

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

AD 671082

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

**PART I. BINARY SYSTEMS**  
**Volume XIV. Constitution of the Hafnium-Vanadium and  
Hafnium-Chromium Systems**

*E. RUDY  
ST. WINDISCH*

*Aerojet-General Corporation*

TECHNICAL REPORT AFML-TR-65-2, PART I, VOLUME XIV

MAY 1968



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**AIR FORCE MATERIALS LABORATORY  
AIR FORCE SYSTEMS COMMAND  
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## FOREWORD

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

The project, which includes the experimental and theoretical investigations of ternary and related binary systems in the system classes  $Me_1$ - $Me_2$ -C, Me-B-C,  $Me_1$ - $Me_2$ -B, Me-Si-B and Me-Si-C, was initiated on 1 January 1964. An extension effort to this contract commenced in January 1966.

The phase diagram work on the binary systems described in this report were carried out by E. Rudy and St. Windisch. Assisting in the investigations were: J. Hoffman (Metallographic preparations), J. Pomodoro (sample preparation), and R. Cobb (X-ray exposures and photographic work). C.E. Brukl assisted in some of the lattice parameter measurements.

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

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

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

### Part I. Related Binaries

- |              |   |
|--------------|---|
| Volume I.    | Mo-C System   |
| Volume II.   | Ti-C and Zr-C Systems   |
| Volume III.  | Systems Mo-B and W-B  |
| Volume IV.   | Hf-C System   |
| Volume V.    | Ta-C System. Partial Investigations in the Systems V-C and Nb-C |
| Volume VI.   | W-C System. Supplemental Information on the Mo-C System         |
| Volume VII.  | Ti-B System   |
| Volume VIII. | Zr-B System   |
| Volume IX.   | Hf-B System   |
| Volume X.    | V-B, Nb-B, and Ta-B Systems                                     |
| Volume XI.   | Final Report on the Mo-C System                                 |
| Volume XII.  | Revision of the Vanadium-Carbon and Niobium-Carbon Systems      |
| Volume XIII. | The Systems Zr-Si and Hf-Si                                     |

## FOREWORD (cont'd)

### Part II. Ternary Systems

- Volume I. Ta-Hf-C System
- Volume II. Ti-Ta-C System
- Volume III. Zr-Ta-C System
- Volume IV. Ti-Zr-C, Ti-Hf-C, and Zr-Hf-C Systems
- Volume V. Ti-Hf-B System
- Volume VI. Zr-Hf-B System
- Volume VII. Systems Ti-Si-C, Nb-Si-C, and W-Si-C
- Volume VIII. Ta-W-C System
- Volume IX. Zr-W-B System, Pseudo-Binary System  
TaB<sub>2</sub>-HfB<sub>2</sub>
- Volume X. Systems Zr-Si-C, Hf-Si-C, Zr-Si-B, and  
Hf-Si-B
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- Volume XIII. Phase Diagrams of the Systems Ti-B-C,  
Zr-B-C, and Hf-B-C
- Volume XIV. The Hafnium-Iridium-Boron System
- Volume XV. Constitution of Niobium-Molybdenum-Carbon  
Alloys
- Volume XVI. The Vanadium-Niobium-Carbon System
- Volume XVII. Constitution of Ternary Ta-Mo-C Alloys

### Part III. Special Experimental Techniques

- Volume I. High Temperature Differential Thermal Analysis
- Volume II. A Pirani-Furnace for the Precision Determina-  
tion of the Melting Temperatures of Refractory  
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### Part IV. Thermochemical Calculations

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

This technical report has been reviewed and is approved.



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Air Force Materials Laboratory

## ABSTRACT

The binary systems hafnium-vanadium and hafnium-chromium were investigated by means of X-ray, melting point, DTA, and metallographic techniques. Phase diagrams of both systems from approximately 1100°C through the melting range were established.

In the hafnium-vanadium system, the vanadium-stabilized  $\beta$ -Hf solid solution decomposes in a rapid eutectoid reaction at  $1190 \pm 25^\circ\text{C}$  and 19 At% V into the  $\alpha$ -modification and  $\text{HfV}_2$ . The maximum vanadium exchange in  $\beta$ -Hf is 23.5 At% at  $1456^\circ\text{C}$ , whereas the solid solubility in  $\alpha$ -hafnium is less than 2 At%. Vanadium dissolves up to  $\sim 4$  At% hafnium.

The only intermediate compound,  $\text{HfV}_2$ , has a fcc cubic, C15 type structure, with  $a = 7.398 \text{ \AA}$  at the hafnium-rich, and  $a = 7.386 \text{ \AA}$  at the vanadium-rich homogeneity limit. The phase melts congruently at  $1550 \pm 10^\circ\text{C}$  at the stoichiometric composition.

Eutectic equilibria are formed between  $\text{HfV}_2$  and  $\beta$ -Hf at 43 At% V and  $1456^\circ\text{C}$ , and between  $\text{HfV}_2$  and V at 69 At% V and  $1520^\circ\text{C}$ .

The hafnium-chromium system contains one intermediate phase,  $\text{HfCr}_2$ , with a hexagonal, C14-type of structure. The phase, which extends from approximately 64 At% Cr ( $a = 5.090 \text{ \AA}$ ;  $c = 8.25 \text{ \AA}$ ), to  $\sim 67$  At% Cr ( $a = 5.056 \text{ \AA}$ ;  $c = 8.21 \text{ \AA}$ ) at  $1500^\circ\text{C}$ , melts congruently at  $1870 \pm 15^\circ$  at the stoichiometric composition.

Beta-hafnium takes a maximum of 13 At% Cr into solid solution ( $1170^\circ\text{C}$ ), and the  $\beta$ -solid solution containing 11.5 At% Cr decomposes in a rapid eutectoid reaction at  $1355 \pm 15^\circ$  into  $\alpha$ -hafnium and  $\text{HfCr}_2$ . The maximum solubilities in  $\alpha$ -Hf and in Cr are less than 2 At%.

Eutectic equilibria are formed between the  $\beta$ -Hf phase and  $\text{HfCr}_2$  at 41 At% Cr and  $1510 \pm 8^\circ$ , and between  $\text{HfCr}_2$  and Cr at 87 At% Cr and  $1690 \pm 15^\circ\text{C}$ .

