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PHASE EQUILIBRIA INVESTIGATION OF BINARY, TERNARY, AND HIGHER ORDER SYSTEMS. PART VI. THE PHASE EQUILIBRIA IN THE METAL-RICH REGION OF THE HAFNIUM-TANTALUM-NITROGEN SYSTEM

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Sacramento, California

December 1969

AFML-TR-69-117
PART VI

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

PART VI. THE PHASE EQUILIBRIA IN THE METAL-RICH REGION OF THE HAFNIUM-TANTALUM-NITROGEN SYSTEM

P. H. BOOKER and C. E. BRUKL
Aerojet-General Corporation

TECHNICAL REPORT AFML-TR-69-117, PART VI

DECEMBER 1969

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PART VI. THE PHASE EQUILIBRIA IN THE METAL-RICH REGION OF THE HAFNIUM-TANTALUM-NITROGEN SYSTEM

P. H. BOOKER and 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 authors wish to thank Dr. E. Rudy for his advice and help during the course of this investigation; they further wish to thank R. Taylor, J. Pomodoro, R. Cobb and O. Catrino for their valuable help in various aspects of the experimental work.

Finally, the authors wish to acknowledge the following persons for their help in the preparation of this manuscript: Mr. R. Cristoni and Mrs. Donna Breuer for the preparation of the drawings and the final typing.

The manuscript of this report was released by the authors in Oct 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 System

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 Nb-Ta-C System

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

This technical report has been reviewed and is approved.

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ABSTRACT

The ternary alloy system tantalum-hafnium-nitrogen was investigated by means of melting point, X-ray, differential thermal analytical, and metallographic techniques. Also investigated were the two binary systems of tantalum-nitrogen and hafnium-nitrogen.

In the ternary system, seven isothermal reactions occur: three, Class II - type four-phase reactions and four limiting tie line reactions.

The observed phase relationships established during the course of this investigation are discussed, and isothermal sections from 1000°C to 3200°C as well as an isometric view of the ternary system are presented. In addition to the ternary system, phase diagrams for the two binary systems of tantalum-nitrogen and hafnium-nitrogen are also presented.

Subsequent studies after the completion of this investigation and report have shown that two new phases instead of one are present in the hafnium-nitrogen binary system in the region near 33 atomic percent nitrogen.

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I. INTRODUCTION AND SUMMARY

A. INTRODUCTION

Refractory nitrides and borides, as well as carbides, are known for their extreme hardness, and it is quite natural that attempts should be made to utilize the hardness properties of refractory nitrides in new alloys for cutting tool applications. In complete analogy to the fabrication of refractory carbide-refractory metal cutting tool alloys, the fabrication of refractory nitride-refractory metal containing alloys must take place at elevated temperatures. In order to guarantee not only the proper selection of compatible components, but also to guard against unwanted reactions during fabrication which would destroy the integrity of the composite cutting tool alloy; the high-temperature phase equilibria of any desired material combination must be thoroughly known.

These features, then, are the underlying initiatives for the investigation of the hafnium-tantalum-nitrogen system which contains the hafnium-nitride-based solid solution with physical properties making it a possible candidate for consideration as a cutting tool alloy component. When the particular high-temperature phase equilibria of the hafnium-tantalum-nitrogen system are known, intelligent combinations containing compatible nitride-metal alloys may be chosen.

B. SUMMARY

The alloy systems tantalum-nitrogen, hafnium-nitrogen, and tantalum-hafnium-nitrogen were investigated by means of x-ray, D.T.A., metallographic, and melting point techniques. The phase relationships in the ternary and two binary systems are summarized as follows:

1. Binary Systems

a. The Tantalum-Nitrogen System

From the melting point of pure tantalum at 3014°C, the solidus temperatures of the metal solid solution decrease to 2870° ± 15°C, the temperature of the Ta-Ta_2N eutectic. At the eutectic temperature, the metal solid solution extends to 9 At.% nitrogen, and the metal-rich phase boundary of the hexagonal Ta_2N phase is located at 29 At.% N.

The Ta_2N phase melts congruently at a temperature of 2950°C (~35 At.% N). The tantalum mononitride phase was not detected in alloys with nitrogen contents of 39 atomic percent, the maximum nitrogen containing alloys used in this investigation.

The partial constitution diagram of the binary Ta-N system is presented in Figure 6.

b. The Hafnium-Nitrogen System

The low temperature, hexagonal α-hafnium phase transforms at 1770° ± 30°C(1) into the body centered cubic (β) allotropic form. The α-modification takes ~28 At.% nitrogen into solid solution and is stabilized to a temperature of 2911° ± 14°C. At this temperature, the α-Hf-ss melts peritecticly to form liquid plus HfN_{1-x} (~34 At.% N). A eutectic at 2190° ± 8°C and ~2 At.% nitrogen is formed between the α-Hf-ss (~3 At.% N) and the β-Hf-modification (< 1 At.%N).

Hafnium mononitride, with a face centered cubic B1-type crystal structure, melts congruently at a temperature of 3387° ± 25°C at a nitrogen concentration of ~49 At.%. At 2100°C, the low nitrogen boundary of the HfN_{1-x} phase is located at 40 At. % N (a = 4.536Å), and at 1500°C the boundary is at 43 At.% N (a = 4.522Å).

As was previously reported by E. Rudy and F. Benesovsky(2), a subnitride phase of hafnium (Hf_2N) occurs in this system. The phase forms in a peritectoid reaction at ~1970°C from α-Hf-ss and mononitride according to the reaction scheme:

$$\alpha\text{-Hf-ss}(\sim 25\ \text{At.\% N}) + \delta\text{-HfN}_{1-x}\ (\sim 40\ \text{At.\% N}) \rightleftarrows$$

$$\epsilon - \text{Hf}_2\text{N}\ (\sim 33\ \text{At.\% N}).$$

The proposed constitution diagram of the binary Hf-N system is presented in Figure 14. The equilibria between melt, mononitride, and nitrogen were not studied in this investigation and hence are not shown in the diagram.

2. Ternary System

a. The Tantalum-Hafnium Nitrogen System

The phase relationships in the ternary system tantalum-hafnium-nitrogen are summarized as follows:

The only complete solid solution formation in the system exists above 1770°C in the body centered cubic β-(Ta, Hf)-ss. At ~ 2260°C, the α-Hf-ss (a = 3.217Å, c = 5.128Å at 10 At.% N) takes a maximum tantalum exchange of 22 atomic percent into solution (a = 3.189Å; c = 5.086Å at ~10 At.% N).

At 2100°C, the (Hf, Ta)N_{1-x}-ss takes into solution a maximum tantalum exchange of 47 atomic percent (a = 4.510Å at 45 At.% N) . Above the temperature of 2100°C, the maximum solubility of tantalum in the (Hf, Ta)N_{1-x}-ss at the mononitride phase boundary of the two-phase field, γ-Ta_2N-ss + (Hf, Ta)N_{1-x}-ss retracts towards the hafnium mononitride side.

The maximum solubility of hafnium in γ-Ta_2N is 9.5 atomic percent at 2800°C and 30 % At.% N (a = 3.062Å, c = 4.937Å) for the solid solution at the three-phase boundary:

$$\beta\text{ - (Ta, Hf)-ss} + \gamma\text{ - (Ta, Hf)}_2\text{N} + \delta\text{ - (Hf, Ta) N}_{1-x}.$$

The equilibrium β - (Ta, Hf)-ss + δ - (Hf, Ta)N_{1-x}-ss remains stable at all temperatures up to melting.

Three, class I four-phase reactions occur in the ternary system. These reaction isotherms are listed in order of decreasing temperature:

(1) 2800°C: $L + \gamma\text{ - Ta}_2\text{N-ss} \rightleftharpoons \beta\text{ - (Ta, Hf)-ss} + \delta\text{ - (Hf, Ta)N}_{1-x}\text{-ss}$

(2) 2260°C: $L + \delta\text{ - (Hf, Ta)N}_{1-x}\text{ -ss} \rightleftharpoons \beta\text{ - (Ta, Hf)-ss} + \alpha\text{-Hf-ss}$

(3) 1950°C: $\alpha\text{-Hf-ss} + \delta\text{ - (Hf, Ta) N}_{1-x}\text{-ss} \rightleftharpoons \beta\text{ - (Ta, Hf)-ss} + \epsilon\text{ - Hf}_2\text{N-ss}$

In addition to the four-phase reaction planes, four limiting tie lines occur in the system.

(1) A pseudo binary eutectic reaction occurs at 2920°C, between the pair γ-Ta_2N-ss and δ-$(Hf, Ta)N_{1-x}$-ss. The reaction is represented by:

$$\text{Liquid} \underset{T > 2920^\circ C}{\overset{T < 2920^\circ C}{\rightleftharpoons}} \gamma\text{-}Ta_2N\text{-ss} \quad \delta\text{-}(Hf, Ta)N_{1-x}\text{-ss}$$

(2) The minimum tie line at 2110°C represents a quasibinary eutectic point in the ternary system:

$$\text{Liquid} \underset{T > 2110^\circ C}{\overset{T < 2110^\circ C}{\rightleftharpoons}} \beta\text{-}(Ta, Hf) + \alpha\text{-}Hf\text{-ss}$$

(3) A critical tie line occurs at 1265°C in the ternary system due to the formation of the miscibility gap in the Hf-Ta binary system. One, three-phase equilibrium results from this reaction towards lower temperatures.

The resulting three-phase field of β-(Ta-Hf) + β'-(Ta, Hf) + α-Hf-ss, mentioned above, is terminated in a critical tie line at 1070°C due to the eutectoid decomposition of the β'-phase in the metal binary system; the two-phase equilibrium β-(Ta, Hf) + α-Hf-ss results from this reaction at lower temperatures.

Using the isothermal sections (Figures 58 through 70), an isometric view of the partial ternary system was constructed for temperatures above 1000°C (Figure 1). The three-dimensional space model is supplemented by an isopleth at ~33 atomic percent nitrogen, exhibiting the principal phase equilibria in the metal-rich portion of the system (Figure 2).

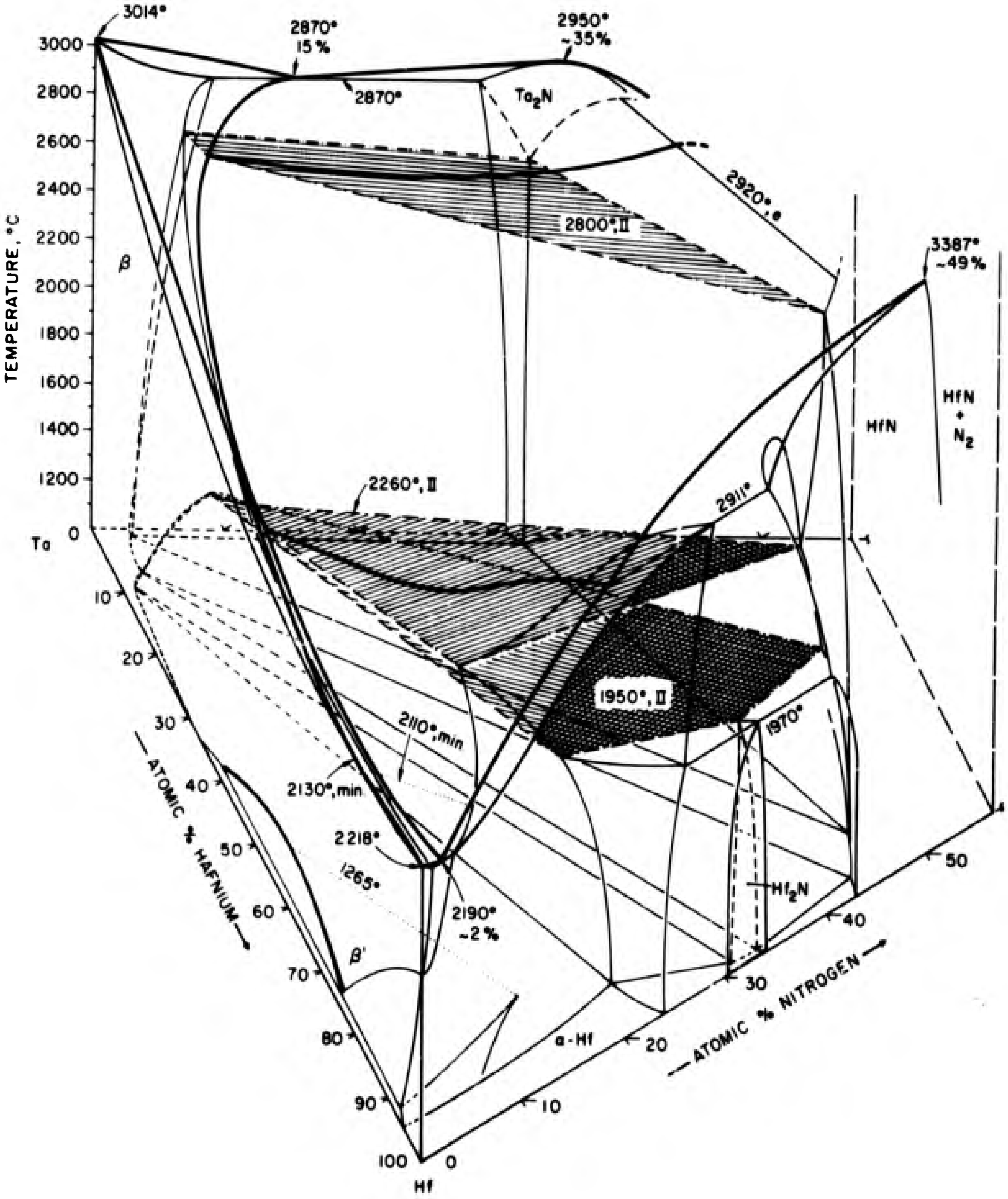

Figure 1. Hf-Ta-N: Partial Isometric View

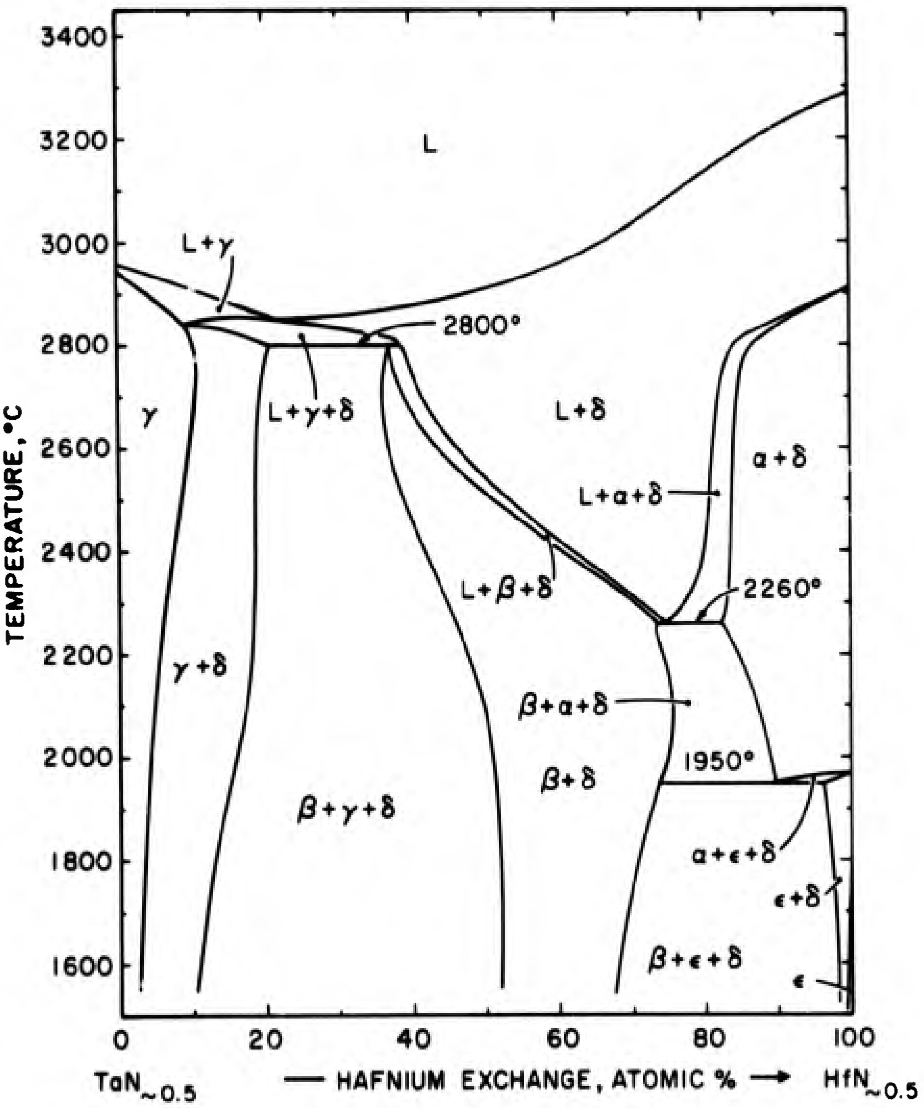

Figure 2. Hf-Ta-N: Isopleth at ~33 At.% Nitrogen

II. LITERATURE REVIEW

A. BINARY SYSTEMS

1. The Tantalum-Hafnium System

A tentative phase diagram for the tantalum-hafnium binary system has been proposed by D. K. Deardorff(3); the solidus curve shows a minimum at about 2100°C and 80 At.% hafnium. The complete series of solid solutions between β-Hf and the BCC form of tantalum existing at high temperatures is interrupted by the formation of a miscibility gap at about 1500°C between the two body centered cubic structures; the miscibility gap is terminated toward lower temperatures by a eutectoid reaction in which the body centered cubic solid solution reacts to a Ta-rich solid solution and the hexagonal α - Hf solid solution at about 1050°C. A somewhat higher critical temperature for the miscibility gap was found by Kato and Copeland(4).

Figure 3 shows a revised diagram of the tantalum-hafnium system by Oden et al(1). In this phase diagram the basic change is a more accurate determination and location of the critical temperature of the body centered cubic miscibility gap.

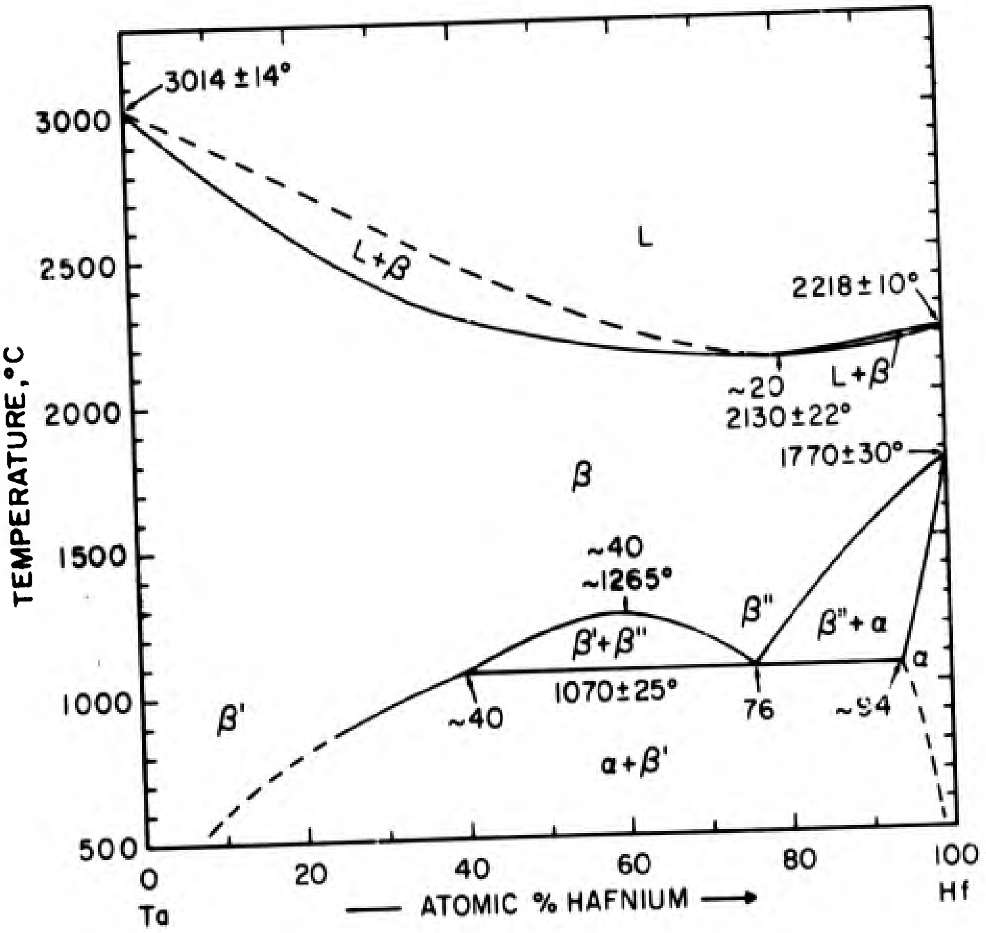

Figure 3. Ta-Hf: Revised Constitution Diagram(1).

2. The Tantalum-Nitrogen System

Some of the first, not precisely defined, tantalum nitrides were prepared by M. A. Joly(5) in 1876 and in 1907 by Muthmann et al (6). Van Arkel(7) determined that the structure of TaN was hexagonal and gave lattice parameters of a = 3.05 and c = 4.94Å. The melting point of TaN was determined at 3360 ± 50°C by C. Agte and K. Moers(8) in 1931. Aschermann, Friederich, Justi, and Kramer,(9) while performing superconductivity experiments, prepared a Ta_2N with lattice parameters of a = 3.06 and c = 4.95Å. Horn and Ziegler(10) prepared a TaN with 50.2 At.% N, but were unable to determine the crystal structure of the complex X-ray pattern. P. Chiotti(11), in agreement with Rundle(12), came to the conclusion that the hexagonal close packed structure for TaN reported by Van Arkel(7) was in reality a Ta_2N compound, and reported, furthermore, that the structure of mononitride is apparently complex; this is in agreement with the result of Aschermann et al(9). In addition, Chiotti stated that the mononitride tends to decompose and reverts to Ta_2N at temperatures near 2000°C. In 1954, N. Schönberg(13) confirmed the close packed hexagonal structure of Ta_2N with the lattice parameters of a = 3.041 - 3.048 and c = 4.907 - 4.918Å, determined a hexagonal structure (D_{6h}^{1}) for the mononitride TaN with lattice parameters of a = 5.185 and c = 2.908Å, and found, in addition, a cubic superlattice structure at about 5 At.% N with a lattice parameter of 10.11Å and a hexagonal phase between 44.4 and 47.4 At.%N with lattice parameters of a = 2.925 - 2.938 and c = 2.876 - 2.883Å. At about the same time (1954) G. Brauer and K. Zapp(14) investigated the crystal structures in the tantalum-nitrogen system and found only three phases: TaN, hexagonal - a = 5.1808, c = 2.9049; kxE; Ta_2N, hexagonal close packed - a = 3.042 and c = 4.909 kxE; and Ta cubic solid solution which contains about 4 At. %N.

E. Gebhardt(15) et al reported finding a tetragonally distorted metallic phase at very low nitrogen contents. In studies on the solubility of nitrogen in tantalum, A. Vaughan(16) et al gave the following results: 3.7 At.% at 1500°C, 2.75 At.% at 1000°C and 2.5 At.% at 500°C; in addition, these authors found a phase near the tantalum solid solution boundary which confirmed N. Schönberg's(13) description of a superlattice near the tantalum solid solution. D. P. Seraphim(17) et al have also confirmed the superlattice structure in the range of 0.1 - 4 At.% nitrogen with a lattice constant of 10.1Å; they also report that the appearance or chance of this superstructure is dependent on the thermal history of the sample. Recently, G. Brauer, J. Weidlein and J. Strahle(18) have reported finding a thermally unstable nitride Ta_3N_5 which has a tetragonal unit cell and lattice parameters of $a = 10.264$ and $c = 3.893$Å.

