PHASE EQUILIBRIA INVESTIGATION OF BINARY, TERNARY, AND HIGHER ORDER SYSTEMS

PART IV

The Effect of Molybdenum and Tungsten on the Subcarbide Solutions in the Vanadium-Tantalum-Carbon and Niobium-Tantalum-Carbon Systems

C. E. BRUKL

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FOREWORD

The work described in this technical report was carried out at the Materials Research Laboratory, Aerojet-General Corporation, Sacramento, California. The principal investigator for this project is Dr. E. Rudy, under USAF Contract AF 33(615)-67-C-1513. This contract was initiated in April 1967 under the direction of Capt. P. J. Marchiando.

The author wishes to thank Dr. E. Rudy for his advice and help during the course of this investigation; he further wishes to thank R. Taylor, J. Pomodoro, R. Cobb and O. Catrino for their valuable help in various aspects of the experimental work.

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The manuscript of this report was released by the author in May 1969 for publication as a Technical Report.

The other reports issued under USAF Contract F33(615)-67-C-1513 were:

Part I:	The Phase Diagrams of the Ti-Nb-C, Ti-Ta-C, and Ti-Mo-C Systems
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

This technical report has been reviewed and is approved.

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ABSTRACT

The phase equilibria of the Ta_2C-V_2C pseudo binary pair, as well as that of the pseudo ternary subcarbide systems, Ta_2C-Nb_2C-Mo_2C, Ta_2C-Nb_2C-W_2C, Ta_2C-V_2C-Mo_2C, and Ta_2C-V_2C-W_2C have been determined primarily by Debye-Scherrer X-ray analysis of alloys heat treated at 1650° and 2000°C.

The subcarbides Ta_2C and V_2C form a continuous series of solid solutions. The phase equilibria of the pseudo ternary combinations Ta_2C-Nb_2C-Mo_2C and Ta_2C-Nb_2C-W_2C are quite similar: a two-phased region, metal + monocarbide divides the two subcarbide solid solutions based on Mo_2C or W_2C and $(Ta,Nb)_2C$.

Miscibility gaps showing the presence of metal + monocarbide phases (and the associated three-phase regions of metal + monocarbide + subcarbide) originate in the Ta_2C-Mo_2C and Ta_2C-W_2C pseudo binary systems of the respective pseudo ternary systems Ta_2C-V_2C-Mo_2C and Ta_2C-V_2C-W_2C; these miscibility gaps extend into the pseudo ternary subcarbide single phase regions of $(Ta,V,Mo)_2C$ and $(Ta,V,W)_2C$.

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I. INTRODUCTION AND SUMMARY

A. INTRODUCTION

The phase equilibria investigations described in this report are in direct support of Air Force sponsored cutting tool research programs. The results reported here are expected to serve as direct guidelines for the selection of possible candidate cutting tool alloys.

Since the making of carbide cutting tools with refractory metal binder phases must depend on high temperature fabrication techniques, it is mandatory that thermochemical equilibria be attained and maintained within the proposed alloys to guarantee the physical and mechanical integrity of the cutting tools. The investigation of the high temperature phase equilibria of possible alloy combinations is, therefore, a prerequisite for the fabrication of even test alloys.

It was recognized during the phase equilibria investigations of the Ta-W-C and Ta-Mo-C ternary systems under another Air Force sponsored program (AF 33(615)-1249) that the subcarbide solid solutions in each of these two ternary systems undergo a disproportionation reaction to yield a thermodynamically stable mixture of tantalum carbide-rich monocarbides and tungsten or molybdenum-rich metal alloys respectively. The structure of these disproportionated alloys is that of a very fine lamellar carbide phase in an equally fine lamellar metal matrix. These alloys with this structure are deemed promising for cutting tool applications.

The purpose of these studies is to investigate the solid state phase equilibria of the above mentioned disproportionating subcarbides with additions of V_2C and Nb_2C, since vanadium and niobium are valuable additives to carbide cutting tool alloys.

Whether these subcarbide combinations are looked at from the viewpoint of W_2C and Mo_2C additions to the Ta_2C-V_2C and Ta_2C-Nb_2C pseudo binary systems or from the viewpoint described above, the results will be the same; since the primary characteristic of these pseudo-ternary subcarbide systems is the disproportionation reaction, these investigations are described from the viewpoint discussed in the preceding paragraph.

B. SUMMARY

1. The Ta_2C-Nb_2C-Mo_2C Pseudo Ternary System

The phase equilibria at both 1650°C and 2000°C are quite similar. The two subcarbide solid solutions based on Mo_2C and $(Ta, Nb)_2C$ are divided by a two-phased region, monocarbide + metal and the associated three-phase fields, monocarbide + metal + subcarbide. The section at 2000°C is shown in Figure 1.

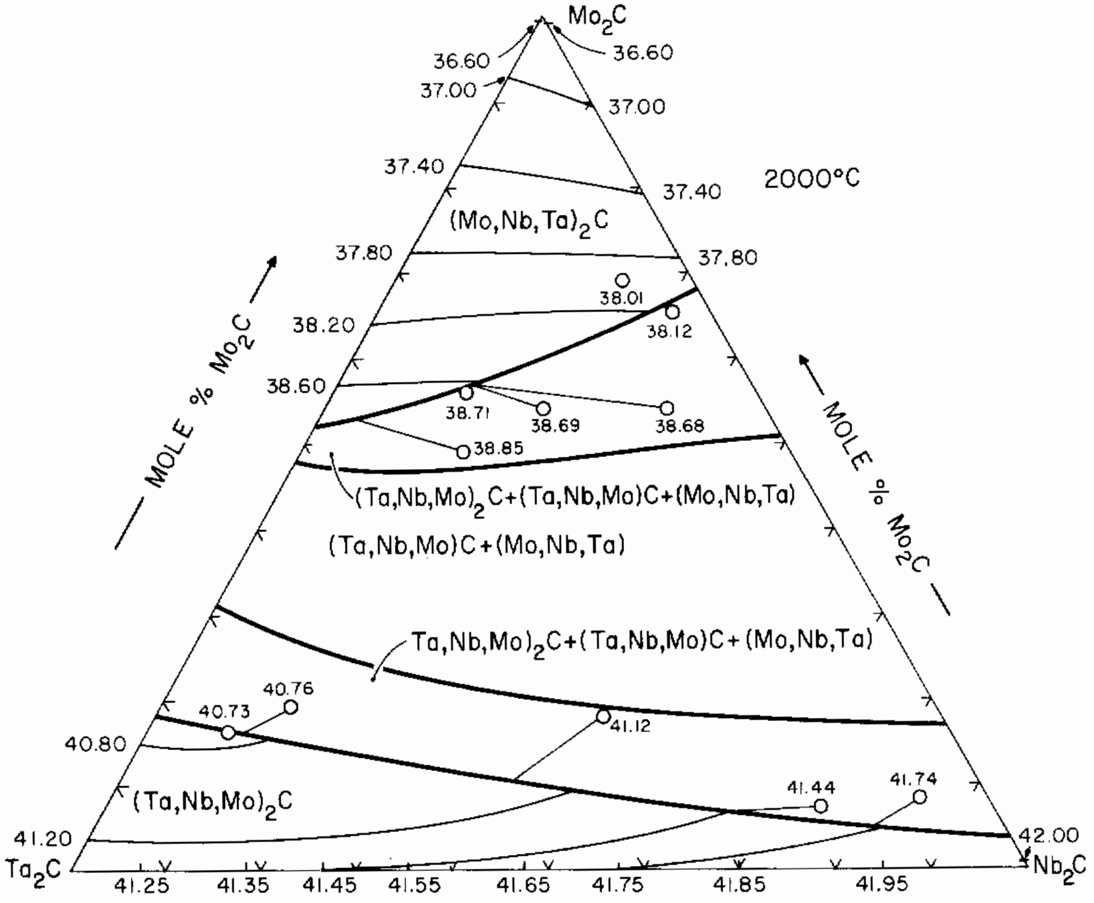

Figure 1. Nb-Ta-Mo-C: Phase Equilibria of the Ta_2C-Nb_2C-Mo_2C Pseudo Ternary System at 2000°C with Isovolumetric Unit Cell Dimensions (Å^3) and Tie Lines Indicating Co-existing Subcarbide Compositions.

2. The Ta_2C-Nb_2C-W_2C Pseudo Ternary System

The phase equilibria of this system at 2000°C, which is very similar to that of the Ta_2C-Nb_2C-Mo_2C system above, is shown in Figure 2 below.

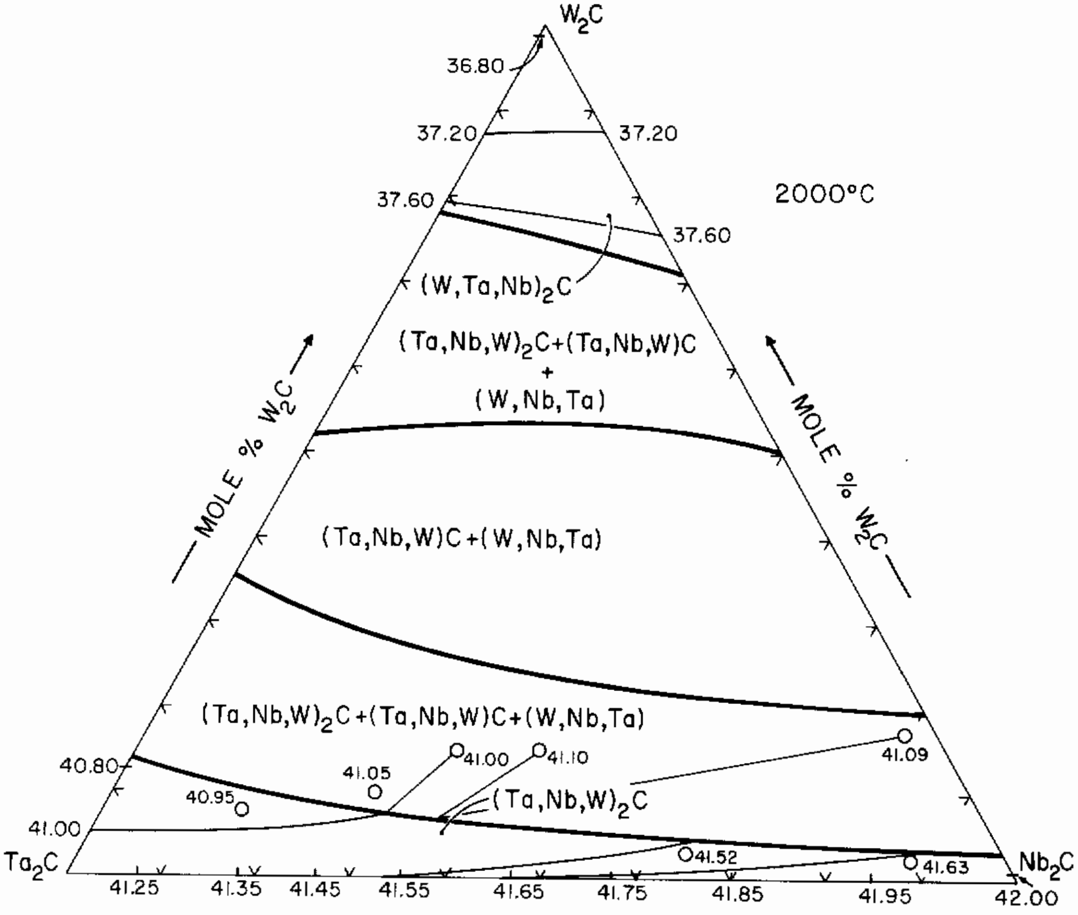

Figure 2. Nb-Ta-W-C: Phase Equilibria of the Ta_2C-Nb_2C-W_2C Pseudo Ternary System at 2000°C with Isovolumetric Unit Cell Dimensions (Å^3) and Tie Lines Indicating Coexisting Subcarbide Compositions.

3. The Ta_2C-V_2C-Pseudo Binary System

Tantalum and vanadium subcarbides form a complete series of solid solutions at both 1650°C and 2000°C; there is some indication of a miscibility gap between the two subcarbide solid solutions at lower temperatures. Figure 3 shows the lattice parameters of the $(Ta,V)_2C$ solid solution at 1650°C.

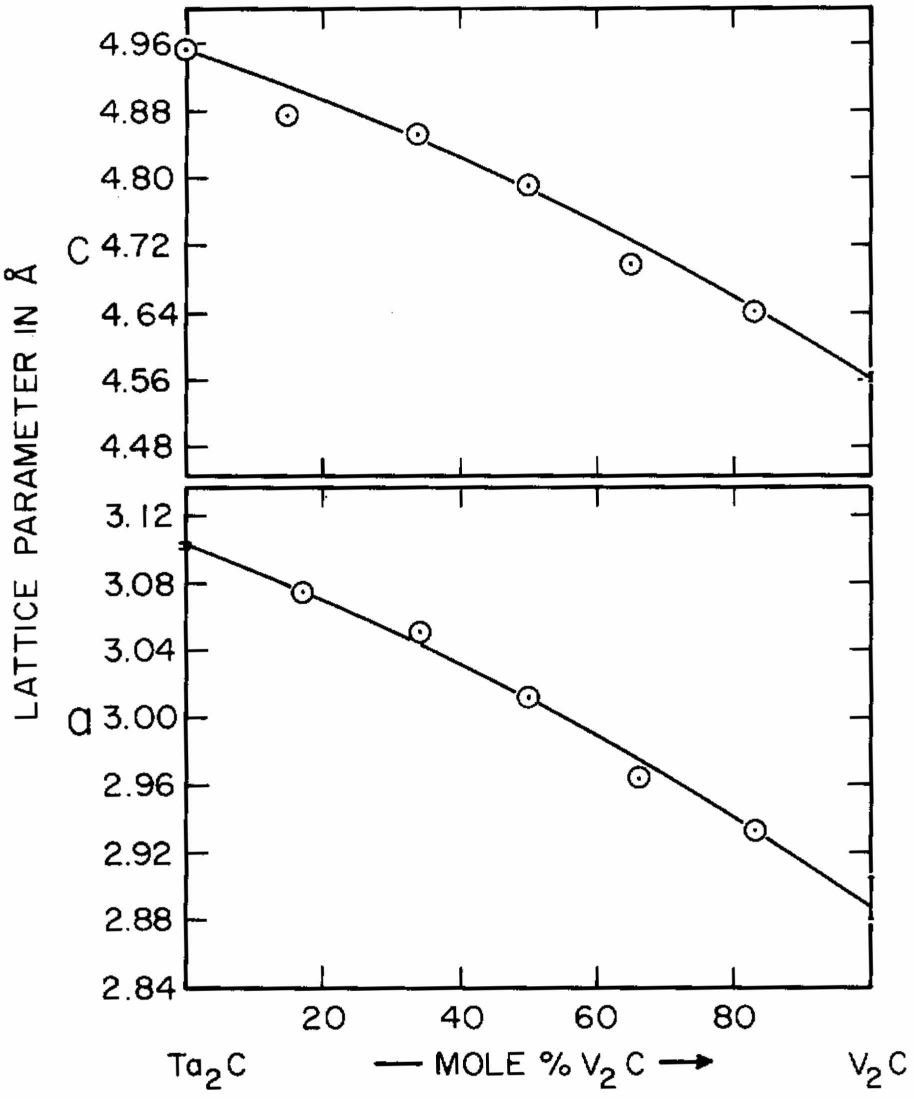

Figure 3. Ta-V-C: Lattice Parameters of the $(Ta,V)_2C$ Solid Solution at 1650°C.

4. The Ta_2C-V_2C-Mo_2C Pseudo Ternary System

The phase equilibria of this system at 1650°C and 2000°C are quite similar. A two-phased, metal + monocarbide, miscibility gap originating in the Ta_2C-Mo_2C pseudo binary system (with its associated three-phased areas) extends into the single phased pseudo ternary subcarbide solid solution region. Figure 4 shows the phase equilibria at 1650°C.