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## I. INTRODUCTION AND SUMMARY OF PREVIOUS WORK

In the course of our work on ternary systems of refractory transition metals with carbon, boron, and silicon<sup>(1)</sup>, it also was necessary to examine or redetermine the phase relationships in some of the metal boundary systems<sup>(2)</sup>.

A tentative diagram for the hafnium-vanadium system was published by Komjathy<sup>(3)</sup>. According to this work, the only intermediate phase,  $\text{HfV}_2$ , melts congruently at temperatures above 2000°C. Eutectic equilibria are formed between  $\text{HfV}_2$  and V at 1600°C, and between  $\text{HfV}_2$  and Hf at  $1550 \pm 15^\circ$  and 53 to 72 At% Hf. The solid solubility of hafnium in vanadium at 1500°C was said to lie between 7 and 8 wt% (2.1 to 2.4 At%).

Using high purity ingredients, the entire system was reinvestigated recently by Deardorff et al.<sup>(4)</sup>. According to the latter authors,  $\text{HfV}_2$  forms peritectically from melt and vanadium at 1480°C. The maximum solubility of vanadium in  $\beta$ -hafnium amounts to  $\sim 8$  wt% (23 At%) and the vanadium-stabilized  $\beta$ -Hf solid solution was shown to decompose eutectoidally at 1165°C and 6 wt% (18 At%) vanadium into the  $\alpha$ -modification and  $\text{HfV}_2$ . A eutectic equilibrium between  $\beta$ -Hf and  $\text{HfV}_2$  was placed at 20 wt% (47 At%) vanadium and 1395°C. Vanadium dissolved approximately 11 wt% (3.5 At%) hafnium, at 1480°C with the solubility rapidly decreasing as the temperature is lowered.

The phase  $\text{HfV}_2$  has a fcc-cubic, C15 type of structure<sup>(5)</sup>, with  $a = 7.386 \text{ \AA}$ <sup>(5)</sup>. Other measurements included  $a = 7.38 \text{ \AA}$ <sup>(4)</sup>, and  $a = 7.400 \text{ \AA}$ <sup>(6)</sup>.

The only information available on the hafnium-chromium systems concerns the structure of the intermediate phase  $\text{HfCr}_2$ : Elliott<sup>(7)</sup>, in his investigation of Laves type intermediate phases, first assigned a hexagonal, C36 ( $\text{MgNi}_2$ ) type of structure with  $a = 5.057 \text{ \AA}$  and  $c = 16.358 \text{ \AA}$ , but did not rule out the possibility of a transformation to the C14 ( $\text{MgZn}_2$ ) type at lower temperatures. In a reinvestigation of the compound by the same author<sup>(6)</sup>,  $\text{HfCr}_2$  was shown to be dimorphic, having the C14-type structure, with  $a = 5.067 \text{ \AA}$  and  $c = 8.237 \text{ \AA}$  up to 1000°C. At 1200°C, the cubic C15 type with  $a = 7.15 \text{ \AA}$  appeared. The  $\text{MgZn}_2$ -type structure was confirmed by Alisova et al.<sup>(8)</sup>, but

was attributed to the high temperature polymorph; the C15-type ( $a = 7.260 \text{ \AA}$ ) was said to be stable below  $1100^\circ\text{C}$ .

## II. EXPERIMENTAL

### A. STARTING MATERIALS AND ALLOY PREPARATION

The powdered elements were used in the preparation of the experimental alloys.

Hafnium metal powder (Wah Chang Corp., Albany, Oregon) was available in two grades, of which one contained 1.35 wt% (2.6 At%) Zr, whereas the other was essentially zirconium-free (175 ppm). Samples were prepared from both materials. The results were identical and hence no distinction of the specimens prepared from the two different grades will be necessary.

The chemical analysis of both powders were as follows (in ppm, values in brackets refer to the low zirconium grade): Al-60 (39); C-60 (360); Nb-<100 (200), Fe-120 (165), H-not dt. (160); Fe-120 (165); Mg-250 (10); N-100 (485); O-1100 (980); Si-<40 (150); Ta-<200 (<200); sum of other metallic impurities-<200 (<200). The lattice parameters measured for both materials were  $a = 3.195 \text{ \AA}$  and  $c = 5.051 \text{ \AA}$ .

High purity chromium powder (>99.9%) was obtained from H.C. Starck Corporation, Berlin, Germany. The main impurities included, in ppm: Fe, ~200; Mg, ~100, and O + N, 250.

The vanadium powder, as purchased, had an overall purity of better than 99.65%. The supplier was Oregon Metallurgical Corporation, Albany, Oregon. The major impurities included oxygen (810 ppm) nitrogen (140 ppm), and iron (450 ppm). The vanadium had a lattice parameter of  $a = 3.026 \text{ \AA}$ .

After cold compaction of the well-mixed powders, the specimens from both systems were prehomogenized under vacuum ( $<2 \times 10^{-6}$  Torr) for 2 hrs at  $1250^\circ\text{C}$  in a tungsten-mesh element furnace. For added protection

of the samples, the top of the tantalum sample container was filled with zirconium sponge to act as getter for rest gases contained in the furnace.

After the melting experiments in the Pirani-furnace, the specimens were cut into several pieces and used for studies of the solid state sections of the systems. Homogenization treatments for hafnium-vanadium alloys were 4 hrs at 1300°C, 6 hrs at 1150°C, and 220 hrs at 900°C. The hafnium-chromium alloys received, after melting, heat treatments at 1400°C (1 hr), 1200°C (7 hrs) and 900°C (220 hrs).

A selected number of specimens, mostly for metallographic purposes and for DTA-studies, were arc melted under high purity helium in a nonconsumable electrode arc furnace.

#### B. DETERMINATION OF MELTING TEMPERATURES AND DIFFERENTIAL THERMAL ANALYSIS

The melting temperatures of the alloys were determined using the method devised by Pirani and Alterthum<sup>(9)</sup>. Details of the apparatus used in this laboratory as well as temperature calibration and correction data have been described elsewhere<sup>(10)</sup>.

For the measurements on hafnium-vanadium and hafnium-chromium alloys, samples having black-body holes 0.4 to 0.6 mm in diameter and 3 mm deep were employed. Independent experiments conducted with graphite as a comparison standard ascertained emissivity coefficients of better than 0.995 for this hole geometry, thus leaving only a small temperature correction due to non-black body conditions<sup>(10)</sup>.