Table I lists the ascertained Ta-N phases and their crystal structures with lattice parameters.

TABLE I - Ascertained Tantalum-Nitrogen Phases with Crystal Structures and Lattice Parameters

Phase	Crystal Structure	Lattice Parameter	Literature
$Ta_{27}N$	Cubic Superlattice to BCC	10.14Å	13, 16, 17
Ta_2N	Hexagonal Close Packed	$a = 3.042$ $c = 4.909$kx	11, 12, 13, 14
TaN	Hexagonal - $T_{6}{}^{1}_{h}$	$a = 5.185$ $c = 2.908$Å	13, 14

To date, there has been no published constitution diagram of the Tantalum-Nitrogen system.

3. The Hafnium-Nitrogen System

Hafnium mononitride had been prepared by several investigators(19, 20, 21); F. Glaser et al(22) prepared a HfN and reported a lattice parameter of 4.52 ± 02Å for this phase with a cubic B-1 type structure.

H. Nowotny(23) et al presented a proposed phase diagram (not available) of the Hf-N system which was quite similar to the Hf-C system. In 1961 E. Rudy and F. Benesovsky(24), in addition to finding a mononitride with a defect nitrogen structure (B-1, cubic), found a phase of the approximate composition "Hf_2N" which appeared to have metastable character; the crystal structure of this compound was not able to be determined. In addition, they reported that at 1700°C, the solubility of nitrogen in α-Hf is about 29 At.%; also the α-β transformation temperature of hafnium is raised by nitrogen additions. A homogeneous range for the HfN_{1-x} solid solution from about 42 to 52 At.% nitrogen where the lattice parameters vary from 4.52_4 to about 4.51_5Å with increasing nitrogen content was given. Recently, M.E. Straumanis and C. A. Faunce(25) have indicated that HfN is of stoichiometric composition with a lattice parameter of 4.5118Å; furthermore, these authors indicate that hafnium nitride has vacancies in both of the sublattices.

B. TERNARY SYSTEM

1. The Hafnium-Tantalum-Nitrogen System

H. Nowotny, F. Benesovsky, and E. Rudy(26) investigated the solid solution of HfN-TaN and found that HfN takes about 75 Mol. % TaN into solution in the cubic (B-1) crystal structure.

III. EXPERIMENTAL PROCEDURES

A. STARTING MATERIALS AND PREPARATION OF MASTER ALLOYS

1. Starting Materials

The elemental powders of tantalum and hafnium, as well as specially prepared master alloys of Ta-N and HfN, served as the starting materials for the preparation of the experimental alloys.

a. 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 Kα Debye-Scherrer X-ray powder of this material was measured and yielded a lattice parameter of 3.304Å .

b. Hafnium

The hafnium metal powder used was purchased from the Wah Chang Corporation, Albany, Oregon; this powder was sized between 44 and 74 micrometers and had the following major impurities as cited by the vendor (in ppm): Aluminum-<25, Carbon-<40, Niobium-<100, Copper-<40, Iron-<20, Nitrogen-67, Oxygen-620, Silicon-<40, Tantalum-<200, Titanium-<37, Tungsten-<20, sum of all other impurities-<86; the zirconium content of this hafnium was 3.1 Wt.%. A Debye-Scherrer X-ray powder photograph showed only the A-3 type hexagonal structure with lattice parameters of $a = 3.19_5$ and $c = 5.05_6$ Å .

The second batch of hafnium used was hafnium sponge for the preparation of the hafnium nitride starting powder; this hafnium was also purchased from Wah Chang in Albany, Oregon. The material was sized between 10 and 1 mm and had the following major impurities (in ppm): Aluminum-94, Copper-<40, Iron-185, Uranium-100, Magnesium-450, Nitrogen-30, Oxygen-680, Silicon-<40, Titanium-<250, Tungsten-<20, and sum of all other impurities -<66; the zirconium content of this hafnium powder was 2.1 Wt. %.

c. Nitrogen

Nitrogen gas was supplied by the Victor Equipment Company, Sacramento Branch; according to the vendor's analysis, the guaranteed purity was 99.995 Vol. % Nitrogen; the dew point was -90°F, and the maximum impurities by volume were (in ppm): Oxygen-20 and Argon-3; there were also traces of hydrogen, methane, and carbon dioxide present.

2. Master Alloy Preparation

The nitrogen was introduced to the ternary and binary alloys in the form of both hafnium and tantalum nitrides which were made in the following manner:

For the hafnium nitride, hafnium sponge was packed loosely into a tungsten can hung in the middle of a quartz tube sealed at both ends. The quartz tube was supported in the center of an RF induction coil powered by a Leco generator. The glass enclosure was extensively flushed for about an hour with atomic grade helium which was first passed through a titanium sponge getter at about 850°C. With induction heating, the temperature of the hafnium sponge was raised to about 1000°C and nitrogen slowly mixed to the inflowing helium to control the exothermic reaction. When the temperature had stabilized, and a pure flowing nitrogen was established, the temperature was raised to 1500°C and held for four hours. At the end of this first nitriding operation, the hafnium nitride chunks were removed, crushed by hand to approximately 1 mm particle size and reloaded in the tungsten can. The nitriding process described above was repeated. The final product, which was light lemon yellow in color was ground in a carbide ball mill and sieved to a particle size of smaller than 74 micrometers. A Debye-Scherrer X-ray powder photograph of this material showed only the B-1 cubic pattern of the HfN; the lattice parameter measured was 4.51_0 Å. A nitrogen analysis performed by the Aerojet Chemicals and Plastics Testing Division, yielded a total nitrogen content of 7.41 Wt. % or 50.5 At.%.

For the tantalum nitride, the nitriding procedure was the same as for hafnium nitride, with the exception that the final heat treating temperature under nitrogen was held to 1400°C, for there were indications that the TaN phase decomposes at higher temperatures.

The X-ray film of this starting material showed a mixture of the hexagonal TaN phase with sizeable quantities of the subnitride, Ta_2N. For the TaN component the lattice parameters measured were $a = 5.19$ and $c = 2.91$.Å, while for the Ta_2N the lattice parameters were $a = 3.04$, and $c = 4.91_6$ Å. The nitrogen content of this tantalum nitride, by chemical analysis, was 5.25 Wt. % or 41.7 At. %.

B. ALLOY PREPARATION

The majority of the alloys in the ternary and two binary systems were prepared by short duration hot-pressing(27) of the blended powders in graphite dies at temperatures of about 1500°C. After hot-pressing, the graphite-contaminated surface zone was removed by grinding, and the cores of the samples were then used for the melting point and solid state investigations of the systems. Metal-rich alloys were prepared by cold-pressing the powder mixtures followed by an equilibration treatment under a slightly positive pressure of argon.

Two principal equilibration temperatures, 1500°C and 2100°C were selected for the solid state investigations of the systems. The heat treatments were carried out under a 1 atmosphere pressure of high purity argon in a tungsten mesh element furnace manufactured by the R. Brew Company.

Altogether, approximately 134 alloys were prepared for the investigation of the ternary and two binary systems.

C. DETERMINATION OF MELTING TEMPERATURES

The melting temperatures of approximately 104 alloys were measured using the technique devised by M. Pirani and H. Alterthum(28) The temperature of the solid-liquid phase change was measured with a disappearing-filament-type pyrometer aimed at a black body hole located in the center of the bar shaped melting point specimens. The melting point furnace, as well as temperature calibration and correction procedures, have been described in previous reports(27, 29) published by this laboratory and hence need not be treated at length here.

Figure 4 shows the location of the melting point samples in both the ternary and two binary systems. The melting temperatures of the binary Ta-N alloys as well as ternary alloys containing 15 to 20 atomic percent hafnium were measured under a slightly positive pressure of nitrogen. The remaining melting point samples were run under a protective atmosphere of high purity argon at a pressure of ~2 atmospheres.

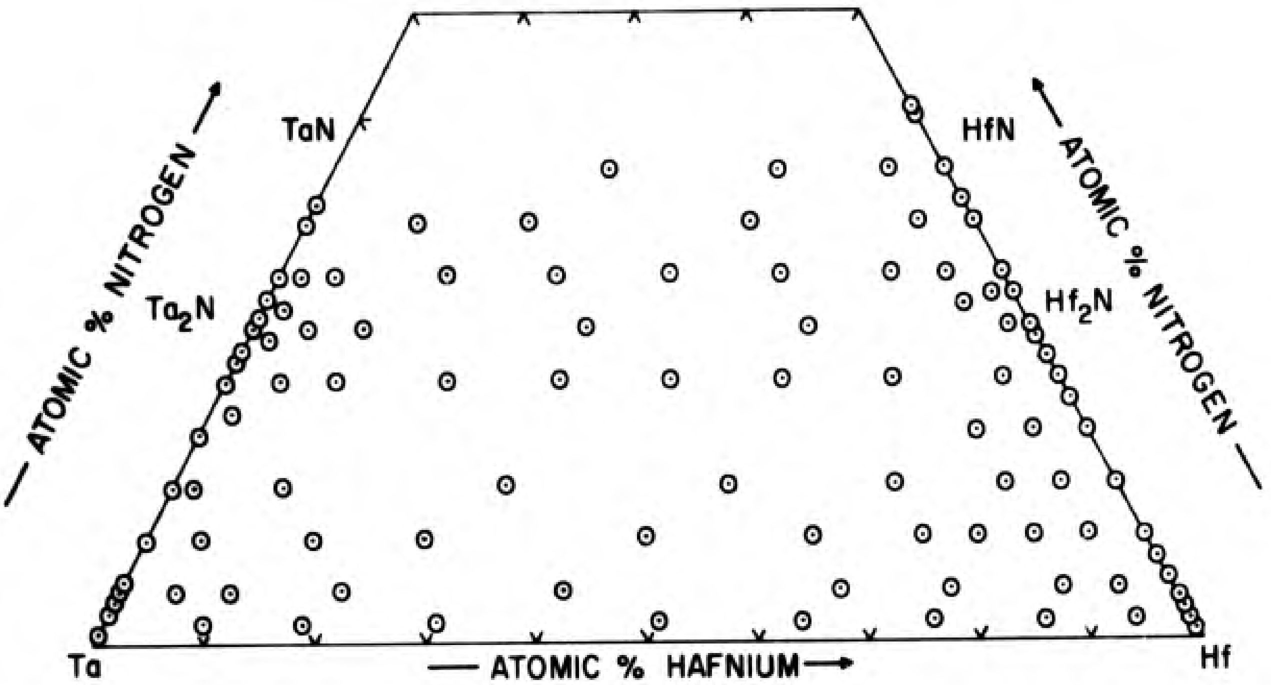

Figure 4. Ta-Hf-N: Compositions of Melting Point Samples.

D. DIFFERENTIAL THERMAL ANALYSIS

Differential thermoanalytical studies(27, 30) were carried out on 18 ternary alloys and 11 binary alloys from the Hf-N system. Figure 5 shows the sample locations of the alloys which were investigated. Graphite sample containers with tantalum inserts placed between the sample compacts and graphite were used in all experiments. The D.T.A. runs were performed under a high purity argon atmosphere.

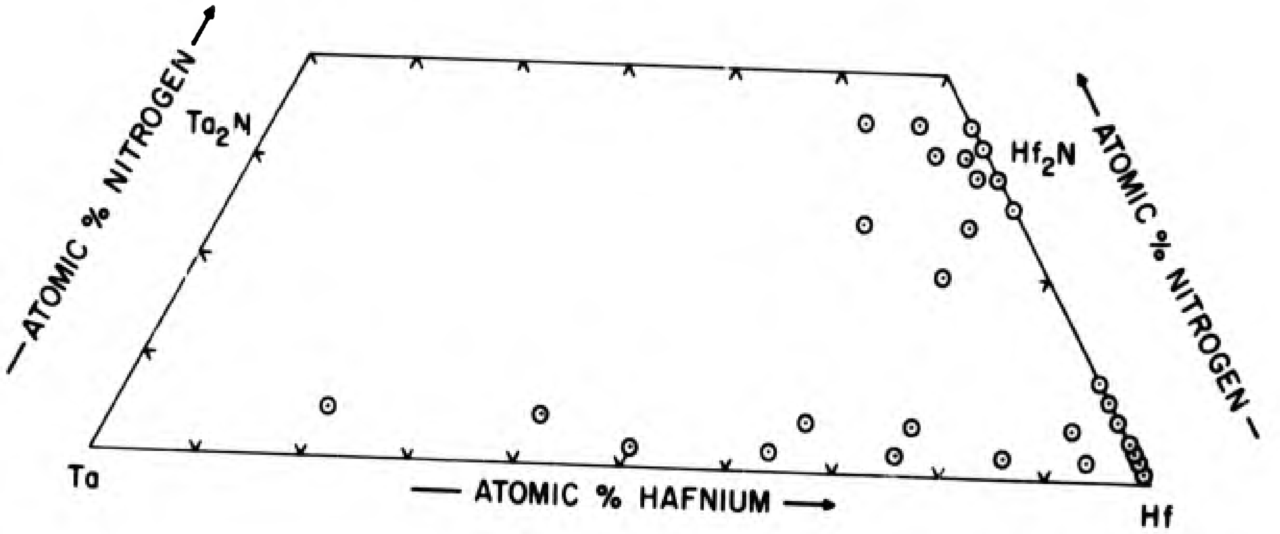

Figure 5. Ta-Hf-N: Compositions of DTA-Samples.

E. X-RAY ANALYSIS

Debye-Scherrer X-ray powder diffraction patterns using Cu-Kα radiation were made of all melting point, heat treated, and D.T.A. samples. The film strips were measured on a Siemens-Kirem coincidence scale with micrometer (0.01mm scale divisions) attachment. All crystal structures were known from previous work, except for the subnitride phase Hf_2N.

All film exposures were evaluated with respect to the nature of the phases present; the lattice parameters were measured to determine the compositions of the coexisting phases in the various two-phase fields, as well as to locate the boundary tie lines of the three-phase equilibria occurring in the system.

F. METALLOGRAPHY

The microscopic examination of melting point as well as heat treated alloys, made on a Zeiss Ultraphot II microscope, were used to locate the eutectic trough and homogeneity boundaries of the phases. For the metallographic studies, the specimens were mounted in a mixture of diallyl-phthalate-lucite coated copper powder and ground on varying grit sizes of silicon carbide paper. The final polishing was performed on a microcloth using a slurry of 0.3 micrometer alumina in a 5% chromic acid solution.

Etchants and etching procedures varied with the metal and nitrogen concentrations of the alloys. For tantalum alloys with nitrogen concentrations <40 At.% and hafnium concentrations <40 At.% the alloys were electroetched in a solution of 30 parts lactic acid, 10 parts HNO_3, 10 parts HF, and 50 parts H_2O. Hafnium alloys, with nitrogen concentrations <35 At.%, were electroetched in a 10% oxalic acid solution. For alloys in the range of the hafnium mononitride solid solution, the samples were dip-etched in a dilute aqueous solution of aqua regia and hydrofluoric acid (60% HCl, 20% HNO_3, 20% HF). A concentrated solution of this acid was used on alloys in the single phase mononitride region.

G. CHEMICAL ANALYSIS

Chemical analysis for nitrogen by a vacuum fusion method was performed on approximately 1/6 of the experimental alloy samples plus the binary nitride master alloys of hafnium and tantalum. No metal analyses were performed since the relative metal concentrations were assumed not to change significantly during the various treatments.

In general, it was found that the analyzed sample nitrogen content agreed to within two to three atomic percent of the nominal compositions. The analyses also showed that samples exposed to high temperatures during either arc melting or at high temperature equilibration, in particular those samples containing large amounts of nitrogen, showed nitrogen losses as great as 15 to 20 atomic percent. These results were supported by the X-ray findings and were taken into account during the interpretation of the experimental results.

IV. RESULTS

A detailed description of the phase equilibria in the tantalum-hafnium-nitrogen system will be covered in this section. Because of the lack of literature data covering the two metal-nitrogen binary systems of tantalum and hafnium, these systems were also investigated. The first two portions of this section will partially cover these investigations, and data not presented here will be included in the description of the ternary system.

A. TANTALUM-NITROGEN SYSTEM

The partial constitution diagram of the binary tantalum-nitrogen system is presented in Figure 6. This figure gives a summary of the melting temperatures and qualitative X-ray evaluation of solid state alloys used in the present investigation.

The solidus temperature of tantalum is lowered by the addition of nitrogen to the Ta-Ta_2N eutectic temperature of 2870°C. The melting of alloys with nitrogen concentrations up to the congruent melting subnitride phase was fairly sharp; this behavior indicates a rather narrow two-phase field of solid plus liquid on either side of the tantalum-tantalum subnitride eutectic at 15 atomic percent nitrogen.

The maximum solubility of nitrogen in tantalum was determined by means of metallographic inspection and X-ray evaluation of alloys quenched from melting. Figure 7 shows the lattice parameter variation of the cubic tantalum solid solution up to its maximum nitrogen solubility of approximately 9 atomic percent (a = 3.303 to 3.326Å at 9 At.% N).

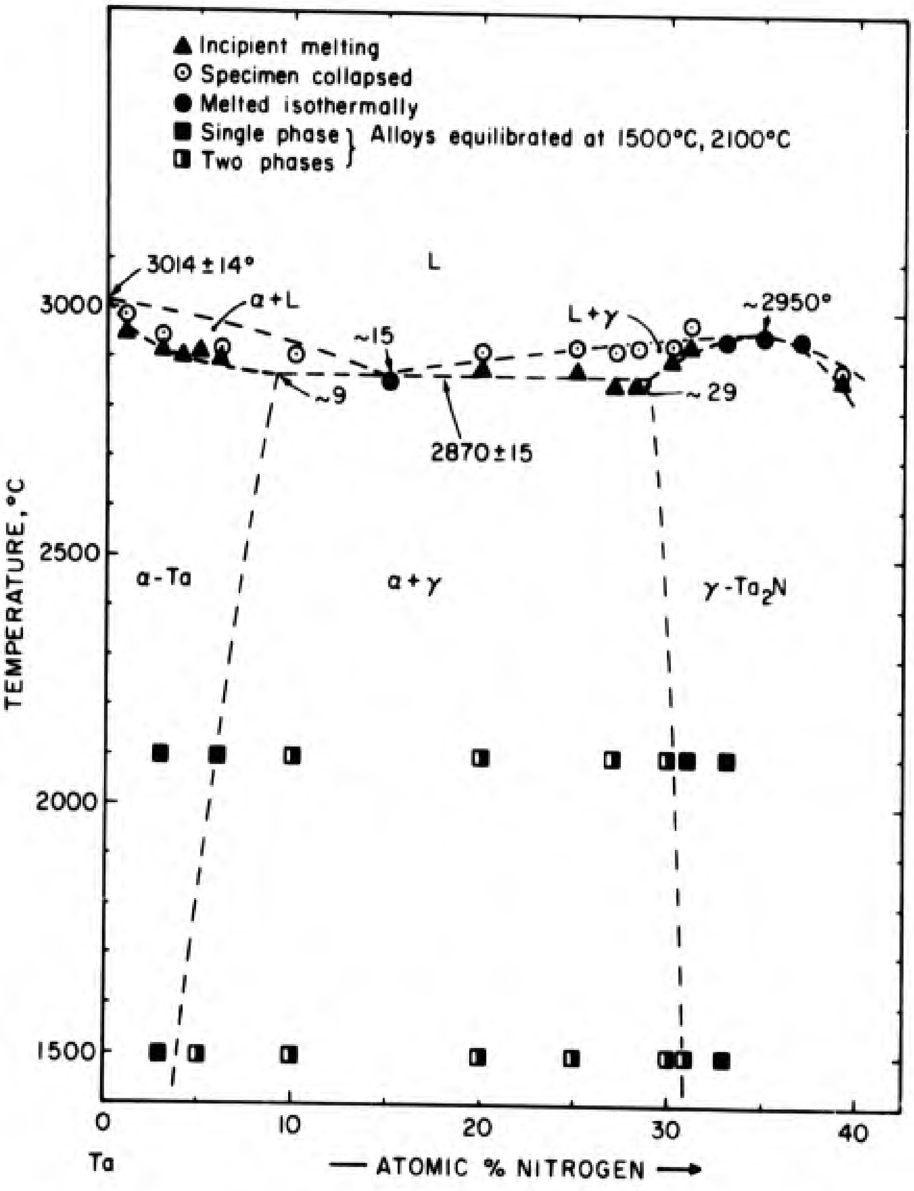

Figure 6. Ta-N: Partial Constitution Diagram, Melting Temperatures and Qualitative X-ray Evaluated Alloys for the Investigation of the Solid State Portion of the System.

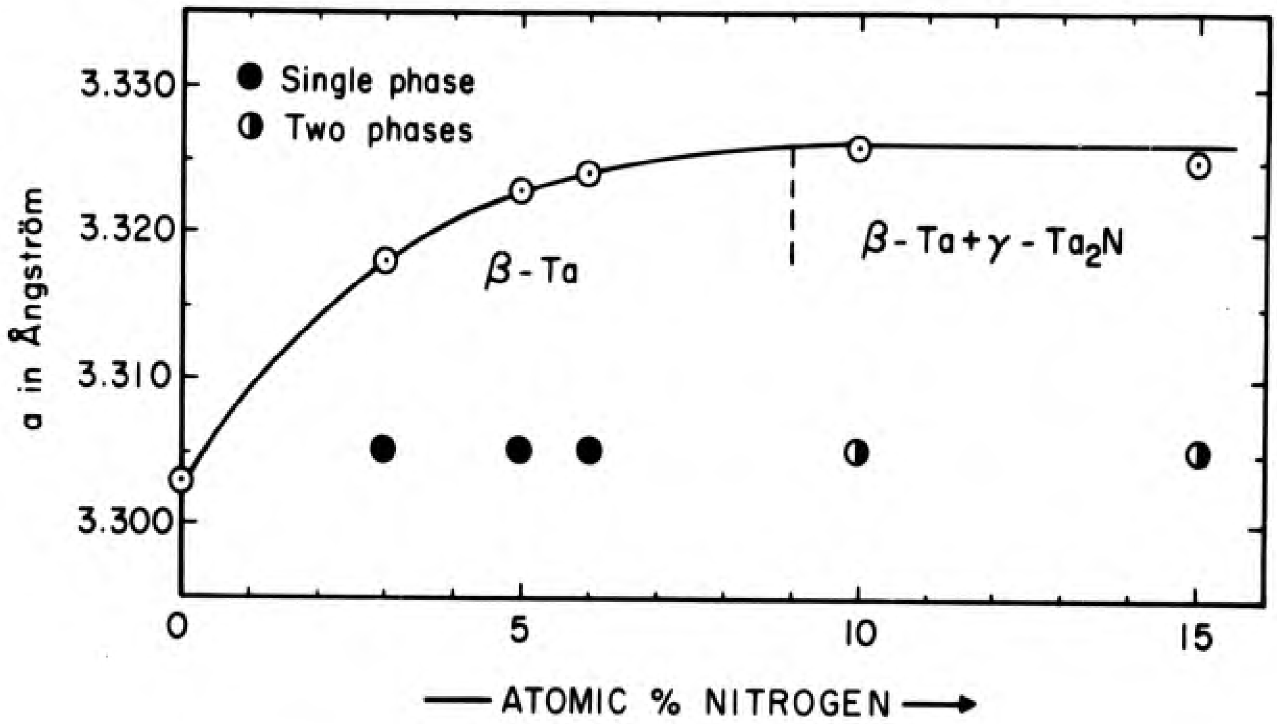

Figure 7. Ta-N: Lattice Parameter Variation of β-Ta Solid Solution. Alloys Quenched from Melting.

