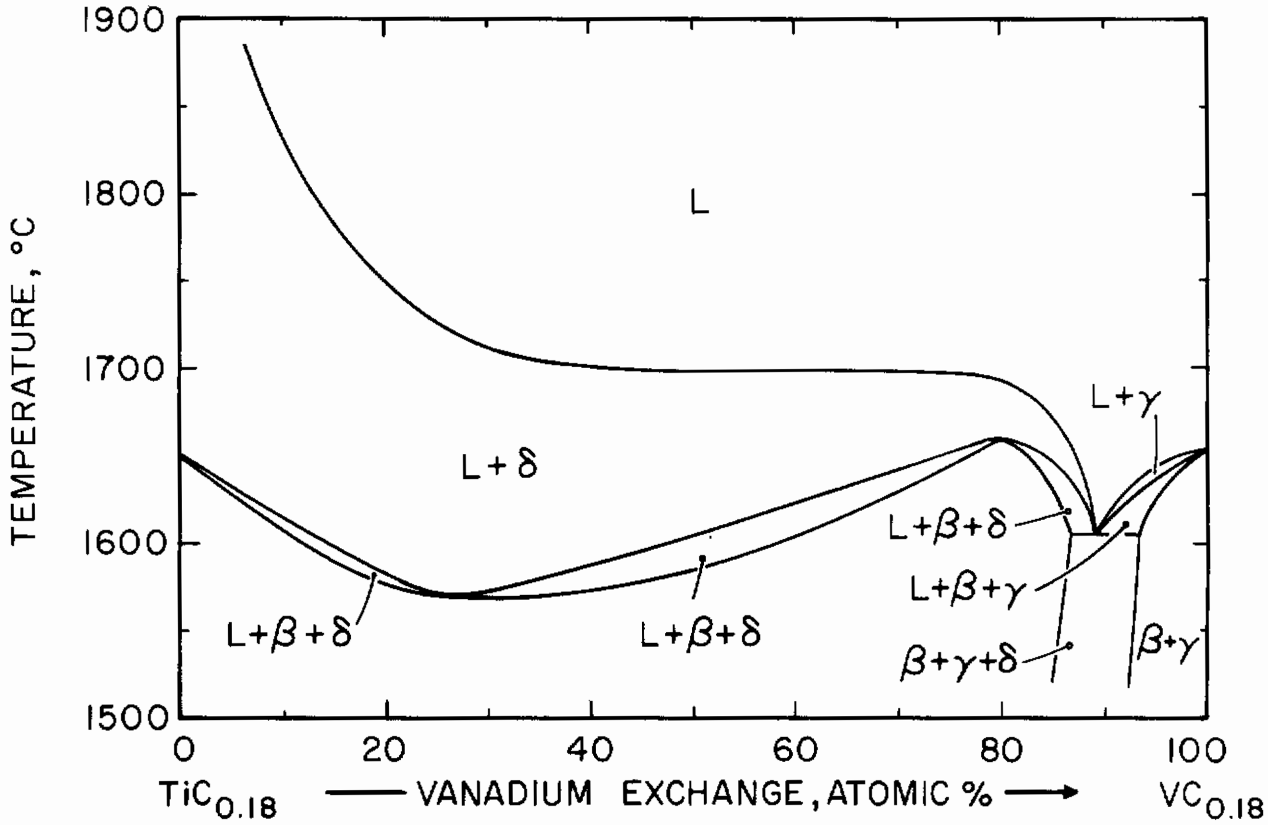

Figure 46. Isopleth at 15 At.% C.