After loading the specimen into the furnace, the chamber was repeatedly evacuated and refilled with high purity helium and finally pressurized to 1.1 atmospheres. Residual gaseous impurities contained in the helium were gettered by a strip of titanium foil heated resistively inside the furnace. The specimens were then rapidly heated to within approximately 50°C of the suspected melting temperatures, and then the temperature gradually raised until

melting was detected. The temperatures were measured with a disappearing-filament type pyrometer, sighting through a quartz port in the furnace wall. To enhance the sensitivity in detecting incipient melting, a photoelectric transducer system<sup>(11)</sup> was employed for very heterogeneously melting alloys.

The differential-thermoanalytical studies were carried out using an apparatus which has been described in an earlier publication<sup>(12)</sup>. The runs were made under vacuum as well as under high purity helium (1.1 atm). Annealed tantalum served as comparison standard and tantalum-clad graphite as crucible material. Because the maximum temperatures reached in the experiments were as a rule less than 1600°C, no adverse interaction effects were noticeable.

### C. METALLOGRAPHIC, X-RAY, AND CHEMICAL ANALYSIS

For the microscopic examinations, the specimens were mounted in a mixture of diallylphtalate and lucite-coated copper powder and preground on silicon-carbide papers in the order of decreasing degrees of coarseness. They were polished on microcloth, using a slurry of Linde "B" alumina (0.05  $\mu$ ) in 5% chromic acid solution. The hafnium-chromium alloys were electroetched in a 0.5% aqueous oxalic acid solution. Hafnium-vanadium alloys containing up to 40 At% vanadium were first electroetched in 0.5% oxalic acid solution, and subsequently treated with a 25% acid solution (6 parts HNO<sub>3</sub>, 2 parts HCl, and 2 parts HF) to remove the stain from the anodizing treatment.

Approximately one-fourth of the processed samples were analyzed for oxygen and nitrogen, using a gas-fusion analyzer. No increase of these impurities in respect to the contaminant levels of starting materials were detected. Although no metal analyses were performed, weighing of the samples before and after each processing step indicated only negligible changes in respect to the weighed-in compositions.

Since the structures of the phases occurring in both systems were known from previous work, only powder diffraction patterns, using

Cu-K<sub>α</sub> as well as Cr-K<sub>α</sub> radiation, were prepared from all experimental alloys and the film strips evaluated.

### III. RESULTS

#### A. THE HAFNIUM-VANADIUM SYSTEM

The melting point data in Figure 1 clearly indicate the formation of two eutectic equilibria on both sides of the congruently melting, intermediate phase HfV<sub>2</sub>; this result was independently verified by metallographic analysis.

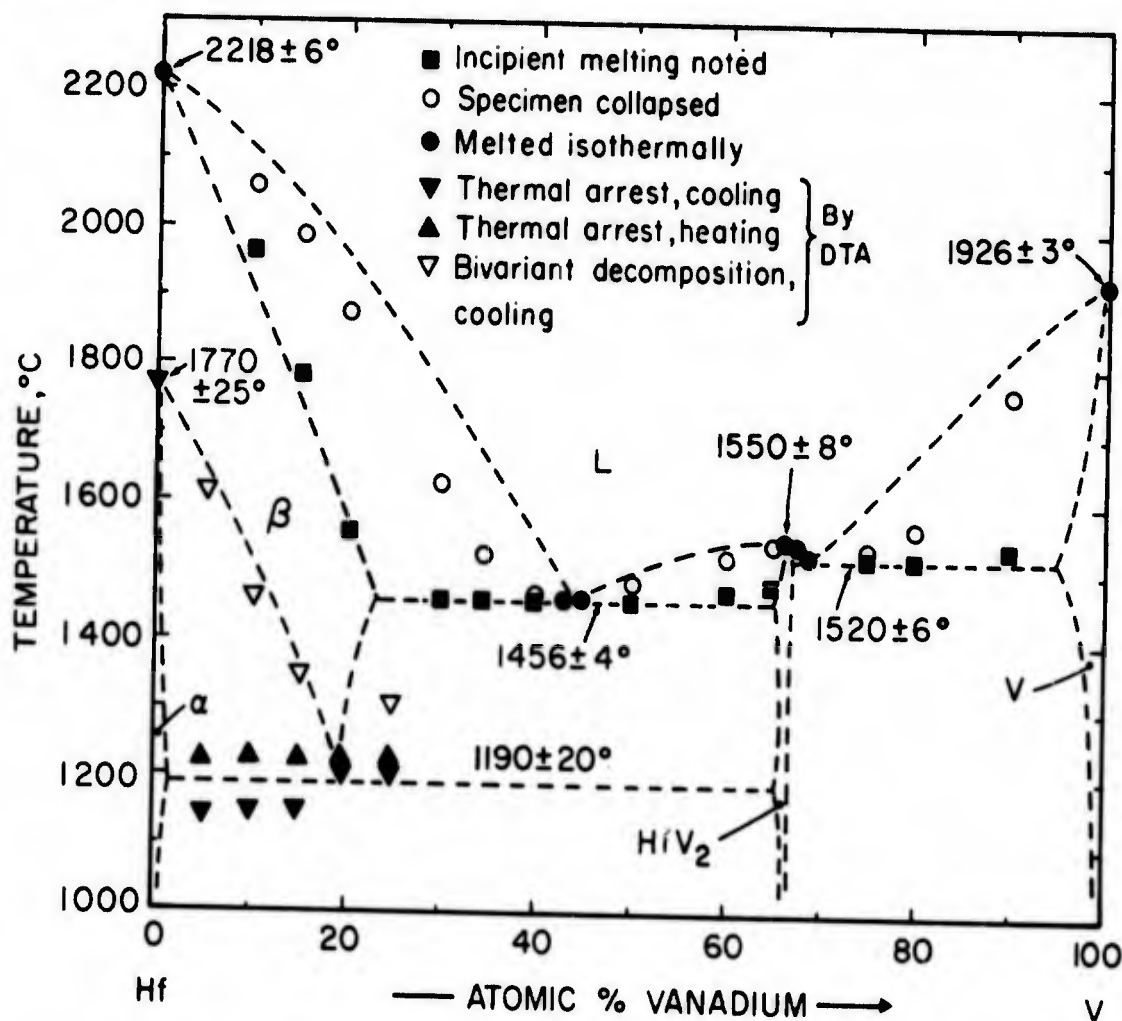


Figure 1. Melting Temperatures and Solid State Isotherms in the Hafnium-Vanadium System