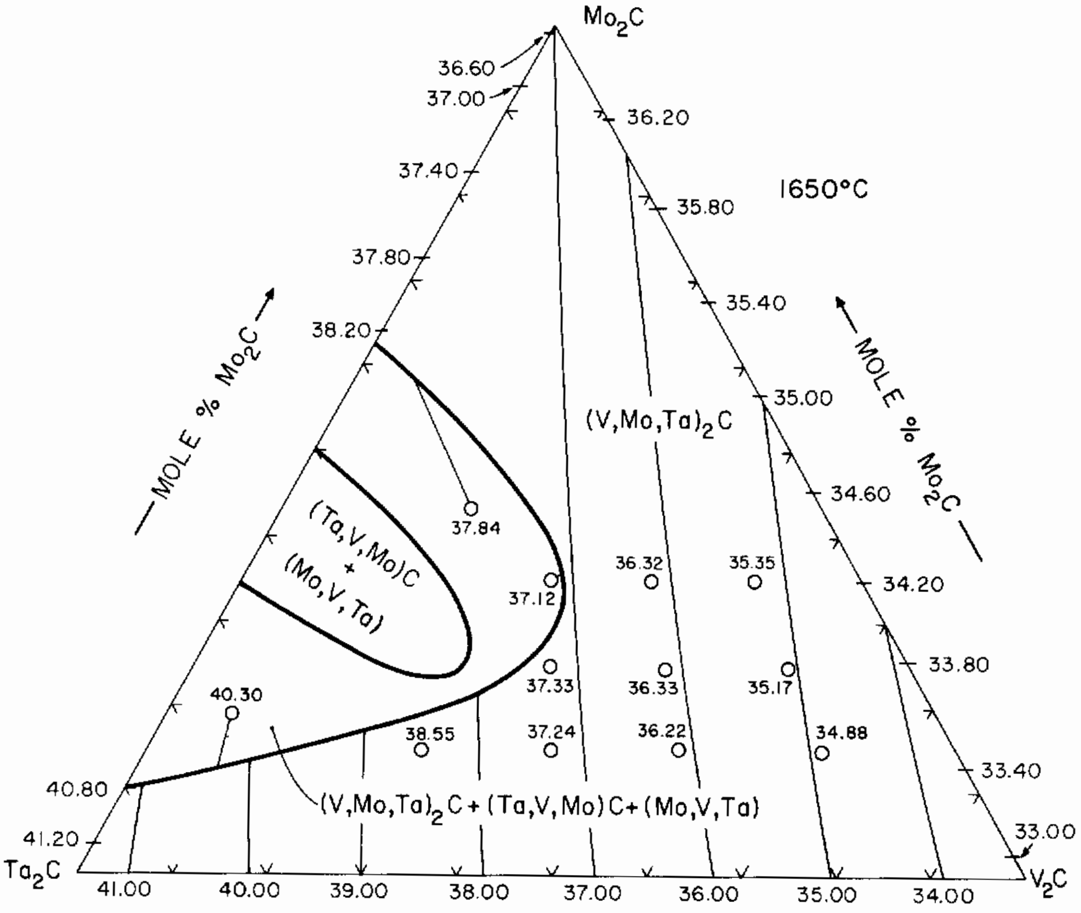

Figure 4. V-Ta-Mo-C: Phase Equilibria of the Ta_2C-V_2C-Mo_2C Pseudo Ternary System at 1650°C with Isovolumetric Unit Cell Dimensions (A^3) and Tie Lines Indicating Co-existing Subcarbide Compositions.

5. The Ta_2C-V_2C-W_2C Pseudo Ternary System

The phase equilibria of this system at both 1650° and 2000°C is very similar to that of the Ta_2C-V_2C-Mo_2C system described above; Figure 5 shows the phase equilibria at 1650°C.

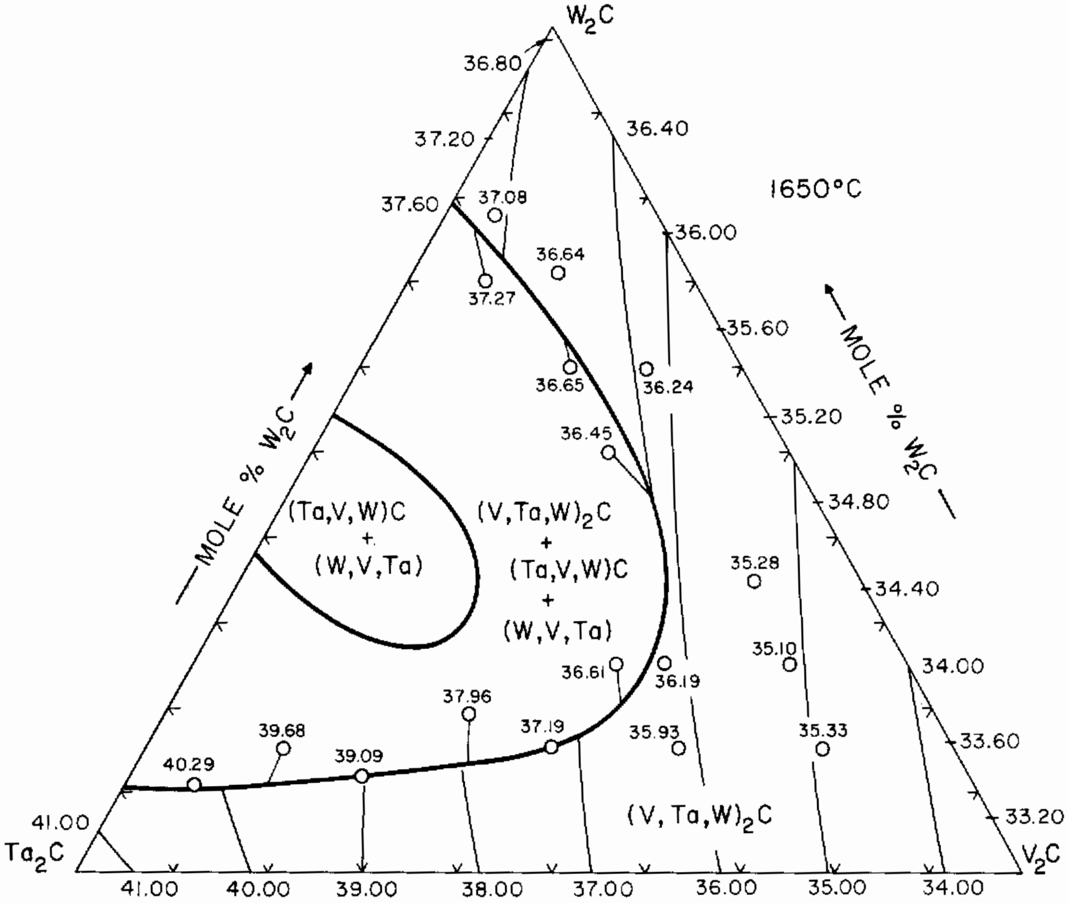

Figure 5. V-Ta-W-C: Phase Equilibria of the Ta_2C-V_2C-W_2C Pseudo Ternary System at 1650°C with Isovolumetric Unit Cell Dimensions ($Å^3$) and Tie Lines Indicating Coexisting Subcarbide Compositions.

II. LITERATURE REVIEW

A. THE Ta_2C-Nb_2C PSEUDO BINARY SYSTEM

This section has been investigated by Booker and Rudy$^{(1)}$ as part of the investigation in the Niobium-Tantalum-Carbon system. The pair of binary compounds form a complete series of solid solutions at all temperatures up to melting. The crystal structural modifications of both Nb_2C and Ta_2C and their contributions to the overall phase equilibria of the Nb-Ta-C system are abundantly described by Booker and Rudy$^{(1)}$. The variation of lattice parameters of the subcarbide solid solution based on the hexagonal L'-3 indexing is given in Figure 6.

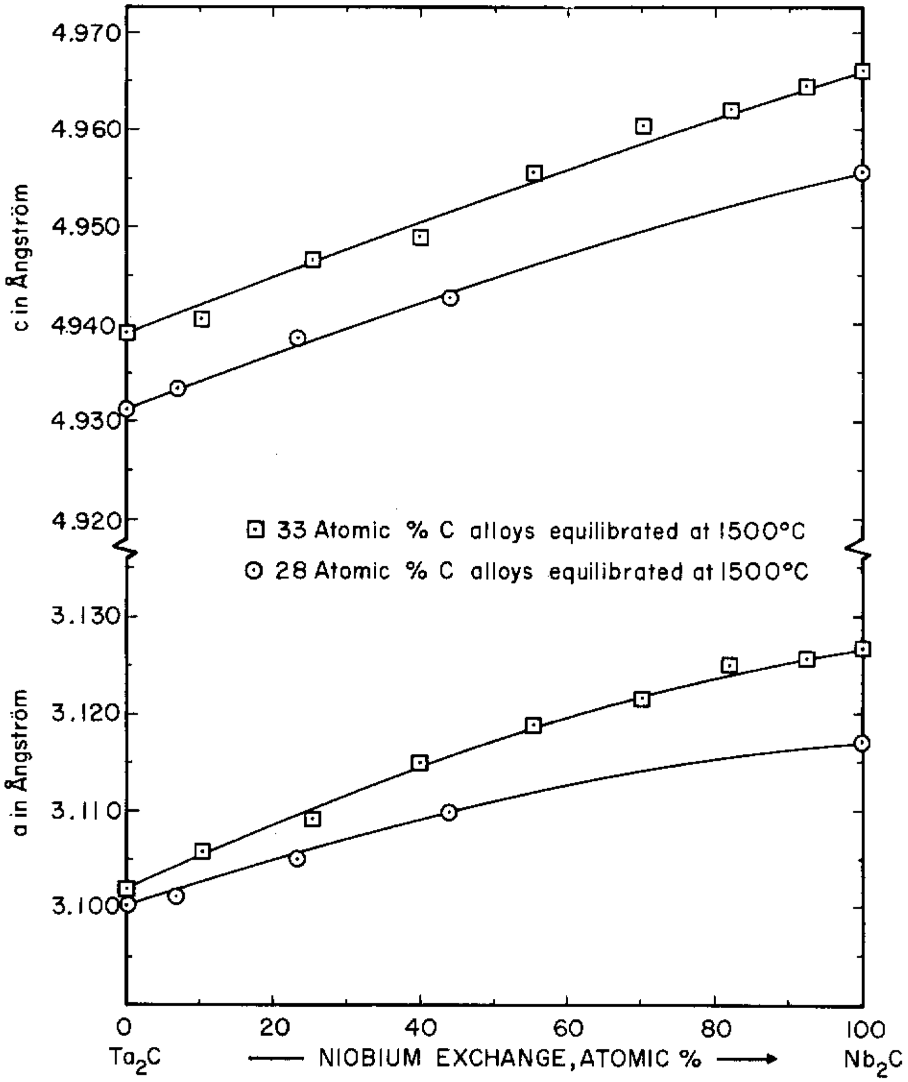

Figure 6. Ta-Nb-C: Lattice Parameters of the $(Ta, Nb)_2C$ Solid Solution$^{(1)}$

B. THE Ta_2C-Mo_2C PSEUDO BINARY SYSTEM

Investigation of the Ta-Mo-C Ternary system by Rudy, Windisch and Brukl(2) showed that the subcarbides Ta_2C and Mo_2C increase their mutual solubility with increasing temperature and form a complete series of solid solutions above 2230°C. This solid solution disproportionates on cooling below 2230°C to yield a mixture of mono-carbide and metal phases. Figure 7 shows the solid state phase equilibria of the Ta_2C-Mo_2C pseudo binary section.

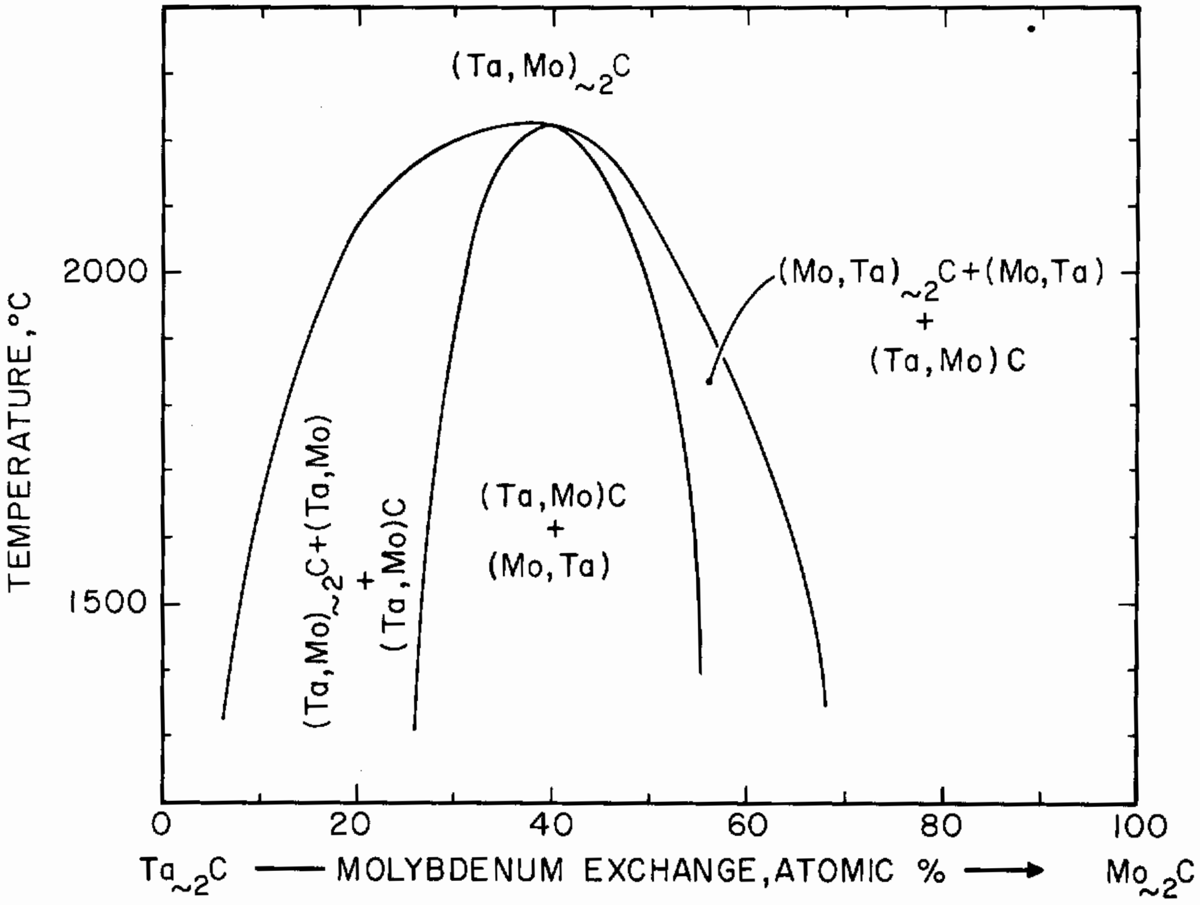

Figure 7. Ta-Mo-C: The Ta_2C-Mo_2C Pseudo Binary System(2)

C. THE Ta_2C-W_2C PSEUDO BINARY SYSTEM

In 1966 E. Rudy(3) investigated the Ta-W-C high temperature phase equilibria and found that above 2450°C Ta_2C and W_2C form a complete series of solid solutions; below this temperature the single phase subcarbide disproportionates into a mixture of monocarbide and metal phases; Figure 8 shows the solid state phase equilibria of this subcarbide section.