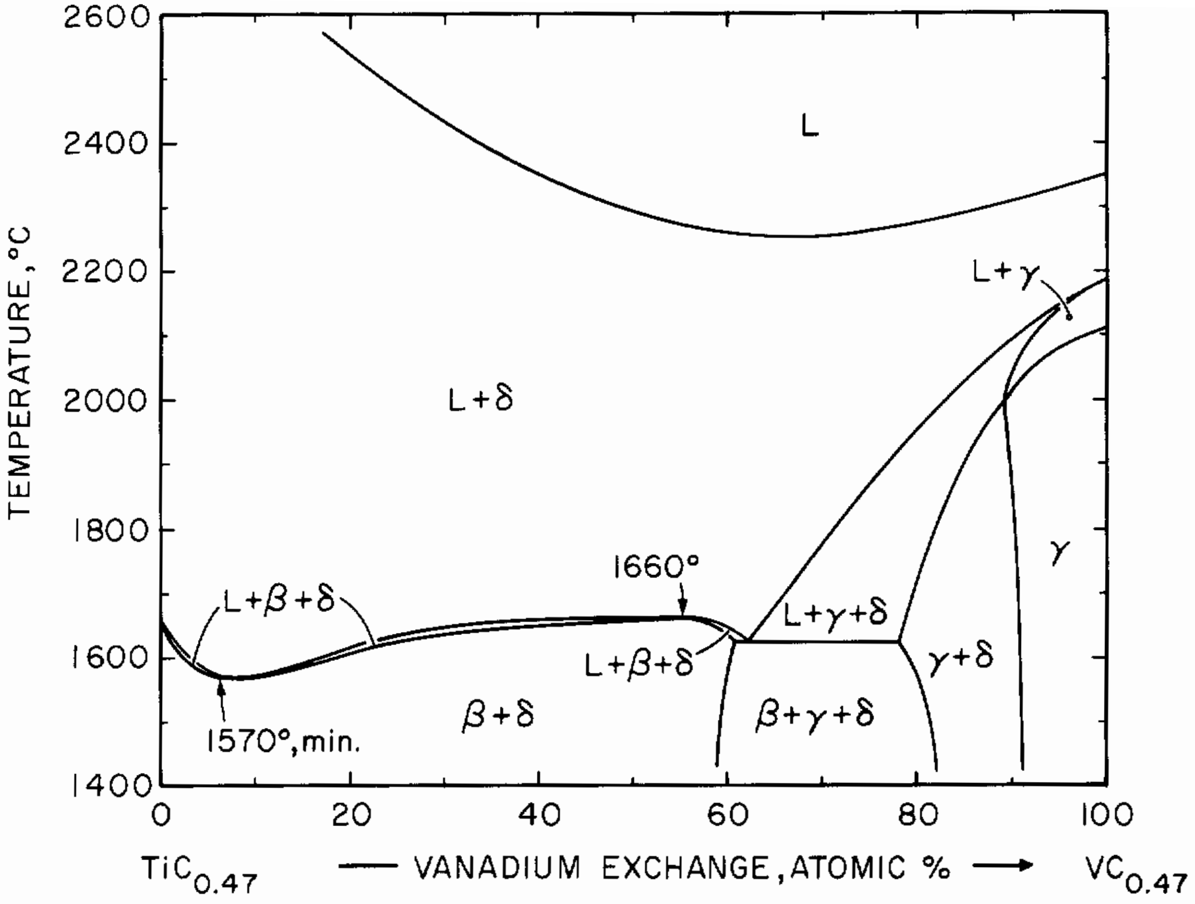

Figure 47. Isopleth at 32 At.% C.