A typical photomicrograph showing the precipitation reaction of the subnitride phase from the tantalum solid solution is presented in Figure 8. The subnitride precipitates within the metal grains show a more or less random orientation and tend to agglomerate at the metal grain boundaries. The next photomicrograph (Figure 9) of an alloy with 15 atomic percent nitrogen exhibits the metal matrix type eutectic structure found in this system.

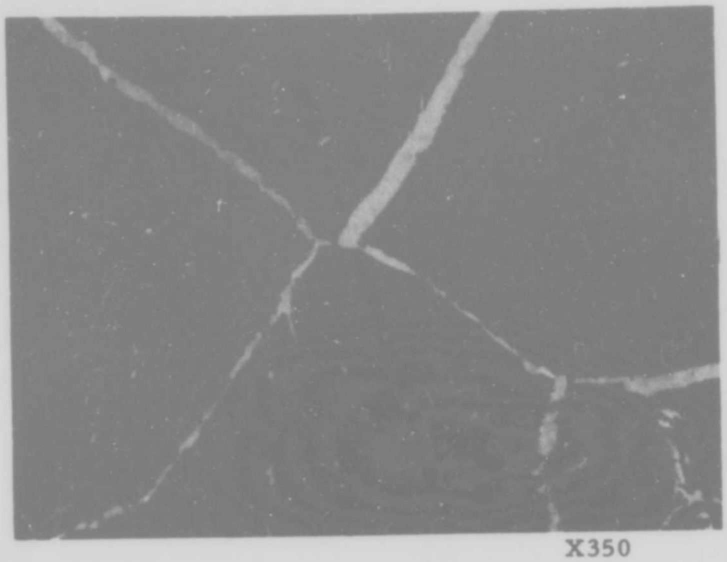

Figure 8. Ta-N (90-10 At.%) Melting Point Sample Quenched from 2910°C and Equilibrated at 1500°C.

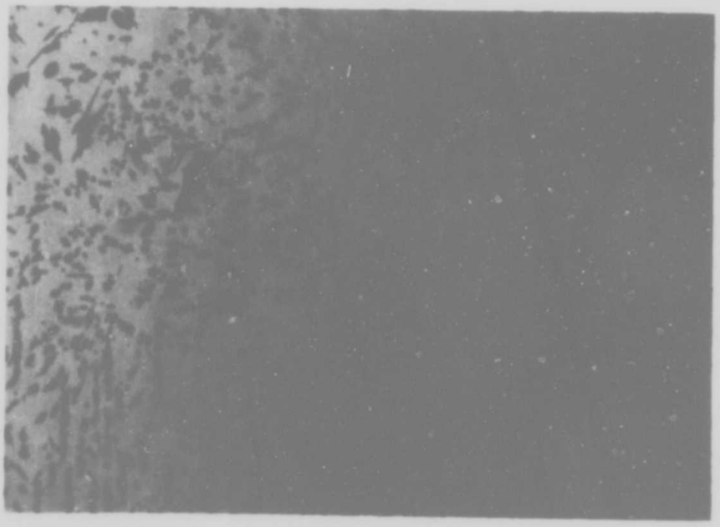

Figure 9. Ta-N (85-15 At.%) Melting Point Sample Quenched from 2860°C. Polarized Light X270

Trace of Primary Ta_2N in $Ta+Ta_2N$ Eutectic Matrix.

Hypereutectic alloys with nitrogen concentrations increasing up to the metal-rich boundary of the Ta_2N-phase show varying amounts of the primary subnitride phase in a Ta + Ta_2N-depleted eutectic matrix (Figures 10 thru 12). The metal-rich homogeneity limit of the subnitride phase at the eutectic temperature is located at approximately 29 atomic percent nitrogen as shown in Figure 12. Alloys with nitrogen concentrations greater than 29 atomic percent exhibited the single phase Ta_2N structure (Figure 13).

As was previously mentioned in the literature review of the tantalum-nitrogen binary system, four different investigations (13, 15, 16, 17) of the solid state portion of this system revealed the presence of a tantalum-nitrogen phase in the range of 0.1 to 4 At.% nitrogen. Alloys prepared in the present investigation at this low nitrogen concentration did not reveal the presence of this phase. The absence of the phase was probably due to the manner in which the alloys were prepared as reported by D. P. Seraphim et al. (17).

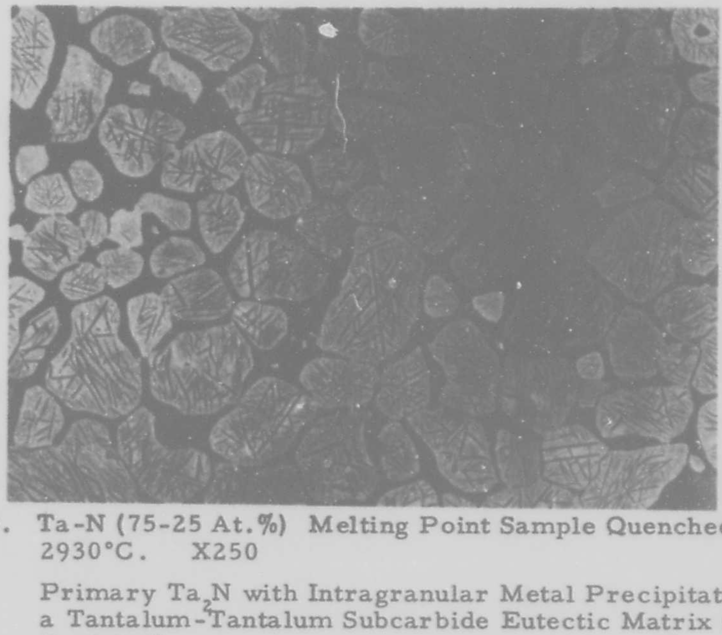

Figure 10. Ta-N (75-25 At.%) Melting Point Sample Quenched from 2930°C. X250

Primary Ta_2N with Intragranular Metal Precipitations in a Tantalum-Tantalum Subcarbide Eutectic Matrix (Ta_2N-Depleted).

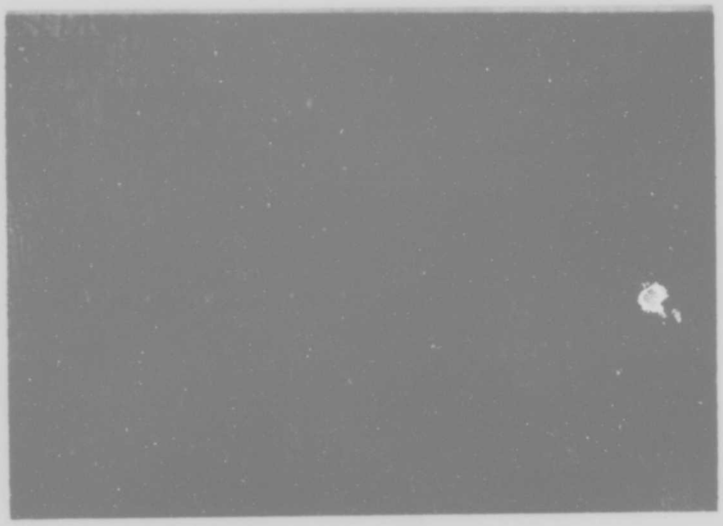

Figure 11. Ta-N (71-29 At.%) Melting Point Sample Quenched from 2930°C. X220

Tantalum Subnitride with Intragranular Metal Precipitates with Traces of Tantalum-Tantalum Subnitride Depleted Eutectic at the Grain Boundaries.

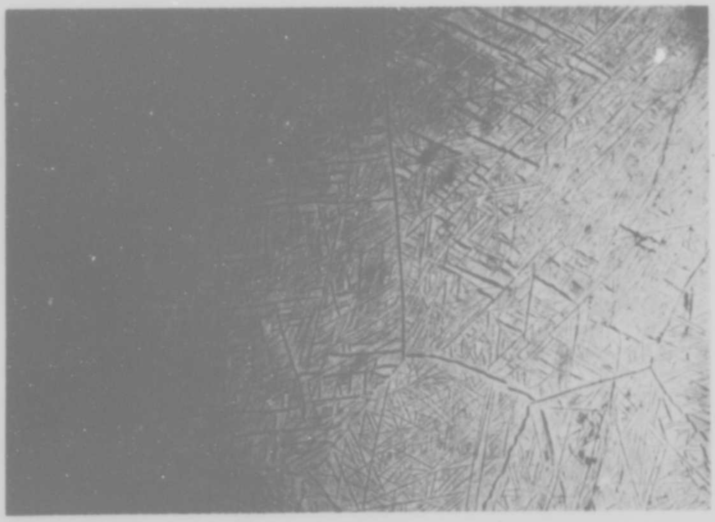

Figure 12. Ta-N (71-29 At.%) Melting Point Sample Quenched from 2930°C. X220

Originally Single Phased Tantalum Subnitride. Intragranular Tantalum Precipitated During Cooling.

Figure 13. Ta-N (65-35 At.%), Melting Point Sample Quenched from 2955°C. X1000

Single Phase Ta_2N

The maximum analyzed nitrogen concentration in both melting point and heat-treated alloys was found to be 39 atomic percent nitrogen. At this concentration, the appearance of the tantalum mononitride phase was not detected by either metallography or X-ray analysis of melting point and heat treated alloys.

B. HAFNIUM-NITROGEN SYSTEM

The proposed constitution diagram of the binary system hafnium-nitrogen is presented in Figure 14.

In order to study the effect of nitrogen on the α-β transformation in hafnium, D.T.A. runs were made, as shown in Figure 15, on samples containing 1, 2 and 3 atomic percent nitrogen. With increasing nitrogen content, the onset of the α-β transformation on both the heating and cooling cycles is shifted to higher temperatures. At a nitrogen concentration of 3 atomic percent, the reaction has almost disappeared; in D.T.A. runs made on alloys with nitrogen concentrations of 4, 6, 8 and 10 At.% N, no heat-effects associated with this transformation could be detected.

The formation of a eutectic between the α and β modifications of hafnium was established by means of melting point determinations and D.T.A. runs on metal-rich alloys (<10 At % N). The melting temperatures of these alloys are summarized in Figure 14. Above the eutectic temperature of 2190°C, the α-Hf solid solution is stabilized to a temperature of 2911°C and 28 At.% N where it melts peritectically to form liquid plus hafnium mononitride.

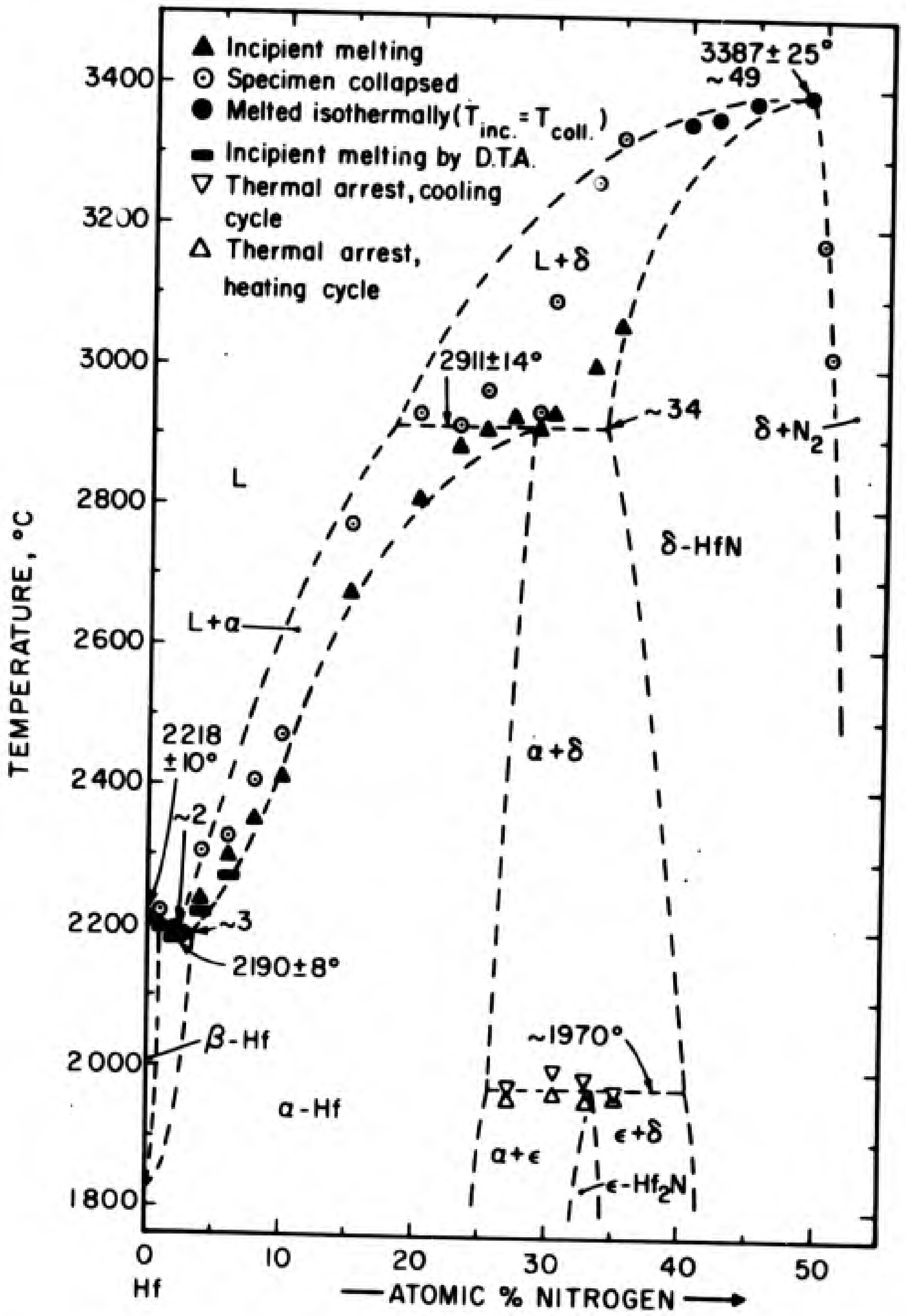

Figure 14. Hf-N: Proposed Constitution Diagram. Experimental Melting Points and Solid State Reactions Included.

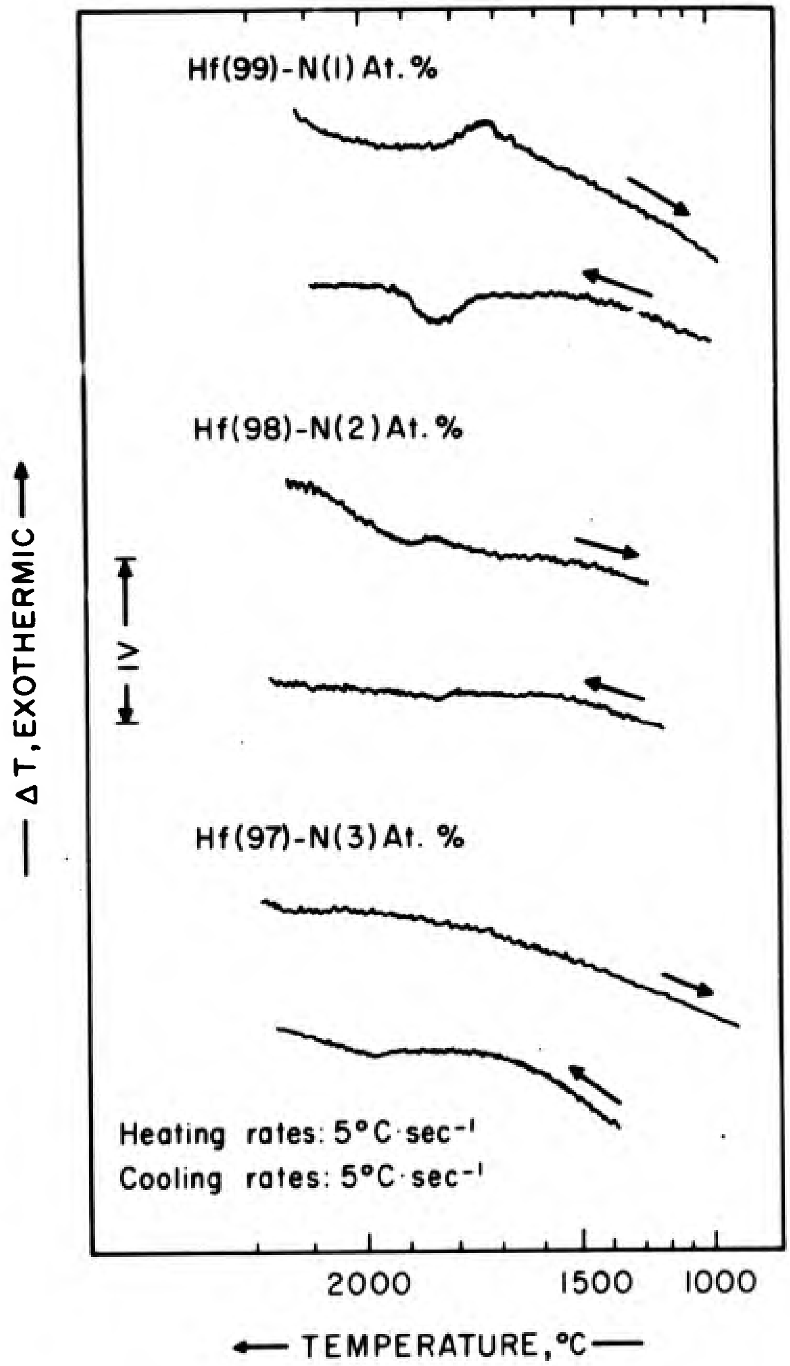

Figure 15. Hf-N: D.T.A. Thermograms (Heating and Cooling) Showing the α-β-Hf Transformation.

The metallographic and X-ray analysis of alloys in the concentration range of 4 to 35 atomic percent nitrogen show that the solid solubility of nitrogen in hafnium is not strongly temperature dependent. The maximum solubility of nitrogen in hafnium at 2100°C is ~ 25.5 At.% as shown by the lattice parameter variations of the hexagonal hafnium solid solution in Figure 16 (a = 3.211Å ; c = 5.105Å at 4 At.% N to a = 3.217Å ; c = 5.150Å at 25.5 At. % N).

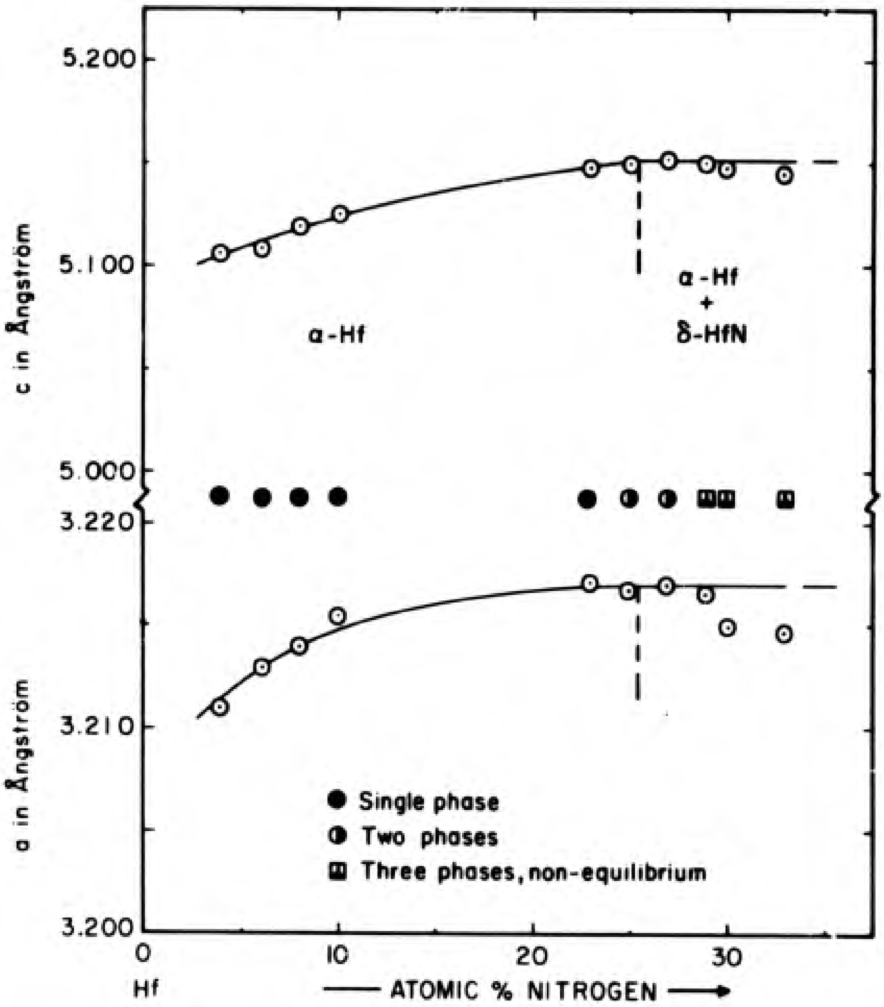

Figure 16. Hf-N: Lattice Parameter Variations of the Hexagonal α-Hf Solid Solution. Alloys Equilibrated at 2100°C.

A photomicrograph of a melting point alloy (Figure 17) at 23 At.% N quenched from 2915°C, shows only the single phase α-Hf-ss. The metallographic examination of alloys which participated in the peritectic reaction at 2911°C showed only the primary phase of hafnium mononitride containing either metal or subnitride precipitates, but in no samples were mononitride precipitates noticed in the hafnium phase (Figures 18 and 19).

Figure 17. Hf-N: (77-23 At.%), Melting Point Sample Quenched from 2915°C. X800

Single Phase α-Hf-ss. Cracks within α-Grains Resulted During Rapid Quenching.

Figure 18. Hf-N: (71-29 At.%), Melting Point Sample Quenched from 2940°C. X300

Primary Hafnium Mononitride with Metal Precipitation and Traces of ϵ-Hf_2N in a Matrix of α-Hafnium.

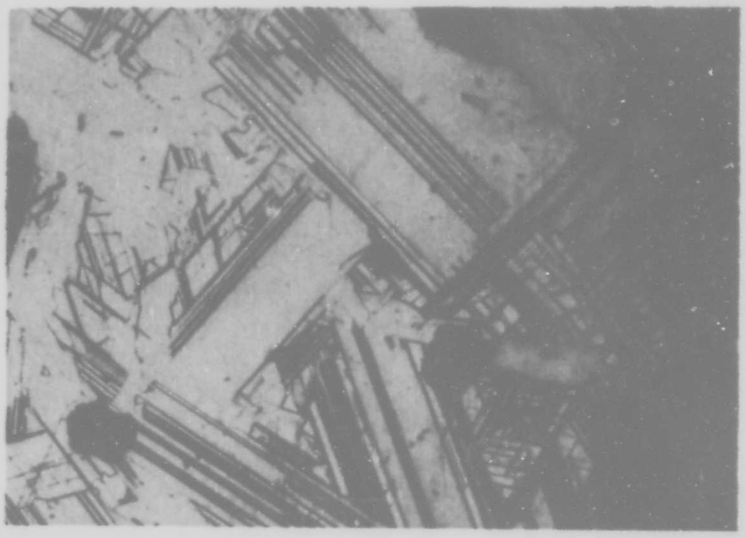

Figure 19. Hf-N: (65-35 At.%), Melting Point Sample Quenched from 3330°C.