(Temperature Error Figures Based on Reproducibility)



DTA-thermograms taken on hafnium-rich alloys indicate a lowering of the  $\alpha$ - $\beta$  hafnium transition temperature by vanadium (Figure 2); in addition to the bivariant transformation reaction at approximately 1600°C, a second, sharper thermal arrest in the vicinity of 1200°C represents the eutectoid decomposition of the  $\beta$ -phase; this sequence of reactions becomes more evident from the series of DTA-thermograms obtained on alloys with gradually increased vanadium contents (Figure 3). The considerable lag of the eutectoid reaction in the hypoeutectoid alloys upon cooling probably is attributable to hindered  $\text{HfV}_2$ -nucleation within  $\beta$ -hafnium. In agreement with this supposition also is the observation that this temperature lag was absent in hypereutectoid alloys, which contained excess  $\text{HfV}_2$  in the form of intragranular precipitates in the  $\beta$ -phase.

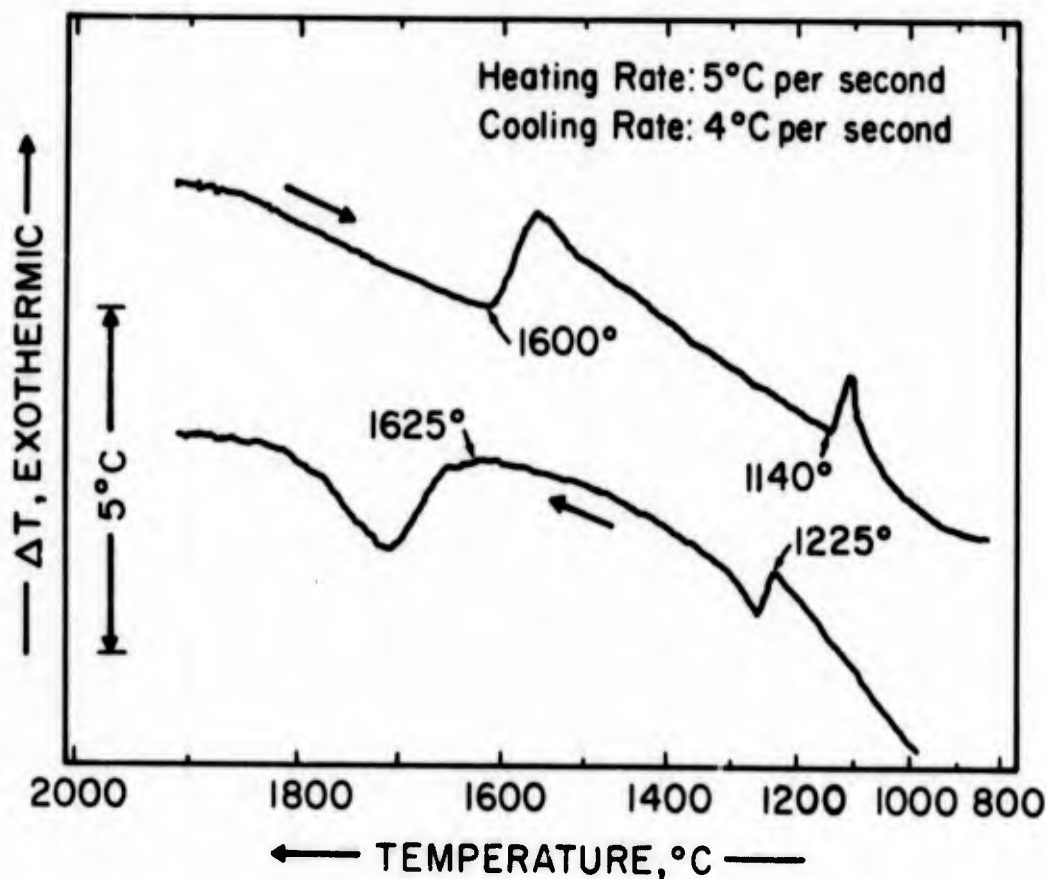


Figure 2. DTA-Thermogram of a Hafnium-Vanadium (95-5 At%) Alloy.