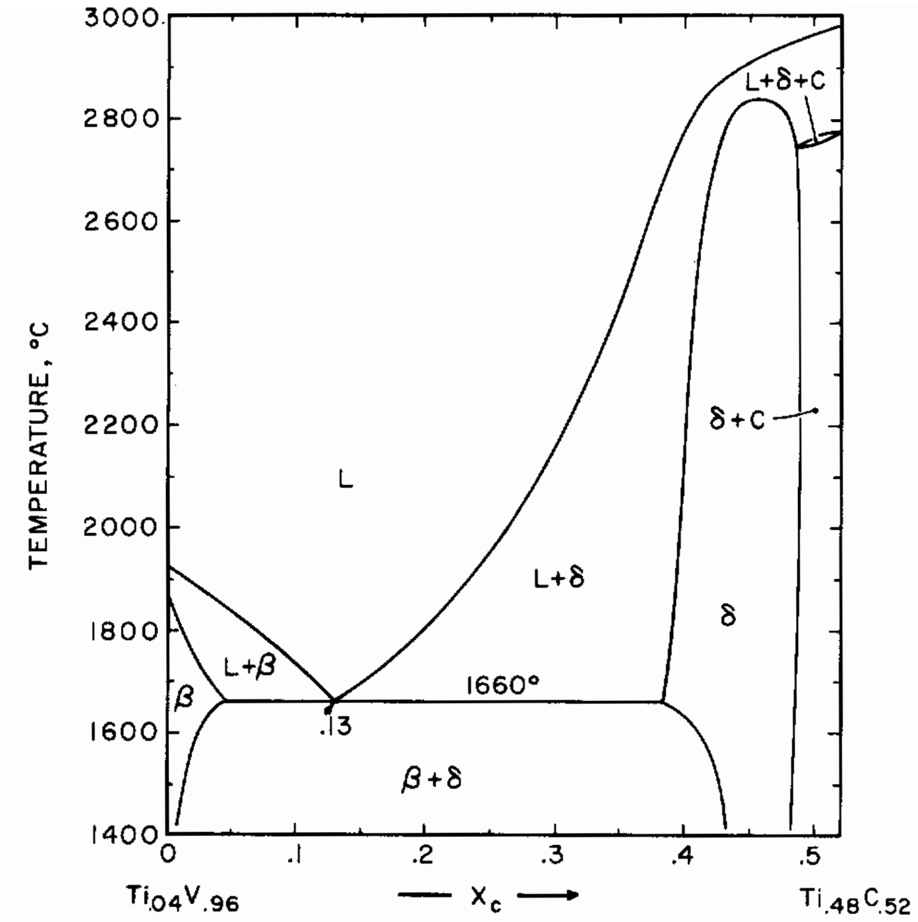

Figure 48. Isopleth at the Pseudobinary Section Metal + Monocarbide.

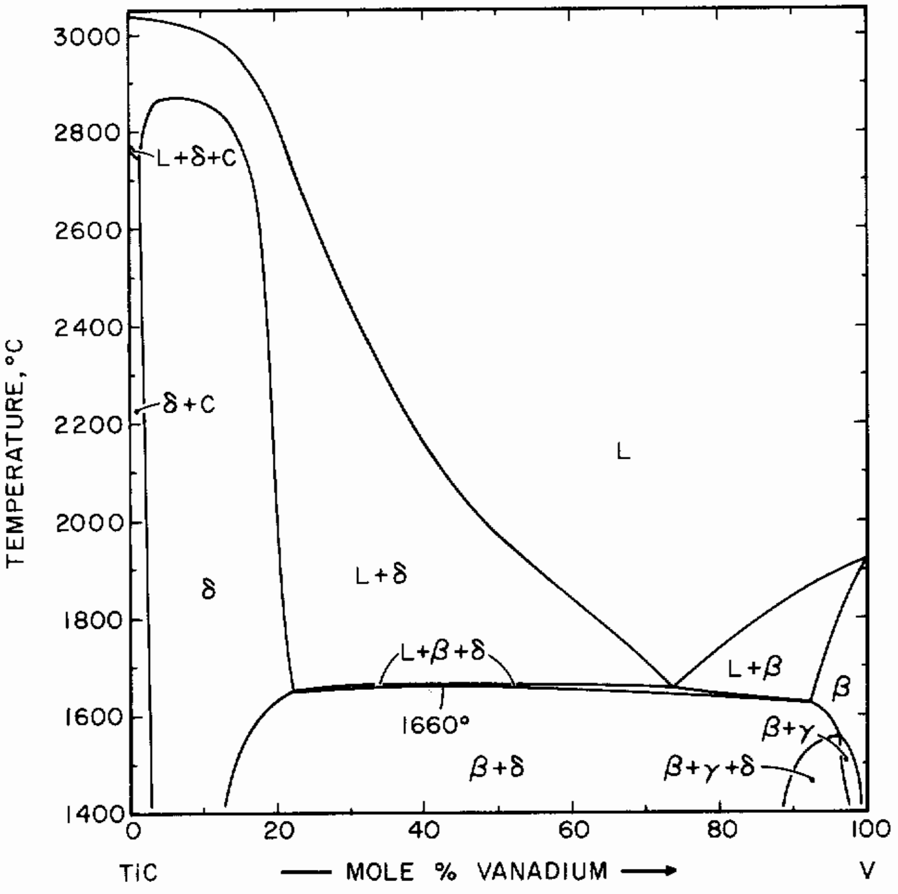

Figure 49. Isopleth TiC-V.