δ-HfN_{1-x} Containing Precipitation Structure of ϵ-Hf_2N Plus Traces of α-Hf. (Pores-Black)

The subnitride phase of hafnium forms in a peritectoid reaction from the α-Hf-ss and δ-HfN_{1-x} phases at a temperature of ∼1970°C. Figure 14 shows the reaction onset during the heating and cooling cycles of the D.T.A. runs; D.T.A. thermograms of alloys participating in the reaction are presented in the next section on the ternary tantalum-hafnium-nitrogen system (Figure 33). Photomicrographs (Figures 20 thru 23) of alloys equilibrated at 1500°C in the concentration range of 26 to 42 atomic percent nitrogen show the phase equilibria resulting from the presence of the subnitride phase, i.e. two phases: α-Hf-ss + ε-Hf_2N, single phase: ε-Hf_2N, and two phases: ε-Hf_2N + δ-HfN_{1-x}. The peritectoid formation of the subnitride phase proceeds at a rapid rate; for from both melting point and heat treated alloys quenched from temperatures above 1970°C, the subnitride phase was always formed.

No attempt was made to classify the crystal structure type of the subnitride phase; from a qualitative evaluation of x-ray films exhibiting the Hf_2N phase, the diffraction patterns contained lines which could be indexed to those belonging to both the hexagonal hafnium and cubic (B-1) hafnium mononitride phases plus many additional lines.

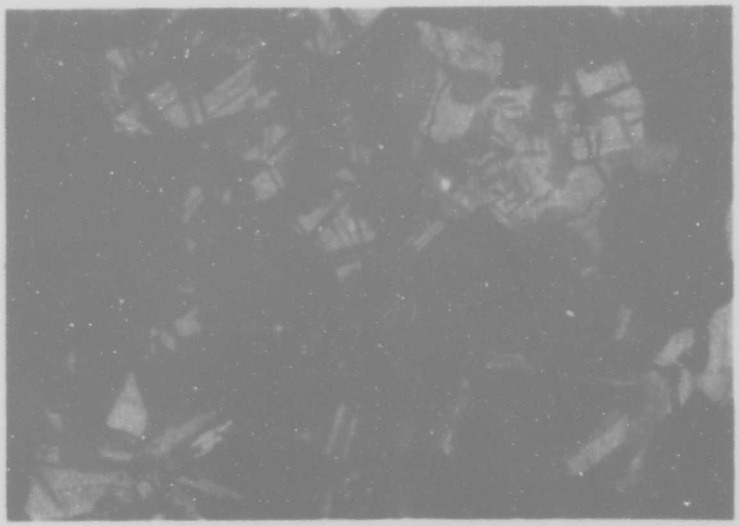

Figure 20. **Hf-N: (73-27 At.%), Melting Point Sample Quenched from 2930°C and Equilibrated at 1500°C. X350**

α-Hf-ss plus Precipitation Structure of ε-Hf_2N.

Figure 21. **Hf-N: (67-33 At.%), Melting Point Sample Quenched** from 3260°C and Heat Treated at 1500°C for 30 hrs. X600

Originally Single Phased Hafnium Mononitride showing Precipitation Structure of ε-Hf_2N.

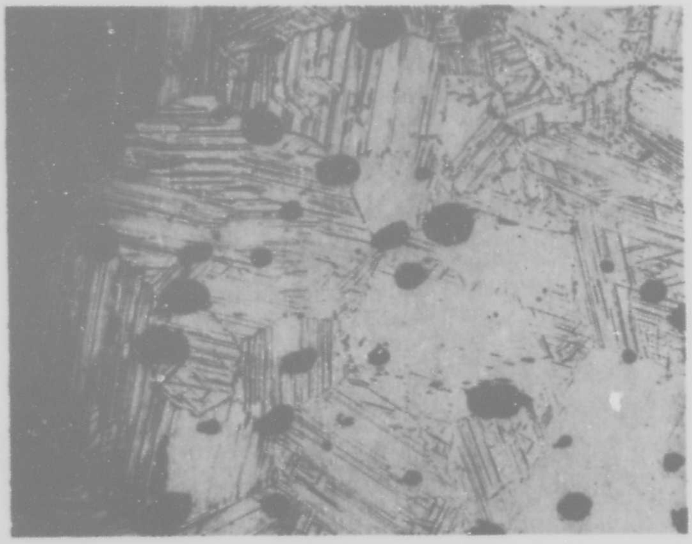

Figure 22. Hf-N: (60-40 At.%), Melting Point Sample Quenched from 3350°C and Equilibrated at 1500°C. X160

δ-HfN_{1-x} Plus Precipitation Structure of ϵ-Hf_2N. (Pores-Black)

The lower solubility limit of the hafnium mononitride phase at 1500°C is located at 43 atomic percent nitrogen (Figure 23); its metal-rich homogeneity limit shifts to lower nitrogen concentrations at higher temperatures: 40 At.% N at 2100°C and ~34 At.% N at 2911°C.

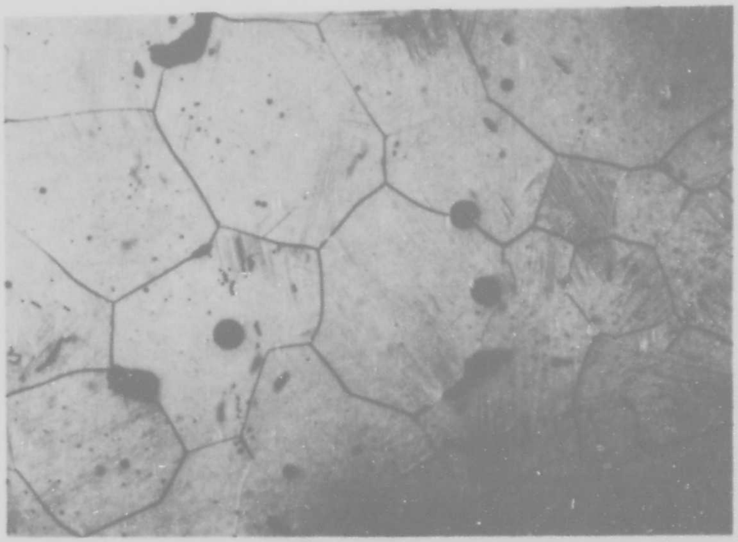

Figure 23. Hf-N: (58-42 At. %), Melting Point Sample Quenched from 3380°C and Equilibrated at 1500°C. X270

δ-HfN$_{1-x}$ Grains Plus Trace of ε-Hf$_2$N. (Pores-Black)

Above the peritectic decomposition temperature of the α-Hf-ss, the solidus temperatures of the hafnium mononitride phase increase rapidly with increasing nitrogen concentration (Figure 14). The δ-HfN$_{1-x}$ phase was found to melt congruently at a temperature of 3387°C at 49 atomic percent nitrogen. At nitrogen contents above the maximum melting composition, the solidus temperatures decrease rapidly, and no melt was observed in the melting point samples with nitrogen concentrations >49 At.%; nitrogen was apparently lost by dissociation. Figures 24 and 25 show photomicrographs of Hf-N alloys located in the single phase mononitride region which were quenched from melting.

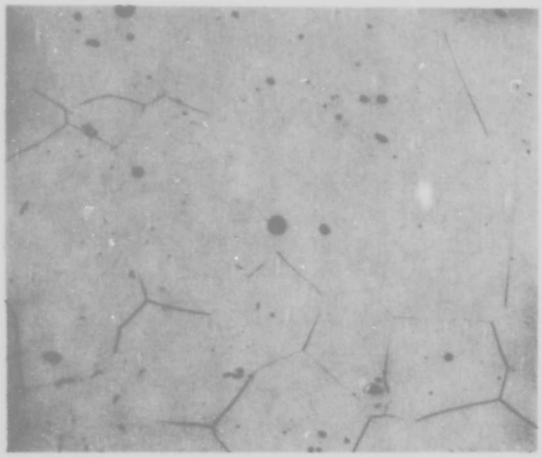

Figure 24. Hf-N: (55-45 At.%), Melting Point Sample Quenched from 3385°C. X200

Single Phase δ-HfN_{1-x}.

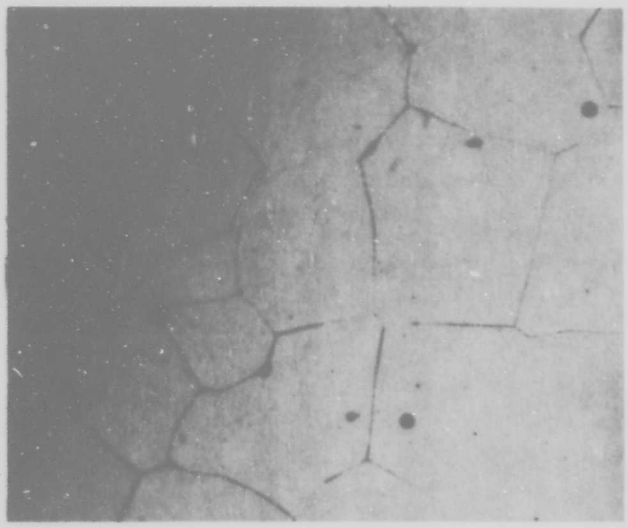

Figure 25. Hf-N: (51-49 At.%), Melting Point Sample Quenched from 3395°C. X400

Single Phase Hafnium Mononitride.

Figure 26 shows the lattice parameter variation of the cubic mononitride phase as a function of the nitrogen concentration at 2100°C. The lattice parameter of the δ-HfN_{1-x} phase in the three-phase non-equilibrium region, hafnium plus hafnium subnitride plus hafnium mononitride, remained constant at a = 4.535Å up to the metal-rich homogeneity limit of the mononitride phase at 40 At.% N. Above this nitrogen concentration in the single phase mononitride region, the lattice parameter dropped to a value of 4.519Å at 50 At.% N. This same lattice parameter variation as a function of the nitrogen content was also observed by E. Rudy et al(24) and M. E. Straumanis et al (25). M. E. Straumanis and C. A. Faunce(25) found by comparing a single phase mononitride sample's X-ray density with its measured density, that the decrease in the lattice parameters of the δ-HfN_{1-x} phase was due to the presence of hafnium atom vacancies in the metal sublattice. No similar comparison was made in the present investigation.

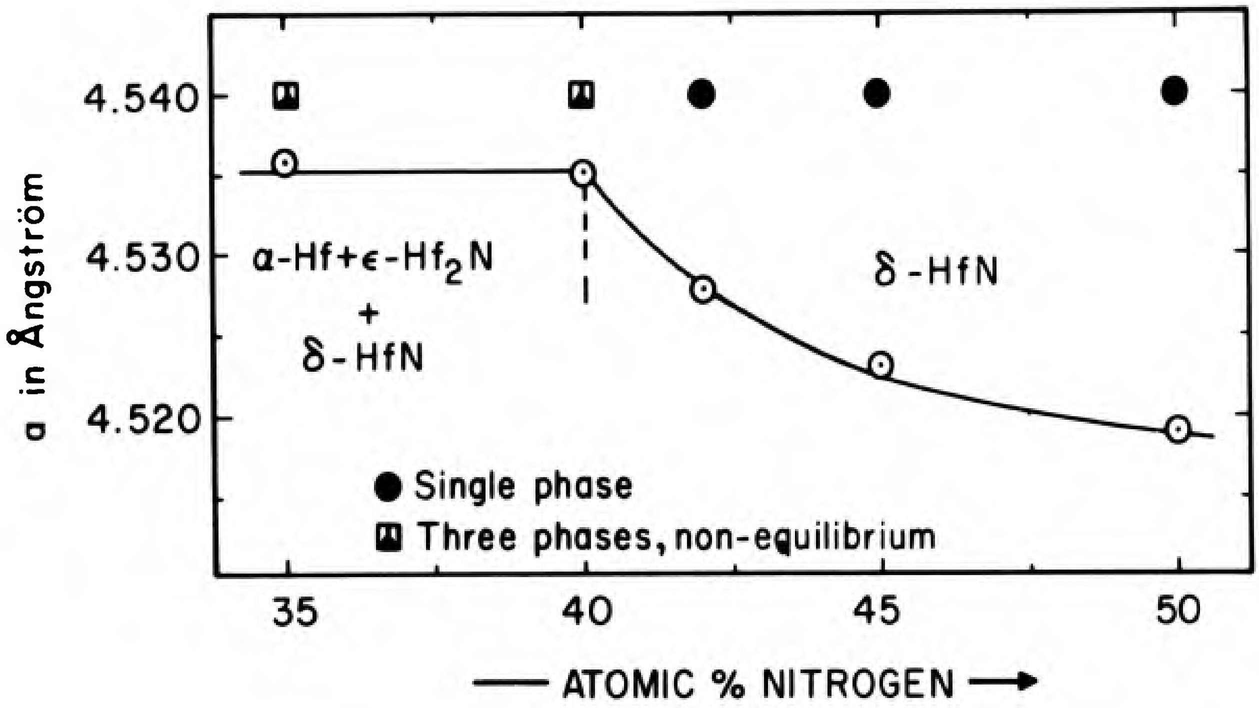

Figure 26. Hf-N: Lattice Parameter Variation of the Cubic Hafnium Mononitride Phase. Alloys Equilibrated at 2100°C.

C. TANTALUM-HAFNIUM-NITROGEN SYSTEM

1. Solid-State Equilibria

The qualitative phase evaluation of both binary and ternary alloys equilibrated at 1500°C and 2100°C resulted in the phase relationships presented in Figures 27 and 28. At 1500°C, the hafnium exchange in γ-Ta_2N (a = 3.041; c = 4.916Å) is approximately 2.9 atomic percent (a = 3.042; c = 4.917Å) and ~6.5 atomic percent at 2100°C (a = 3.053; c = 4.929Å).

The maximum tantalum exchange in the δ-(Hf, Ta)$N_{0.82}$-ss at the mononitride phase boundary of the two-phase field γ-Ta_2N + δ - (Hf, Ta)N_{1-x} is 28.4 atomic percent at 1500°C (a = 4.523 to a = 4.517Å) and 47.5 atomic percent at 2100°C (a = 4.510Å).

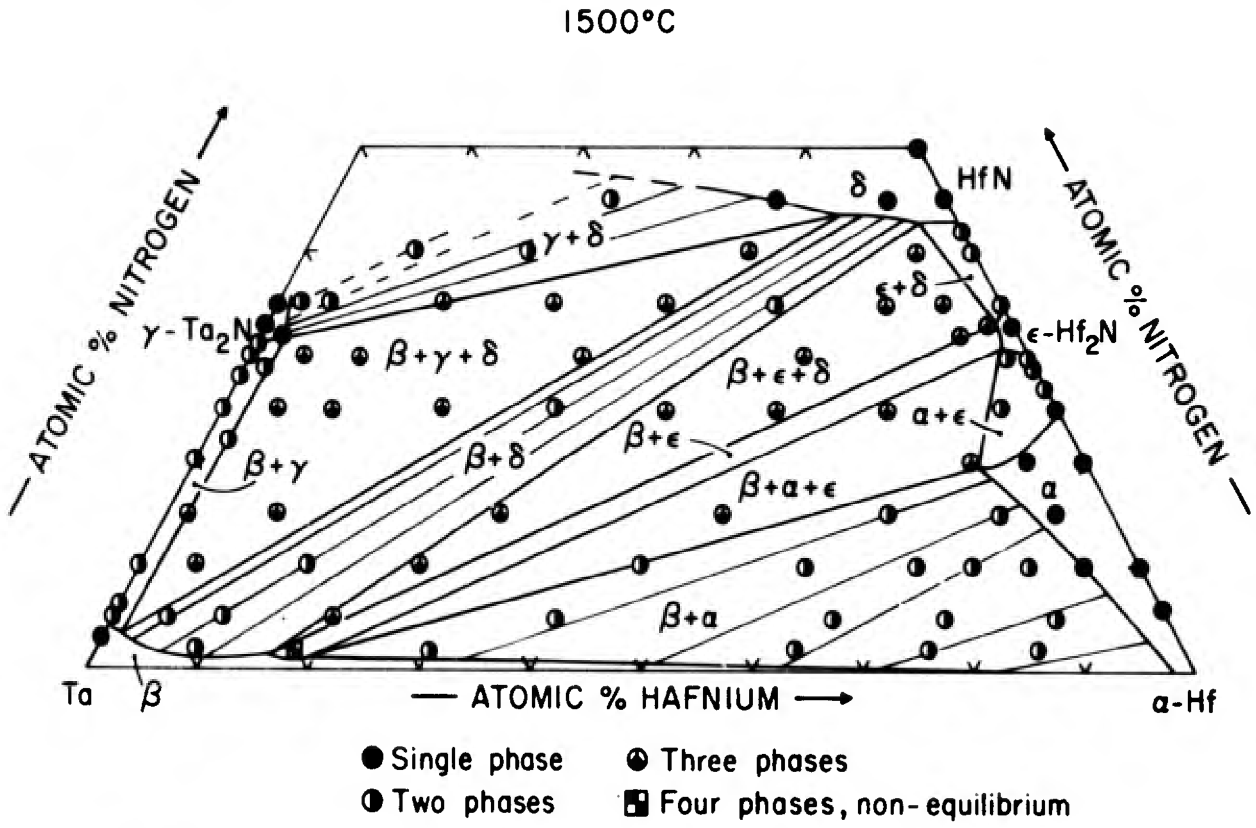

Figure 27. Hf-Ta-N: Qualitative X-ray Evaluation at 1500°C.

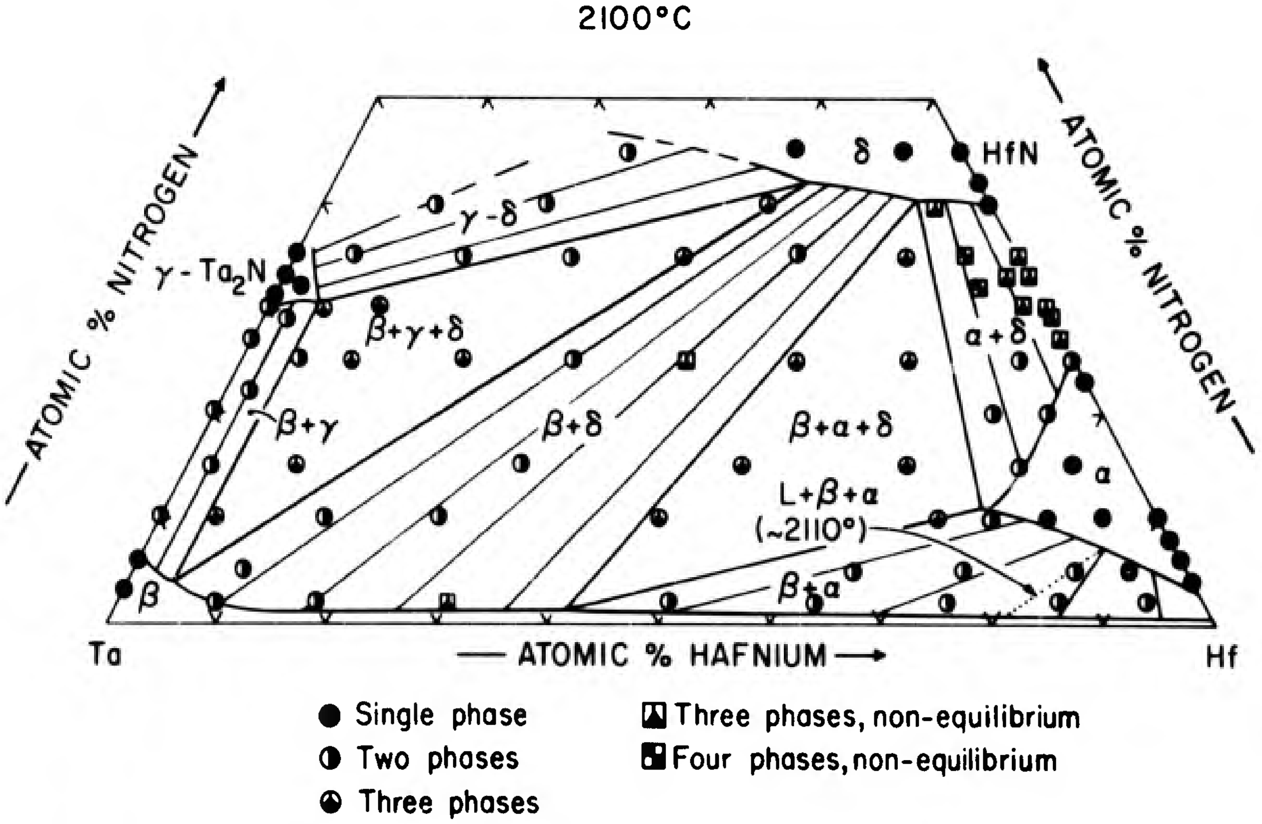

Figure 28. Hf-Ta-N: Qualitative X-ray Evaluation at 2100°C.

Figure 29 shows the lattice parameter variation of the α-Hf-ss as a function of the tantalum exhange at 2100°C. The maximum tantalum exchange at the vertex of the three-phase field α-Hf-ss + β-(Ta,Hf)-ss + δ-(Hf-Ta)N_{1-x} is 16.8 atomic percent (a = 3.198; c = 5.094Å). Below 2100°C, the maximum solubility of tantalum in the α-Hf-ss shifts to higher nitrogen concentrations where at 1500°C and ~20 atomic percent nitrogen, the metal exchange is 12.5 At.% Ta (a = 3.202; c = 5.107Å) at the vertex of the three-phase field α-Hf-ss + β - (Ta,Hf) + ε -Hf_2N).

Below 1500°C, two limiting tie line reactions occur in the ternary system due to the formation of the miscibility gap and the eutectoid decomposition of the β'-phase in the Ta-Hf binary system. The three-phase field: Ta-rich (β)-ss + Hf-rich (β')-ss + α-Hf-ss is formed at temperatures below ~ 1265°C from the two-phase equilibrium β-(Ta,Hf)-ss + α-Hf-ss. At ~1070°C the three-phase field previously mentioned disappears due to the eutectoid decomposition of the Hf-rich (β')-ss phase; the resulting two-phase field of Ta-rich (β)-ss + α-Hf-ss is stable below this temperature.