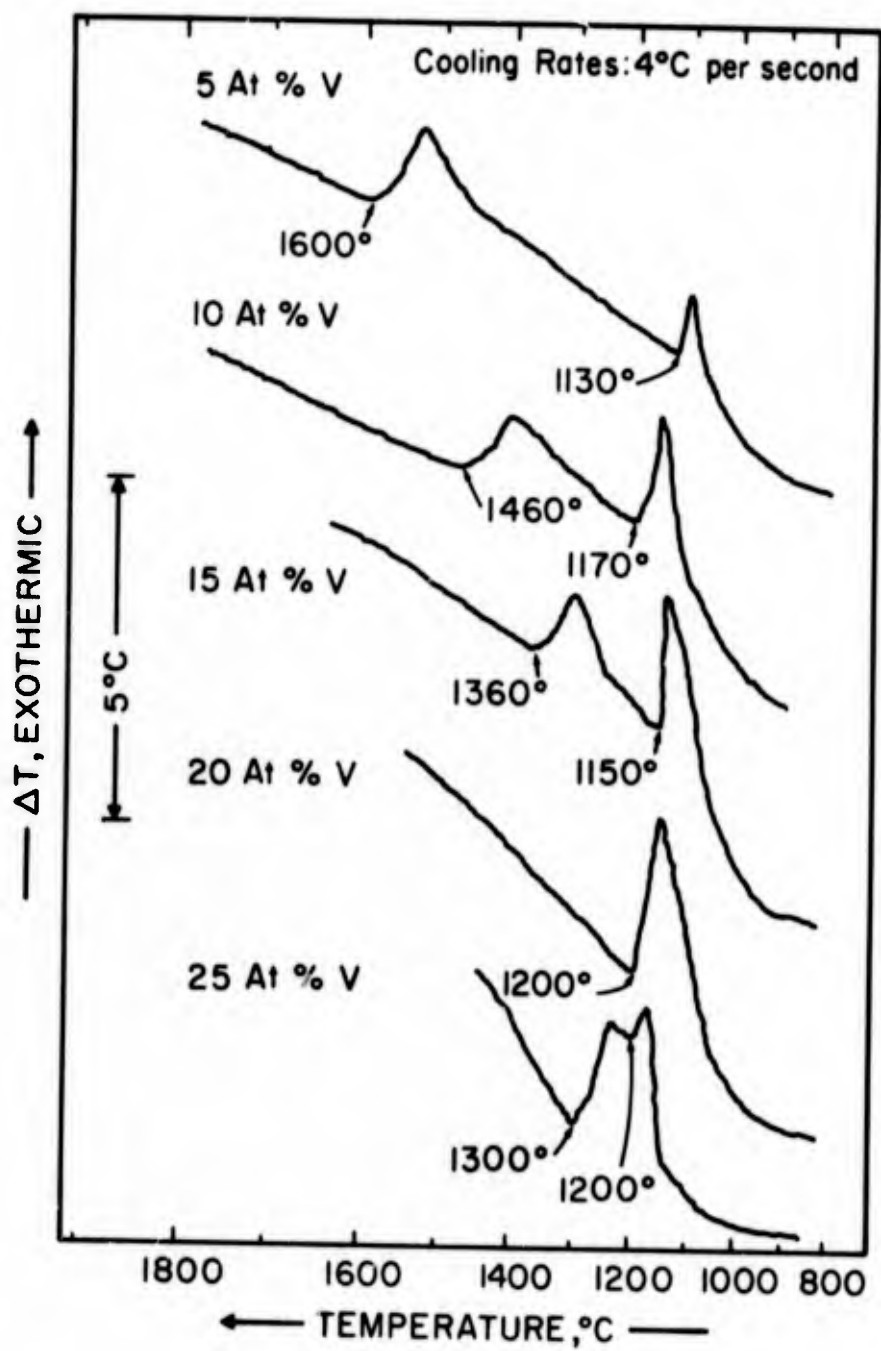
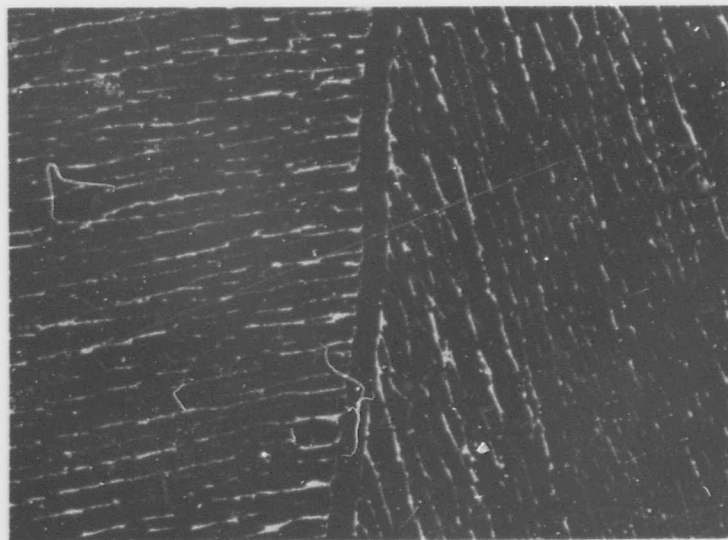


Figure 3. DTA-Thermograms (Cooling) of Hafnium-Rich Hf-V Alloys.



Alloys containing between 2 and 19 At% vanadium and which were equilibrated above 1200°C, contained corresponding amounts of proeutectoid  $\alpha$ -hafnium in a eutectoid matrix [ Figure 4(a) and 4(b) ]. Another alloy Hf-V (81-19 At%) was purely eutectoid (Figure 5), whereas the sample containing 22 At% V is unmistakably hypereutectoid (Figure 6). Based upon the metallographic observations, as well as the DTA-results, the composition of the eutectoid was placed at 19 At%-V and a temperature of  $1190 \pm 20^\circ\text{C}$ . Although an average of the DTA results (Figure 2) would indicate a 10 to 20°C higher temperature than that which was finally adopted, the lower temperature was chosen, since precipitation of  $\text{HfV}_2$  from  $\beta$ -hafnium tended to supplant the eutectoid reaction and thus the isothermal reaction temperature measured in hypereutectoid alloys was too high.



Figures 4(a) and 4(b):  
Proeutectoid  $\alpha$ -Hf (Stained Dark by Electroetch) and Eutectoid (Light).

Figure 4(a): Hf-V (95-5 At%), Cooled at  $12^\circ\text{C}$  per Second X325  
from  $1650^\circ\text{C}$ .

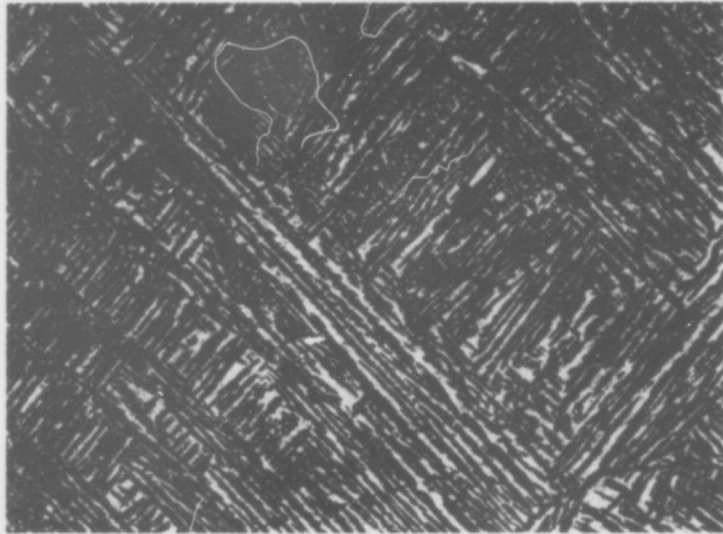


Figure 4(b): Hf-V (85-15 At%), Cooled at 30°C per Second X325  
from 1600°C.



Figure 5. Hf-V (81-19 At%), Cooled at 3°C per Second X2500  
from 1400°C.

$\alpha$ -Hf + HfV<sub>2</sub> Eutectoid.  
(Structure not Completely Resolved)



Figure 6: Hf-V (78-22 At%), Cooled at 3°C per Second  
from 1400°C.

X760

HfV<sub>2</sub> Precipitates in a Eutectoid Matrix.