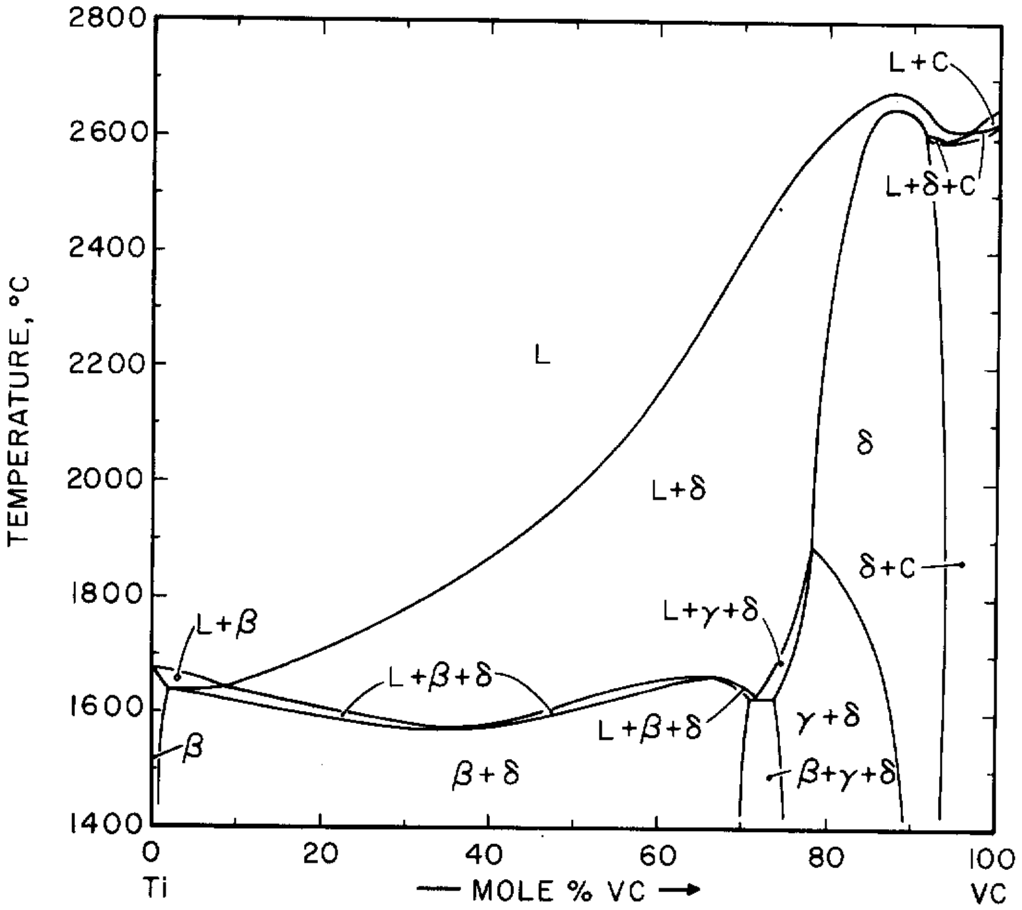

Figure 50. Isopleth Ti-VC

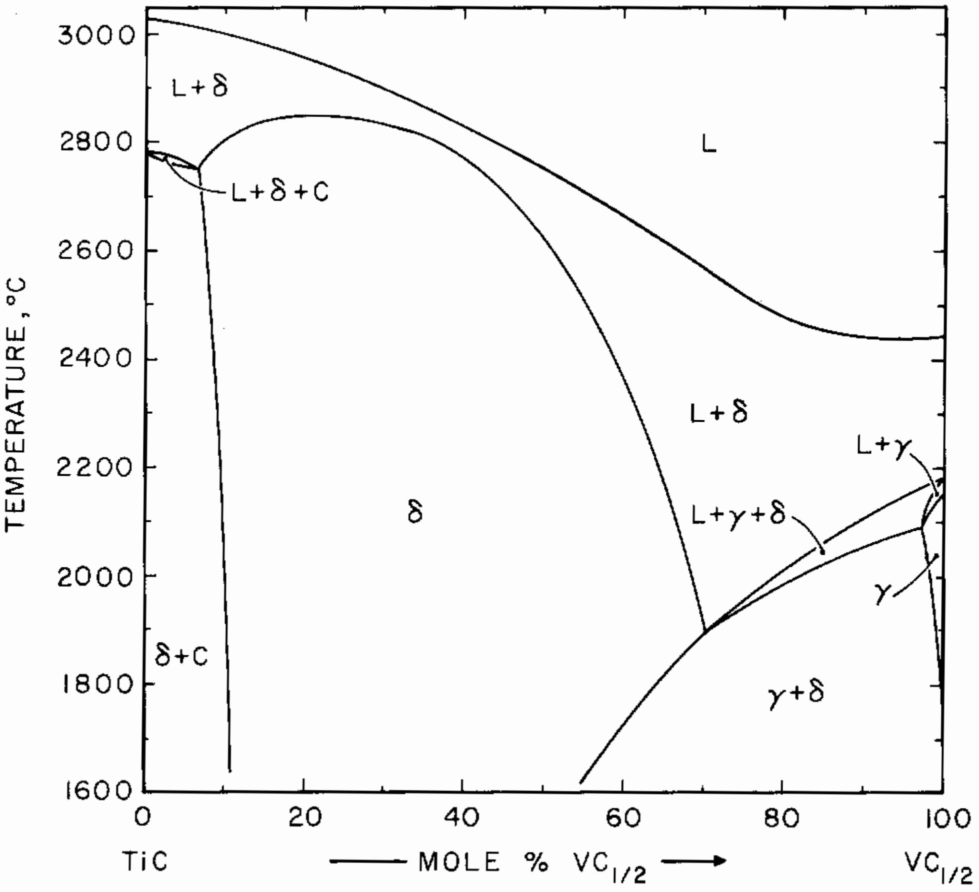

Figure 51. Isopleth TiC-$VC_{1/2}$.