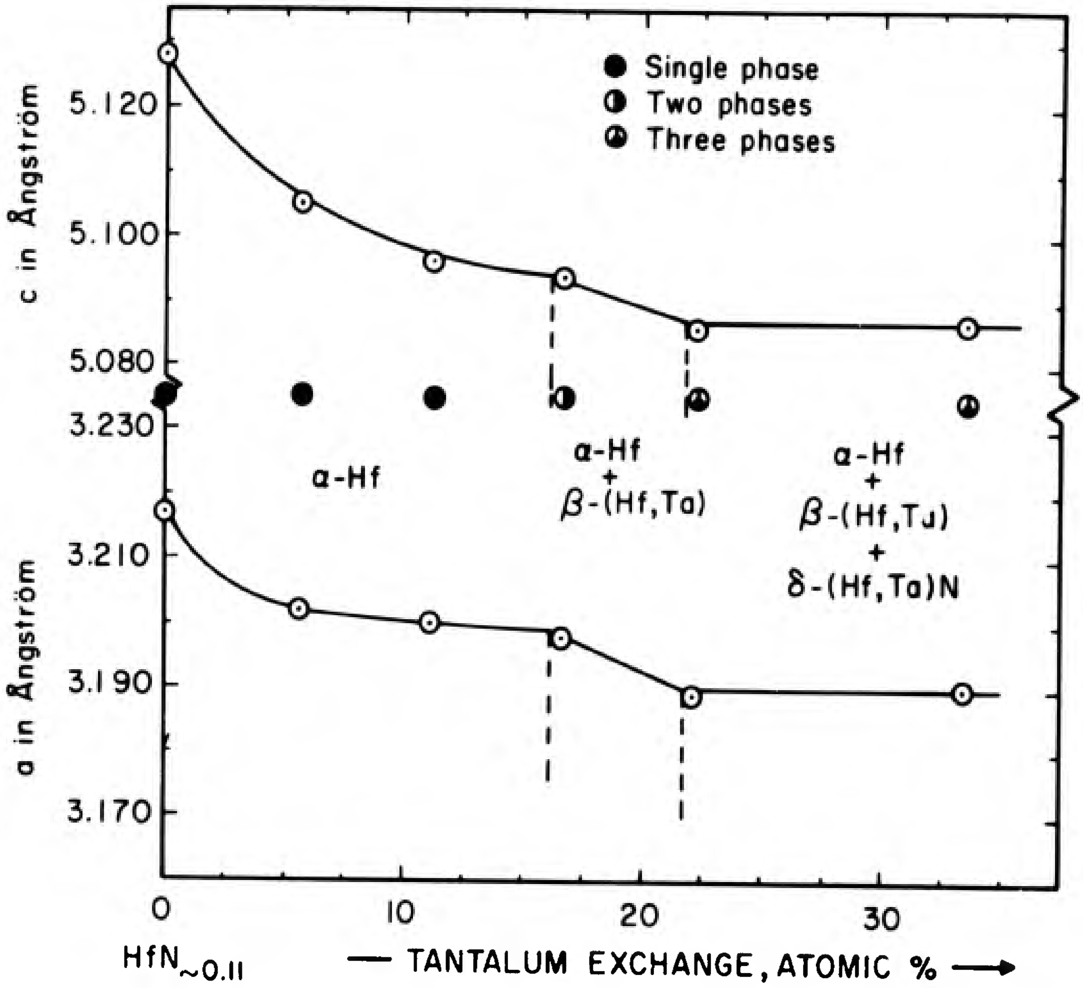

Figure 29. Hf-Ta-N: Lattice Parameter Variation of the Hexagonal α-Hf Solid Solution. Alloys Equilibrated at 2100°C.

The disproportionation of ternary alloys located close to the Ta-Hf binary system occurs relatively rapid and the quenching rates used in this investigation were not fast enough to retain the high temperature (β') form of the Hf-rich (Ta, Hf)-ss phase. Photomicrographs of ternary alloys showing the α-Hf-ss phase and the decomposed β'-(Ta, Hf)-ss are presented in Figures 30, 31 and 32.

Figure 30. Hf-Ta-N: (75-23-2 At. %), Melting Point Sample Quenched from 2140°C. X440

Traces of Primary α-Hf-ss in Partially Decomposed β'-(Ta, Hf)-ss Matrix.

Figure 31. Hf-Ta-N: (85-13-2 At.%), Melting Point Sample Quenched from 2150°C. X560

Decomposed β'-(Ta, Hf)-ss plus Traces of α-Hf-ss.

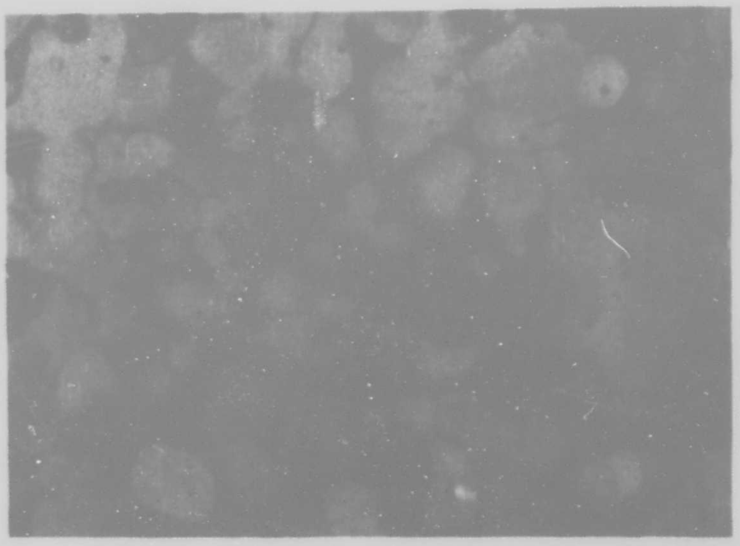

Figure 32. Hf-Ta-N: (85-10-5 At.%), Melting Point Sample Quenched from 2290°C. X400

Primary α-Hf-ss plus Trace of Partially Decomposed β' at the Grain Boundaries.

2. High Temperature Equilibria

The eutectoid reaction observed in the Hf-N binary system at 1970°C which is associated with the formation of the ϵ-Hf_2N phase appears in the ternary system at a slightly lower temperature of ~1950°C. D.T.A.-thermograms of ternary alloys participating in the four-phase reaction are presented in Figure 33. The class II-type, four-phase isothermal plane at 1950°C is represented by:

$$\alpha\text{-Hf-ss} + \delta\text{-(Hf, Ta)}N_{1-x} \rightleftarrows \beta\text{-(Ta, Hf)-ss} + \epsilon\text{-}Hf_2N$$

Photomicrographs of ternary alloys exhibiting either 3 or 4 phase non-equilibrium mixtures of β, α, ε, and δ cooled from temperatures above the four-phase reaction plane at 1950°C are shown in Figures 34 through 37.

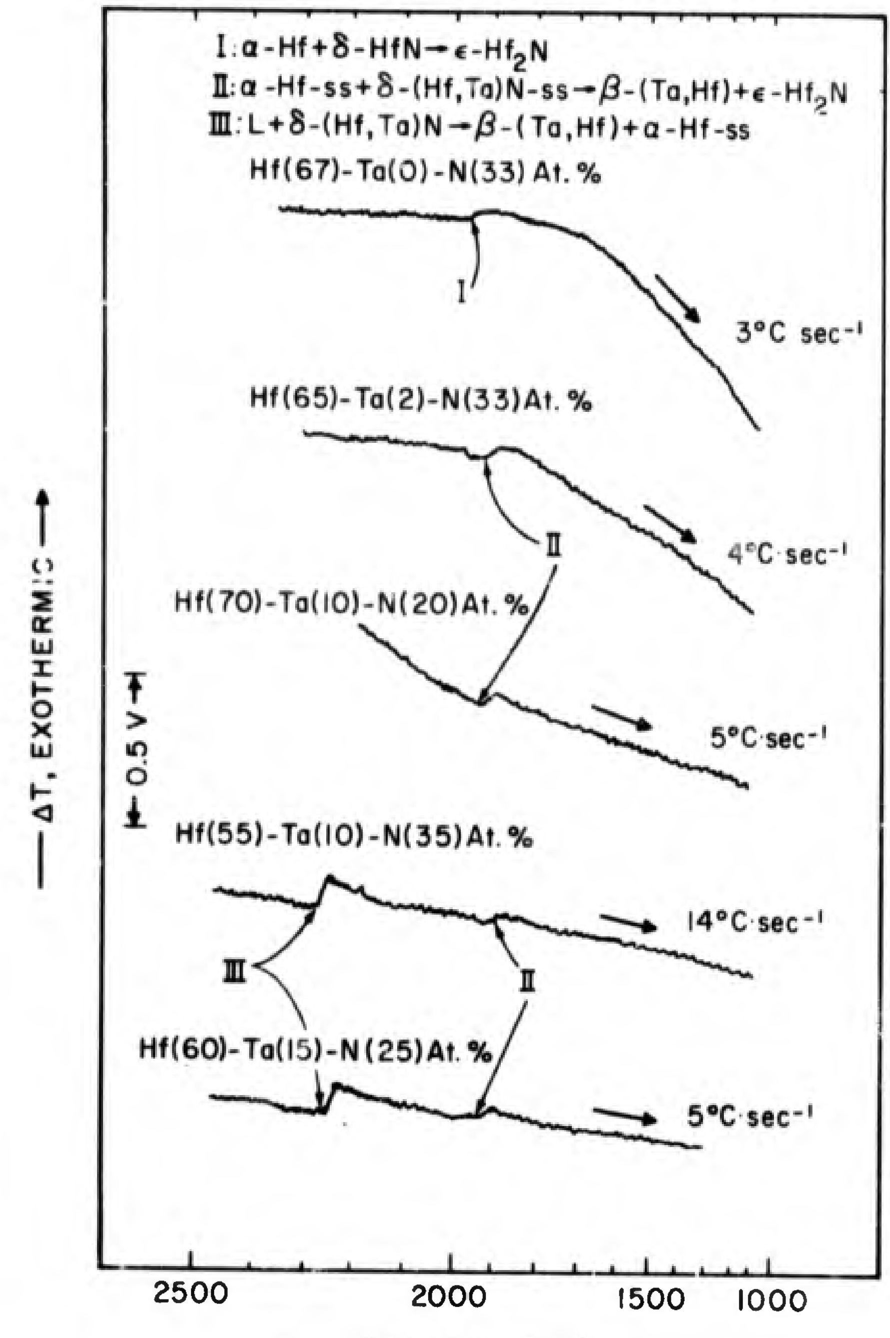

Figure 33. Hf-Ta-N: DTA-Thermograms (Cooling) of Alloys Participating in the Four-Phase Reactions at 1950°C and 2260°C.

Figure 34. Hf-Ta-N: (60-15-25 At.%), Melting Point Sample Heat-Treated at 2100°C for 15 hours and Quenched. X400

Primary δ-(Hf, Ta)N_{1-x} Containing Precipitation Structure of ε-Hf_2N in a Matrix of α-Hf (Light Gray) and β-(Ta, Hf) (Dark Gray). Pores-Black.

Figure 35. Hf-Ta-N: (55-10-35 At.%), Melting Point Sample Heat Treated at 2100°C for 15 hours and Quenched. X760

δ-(Hf, Ta)N_{1-x} Containing Precipitation Structure of ε-Hf_2N plus β-(Ta, Hf) (Dark Gray) and Trace Amounts of α-Hf (Light Gray). Pores-Black.

Figure 36. Hf-Ta-N: (68-2-30 At.%), Melting Point Sample Quenched from 3113°C. X640

δ-(Hf, Ta)N_{1-x} + ϵ-Hf_2N in a α-Hf-ss Matrix. X-ray Analysis - Trace Amounts of β-(Ta, Hf)-ss + δ-(Hf, Ta)N_{1-x} + ϵ-Hf_2N + α-Hf-ss.

Figure 37. Hf-Ta-N: (65-2-33 At.%), D.T.A. Sample Cooled at 4°C Sec. from 2400°C. X600

δ-(Hf, Ta)N_{1-x} Grains Exhibiting Precipitation Structure of ϵ-Hf_2N. Trace amounts of α-Hf at Grain Boundaries.

Figure 38 shows the melting temperatures and location of the eutectic trough in the metal-rich region of the ternary system. This figure also shows that the eutectic melting temperatures are only slightly below the maximum solidus temperature of the Ta-Hf solid solution indicating that the eutectic trough is located very close to the binary Ta-Hf system. These results are very similar to those obtained by E. Rudy(31) in his investigation of the Ta-Hf-C system.

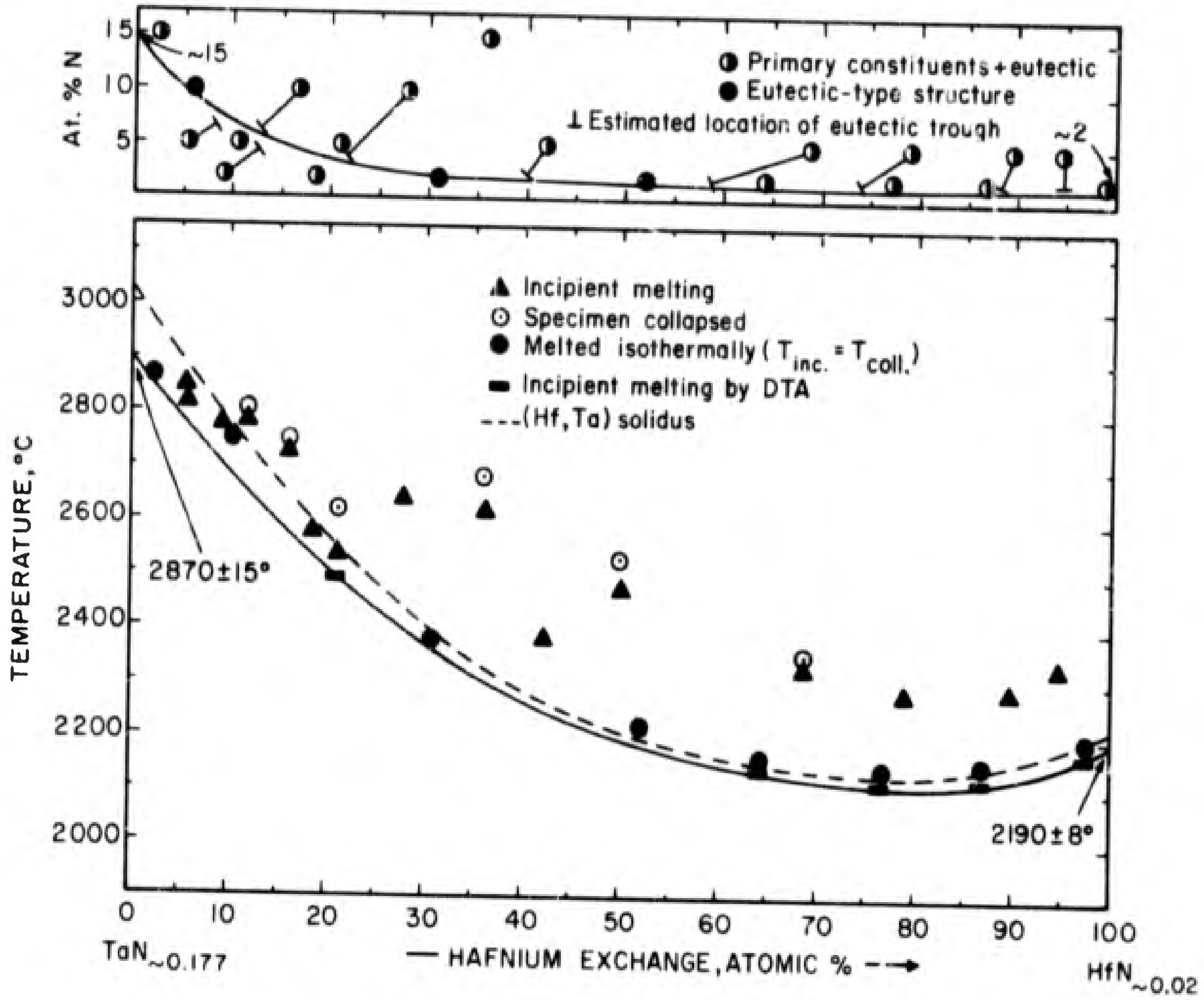

Figure 38. Hf-Ta-N: Melting Temperatures and Location of the Eutectic Trough in the Metal-Rich Region of the Tantalum-Hafnium-Nitrogen System.

The solidus temperatures along the metal-rich eutectic trough decrease smoothly from the binary Ta-Ta_2N eutectic at 2870°C and 15 At.% N and binary α(Hf)-β(Hf) eutectic at 2190°C and ~2 At.% N to the minimum eutectic point in the ternary system, i.e. a minimum tie line reaction at 2110°C according to:

$$\text{Liquid} \longleftrightarrow \beta\text{-(Ta, Hf)} + \alpha\text{-Hf-ss}$$

at a composition of approximately Hf(81) - Ta(17)-N(2) At.% is present. The metallographic examination of Ta-rich ternary alloys exhibited the same type of structures as found in the Ta-N binary system, e.g., primary Ta_2N grains contained metal precipitates in a Ta plus Ta_2N-depleted eutectic matrix (Figure 39).

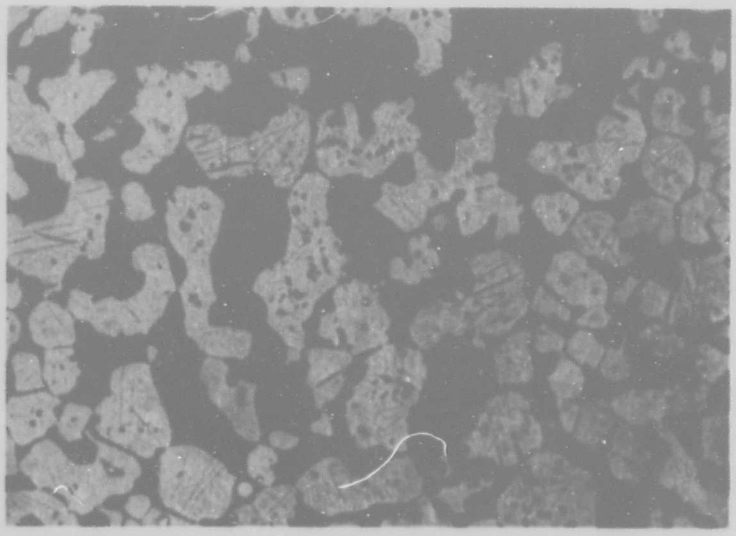

Figure 39. Hf-Ta-N: (2-76-22 At.%), Melting Point Sample Quenched from 2880°C. X400

Primary γ-$(Ta,Hf)_2N$ Containing β-(Ta, Hf) Precipitates in (Ta, Hf) plus $(Ta,Hf)_2N$-Depleted Eutectic Matrix. Trace Amounts of Subnitride and Primary Mononitride in Metal Matrix.

With increasing hafnium content, the ternary alloys exhibited eutectic-like structures as shown in Figures 40 thru 43. These alloys are located in the two-phase field of metal plus mononitride; finally in the two-phase field of β-Ta + α-Hf, eutectic-like structures as presented in Figure 44 were obtained. The more hafnium-rich ternary alloys located close to the eutectic trough did not exhibit very characteristic eutectic structures; this is due to the low nitrogen concentration of the eutectic which is located very close to the maximum solubility limit of nitrogen in the β-(Ta-Hf)-ss phase.

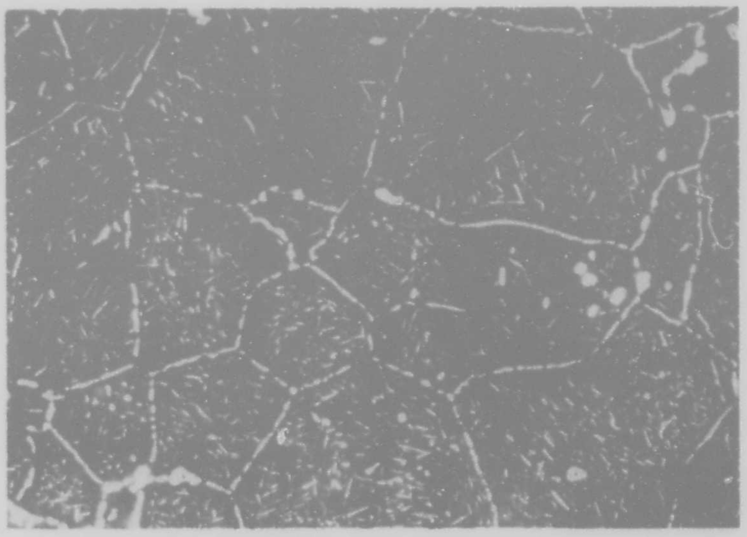

Figure 40. Hf-Ta-N: (5-90-5 At. %), Melting Point Sample Heat-Treated at 2100°C for 15 hours. X400

Primary Metal Grains Containing Mononitride Precipitates and Traces of Metal + Mononitride Eutectic at Grain Boundaries.

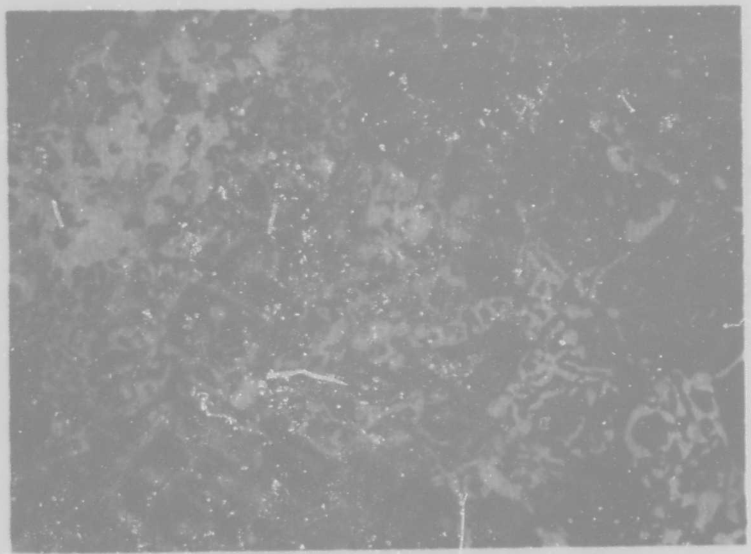

Figure 41. Hf-Ta-N: (15-75-10 At.%), Melting Point Sample Quenched from ~2800°C.

Co-crystallized γ-Ta_2N (Light Gray) and Mononitride (White) in Mononitride plus Metal Eutectic. This Phase Morphology Resulted from the Four-Phase Reaction at 2800°C: Liquid + γ-Ta_2N ⟷ β-(Ta, Hf) + δ-(Hf, Ta)N_{1-x}.

Figure 42. Hf-Ta-N: (35-30-35 At.%), Melting Point Sample Quenched from 3056°C and Equilibrated at 2100°C. X600

Primary Mononitride Grains Containing Metal Precipitates in a Mononitride + Metal Eutectic Matrix. Trace of γ-Ta_2N (Light Gray) in Eutectic Matrix.

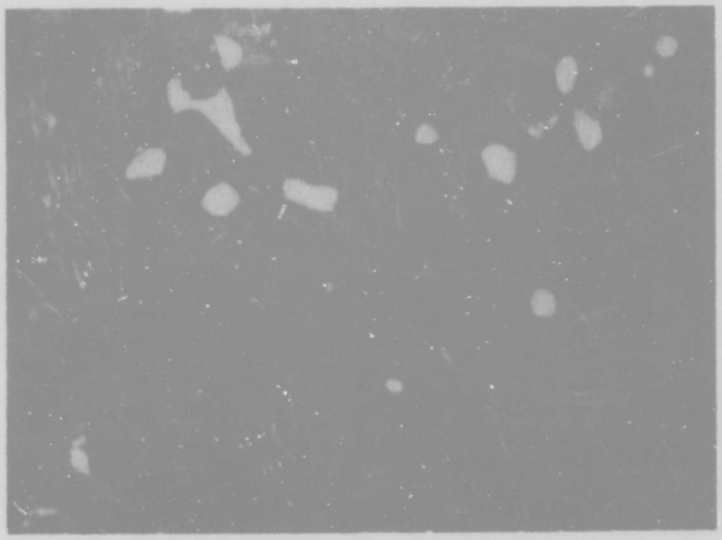

Figure 43. Hf-Ta-N: (20-75-5 At. %), Melting Point Sample Quenched from 2620°C. X1000

Primary δ-(Hf, Ta)N_{1-x} and δ-(Hf, Ta)N_{1-x} + β-(Ta, Hf) Eutectic.