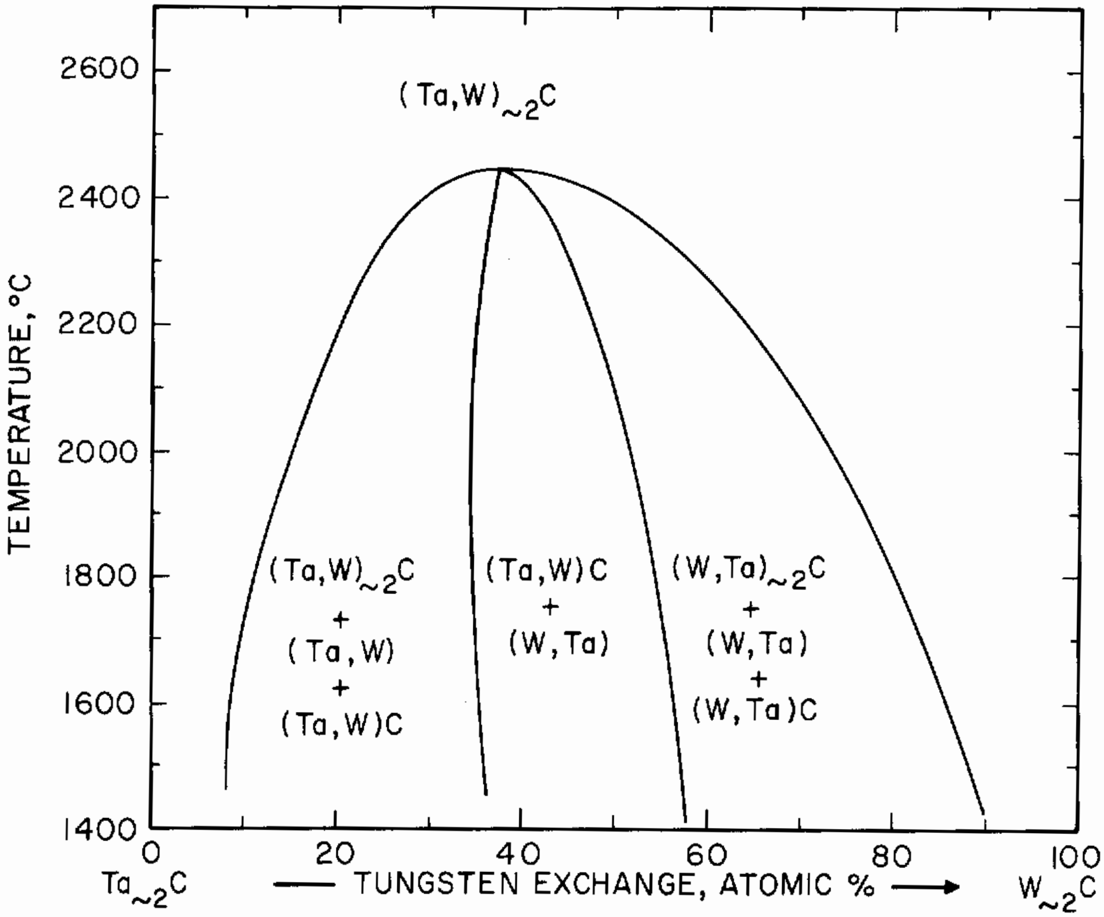

Figure 8. Ta-W-C: The Ta_2C-W_2C Pseudo Binary Section(3)

D. THE Nb_2C-Mo_2C PSEUDO BINARY SYSTEM

In part of the studies in the system Nb-Mo-C this pseudo binary section was recently investigated by Rudy, Brukl and Windisch(4). The partial diagram of the solid state region of interest here (Figure 9) shows that these two subcarbides do not form a continuous series of solid solutions; a rather large two-phased area consisting of (Nb, Mo)C and (Mo, Nb) exist in the middle concentration range and is present up to melting.

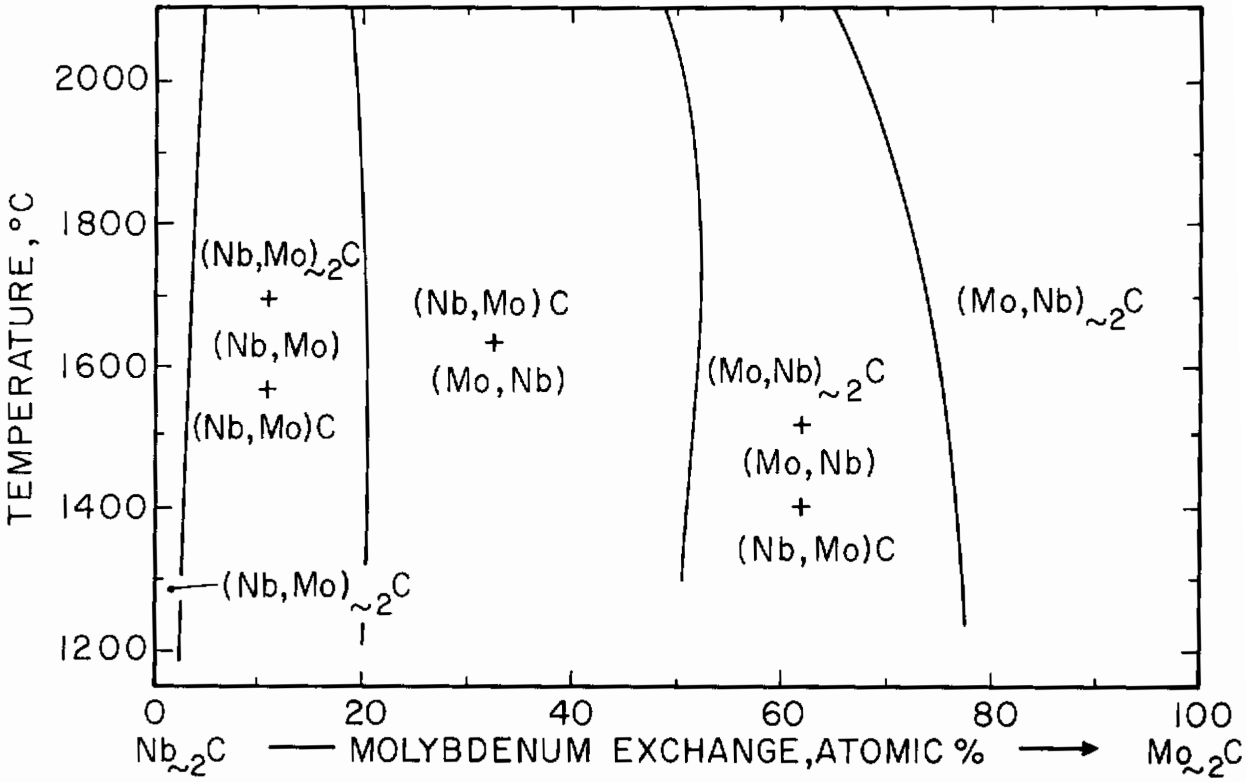

Figure 9. Nb-Mo-C: The Nb_2C-Mo_2C Pseudo Binary Section(4)
(Solid State)

E. THE Ta_2C-V_2C PSEUDO BINARY SYSTEM

A solid state section of this system has been investigated by Rudy and Booker as a part of this report series(1). It was established that Ta_2C and V_2C form a continuous series of solid solutions above about 1500°C; below this temperature a miscibility gap exists between the two subcarbide solid solutions. Figure 10 shows the lattice parameters for subcarbide alloys equilibrated above 1500°C.

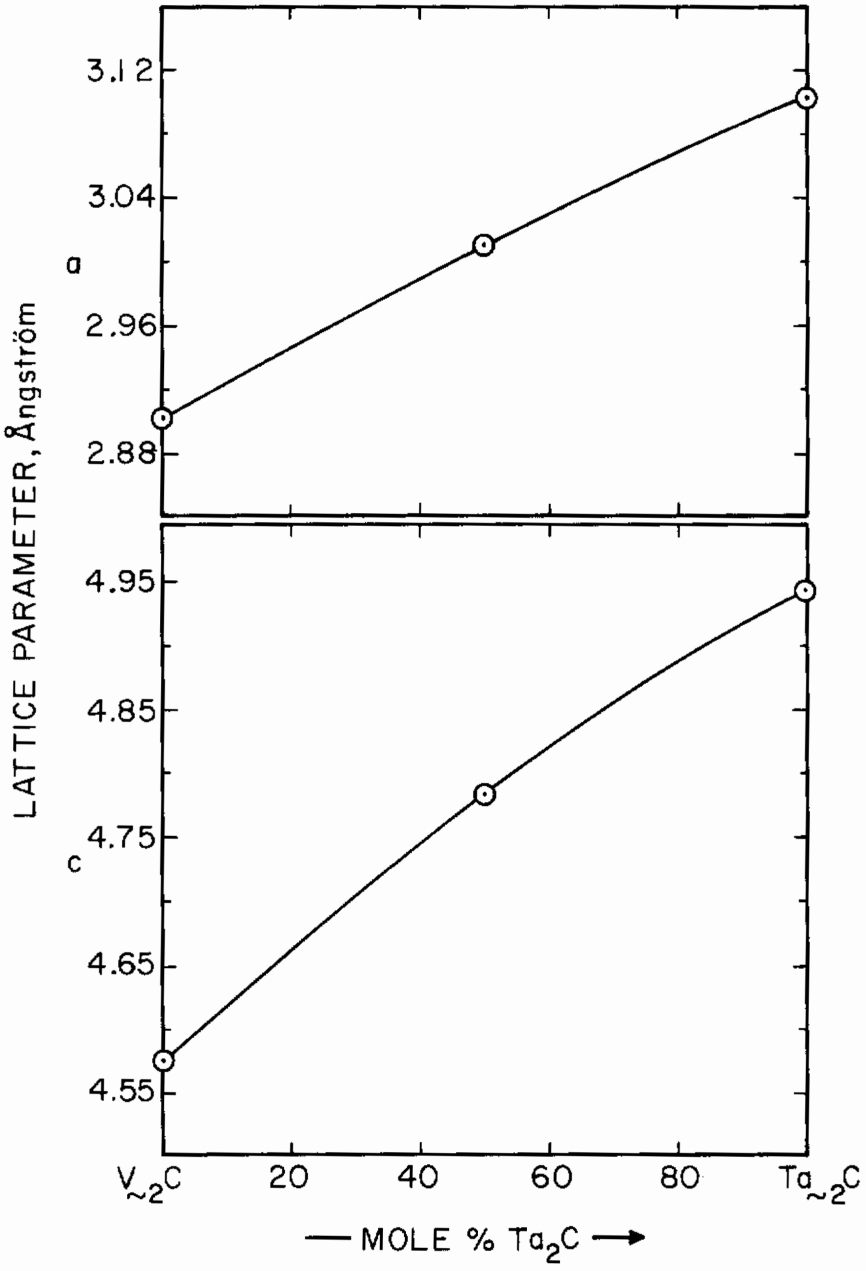

Figure 10. V-Ta-C: Lattice Parameters of $(V, Ta)_2C$ Alloys at Temperatures Above 1500°C

F. THE V_2C-W_2C PSEUDO BINARY SYSTEM

The ternary system to which this pseudo binary section belongs was investigated by E. Rudy et al.(5) These subcarbides form a continuous series of solid solutions; the variation in lattice parameters is shown in Figure 11.

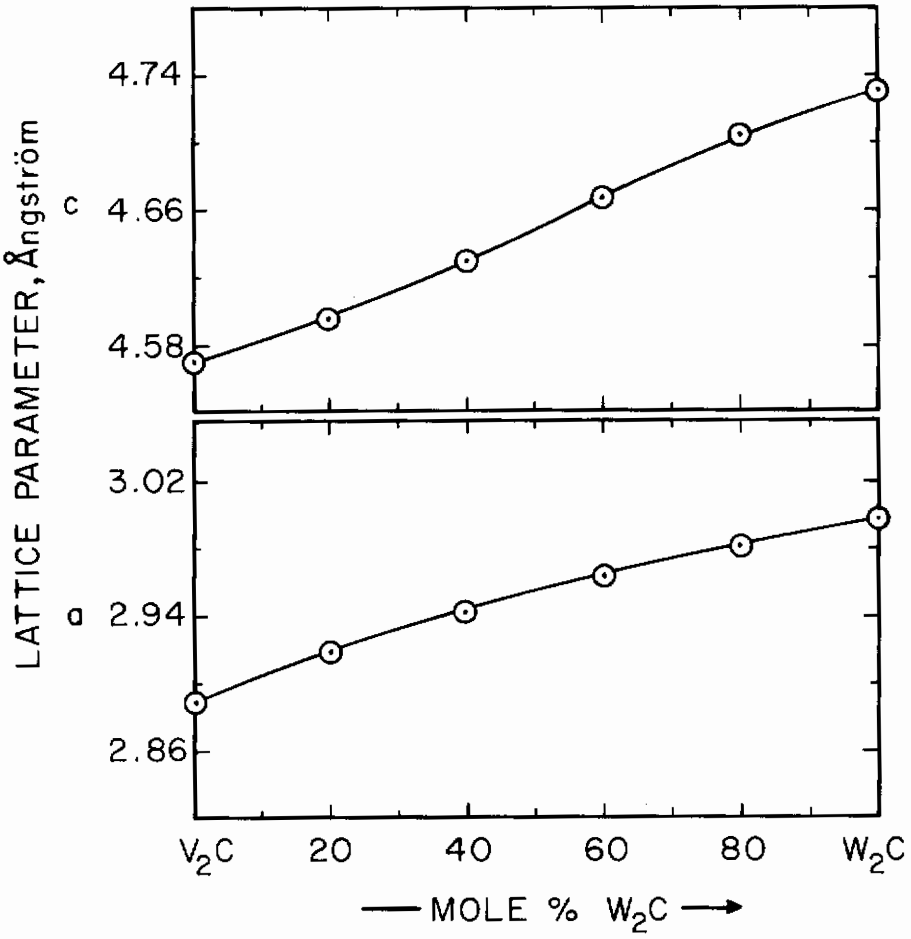

Figure 11. V-W-C: Lattice Parameters of the $(V, W)_2C$ Solid Solution(5)

G. THE V_2C-Mo_2C PSEUDO BINARY SYSTEM

Vanadium subcarbide and molybdenum subcarbide form a continuous series of solid solutions as shown by the investigations of E. Rudy et al.(6) on the ternary V-Mo-C system. Figure 12 shows the variation of the lattice parameters of the$(V,Mo)_2C$ solid solution.

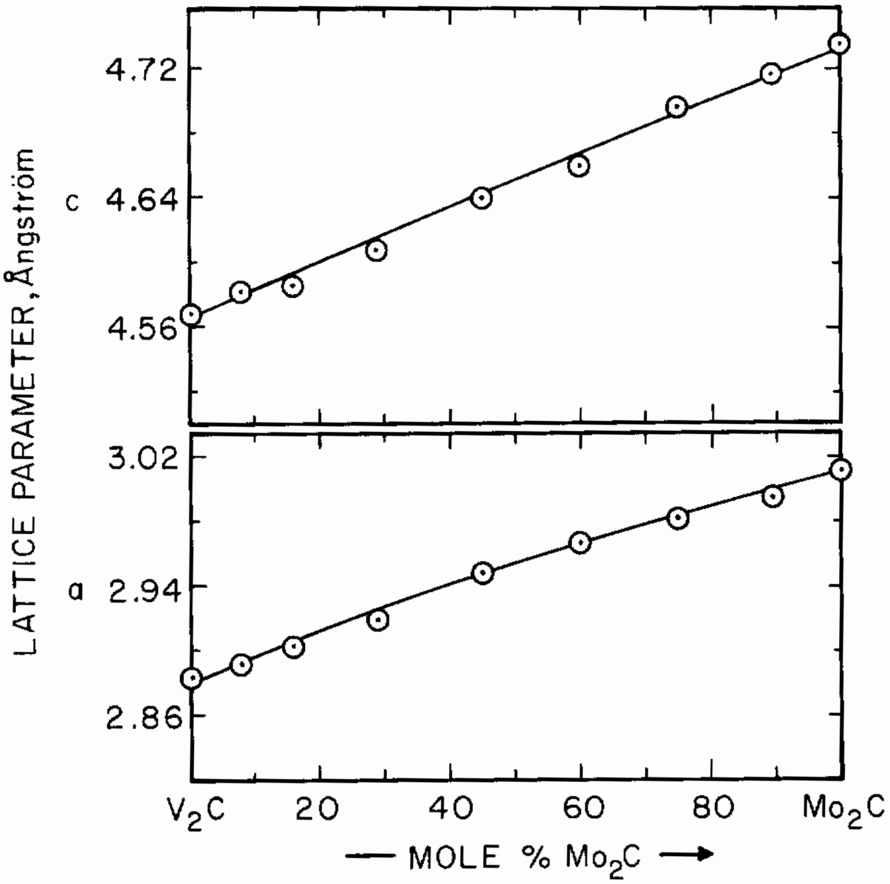

Figure 12. V-Mo-C: Lattice Parameters of the $(V,Mo)_2C$ Solid Solution(6)

H. THE Nb_2C-W_2C PSEUDO BINARY SYSTEM

The Nb-W-C ternary system has been investigated by E. Rudy(7) under a recently completed Air Force Program. The Nb_2C-W_2C pseudo binary section is similar to the Nb_2C-Mo_2C system in as far as the Nb_2C-W_2C pair does not exhibit a complete solid solubility; the middle concentration region is characterized by a two-phased area (Nb, W)C + (W, Nb). This metal-monocarbide region is stable up to melting. Figure 13 shows the solid-state phase equilibria of this pseudo binary pair.