The eutectoid reaction appears to be fast and the  $\beta$ -phase could not be retained even after tin-quenching of the alloys from above peritectoid temperatures. A maximum solid solubility 23.5 At% vanadium in  $\beta$ -hafnium was deduced mainly from a microscopic examination of alloys after equilibration and quenching from the  $\beta$ -Hf + HfV<sub>2</sub> eutectic temperature.

Melted alloys from the concentration range 25 to 42 At% vanadium showed primary crystallized  $\beta$ -Hf in a eutectic matrix (Figure 7). The alloy with 43 At% V was purely eutectic (Figure 8), whereas alloys in the range from 44 to 63 At% V contained primary crystallized HfV<sub>2</sub> and eutectic. Two samples located at 66 and 66.6 At% V were single phase HfV<sub>2</sub> after quenching from the melt; however, the alloy containing 68 At% V already showed approximately 40% eutectic besides primary crystallized HfV<sub>2</sub> (Figure 9).

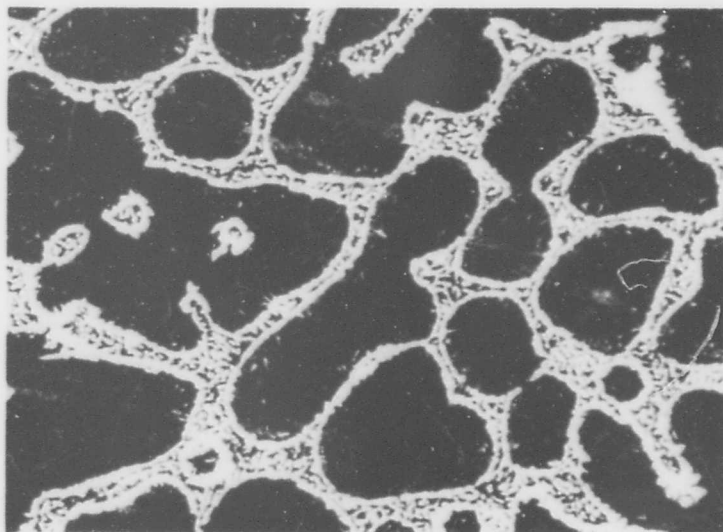


Figure 7: Hf-V (73-27 At%), Cooled at  $\sim 60^{\circ}\text{C}$  per Second X840  
from  $1600^{\circ}\text{C}$ .

Primary  $\beta\text{-Hf}$  (Decomposed, Dark Grains) in a Matrix  
of  $\beta\text{-Hf} + \text{HfV}_2$  Eutectic.

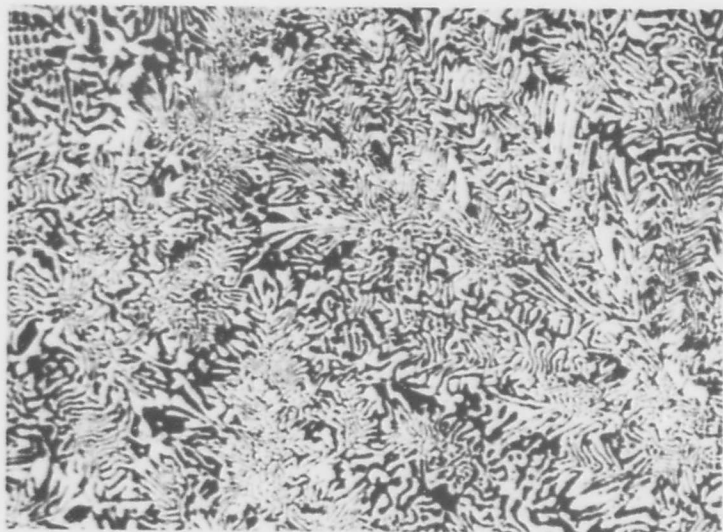


Figure 8. Hf-V (57-43 At%), Cooled at  $20^{\circ}\text{C}$  per Second X1000  
from  $1460^{\circ}\text{C}$ .

$\beta\text{-Hf} + \text{HfV}_2$  Eutectic

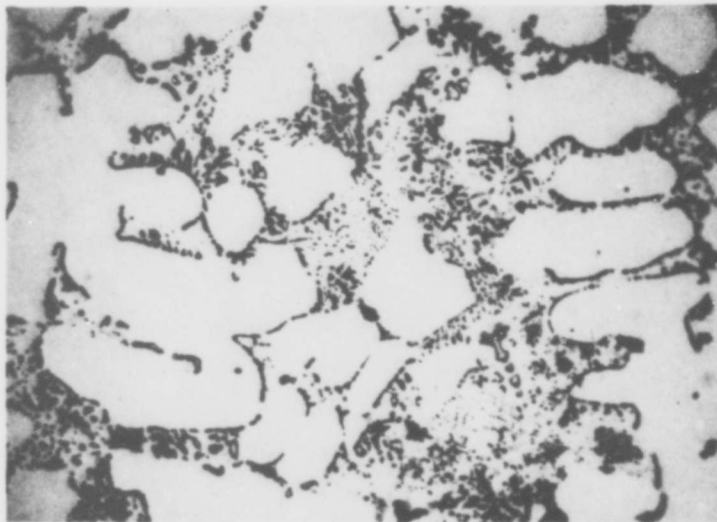


Figure 9: Hf-V (32-68 At%), Rapidly Cooled from 1540°C X600

The solubility of hafnium in vanadium was not specifically investigated, although microscopic examination of a melted alloy containing 95 At% V showed the alloy to be close to the phase boundary at 1500°C. Lattice parameter measurements on alloys quenched from 1500°C yielded an average expansion of the vanadium lattice from  $a = 3.206 \text{ \AA}$ , for pure vanadium, to  $a = 3.046 \text{ \AA}$  for the hafnium-saturated solid solution. In the 1200°C-equilibrated alloys, the parameter of the hafnium saturated solution was  $a = 3.031 \text{ \AA}$ . Taking into account the atomic radii of the alloy partners, these parameters would suggest a maximum hafnium solubility of  $\sim 4 \text{ At\%}$  at 1500°C, and of  $\sim 1 \text{ At\%}$  at 1200°C.