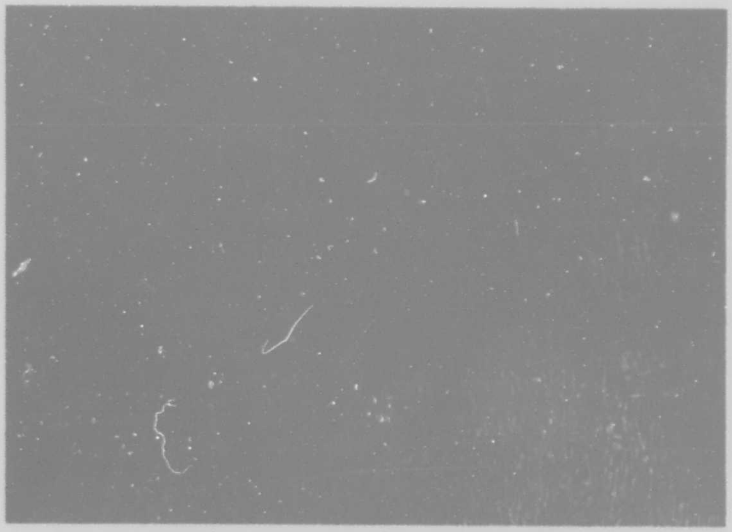

Figure 44. Hf-Ta-N: (63-35-2 At.%), Melting Point Sample Quenched from 2160°C and Equilibrated at 1500°C. X340

Traces of Decomposed β-(Ta, Hf)-ss plus α-β Eutectic.

The maximum tantalum exchange in the α-Hf phase is terminated at the four-phase reaction plane occurring at 2260°C. The Class II-type, four-phase reaction proceeding at this temperature is represented by

$$\text{Liquid} + \delta\text{-(Hf, Ta)N}_{1-x}\text{-ss} \rightleftarrows \beta\text{-(Ta, Hf)-ss} + \alpha\text{-Hf-ss}$$

D.T.A. thermograms of two ternary alloys participating in the four-phase reaction at 2260°C are shown in Figure 33. At this temperature, the tantalum exchange in the α-Hf phase is 22 atomic percent (a = 3.189; c = 5.086Å at ~10 At.% N). Ternary alloys showing the primary α-Hf phase plus trace amounts of the metal solid solution are presented in Figures 45 and 46.

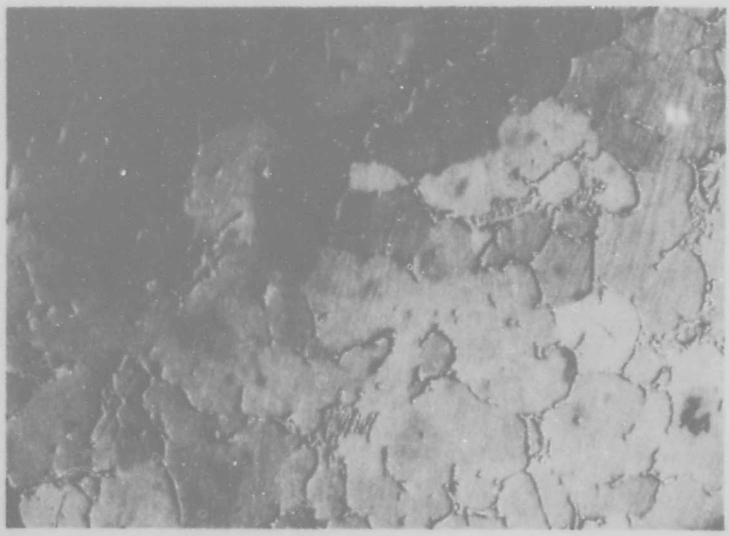

Figure 45. Hf-Ta-N: (75-10-15 At.%), Melting Point Sample Quenched from 2850°C and Heat-Treated for 30 hours at 1500°C. X300
α-Hf-ss Grains plus β-(Ta, Hf) at Grain Boundaries.

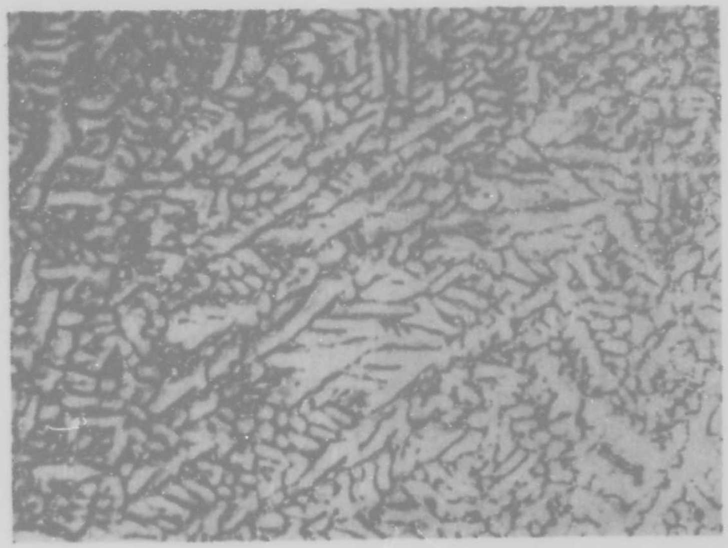

Figure 46. Hf-Ta-N: (75-15-10 At.%), Melting Point Sample Quenched from 2750°C. X320

Primary Dendrites of α-Hf plus Trace Amounts of (Hf, Ta) Metal Solid Solution.

With increasing temperatures, two three-phase fields emerge from the four-phase reaction plane at 2260°C. The one three-phase field of liquid + α-Hf-ss + δ-(Hf, Ta)N_{1-x}-ss moves toward the Hf-N binary system and is terminated at the maximum temperature stability of the α-Hf phase, i.e. the binary peritectic reaction at 2911°C. The second three-phase field of liquid + β-(Ta, Hf)-ss + δ-(Hf, Ta)N_{1-x}-ss proceeds across the ternary system and is terminated in a Class II-type, four phase reaction at a temperature of approximately 2800°C. The reaction scheme representing the four-phase temperature plane at 2800°C may be written as follows:

$$\text{Liquid} + \gamma\text{-}Ta_2N\text{-ss} \rightleftarrows \beta\text{-(Ta, Hf)-ss} + \delta\text{-(Ha, Ta)}N_{1-x}\text{-ss}$$

At this temperature a maximum hafnium exchange of 9.5 atomic percent was observed for the γ-Ta_2N phase (a = 3.044; c = 4.915Å for Ta_2N and a = 3.062; c = 4.937Å at the γ-$(Ta, Hf)_2N$-ss vertex of the three-phase field ($\beta + \gamma + \delta$).

The existence of the four-phase temperature plane at 2800°C was determined from melting point runs with subsequent metallographic examination of these alloys. A photomicrograph showing approximately the maximum extent of the γ-$(Ta, Hf)_2N$-ss phase into the ternary system is shown in Figure 47. As was previously shown in Figures 41 and 42, products of the four-phase reaction at 2800°C are also shown in Figures 48 and 49.

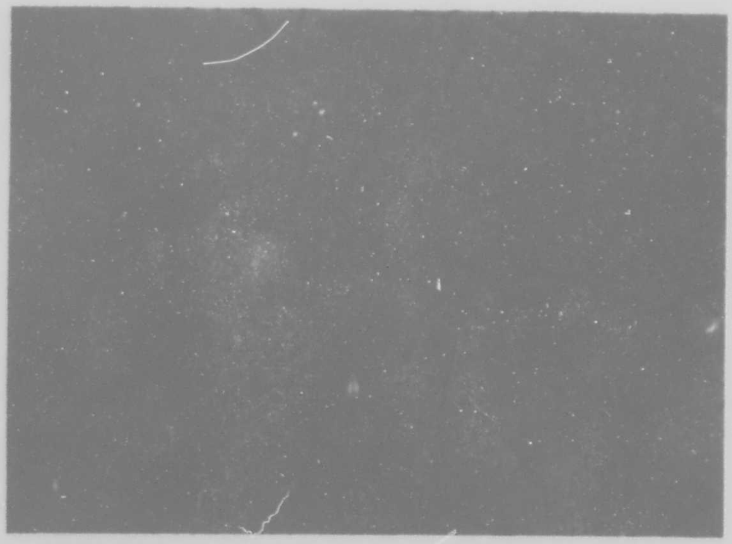

Figure 47: Hf-Ta-N: (10-60-30 At.%), Melting Point Sample Quenched from ~2850°C. X400

Primary γ-Ta_2N-ss with Melting Phase at Grain Boundaries. X-ray Analysis: Subnitride, Metal and Trace Amounts of Mononitride.

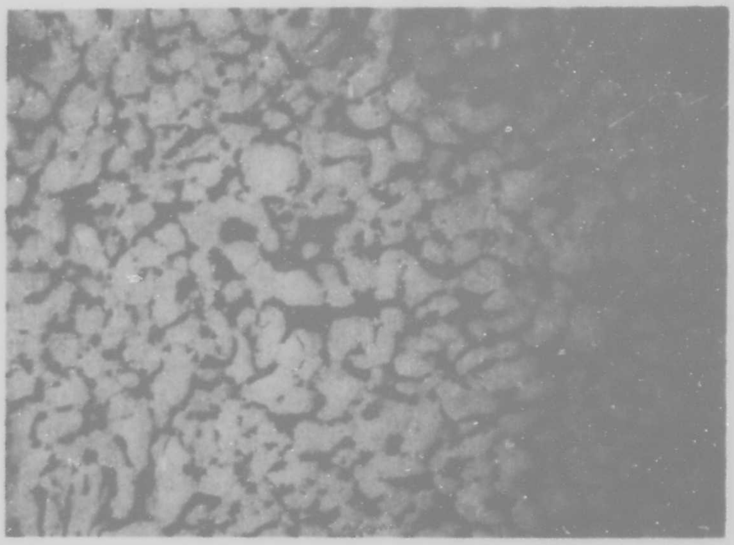

Figure 48. Hf-Ta-N: (27-33-40 At.%), Melting Point Sample Quenched from 3056°C. X400

Primary Mononitride in a γ-Ta_2N Matrix (Light Gray) Containing both Metal (Dark Gray) and Mononitride.

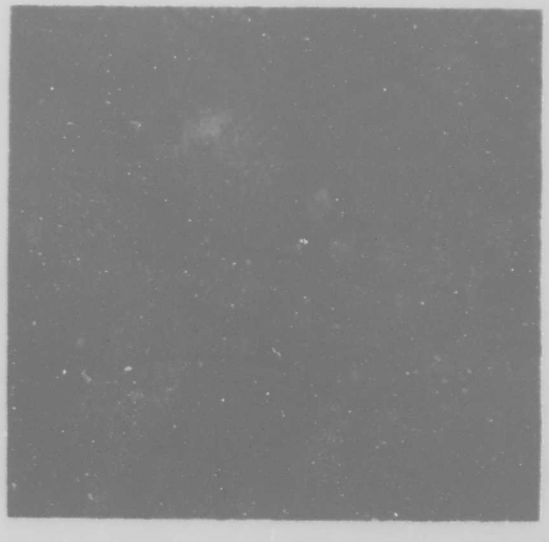

Figure 49. Hf-Ta-N: (5-67-28 At.%), Melting Point Sample Quenched from 2808°C. X280

Primary γ-Ta_2N Containing Intragranular Metal Precipitates in a Metal Matrix (Dark) with Traces of Mononitride (White Spheres).

The two-phase equilibrium β-(Ta, Hf)-ss + δ-(Hf, Ta)N_{1-x}-ss remains stable at all temperatures up to melting. As shown in Figures 50 and 51 of ternary alloys quenched from melting, metal and mononitride are the only phases present. At slightly higher tantalum exchanges the mononitride vertex of the three-phase field β + γ + δ is crossed at a temperature of 2100°C and ~42 At. % N (Figure 52).

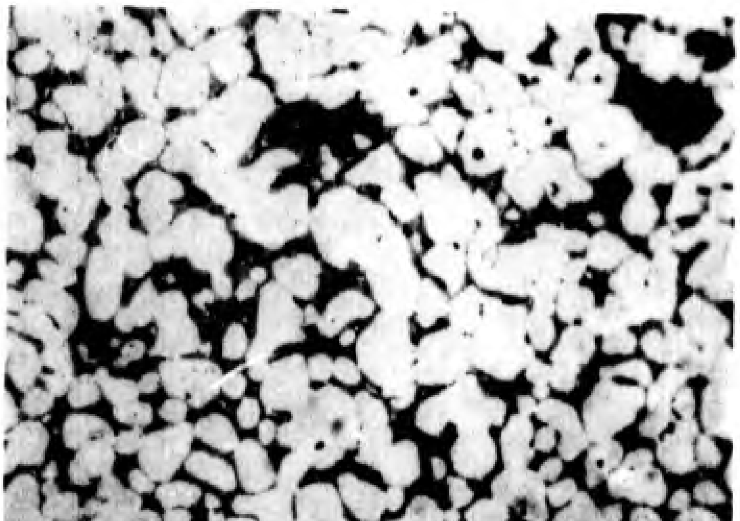

Figure 50. Hf-Ta-N: (45-20-35 At.%), Melting Point Sample Quenched from 2900°C. X640

Primary Hafnium Mononitride Solid Solution in a Mononitride-Metal Eutectic Matrix.
X-ray Analysis: δ-(Hf, Ta)N_{1-x} + β-(Ta, Hf)

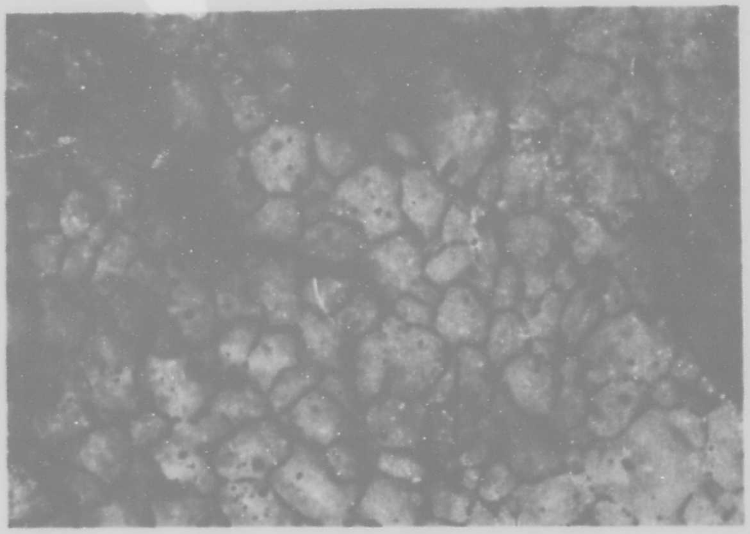

Figure 51. Hf-Ta-N: (55-5-40 At.%), Melting Point Sample Quenched from 3300°C. X400

δ-(Hf, Ta)N_{1-x} plus Slight Trace of β-(Ta, Hf) at Grain Boundaries. (Pores-Black) X-Ray Analysis: δ-(Hf, Ta)N_{1-x} + Slight Trace β-(Ta, Hf).

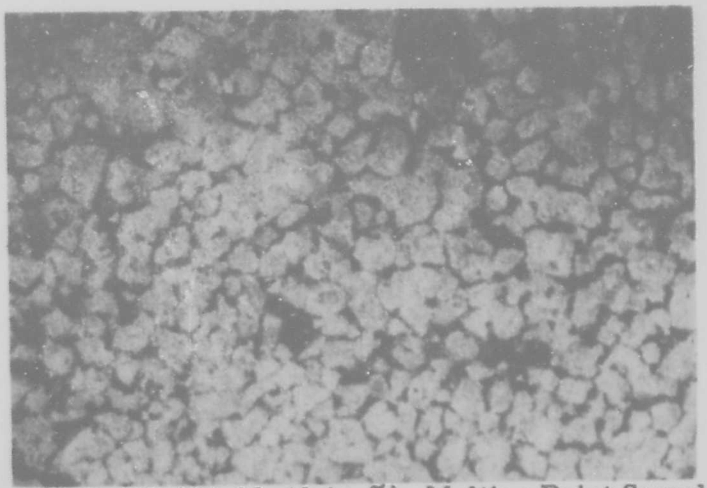

Figure 52. Hf-Ta-N: (40-20-40 At.%), Melting Point Sample Heat-Treated at 2100°C for 15 hours. X400

Mononitride (δ) Grains Containing Metal Precipitates at Grain Boundaries.

X-Ray Analysis: δ-(Hf, Ta)N_{1-x} + β-(Ta, Hf) + Trace γ-Ta_2N.

Above the temperature of 2100°C, the maximum solubility of tantalum in δ-(Hf, Ta)N_{1-x}-ss at the mononitride phase boundary of the two-phase field γ + δ shifts towards the hafnium mononitride phase. Ultimately, the two-phase field of subnitride plus mononitride is terminated in a pseudobinary eutectic reaction at 2920°C. The melting temperatures of ternary alloys located along this section are presented in Figures 53. The reaction occurring at 2920°C is represented by:

$$\text{Liquid} \rightleftarrows \gamma\text{-Ta}_2\text{N-ss} + \delta\text{ - (Hf, Ta)N}_{1-x}\text{-ss}$$

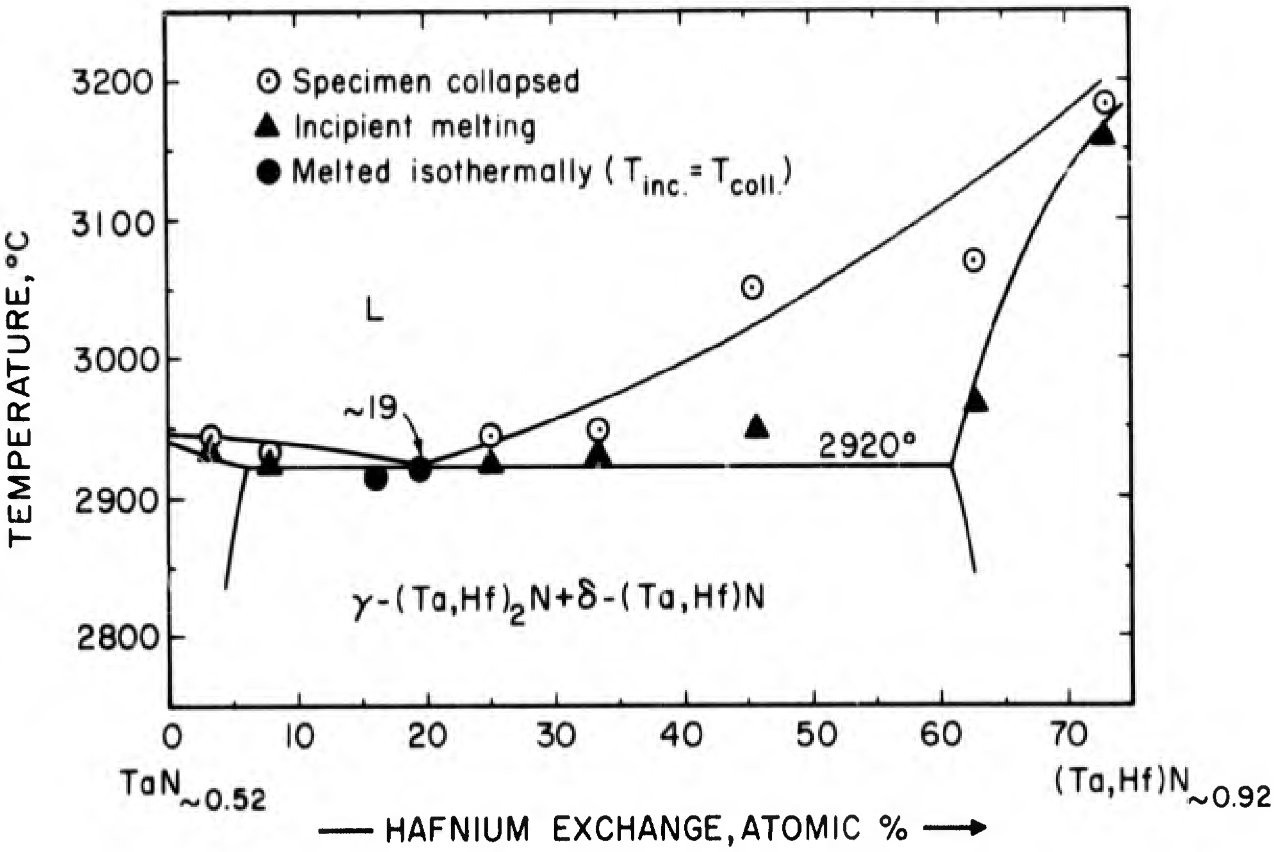

Figure 53. Hf-Ta-N: Melting Temperatures Along the Pseudobinary Section $TaN_{\sim 0.5}$ - $(Ta, Hf)N_{\sim 0.92}$

Photomicrographs of the two end phases participating in the pseudobinary eutectic reaction are shown in Figures 54 and 55; eutectic-like structures were obtained in ternary alloys with hafnium exchanges of ~19 atomic percent. These structures, which are not very characteristic of eutectics, are presented in Figures 56 and 57.

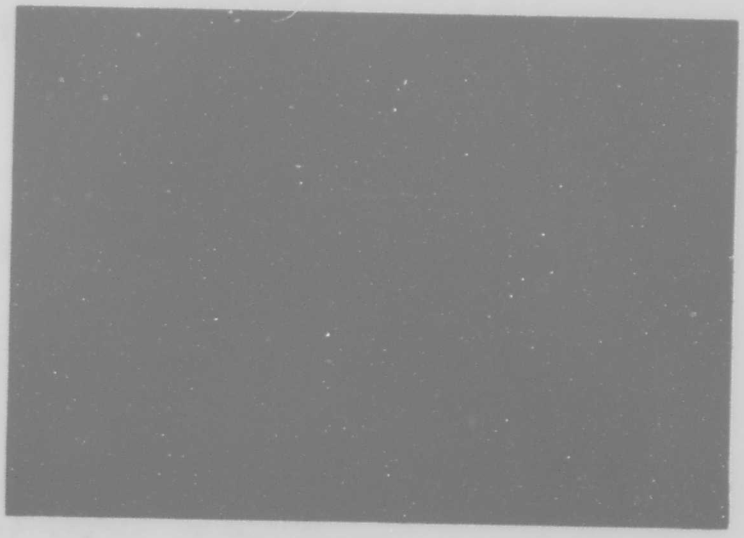

Figure 54. Hf-Ta-N: (5-59-36 At.%), Melting Point Sample Quenched from 2935°C. Polarized Light X760

δ-Ta_2N-ss plus Slight Trace of Mononitride.

Figure 55. Hf-Ta-N: (40-15-45 At.%), Melting Point Sample Quenched from 3180°C. X1000

Single Phase δ-(Hf, Ta)N_{1-x} Solid Solution (Pores-Black).

Figure 56. Hf-Ta-N: (12-50-38 At.%), Melting Point Sample Quenched from 2950°C. Polarized Light X520

Trace of Primary Mononitride (Light Gray) in a Subnitride (Dark Gray)-Mononitride Eutectic-Like Matrix.