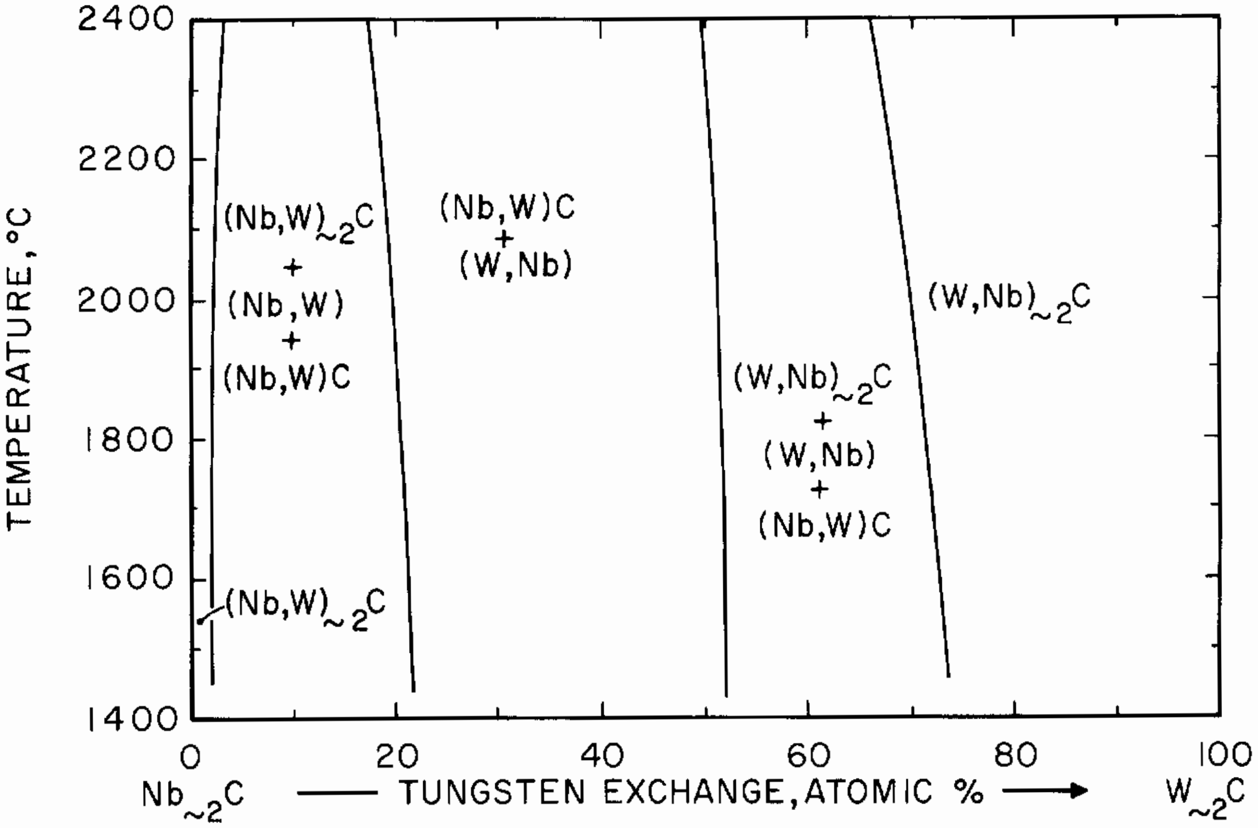

Figure 13. Nb-W-C: The Nb_2C-W_2C Pseudo Binary System(7) (Solid State)

III. EXPERIMENTAL PROCEDURES

A. STARTING MATERIALS

In these investigations, the subcarbide pseudo ternary sections were studied by using samples made with pre-prepared subcarbide master alloys. The subcarbides of tantalum, niobium, molybdenum, tungsten and vanadium were prepared from the elemental metal and graphite powders. These metal powders and graphite had the following vendors' analyses:

Tantalum

Tantalum metal powder with a particle size less than 44 micrometers was purchased from Wah Chang, Albany, Oregon. The analysis was (in ppm): Carbon-50, Niobium-<50, Iron-28, Hydrogen-140, Oxygen-440 and Nitrogen-60. A copper K_α Debye-Scherrer x-ray powder diagram of this material was measured and yielded a lattice parameter of 3.304 Å.

Niobium

Niobium metal powder with a particle size of less than 74 micrometers was purchased from the Fansteel Metallurgical Corporation, Muskogee, Oklahoma. The major impurities cited in the vendor's analysis were (in ppm): Tantalum-492, Tungsten-120, Zirconium-200, Titanium-100, Iron-50, Molybdenum-100, Carbon-84, Oxygen-1125, Nitrogen-24 and Hydrogen-29. An "in house" analysis for oxygen at the Aerojet Chemical and Plastics Testing Laboratory yielded a value of 1360 ppm. A lattice parameter of 3.300 Å was measured for this niobium metal powder.

Molybdenum

The molybdenum metal powder used was supplied by the Wah Chang Corporation, Glen Cove, New York. The analysis accompanying the powder had the following major impurities (in ppm): Aluminum-15, Cobalt-10, Chromium-30, Copper-10, Iron-100, Nickel-20, Oxygen-900, Silicon-80 and Tungsten-100. The lattice parameter of this molybdenum powder was 3.147 Å.

Tungsten

The tungsten powder used was also supplied by Wah Chang in Glen Cove, New York. The vendor's analysis of the main impurities of this tungsten powder whose particle size was less than 44 micrometers was (in ppm): Aluminum-10, Carbon-27, Molybdenum-25, Oxygen-370 and Nickel-10. 3.164 Å was the lattice parameter of this tungsten powder as measured on a Copper K_α powder diagram.

Vanadium

The vanadium used was supplied by the Oregon Metallurgical Corporation, Albany, Oregon. The analysis supplied by the vendor for this less than 44 micrometer particle size powder cited the following major impurities (in ppm): Carbon-520, Hydrogen-42, Oxygen-2000, Nitrogen-660, Iron-390 and Silicon-700. The lattice parameter of this vanadium powder was 3.042 Å.

Graphite

The graphite powder used was supplied by the National Carbon Company and had the following typical impurities (in ppm):

S-110, Si-46, Ca-44, Fe-40, Al-8, Ti-4, Mg-2, V-trace, and ash-800 max. Ninety-nine percent of this graphite powder had a particle size smaller than 44 micrometers. Highly overexposed x-ray films of the graphite powder showed no traces of any impurities.

B. PREPARATION OF SUBCARBIDE MASTER ALLOYS

The preparations of all the subcarbide starting materials were similar for every material made; only the sinter temperatures and times varied slightly for each material.

The weighed in, respective metal powders and graphite were well mixed in a ball mill jar. After the addition of an ether-camphor solution as a binder, the powder was pressed into small bricks; the bricks were loaded into a graphite can and placed in a carbon pot furnace. After being purged several times with helium, the bricks were heated to about 150°C under vacuum to remove the camphor. The starting material was then allowed to react at about 1300°C under helium; after the mild exothermic reaction the samples were sintered at 1550°C-1850°C for 2-3 hours. The sintered bricks were broken down, ball milled, and sieved to a particle size of less than 60 micrometers. The powders were then analyzed for their carbon content by direct carbon analysis and by inspection of their Debye-Scherrer powder photographs. Table I shows the results of these carbon analyses and the x-ray findings.

Table I. Analysis Results of Subcarbide Master Alloys

Material	Atomic % Carbon	Qualitative X-Ray Results
Ta_2C	33.5	Ta_2C Single Phase
Nb_2C	33.3	Nb_2C Single Phase
W_2C	34.5	W_2C, Trace WC
Mo_2C	33.6	Mo_2C Single Phase
V_2C	35.6	V_2C Some VC

Upon adding the appropriate amount of respective metal and mixing well, the alloys were corrected to the stoichiometric carbon content. In the case of the vanadium subcarbide, the metal was always added just prior to the final sample preparation to avoid as much contamination by air oxidation as possible.

C. EXPERIMENTAL ALLOY PREPARATION AND HEAT TREATMENTS

The alloys for heat treatments were prepared from the master subcarbide starting materials by hot pressing the well mixed powders in graphite dies at approximately 1500°C. The hot pressed pellets were surfaced cleaned to eliminate the extraneous carbide layer formed from contact with the graphite die. The cleaned samples were placed in tantalum tubes and heat treated under helium for both 25 hours at 2000°C and 31 hours at 1650°C. In the case of the V_2C containing samples, a tungsten can was used to circumvent the possibility of the formation of low melting eutectics by sample contact with the tantalum cans. Portions of the heat treated samples, after each heat treatment, were subsequently x-rayed using the Debye Scherrer powder technique.

D. X-RAY ANALYSIS

Debye-Scherrer x-ray powder photographs using CuK α, and CrK $_\alpha$ in some cases where higher resolution was desired for the detection of trace amounts of phases where lines coincided with the main phase, were made. All of the patterns presented by the x-ray films of these ternary alloys at 33.3 At. % carbon are known i.e., metal, monocarbide, and subcarbide phases. Almost all of the subcarbide patterns were measured to obtain, by computing the cell volumes, not only compositions of the coexisting phases in three-phase regions, but also to enable the drawing of isoparametric lines in the single-phase subcarbide region. The measurements of the film strips were made using a Siemens-Kirem coincidence scale with a micrometer (.01mm scale divisions) attachment.

IV. RESULTS

Since both W_2C and Mo_2C in combination with Ta_2C exhibit the characteristic of strongly temperature dependent mutual solubilities, coupled with the somewhat unusual behavior of a disproportionation reaction towards low temperatures which yields a very fine eutectoid-like structure of monocarbide and metal phases(2)(3); it is of interest to observe what the effect of varying amounts of W_2C and Mo_2C is on the non-disproportionating subcarbide solid solutions of $(V, Ta)_2C$ and $(Nb, Ta)_2C$, even though Mo_2C and W_2C show different behaviors with V_2C and Nb_2C. In fact, the most logical consideration of these combinations would be the observation of the variation of the phase equilibria of those disproportionating subcarbide systems as a function of Nb_2C and V_2C additions.

Although both the $(Ta, W)_2C$ and $(Ta, Mo)_2C$ subcarbide solid solutions disproportionate, the kinetics of the two separate reactions, as well as the enthalpies detected with differential thermal analysis are different.(2)(3) In the case of $(Ta, W)_2C$, the disproportionation reaction occurs reasonably rapidly with the formation of a well detectable exothermic DTA peak caused by the heat of disproportionation. In the $(Ta, Mo)_2C$ case, however, the disproportionation reaction is often not complete, and the resulting DTA peak is sometimes not sharply defined and uncertain. Nonetheless, a few cursory DTA experiments involving pseudo ternary subcarbide combinations located close to the $(Ta, W)_2C$ and $(Ta, Mo)_2C$ compositions were attempted. As was expected, the DTA results were inconclusive, primarily due to the fact that the added component apparently slowed down the kinetics to a point where the differential thermal analysis equipment could no longer detect the disproportionation reaction. On the basis of these results, it was decided that the investigation of these pseudo ternary alloys would have to rely mainly on the analysis of X-ray data obtained from heat treated samples.

The four, pseudo ternary combinations described below were heat treated at two temperatures, 1650°C and 2000°C.

A. THE Ta_2C-Nb_2C-Mo_2C PSEUDO TERNARY SYSTEM

Figure 14 shows the compositional locations and qualitative phase analysis of the samples heat treated at 1650°C. Since the Nb_2C-Mo_2C pair does not show complete solid solubility, the two phased monocarbide-metal region extends across the full range of Ta_2C compositions joining the similar two-phased area in the Ta_2C-Mo_2C pseudo binary system.

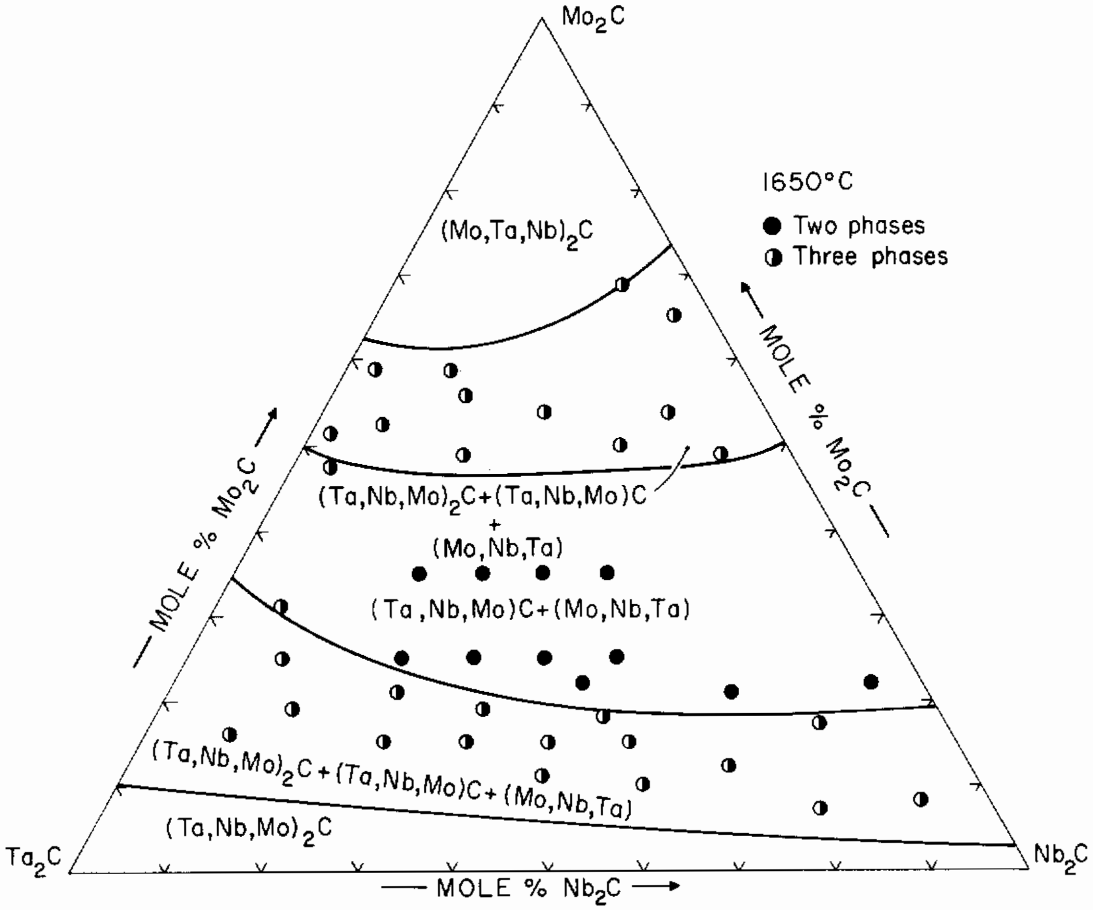

Figure 14. Nb-Ta-Mo-C: Sample Location and Qualitative X-ray Analysis of Ta_2C-Nb_2C-Mo_2C Alloys Heat Treated at 1650°C.

Figure 15 portrays the phase boundaries at 1650°C along with the experimentally determined isovolumetric unit cell parameters in the single-phased subcarbide regions, and also tie lines from individual three-phased samples showing the compositions of co-existing subcarbide phases.

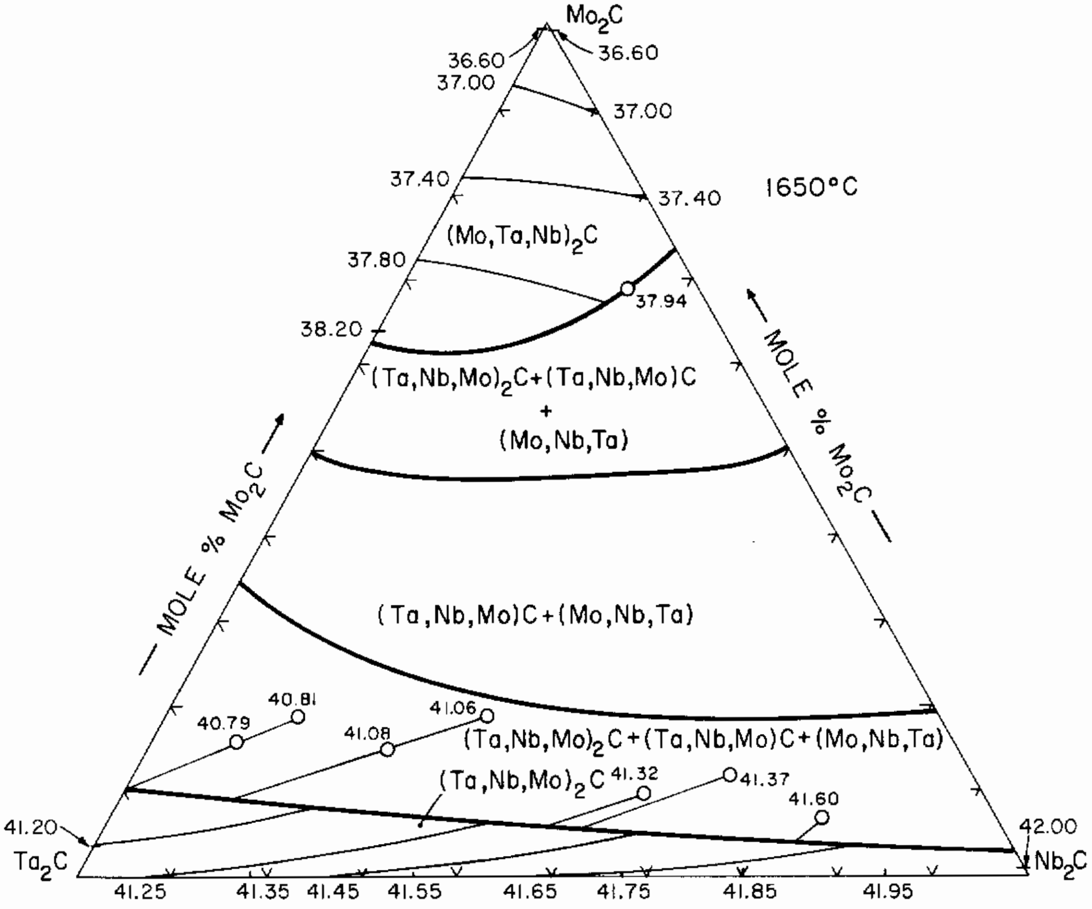

Figure 15. Nb-Ta-Mo-C: Phase Equilibria of the Ta_2C-Nb_2C-Mo_2C Pseudo Ternary System at 1650°C along with Numerically Designated Isovolumetric Unit Cell Dimensions (Å^3), and Tie Lines Indicating Coexisting Subcarbide Compositions.