No additional phases were detected in the lower temperature ( $< 1200^\circ\text{C}$ ) heat-treatments, and the only modification observed for the  $\text{HfV}_2$ -phase was the C15-type. On the average and independent of the composition, a parameter of  $a = 7.388 \text{ \AA}$  was measured in the alloy series heat treated at 1100°C. Towards higher temperatures, the phase seems to exhibit a small homogeneity range as evidenced by the change of the lattice parameter from

$a = 7.398 \text{ \AA}$ , obtained in hafnium-rich alloys, to  $a = 7.386 \text{ \AA}$  in excess-vanadium alloys. The experimental data have been combined to yield the phase diagram of the system depicted in Figure 10.

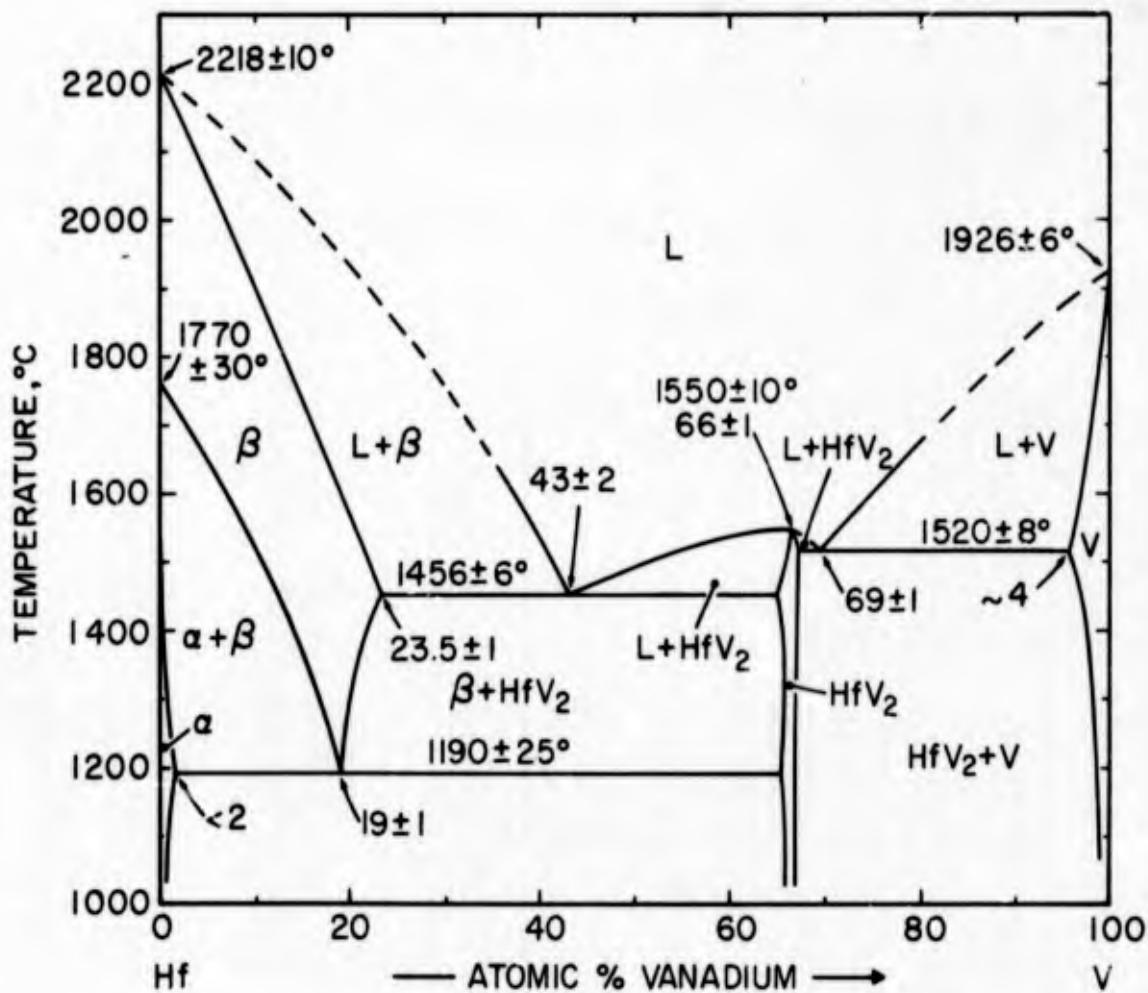


Figure 10. Proposed Constitution Diagram for the Hf-V System. (Temperature Figures Refer to Mean Value and Estimated Overall Uncertainty)

### B. THE HAFNIUM-CHROMIUM SYSTEM

The constitution diagram of the hafnium-chromium system is very similar to that of hafnium-vanadium. Because the experimental techniques were the same as applied for the hafnium-vanadium system, only a brief description of the experimental results will be given.

The measured solidus temperatures and solid state reaction isotherms are recorded in Figure 11. Representative DTA-thermograms of hafnium-rich alloys are shown in Figures 12 and 13, and micrographs in Figures 14 through 19. A proposed phase diagram for the hafnium-chromium system is depicted in Figure 20.