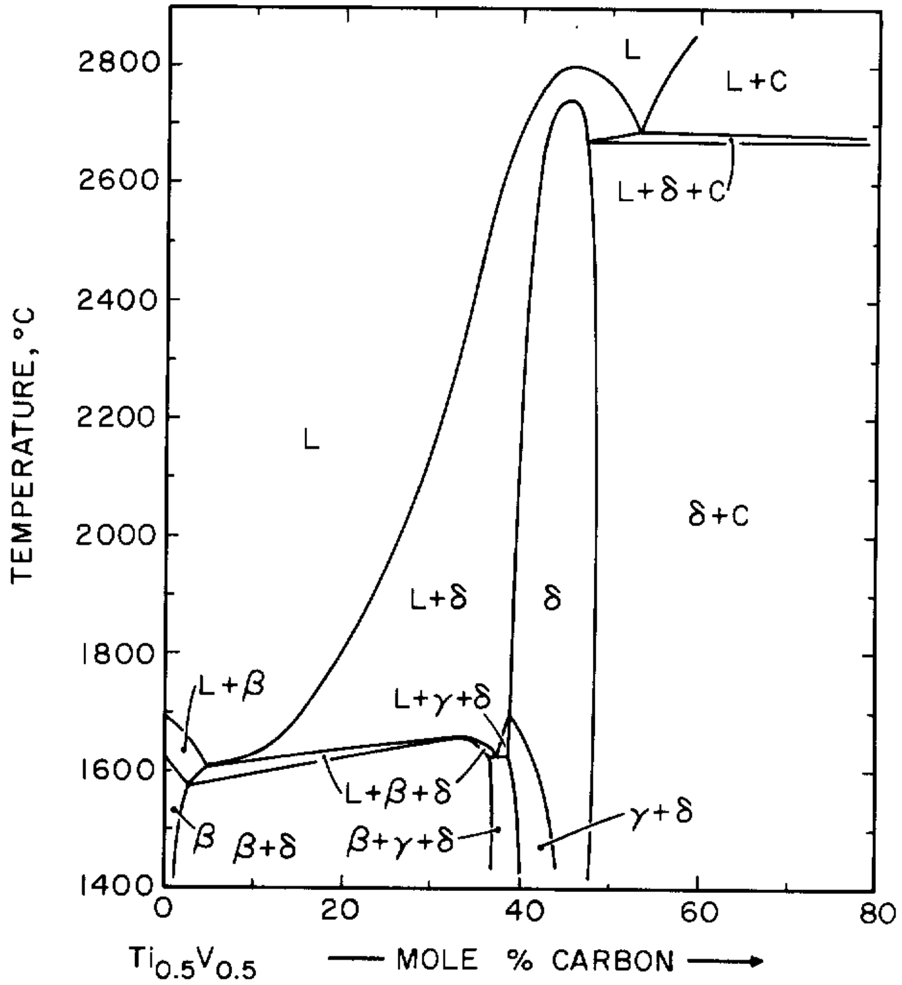

Figure 52. Isopleth $Ti_{0.5}V_{0.5}$-V.

V. DISCUSSION

From a thermodynamic point of view, the most interesting phase diagram feature concerns the formation of a pseudobinary eutectic of the maximum-type between the metal and the monocarbide phase. Analogous equilibria, but involving solid phases only, were observed in the Ta-W-C system(1). In the cited system, the subcarbides Ta_2C and W_2C form a complete series of solid solutions at high temperature. At 2450° C, however, the Me_2C solid solution disproportionates into mixtures of metal and monocarbide phase, with both subcarbide solutions, one rich in tungsten and the other in tantalum, being constrained by three-phase equilibria metal + subcarbide + + monocarbide.

A thermodynamic analysis of the stability of the subcarbide solid solution relative to mixtures of metal and monocarbide alloys indicated that disproportionation reactions of this kind generally can then be expected if the corresponding phases in the boundary systems have low relative stability, but especially if the phases in one of the boundary systems have considerably higher stability than the (isostructural) intermetallic compounds in the other.

This is also the case in the Ti-V-C system, as evidenced by the extreme inclinations of the tie lines in the two-phase field Me + MeC_{1-x} and by a comparison of the free enthalpies of formation of titanium and vanadium carbides. The only difference between the equilibrium type found in the Ti-V-C system and that of the aforecited example, is that the homogeneous high temperature phase in the former consists of melt, which then disproportionates in a pseudobinary eutectic reaction into the two neighboring phases. It should be noted, however, that, in contrast to the true binary eutectic which may be viewed as a degenerate (one) three-phase range, two three-phase equilibria are required (degenerate) to form the pseudobinary eutectic.