Figures 16 and 17 show the sample locations and qualitative X-ray analysis as well as the phase equilibria and iso-volumetric unit cell parameters of samples heat treated at 2000°C.

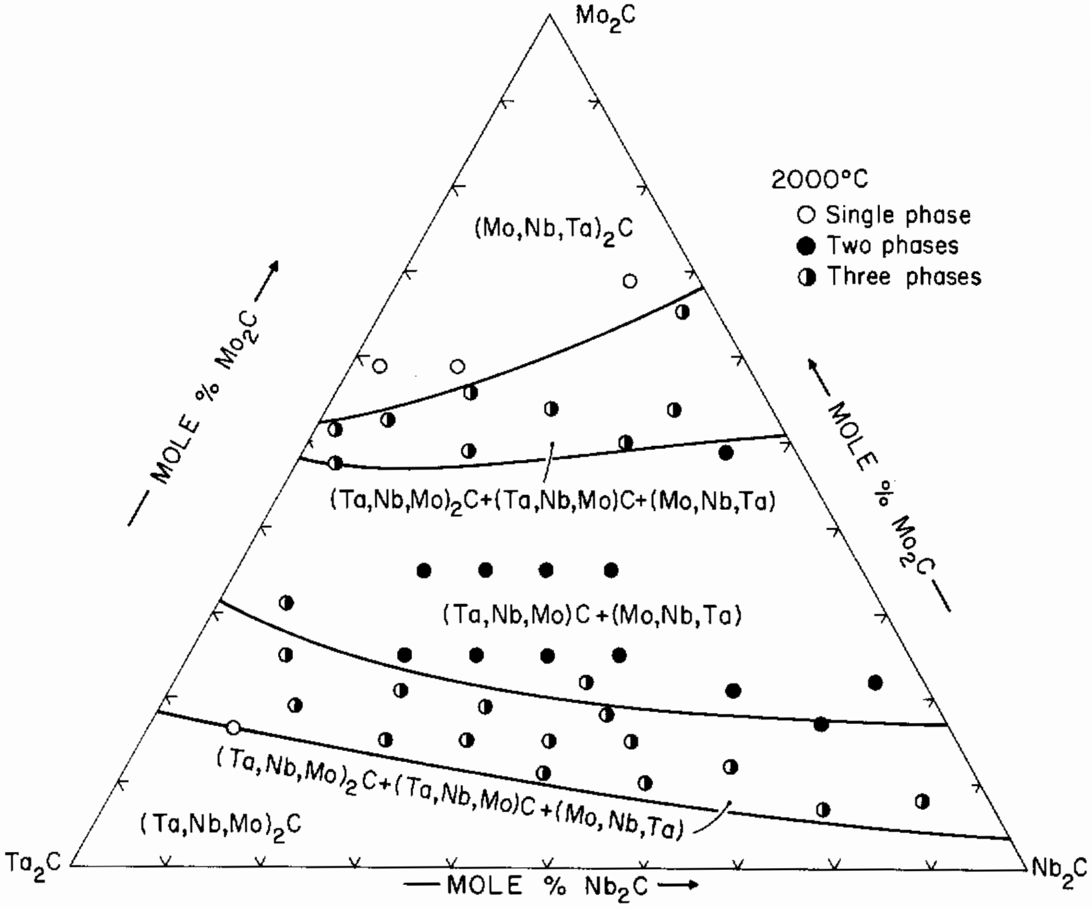

Figure 16. Nb-Ta-Mo-C: Sample Location and Qualitative X-ray Evaluation of Ta_2C-Nb_2C-Mo_2C Alloys Heat Treated at 2000°C.

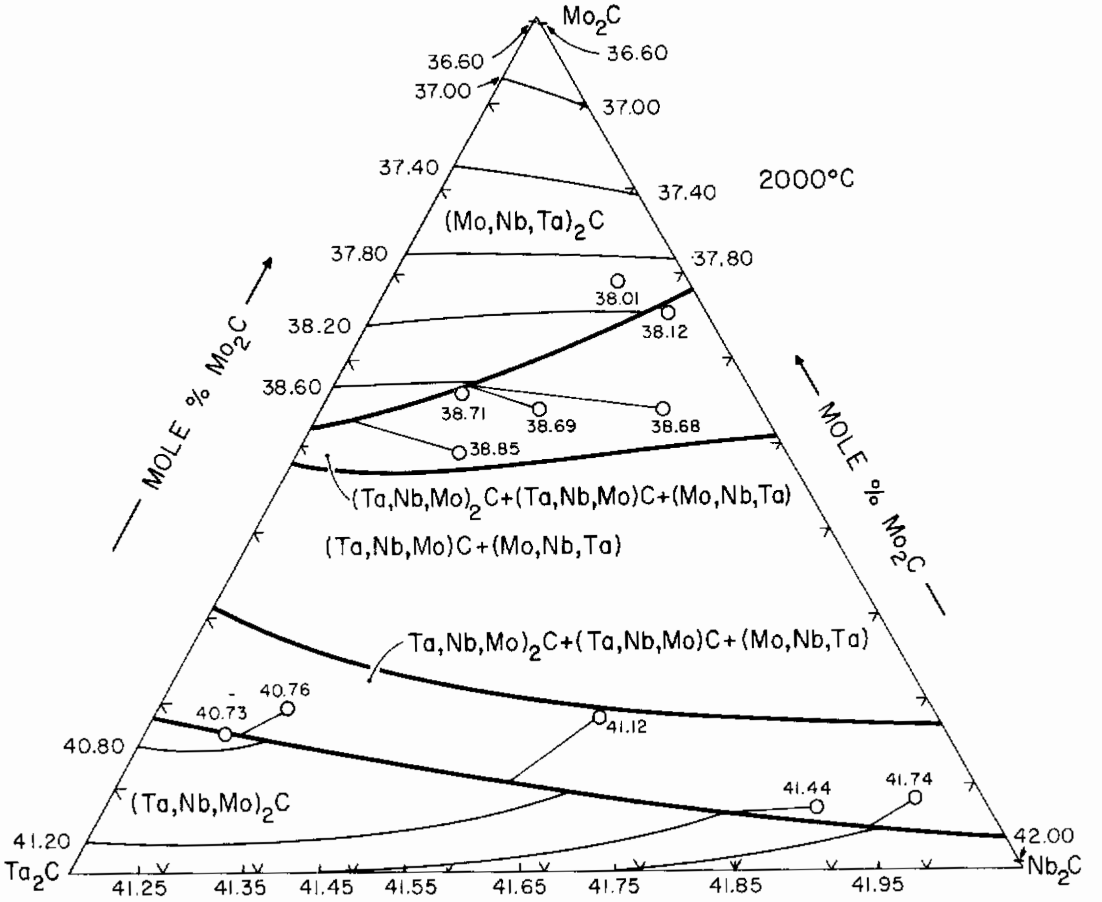

Figure 17. Nb-Ta-Mo-C: Phase Equilibria of the Ta_2C-Nb_2C-Mo_2C Pseudo-Ternary System at 2000°C along with Numerically Designated Isovolumetric Unit Cell Dimensions ($Å^3$), and Tie Lines Indicating Coexisting Subcarbide Compositions

It is seen that there are no extreme changes in the phase equilibria from 1650°C to 2000°C in this system; however, the single phase subcarbide regions increase their size noticably at higher temperatures.

Minor compensations were made in evaluating and locating some of the isovolumetric unit cell lines in the single-phased subcarbide regions. Since the exact location of the single-phased subcarbide regions in the base Me_1-Me_2-C ternary systems is a function of carbon concentration, metal exchange, and temperature; the pseudo ternary subcarbide combinations investigated do not necessarily have their single-phased domains at precisely 33.3 At. % C. Because of this effect, the X-ray films of some samples (all were made nominally at 33.3 At. % C) showed small amounts of the monocarbide phase indicating that the samples (at 33.3 At. % C) were actually located in the two-phased subcarbide + monocarbide region due to the recession of the carbon-rich boundary of the subcarbide phase toward lower carbon contents in these quaternary alloys. This in itself was not misleading in the interpretation of the pseudo ternary subcarbide equilibria, for the true criterion of the location of the three-phased region adjoining the single-phased subcarbide area is the presence of both monocarbide and metal along with the subcarbide phase. However, numerical evaluation of the lattice parameters of those "quasi" single phase subcarbides (i.e. containing some monocarbide) lead to varying results owing to the tie line distribution of the coexisting monocarbide and subcarbide phases. Since it is known that the stability of the monocarbides decrease, in general, in the order VIa<Va<IVa in the periodic table; the monocarbide mixed crystals in equilibrium with the subcarbides will contain more of the metals in the order IVa >Va>VIa; correspondingly, the subcarbides are encriched in the metals in the reverse order VIa>Va>IVa. Similar variations are observed in each individual group also. The result of these facts is that the subcarbide lattice parameters measured in monocarbide containing alloys tend to be smaller than the actual values in corresponding single phase alloys of the same proportionate metals content. These considerations were taken into account in the evaluation of the lines showing isovolumetric unit cell dimensions in not only the Ta_2C-Nb_2C-Mo_2C system, but also in the other combinations.

B. THE Ta_2C-Nb_2C-W_2C PSEUDO TERNARY SYSTEM

Figure 18 shows the compositional location and qualitative X-ray analysis of the pseudo ternary alloys in this system at 1650°C. Figure 19 presents the phase equilibria, isovolumetric unit cell dimensions, and tie lines indicating coexisting subcarbide compositions in the three-phased metal + monocarbide + subcarbide regions at 1650°C.

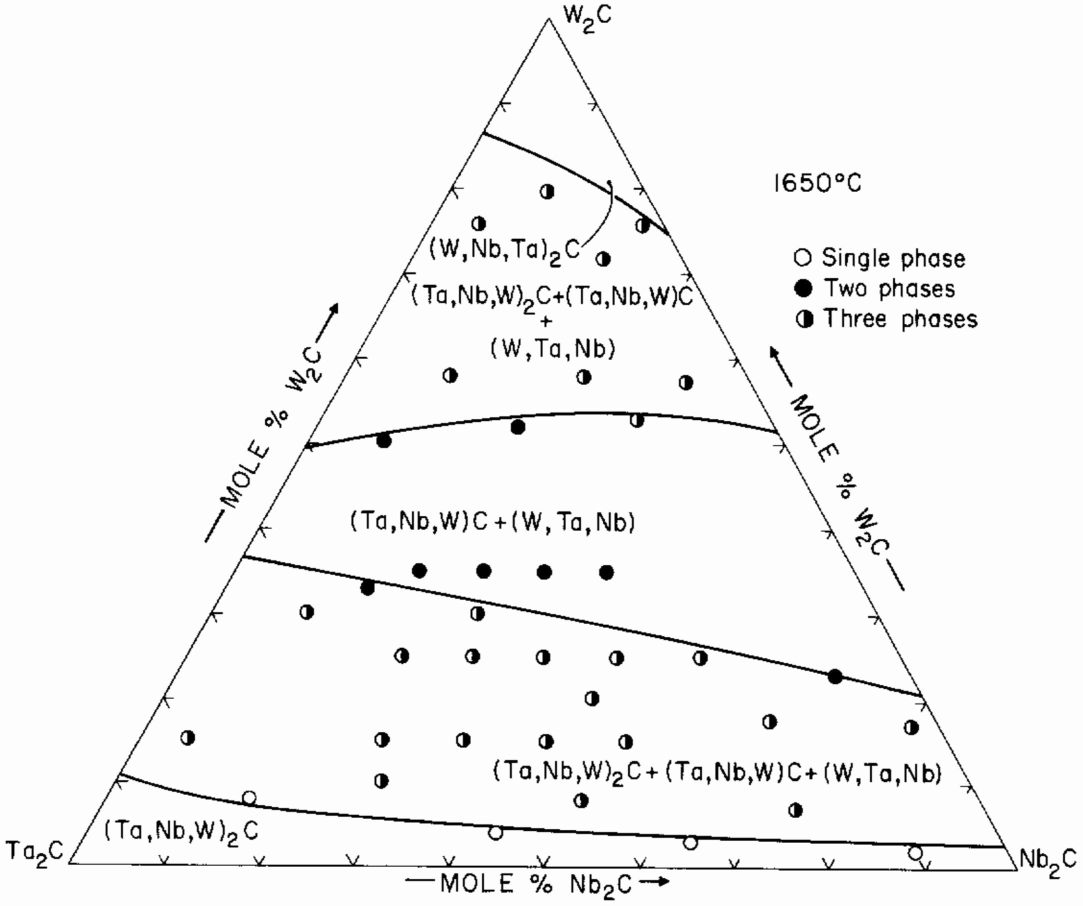

Figure 18. Nb-Ta-W-C: Sample Location and Qualitative X-ray Evaluation of Ta_2C-Nb_2C-W_2C Alloys Heat Treated At 1650°C.

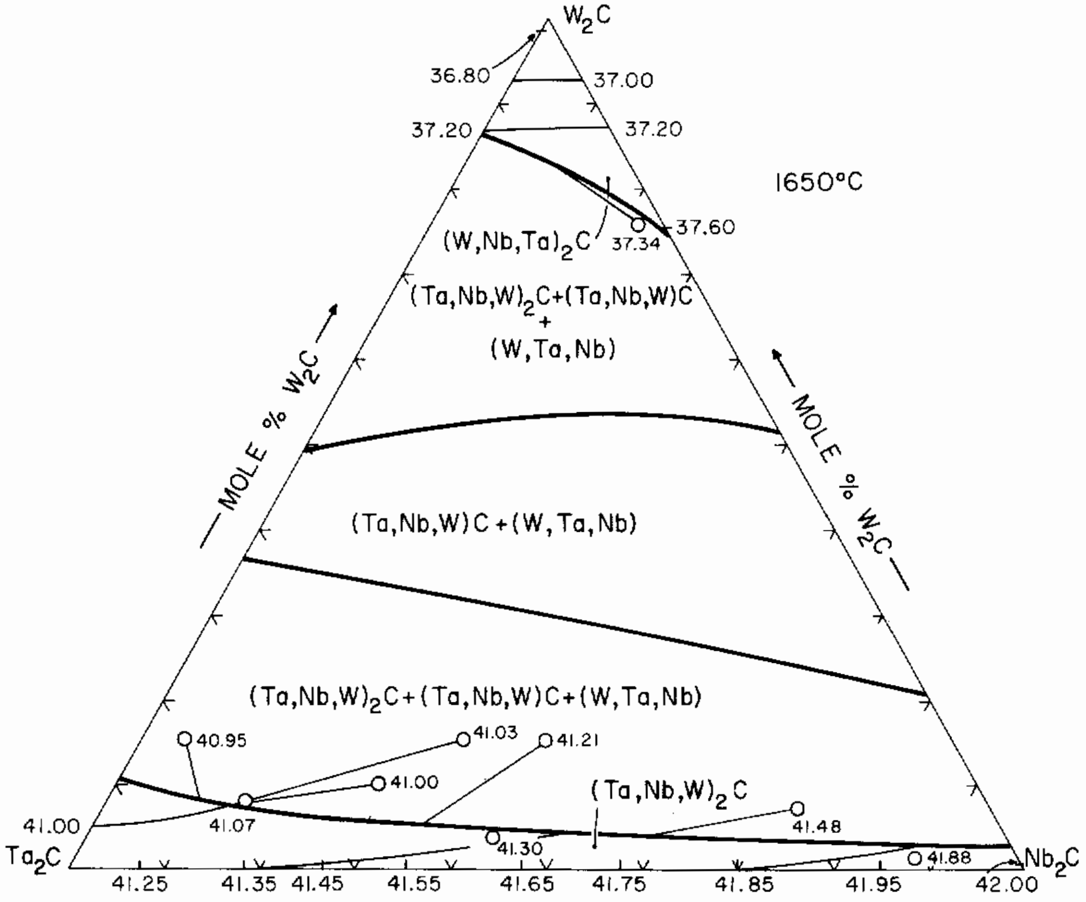

Figure 19. Nb-Ta-W-C: Phase Equilibria of the Ta_2C-Nb_2C-W_2C Pseudo Ternary System at 1650°C along with Numerically Designated Isovolumetric Unit all Dimensions ($Å^3$) and Tie Lines Indicating Coexisting Subcarbide Compositions.