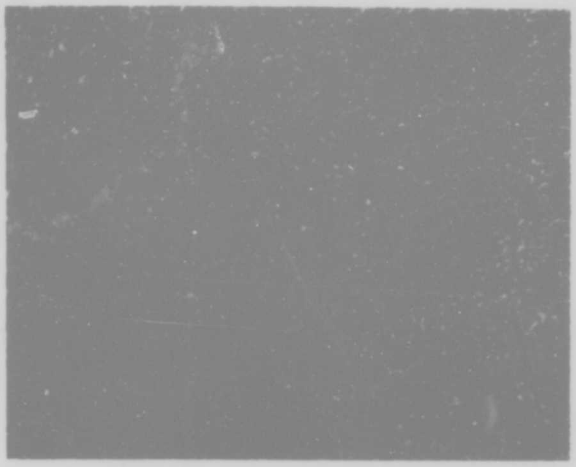

Figure 57. Hf-Ta-N: (20-40-40 At.%), Melting Point Sample Quenched from 2950°C. Polarized Light X 520

Primary Mononitride Dendrites (Light Gray) in a Subnitride-Mononitride Eutectic-Like Matrix.

3. Assembly of the Phase Diagram

The experimental results obtained from the solid state sections, D.T.A., melting point, and metallographic studies were used to construct the isothermal sections from 1000°C to 3200°C (Figures 58 thru 70). Finally, the temperature sections are supplemented by a drawing showing the melting troughs and liquidus projections of the partial ternary system (Figure 71).

The various phase equilibria as presented in the isothermal sections were combined to construct a partial isometric view of the ternary Ta-Hf-N system (Figure 1).

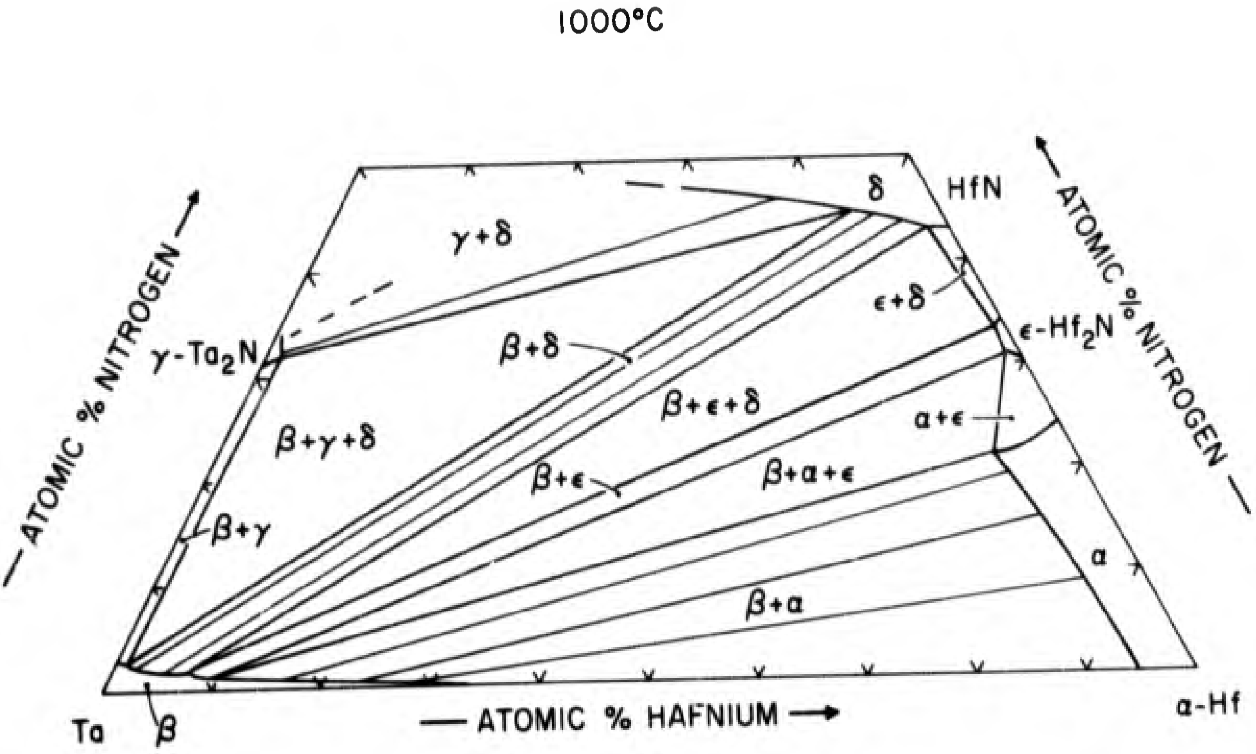

Figure 58. Hf-Ta-N: Isothermal Section At 1000°C.

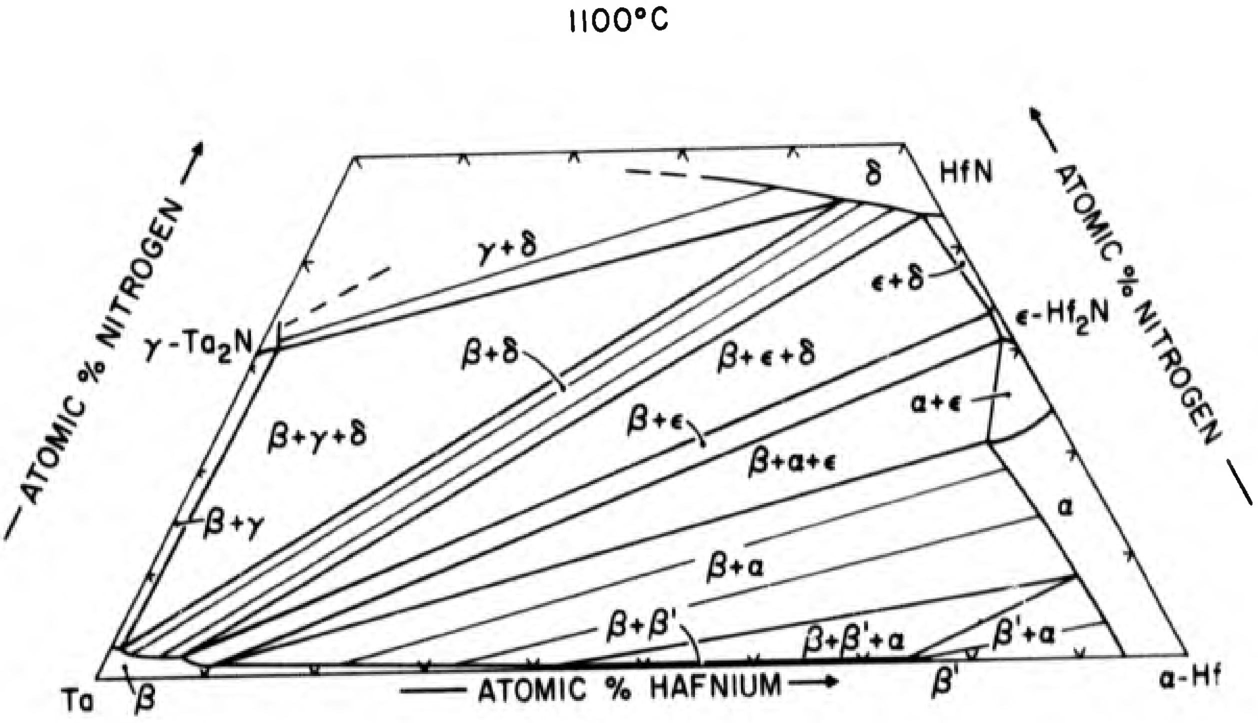

Figure 59. Hf-Ta-N: Isothermal Section at 1100°C.

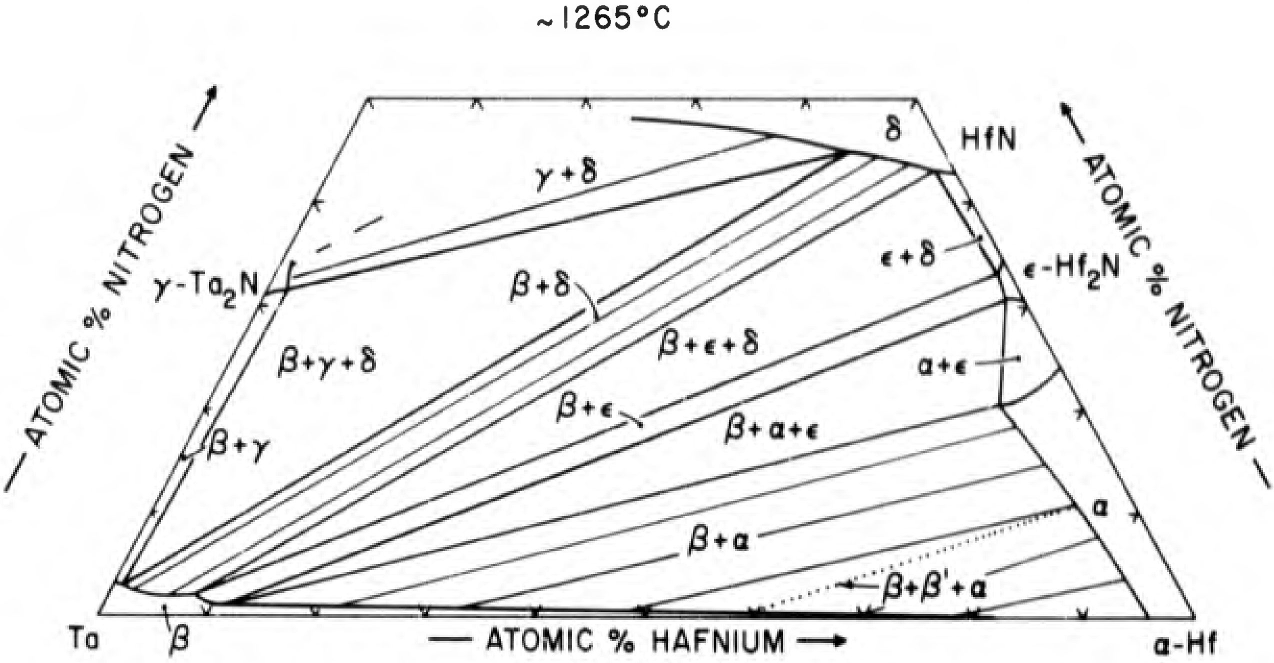

Figure 60. Hf-Ta-N: Isothermal Section at ~1265°C.

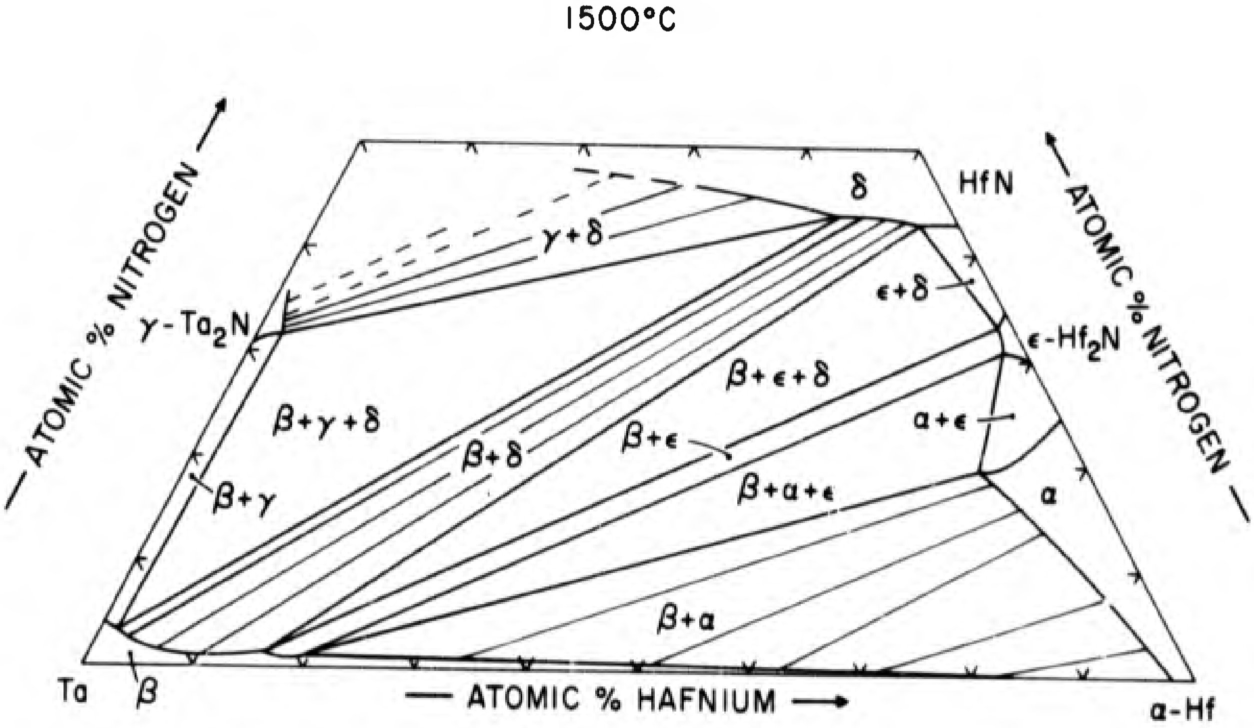

Figure 61. Hf-Ta-N: Isothermal Section at 1500°C.

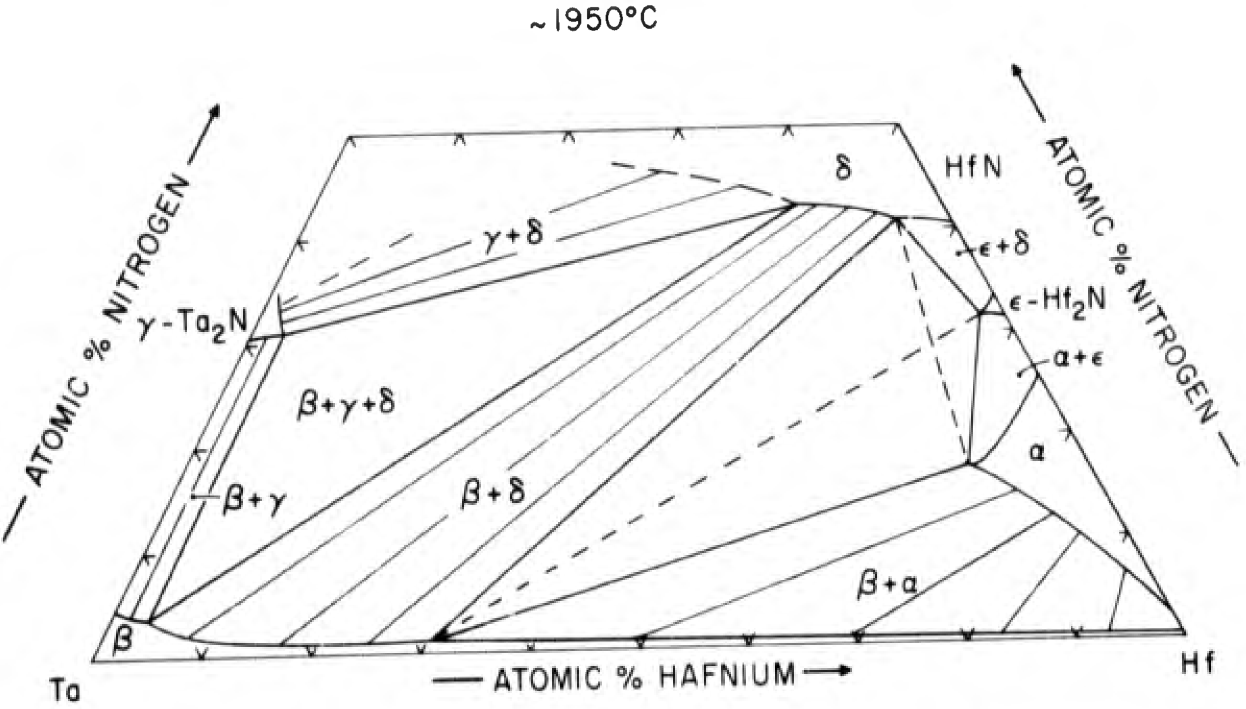

Figure 62. Hf-Ta-N: Isothermal Section at ~1950°C.

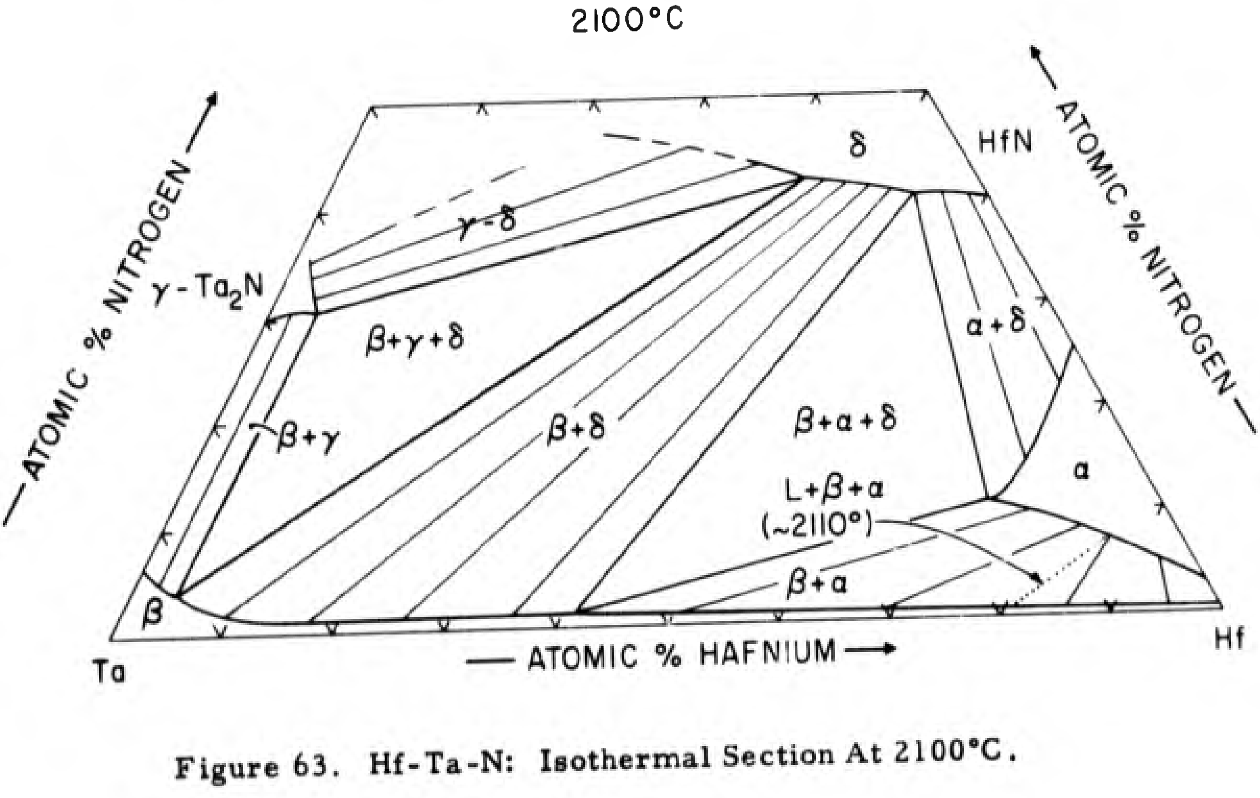

Figure 63. Hf-Ta-N: Isothermal Section At 2100°C.

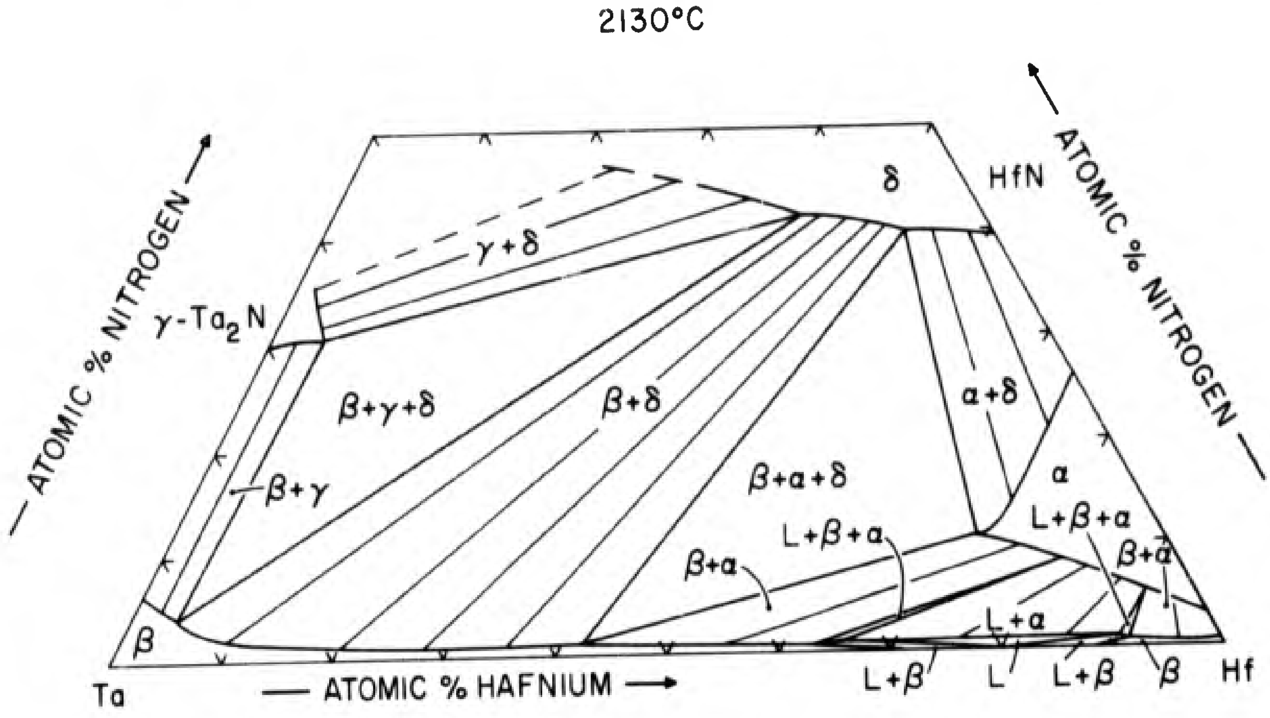

Figure 64. Hf-Ta-N: Isothermal Section at 2130°C.