Expanding the considerations derived from the solid state case in the Ta-W-C system, we may expect to find pseudobinary eutectics preferably in such systems, where

(a) the binary eutectic temperatures and the melting temperatures of the components A, B in one of the edge systems are not too different. Under these circumstances the pseudobinary eutectic temperatures will be not too far apart from the binary eutectic temperatures and the cited condition for low relative stability of the disproportionating phases (liquids) in the edge binaries is fulfilled.

(b) the stability differences between the phases in the A-C and the B-C system are large. This condition has a more pronounced effect on the formation of pseudobinary eutectic equilibria than condition (a).

In the Ti-V-C system both conditions are fulfilled and thus a pseudobinary eutectic is formed. In the Ti-Nb-C and Ti-Ta-C systems, for example, the stability differences between the binary metal-carbon phases are comparatively smaller, while the binary Me + MeC_{1-x} eutectic temperatures are further apart; as a consequence, no pseudobinary eutectics have been observed in these systems.(31) On the other hand, the stability differences between titanium carbides and the carbides of the heavier group VI metals (Mo and W) are even larger than in the case of vanadium, offsetting the large differences in the binary eutectic temperatures; therefore, pseudobinary eutectic temperatures are again found in the Ti-Mo-C(31) and the Ti-W-C(21) systems. Other systems where pseudobinary eutectics occur between metal and monocarbide phases are Ti-Cr-C, Zr-Mo(W)-C, and Hf-Mo(W)-C, the reasons for their occurrence being the same as discussed for the other group IV - group VI metal-carbon systems.