The phase equilibria of the Ta_2C-Nb_2C-W_2C pseudo ternary system at 1650°C and 2000°C are quite similar to the phase equilibria of the Ta_2C-Nb_2C-Mo_2C pseudo ternary system; slight differences in the configuration of the phase boundaries stem from the differences in mutual solubilities of the pseudo binary subcarbides. It is seen that the run of the isovolumetric unit cell dimension lines are about the same in both systems. The temperature section of the Ta_2C-Nb_2C-W_2C system at 2000°C is very similar to the section at 1650°C; again, the noticeable changes occur in the slight extension of the single-phase subcarbide boundaries. The following two figures depict the experimental results at 2000°C.

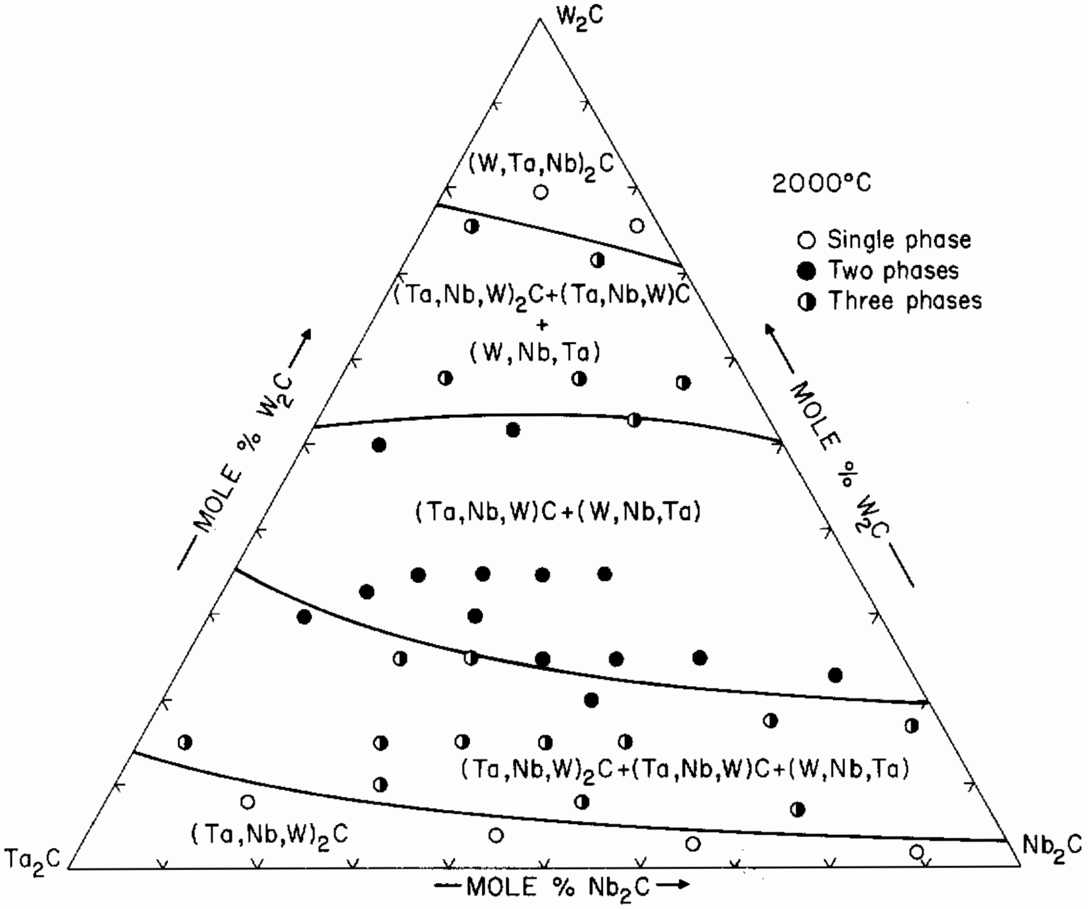

Figure 20. Nb-Ta-W-C: Sample Location and Qualitative X-ray Evaluation of Ta_2C-Nb_2C-W_2C Alloys Heat Treated At 2000°C.

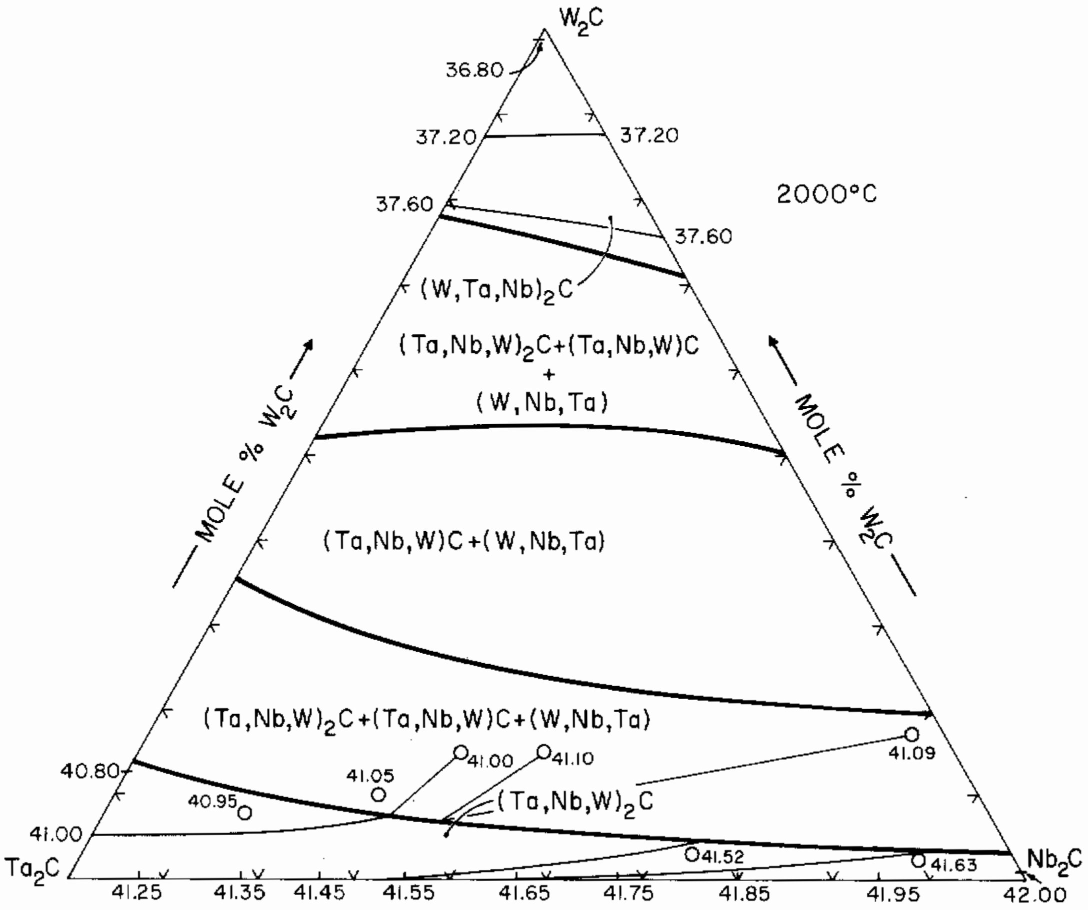

Figure 21. Nb-Ta-W-C: Phase Equilibria of the Ta_2C-Nb_2C-W_2C Pseudo Ternary System at 2000°C Along with Numerically Designated (Å^3) Isovolumetric Unit Cell Dimensions and Tie Lines Indicating Coexisting Subcarbide Compositions.

C. THE Ta_2C-V_2C PSEUDO BINARY SYSTEM

As part of these investigations on the pseudo ternary combinations, it was reaffirmed$^{(1)}$ that the subcarbides Ta_2C and V_2C form a continuous series of solid solutions, at least at temperatures between 1650° and 2000°C. Figures 22 and 23 show the plots of the lattice parameters of the $(Ta,V)_2C$ solid solutions at both 1650° and 2000°C.

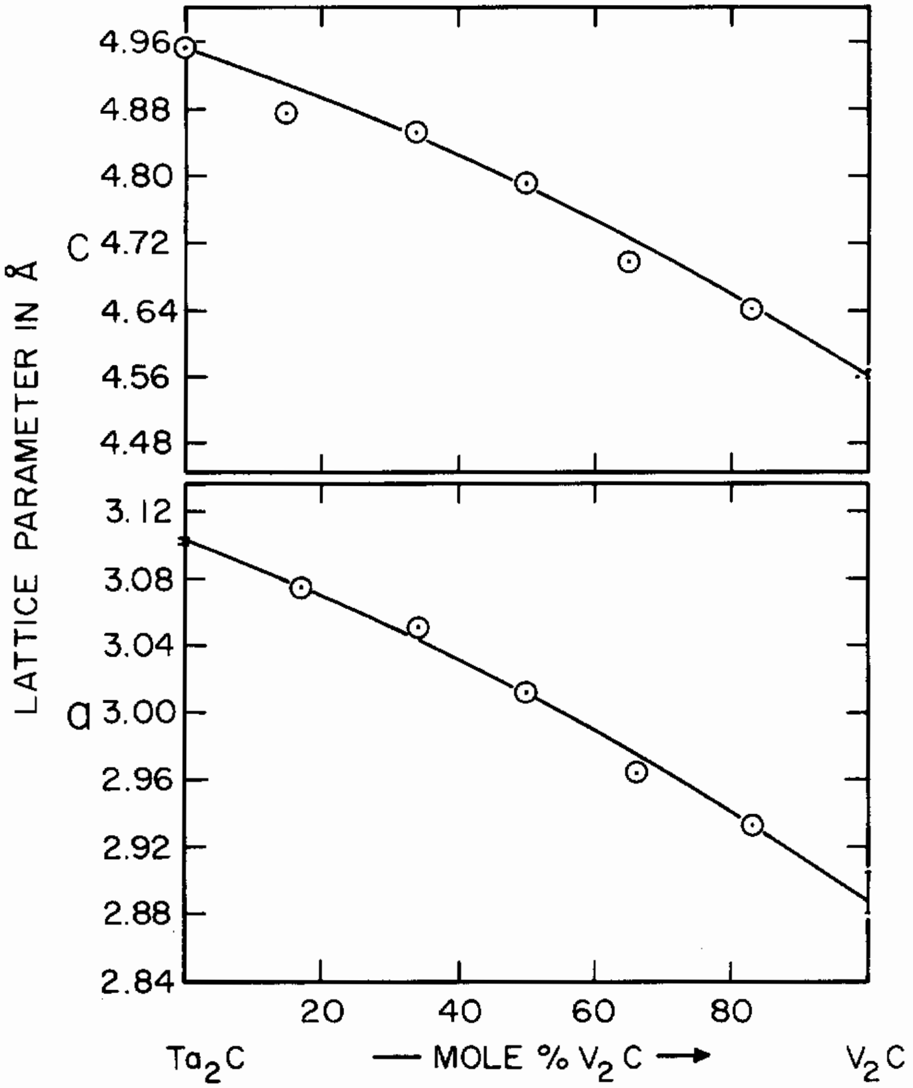

Figure 22. V-Ta-C: Lattice Parameters of the $(V, Ta)_2C$ Solid Solution at 1650°C.

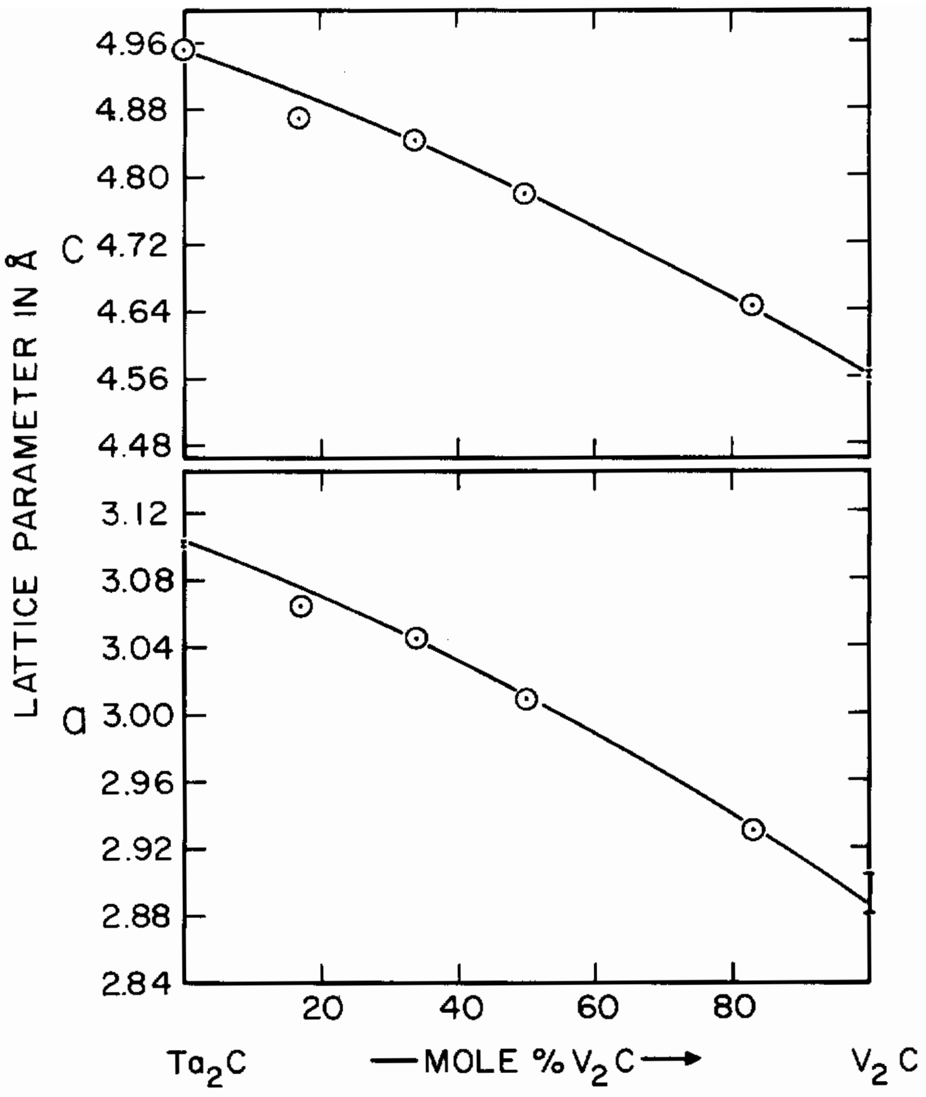

Figure 23. V-Ta-C: Lattice Parameters of the (V, Ta)$_2$C Solid Solution at 2000°C.

It was observed that the Debye-Scherrer X-ray film of the Ta_2C-V_2C sample with 67.5 Mole % V_2C heat treated at 1650°C showed slight signs of decomposition of the single-phased subcarbide structure; this effect was probably caused by the slowness of the furnace cooldown and goes hand in hand with the results reported by Rudy and Booker(1) indicating that a miscibility gap occurs in this subcarbide solid solution at temperatures below about 1500°C.

D. The Ta_2C-V_2C-Mo_2C PSEUDO TERNARY SYSTEM

The phase equilibria configuration of this pseudo ternary system at 1650°C and 2000°C appears significantly different than the preceding two systems, Ta_2C-Nb_2C-Mo_2C and Ta_2C-Nb_2C-W_2C. Figures 24 through 27 portray the sample locations, qualitative X-ray evaluation, phase equilibria, and isovolumetric unit cell dimensions at both 1650° and 2000°C for the Ta_2C-V_2C-Mo_2C pseudo ternary system.