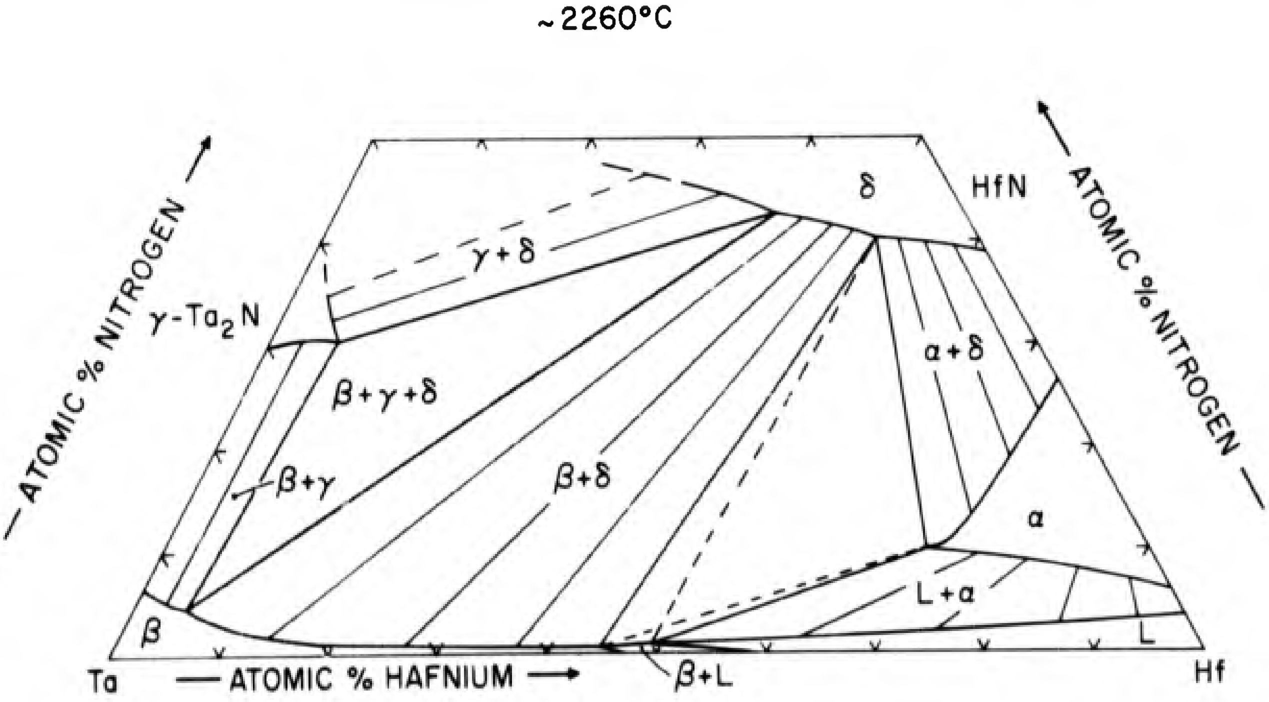

Figure 65. Hf-Ta-N: Isothermal Section at ~2260°C.

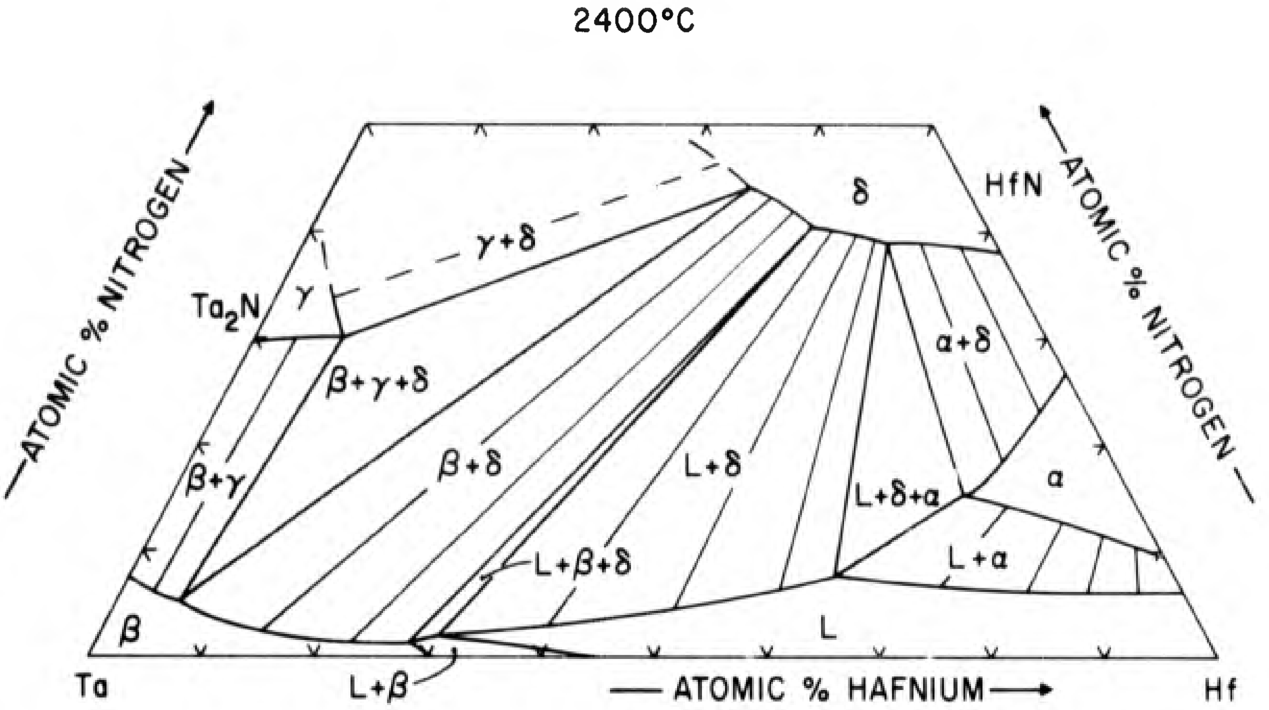
2400°C

Figure 66. Hf-Ta-N: Isothermal Section at 2400°C.

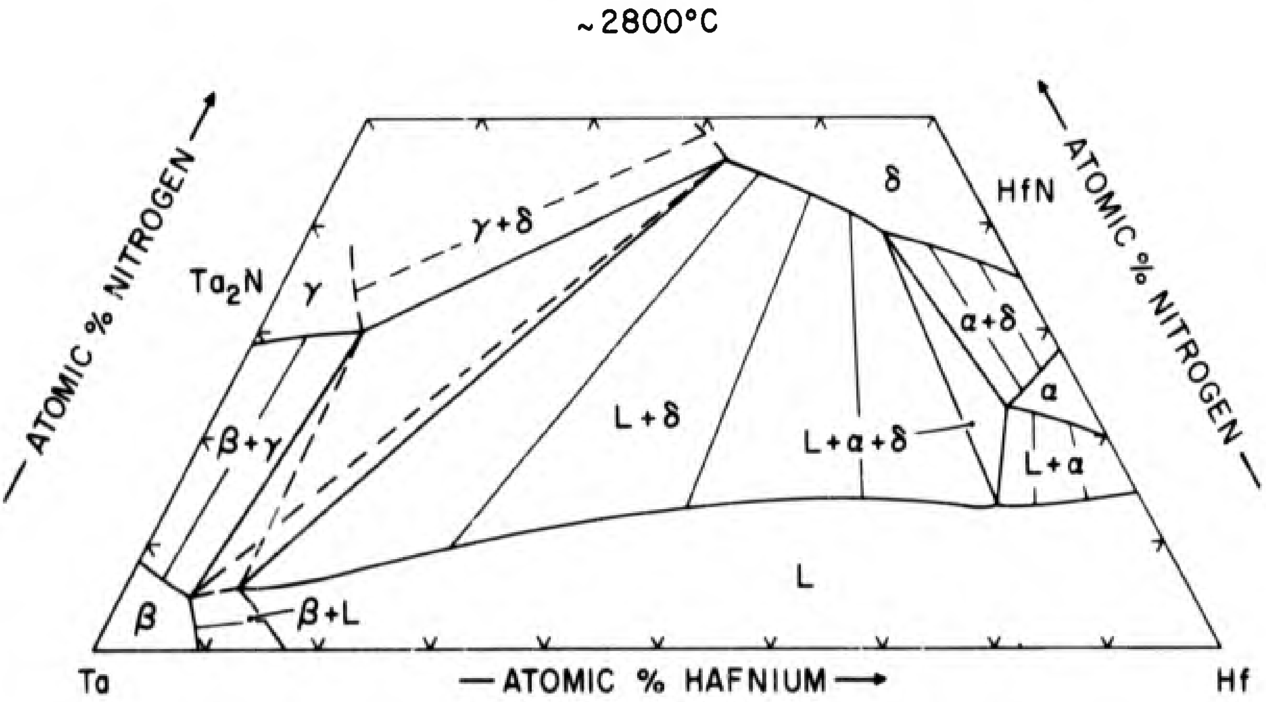
~2800°C

Figure 67. Hf-Ta-N: Isothermal Section at ~2800°C.

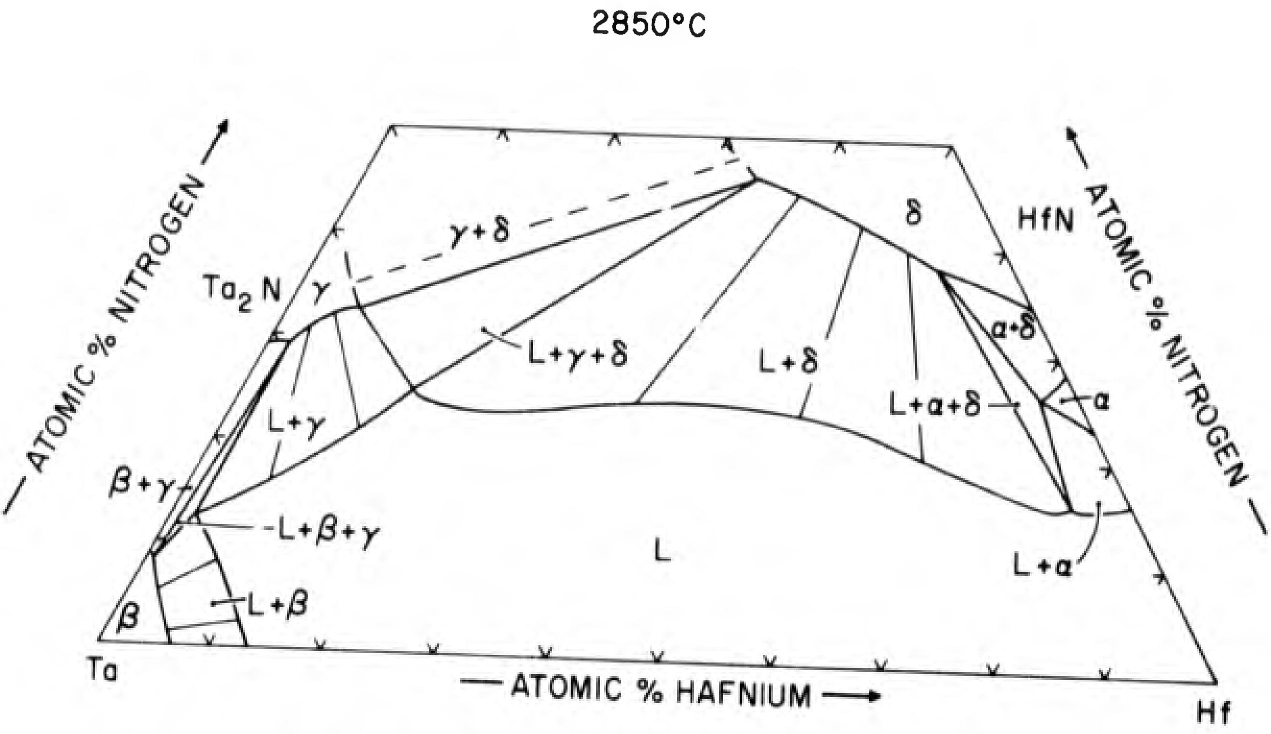

Figure 68. Hf-Ta-N: Isothermal Section at 2850°C.

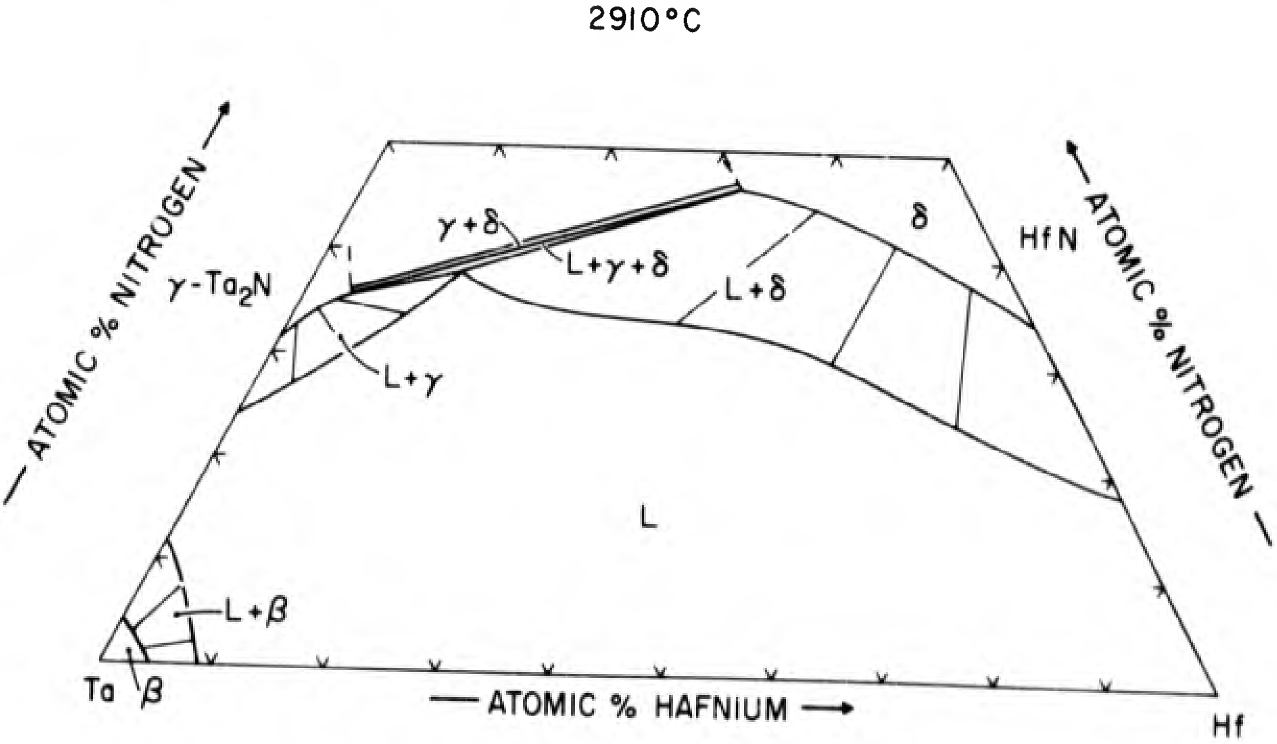

Figure 69. Hf-Ta-N: Isothermal Section at 2910°C.

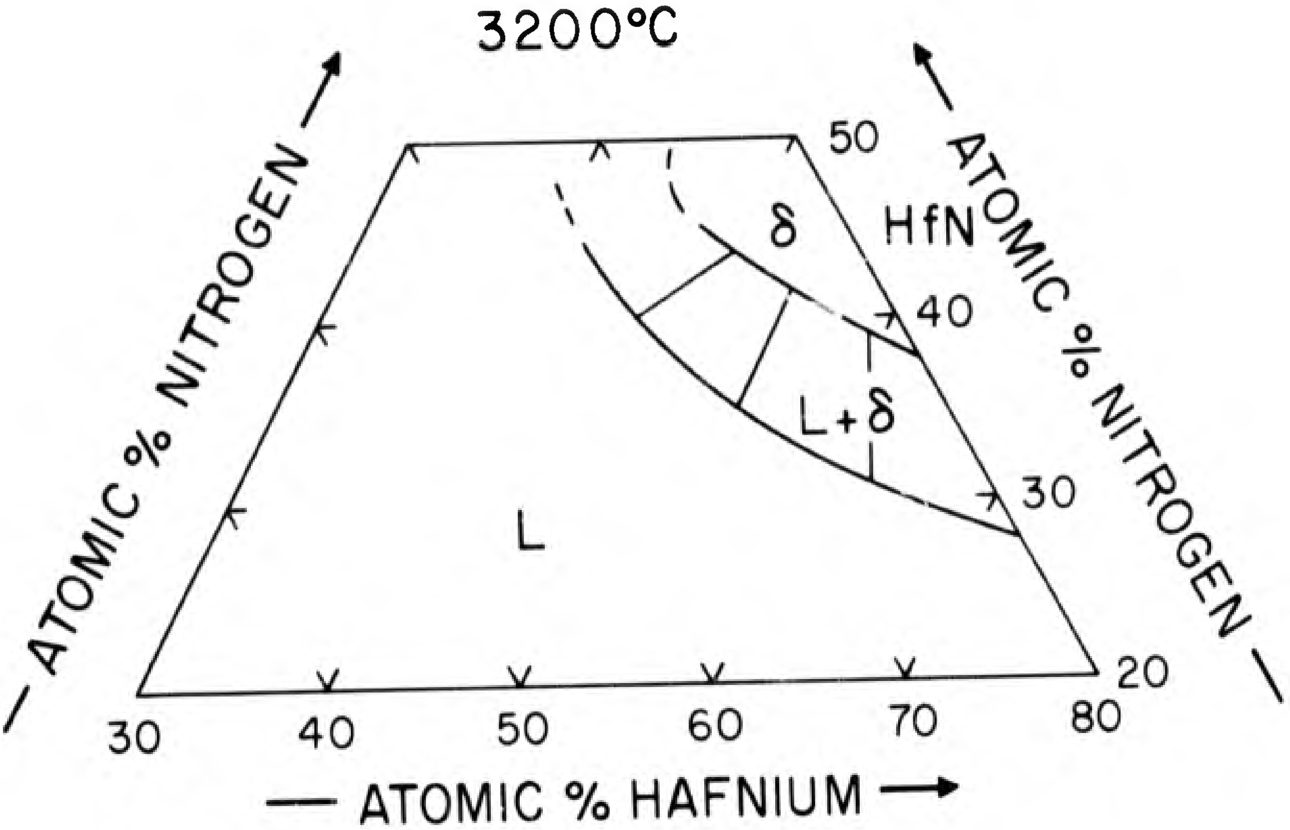

Figure 70. Hf-Ta-N: Isothermal Section at 3200°C.

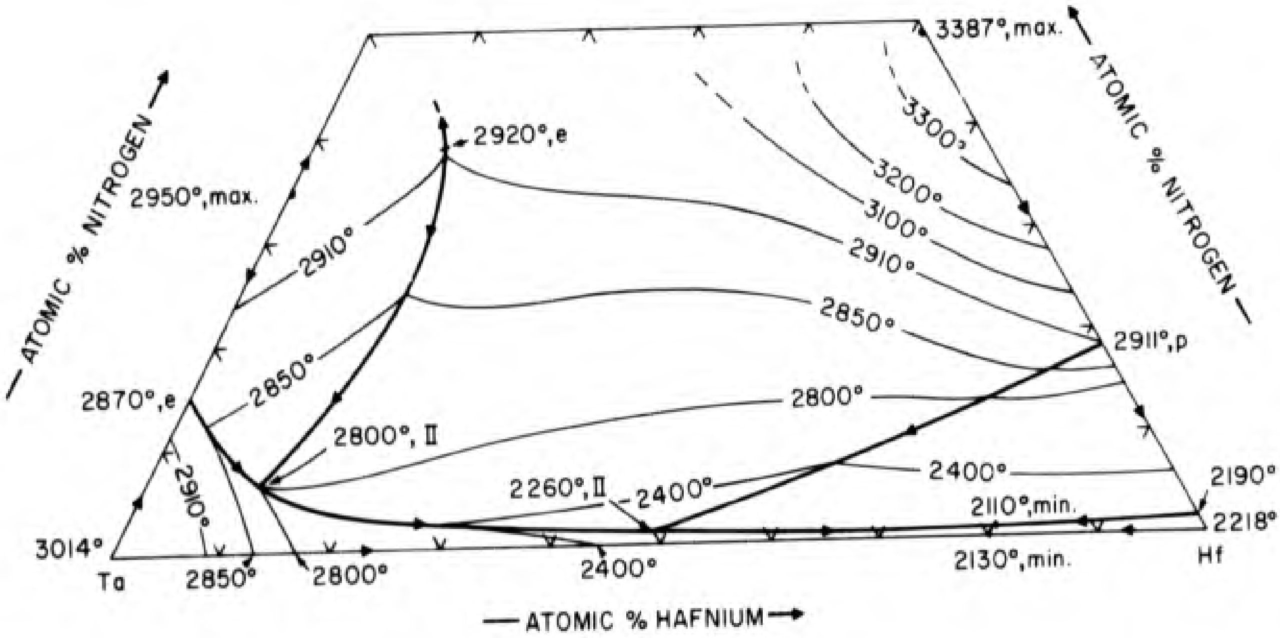

Figure 71. Hf-Ta-N: Liquidus Projections.

V. CONCLUSION AND DISCUSSION

In view of the phase relationships formed in the Ta-Hf-N system, the existence of the two-phase equilibrium, metal and mononitride, seems to offer the best alloy compositions for obtaining refractory nitride-refractory metal composite bodies for cutting tool applications. Depending on the composition of the ternary alloys in the two-phase field, (Ta, Hf) + (Ta, Hf)N_{1-x}; composite bodies can be fabricated which exhibit microstructures of either mononitride grains containing intragranular metal precipitates or primary mononitride grains containing metal precipitates in a metal-mononitride eutectic matrix. Alloy combinations of this type could possibly result in high strength refractory metal alloy reinforced mononitride composite bodies suitable for cutting tool material.

Not only are these two phases compatible, but also, since the two-phase equilibrium (Ta, Hf)-(Ta, Hf)N_{1-x} remains stable at all temperatures up to melting, no solid state reactions can occur during fabrication which would influence the integrity of the composite body. By establishing the appropriate fabrication techniques to obtain the desired phase morphology, ternary alloys from the tantalum-hafnium-nitrogen system seem to offer candidate materials for the development of cutting tools with improved temperature capabilities.

Investigations conducted after the completion of this report have indicated that two nitride phases, and not just one, are present in the hafnium-nitrogen binary system near 33 atomic percent nitrogen. One phase (B) is found at about 36 At. % nitrogen and is formed in a peritectoid reaction from the α-Hf and the mononitride at a temperature somewhat above 2100°C. The second phase (A) lies at about 33 At.% nitrogen and is also formed in a peritectoid reaction from the B phase and α-Hf at about 2000°C. The crystal structures of both these phases are unknown at present. These hafnium subnitride phases partake of the ternary equilibria in the Hf-Ta-N system in a manner similar to that depicted for the "ϵ-Hf_2N" phase; the existence and characteristics of the two-phase region, metal + mononitride, (Ta, Hf)-(Hf, Ta)N_{1-x}, (the area of most interest in this system) are not affected by the presence of these additional equilibria.

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Unclassified
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DOCUMENT CONTROL DATA - R&D

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

1 ORIGINATING ACTIVITY (Corporate author)
Materials Research Laboratory
Aerojet-General Corporation
Sacramento, California

2a REPORT SECURITY CLASSIFICATION
Unclassified

2b GROUP
N/A

3 REPORT TITLE
Phase Equilibria Investigations of Binary, Ternary and Higher Order Systems. Part VI - The Phase Equilibria in the Metal-Rich Region of the Hafnium-Tantalum-Nitrogen System.

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

5 AUTHOR(S) (Last name, first name, initial)
Philip H. Booker and Charles E. Brukl

6 REPORT DATE
May 1969

7a TOTAL NO OF PAGES
73

7b NO OF REFS
31

8a CONTRACT OR GRANT NO
AF 33(615)-67-C-1513

b PROJECT NO

c

d

9a ORIGINATOR'S REPORT NUMBER(S)
69
AFML-TR-117, Part VI

9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

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13 ABSTRACT

The ternary alloy system tantalum-hafnium-nitrogen was investigated by means of melting point, X-ray, differential thermal analytical, and metallographic techniques. Also investigated were the two binary systems of tantalum-nitrogen and hafnium-nitrogen.

In the ternary system, seven isothermal reactions occur: Three, Class II-type four-phase reactions and four limiting tie line reactions are observed.

The observed phase relationships established during the course of this investigation are discussed, and isothermal sections from 1000°C to 3200°C as well as an isometric view of the ternary system are presented. In addition to the ternary system, phase diagrams for the two binary systems of tantalum-nitrogen and hafnium-nitrogen are also presented.

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