A thermodynamic evaluation of the two-phase equilibrium (Ti, V) + + (Ti, V)C_{1-x} according to methods developed earlier(32) yields for the difference of the free enthalpies of formation of carbon-deficient titanium and vanadium monocarbide at 1500° C

$$\Delta G_{f,VC_{\sim 0.75}} - \Delta G_{f,TiC_{\sim 0.75}} = 17{,}450 \text{ cal/gr.-At metal}$$

which yields, using best estimates for the substoichiometric titanium carbide, a value of

$$\Delta G_{f,VC_{\sim 0.75}} \sim -15{,}700 \text{ cal/gr.At. V at } 1500^\circ\text{C}$$

The relative stability of V_2C, measured as its free enthalpy of disproportionation into metal and monocarbide, can be derived(32) from the three-phase equilibrium (Ti, V) + (Ti, V)$_2$C + (Ti, V)C_{1-x}. The value calculated from the experimental section at 1500° C yields

$$\Delta G_{Z,VC_{\sim 1/2}} = 2200 \text{ cal/gr.At. V},$$

while an evaluation of the temperature section at 1450° C proposed by Eremenko et al.(21) leads to:

$$\Delta G_{Z,VC_{\sim 1/2}} = 2500 \text{ cal/gr.At. V}$$

A value of $\Delta G_{Z,VC_{1/2}} \sim 460$ cal/gr.At. V, derived from the phase diagram by Fedorov et al.(22) is incompatible with the observed phase relationships and hence the location of the three-phase vertices reported in this work obviously in error.

The above values for $\Delta G_{f,VC_{\sim 0.75}}$ and $\Delta G_{Z,VC_{\sim 1/2}}$ can now be combined to calculate the free enthalpy of formation of $VC_{1/2}$. With

$$\Delta G_{f,VC_{\sim 1/2}} = 0.67\ \Delta G_{f,VC_{1-x}} - \Delta G_{Z,VC_{\sim 1/2}},$$

one obtains

$$\Delta G_{f,VC_{\sim 1/2}} \simeq -\ 12{,}700\ \text{cal/gr.At. V.}$$

It is interesting to note, that this value agrees very will with values of $\Delta G_{f,VC_{1/2}} = -\ 12{,}260$ and $-12{,}000$ cal/gr.At. V derived independently from the tie line distributions in the Me + Me_2C two-phase fields in the V-Mo-C and V-W-C systems(33).

Expanding the calculations to include the monocarbide, it would appear from the free enthalpy of formation data calculated from the phase diagrams, that the currently accepted free enthalpies of formation for the carbon-saturated VC_{1-x} phase,

$$\Delta G_{f,VC_{0.88}} = -\ 24{,}980 + 1.80T\ [\text{cal/gr.At. V}]^{(10)}$$

should be more positive by about 4000 cal/gr.At. V, i.e. the actual stability of $VC_{0.88}$ seems to be less than currently accepted in the literature.

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13. ABSTRACT

The phase relationships in the Ti-V-C system were experimentally investigated by means of X-ray, melting point, DTA, and metallographic methods on heat-treated and melted specimens, and a phase from 1400° C through the melting range established. The solid state equilibria are characterized by the monocarbide phases, and a limited Ti-exchange in V_2C (15 At.% at 1400° C); a wide two-phase equilibrium is formed between the carbon-deficient monocarbide solid solution and the metal phase. The V_2C-solid solution is terminated by a three-phase equilibrium, V_2C + + $(V,Ti)C_{1-x}$ + (V,Ti)-ss, in the ternary. Four isothermal reactions occur in the system, of which three correspond to pseudobinary eutectic reactions, and the fourth to a ternary eutectic between metal, subcarbide, and monocarbide. The monocarbide solid solution has a minimum melting point of 2625° C at a composition Ti-V-C (6-50-44 At.%).

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