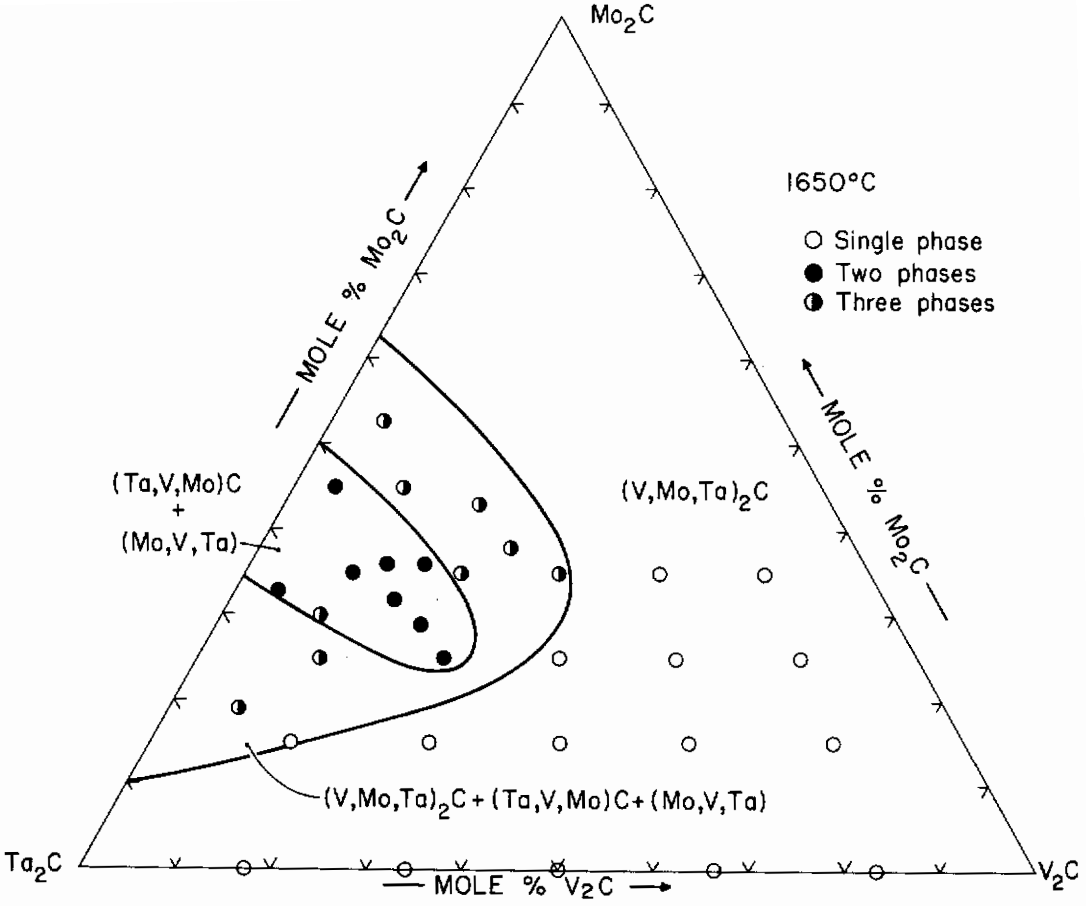

Figure 24. V-Ta-Mo-C: Sample Location and Qualitative X-ray Evaluation of Ta_2C-V_2C-Mo_2C Alloys Heat Treated at 1650°C.

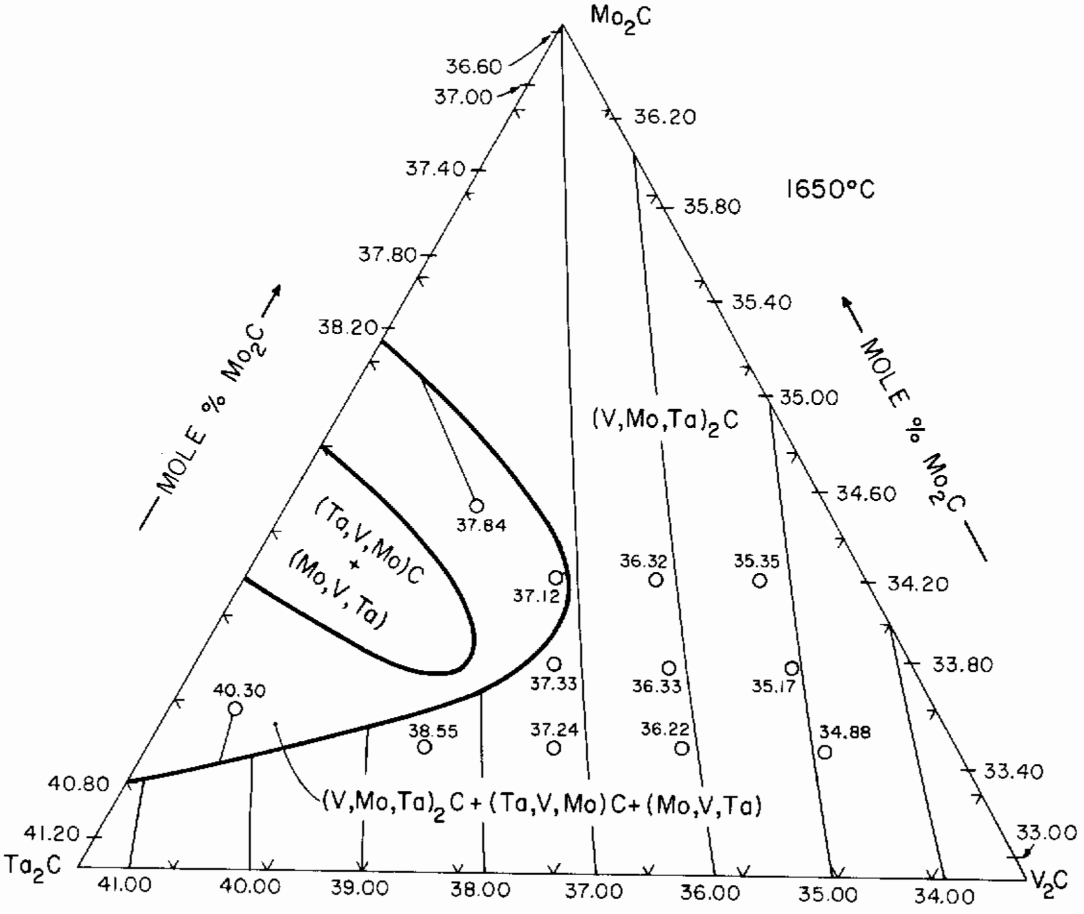

Figure 25. V-Ta-Mo-C: Phase Equilibria of the Ta_2C-V_2C-Mo_2C Pseudo Ternary System at 1650°C Along with Numerically Designated (Å ^{3}) Isovolumetric Unit Cell Dimensions and Tie Lines Indicating Coexisting Subcarbide Compositions.

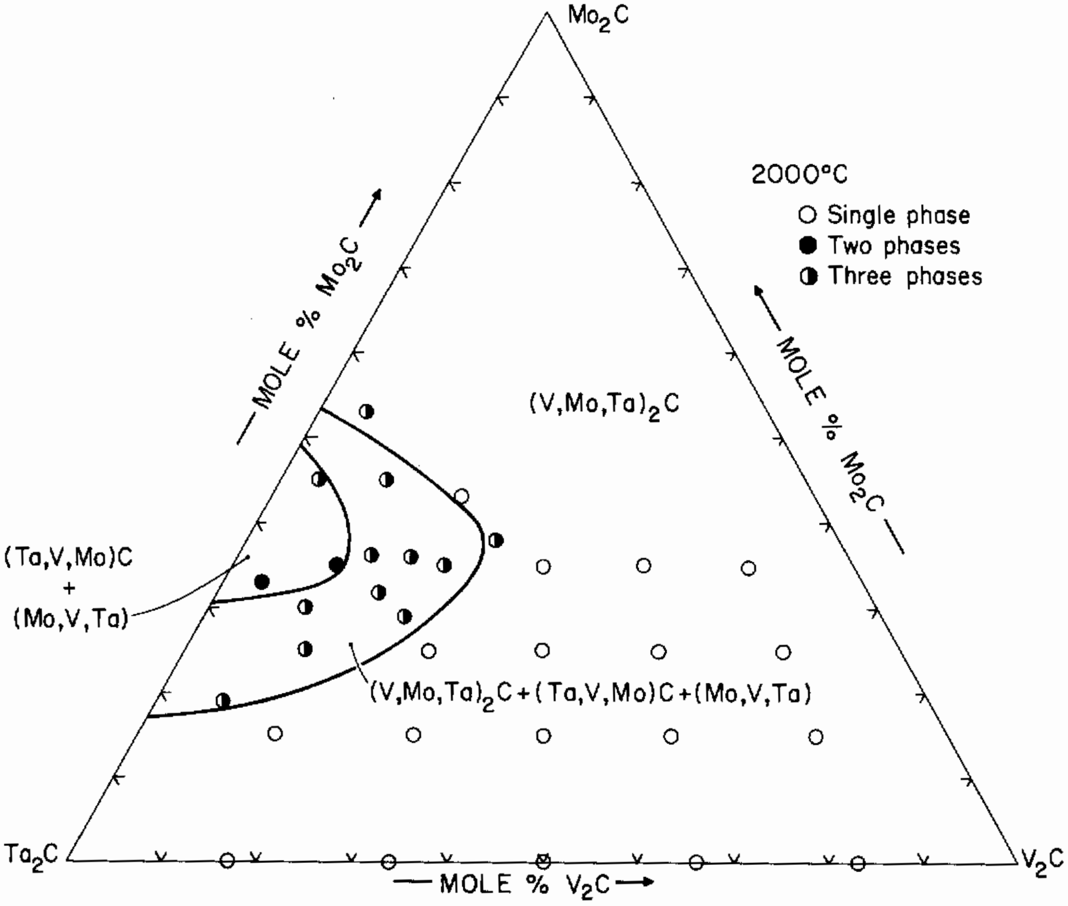

Figure 26. V-Ta-Mo-C: Sample Location and Qualitative X-ray Evaluation of Ta_2C-V_2C-Mo_2C Alloys Heat Treated at 2000°C.

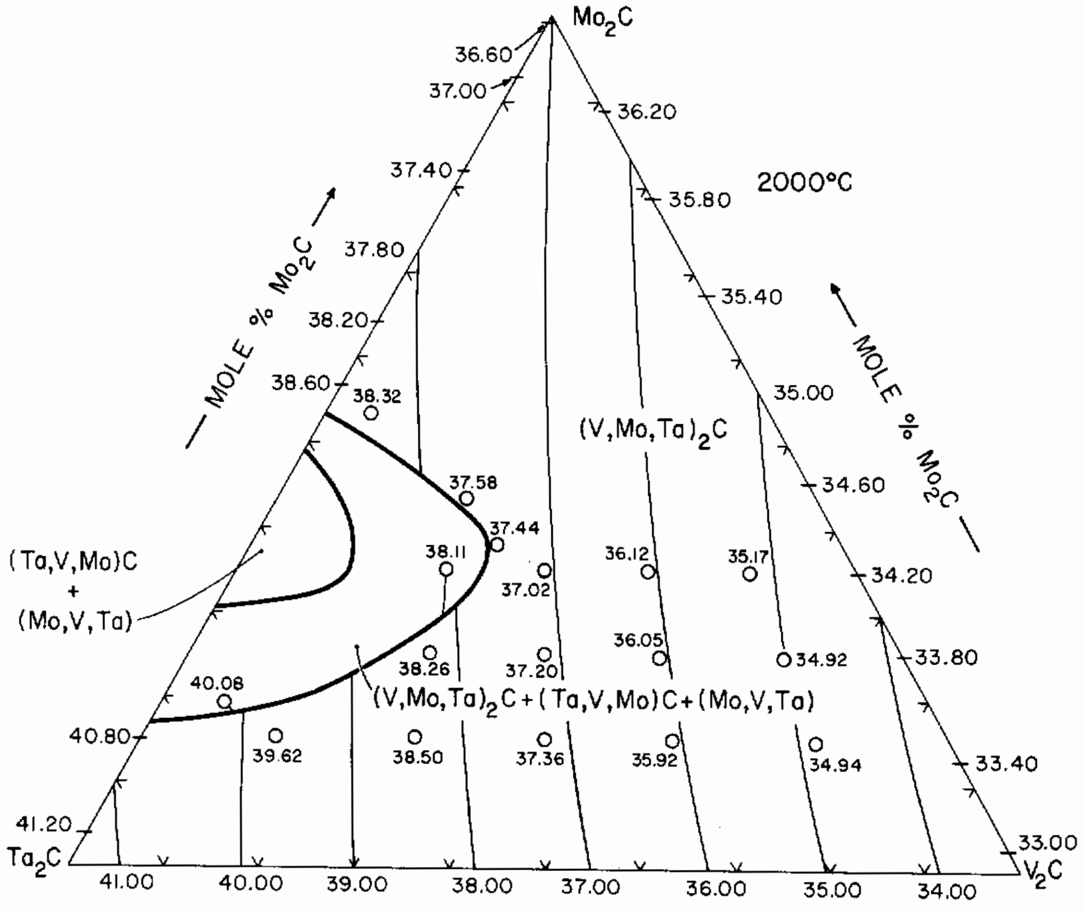

Figure 27. V-Ta-Mo-C: Phase Equilibria of the Ta_2C-V_2C-Mo_2C Pseudo Ternary System at 2000°C Alloy with Numerically Designated (Å^3) Isovolumetric Unit Cell Dimensions and Tie Lines Indicating Coexisting Subcarbide Compositions.

Since V_2C and Mo_2C form a continuous series of solid solutions at all temperatures, the phase equilibria of the pseudo ternary system Ta_2C-V_2C-Mo_2C shows precisely how much V_2C is able to be incorporated into the $(Ta, Mo)_2C$ and $(Mo, Ta)_2C$ solid solutions at 1650°C and 2000°C before the disproportionation reaction based on the subcarbide solid solution in the ternary Ta-Mo-C system: $(Ta, Mo)_2C \longleftrightarrow (Ta, Mo)C + (Mo, Ta)$ is suppressed in favor of the more stable $(Ta, Mo, V)_2C$ subcarbide solid solution. Towards higher temperatures, obviously, the two-phased region, metal and monocarbide, in the pseudo ternary subcarbide system recedes more and more toward the Ta_2C-Mo_2C pseudo binary side and ultimately vanishes as the pseudo ternary system becomes all single phase subcarbide at 2230°C, the critical temperature of the pseudo binary miscibility gap.

E. THE Ta_2C-V_2C-W_2C PSEUDO TERNARY SYSTEM

The phase equilibria of this system at 1650°C and 2000°C is very similar to that of the Ta_2C-V_2C-Mo_2C system in the preceding section in as much as V_2C also forms a complete series of solid solutions with W_2C; the main difference is seen in the size of the two and three phased miscibility gaps that extend into the pseudo ternary region. In the Ta_2C-V_2C-W_2C system the miscibility gap in the pseudo ternary region is larger, primarily due to the smaller mutual solubilities of the Ta_2C-W_2C pair which becomes a single phase subcarbide solid solution at 2450°C; at this temperature, then, the pseudo-ternary Ta_2C-V_2C-W_2C system also becomes a single phase subcarbide solid solution $(Ta, V, W)_2C$.

Figures 28 through 31 show the sample location, qualitative X-ray evaluation, phase equilibria, and isovolumetric unit cell dimensions of the Ta_2C-V_2C-W_2C system at both 1650° and 2000°C.

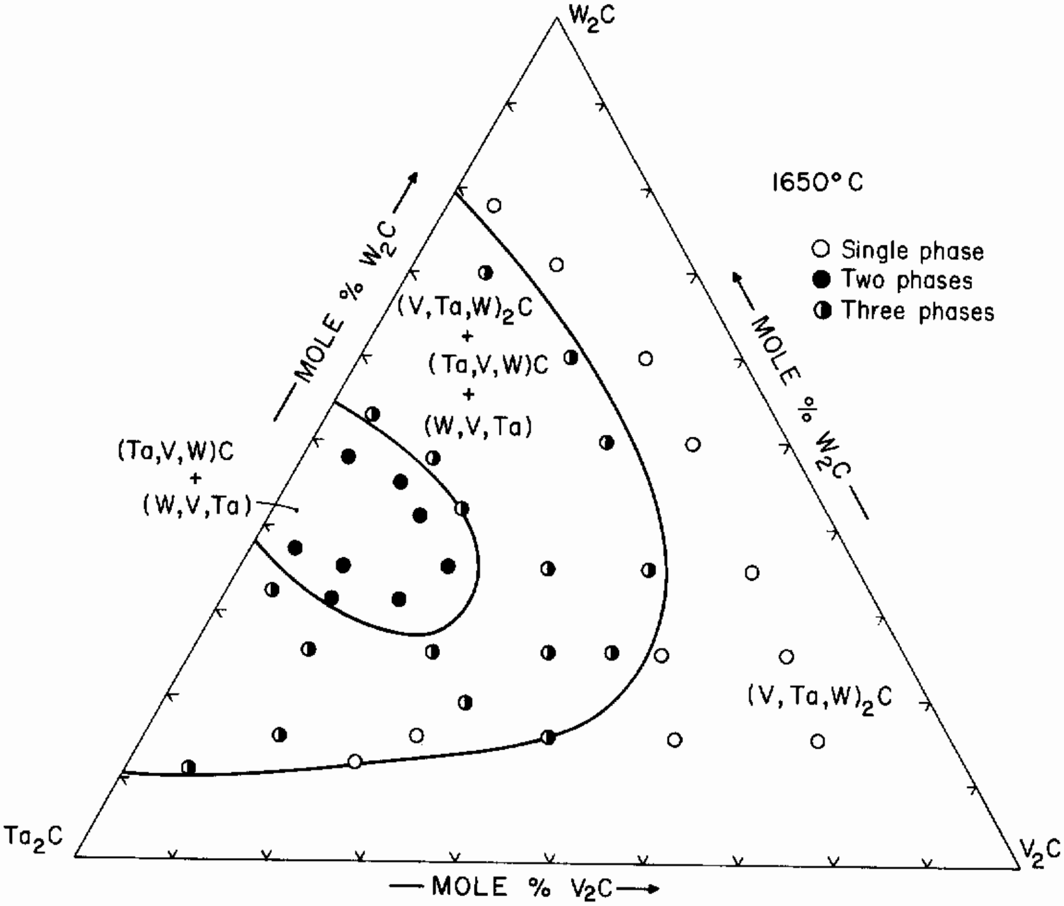

Figure 28. V-Ta-W-C: Sample Location and Qualitative X-ray Evaluation of Ta_2C-V_2C-W_2C Alloys Heat Treated at 1650°C.

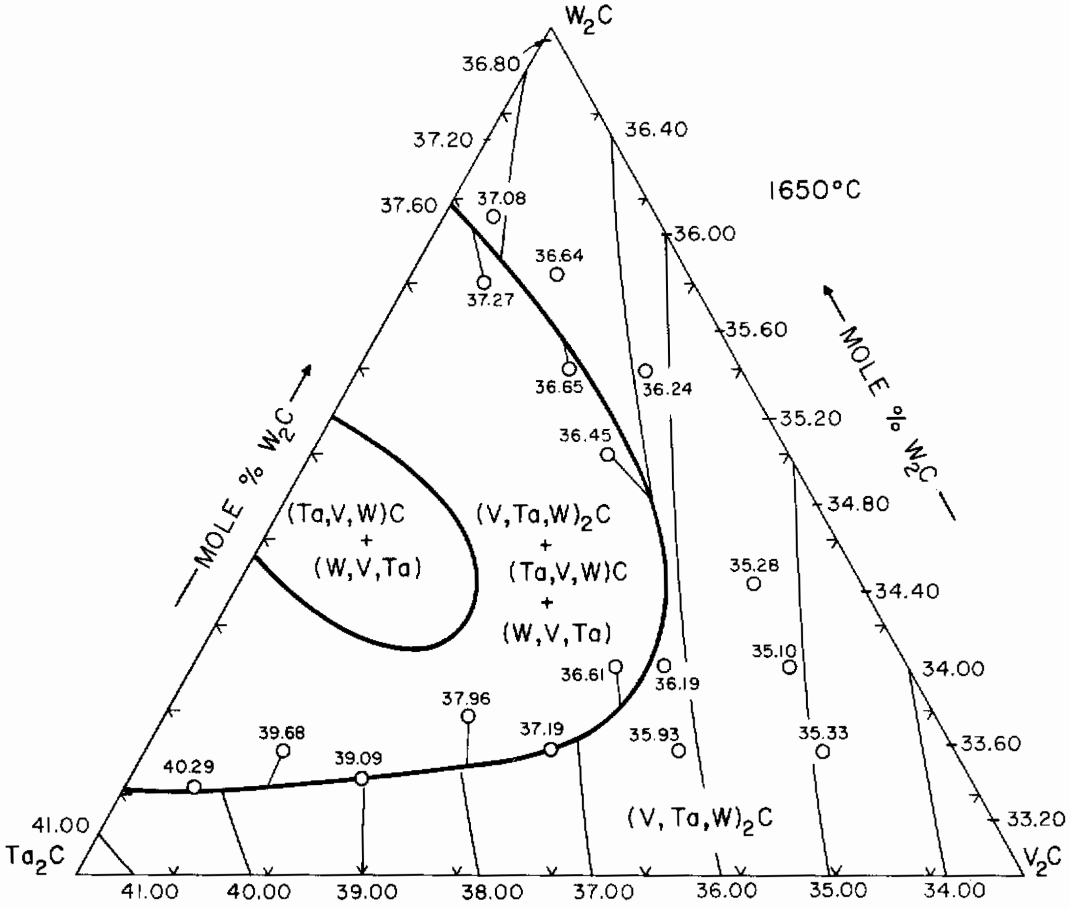

Figure 29. V-Ta-W-C: Phase Equilibria of the Ta_2C-V_2C-W_2C Pseudo Ternary System at 1650°C Along With Numerically Designated (Å^3) Isovolumetric Unit Cell Dimensions and Tie Lines Indicating Coexisting Subcarbide Compositions.

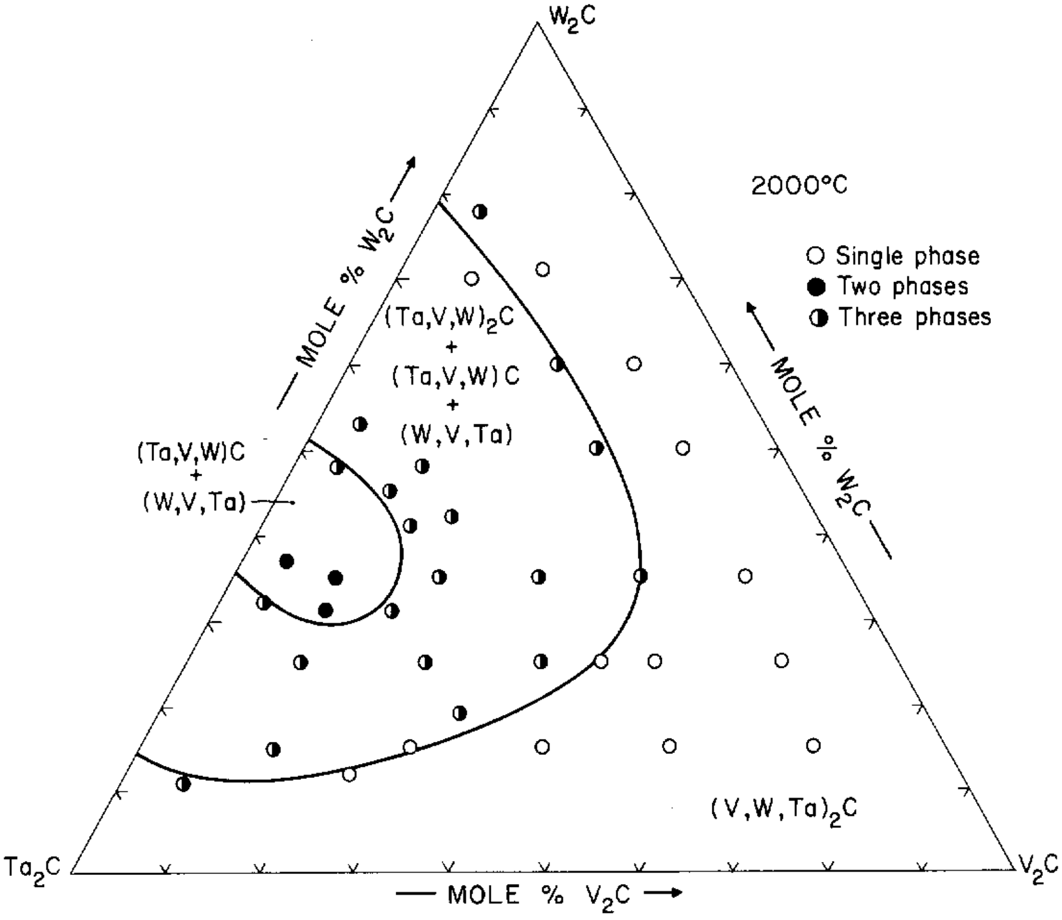

Figure 30. V-Ta-W-C: Sample Location and Qualitative X-ray Evaluation of Ta_2C-V_2C-W_2C Alloys Heat Treated at 2000°C.

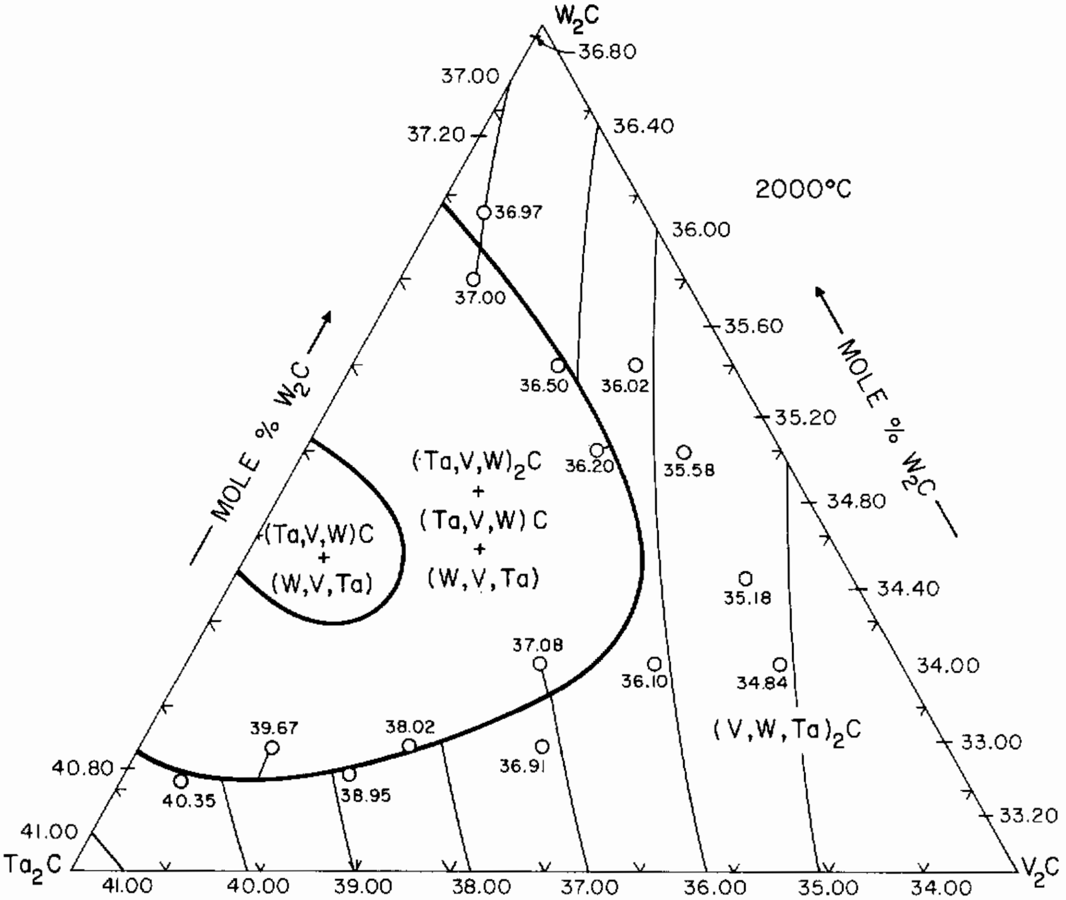

Figure 31. V-Ta-W-C: Phase Equilibria of the Ta_2C-V_2C-W_2C Pseudo Ternary System at 2000°C Along With Numerically Designated (Å ^{3}) Isovolumetric Unit Cell Dimensions and Tie Lines Indicating Coexisting Subcarbide Compositions.

V. DISCUSSION AND CONCLUSION

The phase equilibria of the Ta_2C-Nb_2C-W_2C and Ta_2C-Nb_2C-Mo_2C systems, which show similar phase equilibria characteristics at both 1650° and 2000°C, have not been investigated at temperatures above 2000°C; it is certain, however, that the miscibility gaps in the Ta_2C-W_2C and Ta_2C-Mo_2C pseudo binary systems will close quite near the lowest melting points of the Nb_2C-W_2C and Nb_2C-Mo_2C pseudo binary systems, respectively; how far the melt stretches into the pseudo ternary region from the Nb_2C-W_2C and Nb_2C-Mo_2C pseudo binary sides towards the Ta_2C-W_2C and Ta_2C-Mo_2C sides, respectively, at temperatures slightly above the melting points of the lower melting pseudo binary sides, is an open question. Melting point determinations in the pseudo ternary region in the vicinity of the Ta_2C-Mo_2C and Ta_2C-W_2C pseudo binary sides would be necessary before attempting to heat treat these alloys at these high temperatures. It is not expected that single phased region, resulting from the closing of the miscibility gap in the Ta_2C-Mo_2C and Ta_2C-W_2C pseudo-binary systems, will range excessively far into the pseudo ternary region with increasing temperature before the pseudo ternary alloys melt. If, however, alloys containing approximately ten or perhaps slightly more mole percent Nb_2C with approximately equal proportions of Ta_2C-Mo_2C or Ta_2C-W_2C are able to be made single phase subcarbide, and the resulting disproportionated monocarbide + metal alloys are judged possible candidates for cutting tools (on the basis of possible good wear resistance and mechanical strength); the disproportionation of the single phase subcarbide to a fine lamellar structure of monocarbide and metal phases should proceed at a technically feasible rate owing to the additional tendency of the Nb_2C-W_2C and Nb_2C-Mo_2C pairs not to form complete solid solutions.

By analogy, on the other hand, Ta_2C-Mo_2C and Ta_2C-W_2C based alloys containing excessive amounts of V_2C are not expected to have beneficial kinetic rates of the disproportionation reaction because of the ability of V_2C to form continuous series of solid solutions with both Mo_2C and W_2C.

REFERENCES

1. P. Booker and E. Rudy: Tech. Report AFML-TR-69-117 Part III (1969)

2. E. Rudy, St. Windisch, and C. Brukl: Tech. Report AFML-TR-65-2 Part II, Vol. XVII (December 1967)

3. E. Rudy: Tech. Report AFML-TR-65-2-Part II, Vol. VIII (March 1966)

4. E. Rudy, C. E. Brukl, and St. Windisch: AFML-TR-65-2 Part II, Vol. XV (July 1967)

5. E. Rudy, F. Benesovsky and Elisabeth Rudy: Mh. Chem. 93 (1962) 693

6. E. Rudy, Elisabeth Rudy, and F. Benesovsky: Planseeber. 10 (1962) 42

7. E. Rudy: Tech Report AFML-TR-65-2 Part II, Vol. XVIII (January 1969)

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The phase equilibria of the Ta_2C-V_2C pseudo binary pair, as well as that of the pseudo ternary subcarbide systems, Ta_2C-Nb_2C-Mo_2C, Ta_2C-Nb_2C-W_2C, Ta_2C-V_2C-Mo_2C and Ta_2C-V_2C-W_2C have been determined primarily by Debye-Scherrer X-ray analysis of alloys heat treated at 1650° and 2000°C.

The subcarbides Ta_2C and V_2C form a continuous series of solid solutions. The phase equilibria of the pseudo ternary combinations Ta_2C-Nb_2C-Mo_2C and Ta_2C-Nb_2C-W_2C are quite similar; a two phased region metal + monocarbide divides the two subcarbide solid solutions based on Mo_2C or W_2C and $(Ta,Nb)_2C$.

Miscibility gaps showing the presence of metal + monocarbide phases (and the associated three phase regions of metal + monocarbide + subcarbides) originate in the Ta_2C-Mo_2C and Ta_2C-W_2C pseudo binary systems of the respective pseudo ternary systems Ta_2C, V_2C, Mo_2C and Ta_2C-V_2C-W_2C; these miscibility gaps extend into the pseudo ternary subcarbide single phase regions of $(Ta,V,Mo)_2C$ and $(Ta,V,W)_2C$.

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