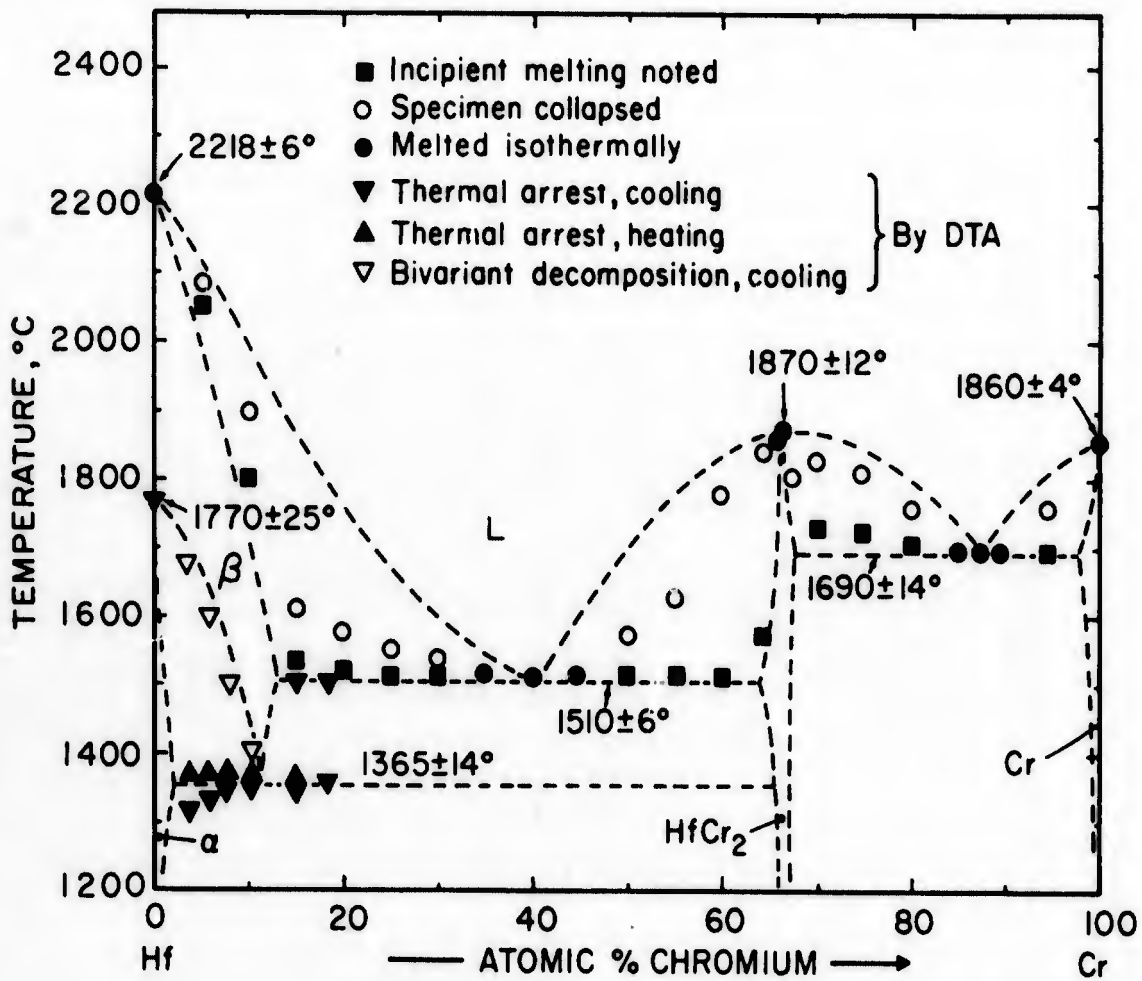


Figure 11. Measured Melting Temperatures and Solid State Isotherms in the Hafnium-Chromium System.

(Temperature Error Figures Based on Reproducibility)

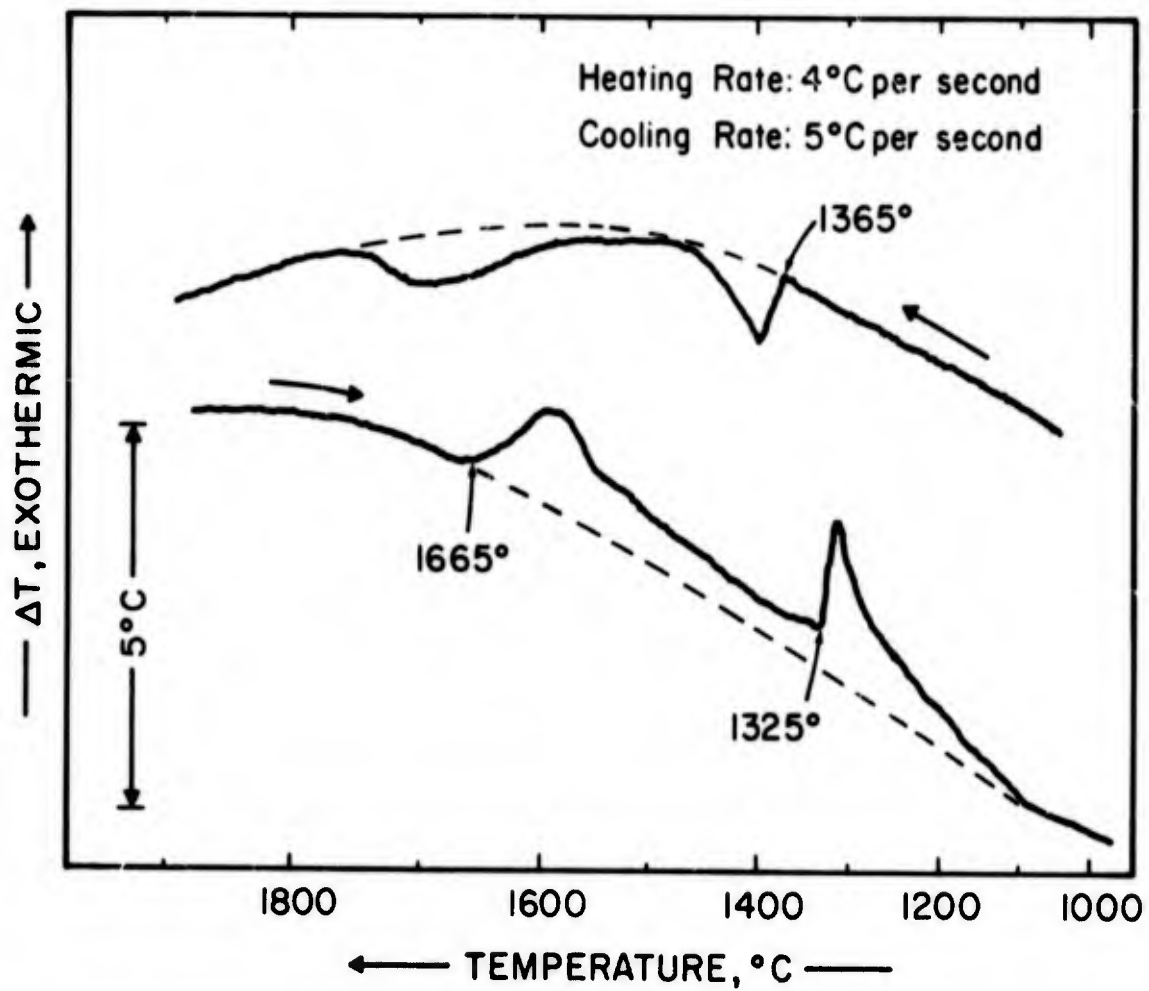


Figure 12. DTA-Thermogram of a Hafnium-Chromium Alloy Containing 4 At% Cr.



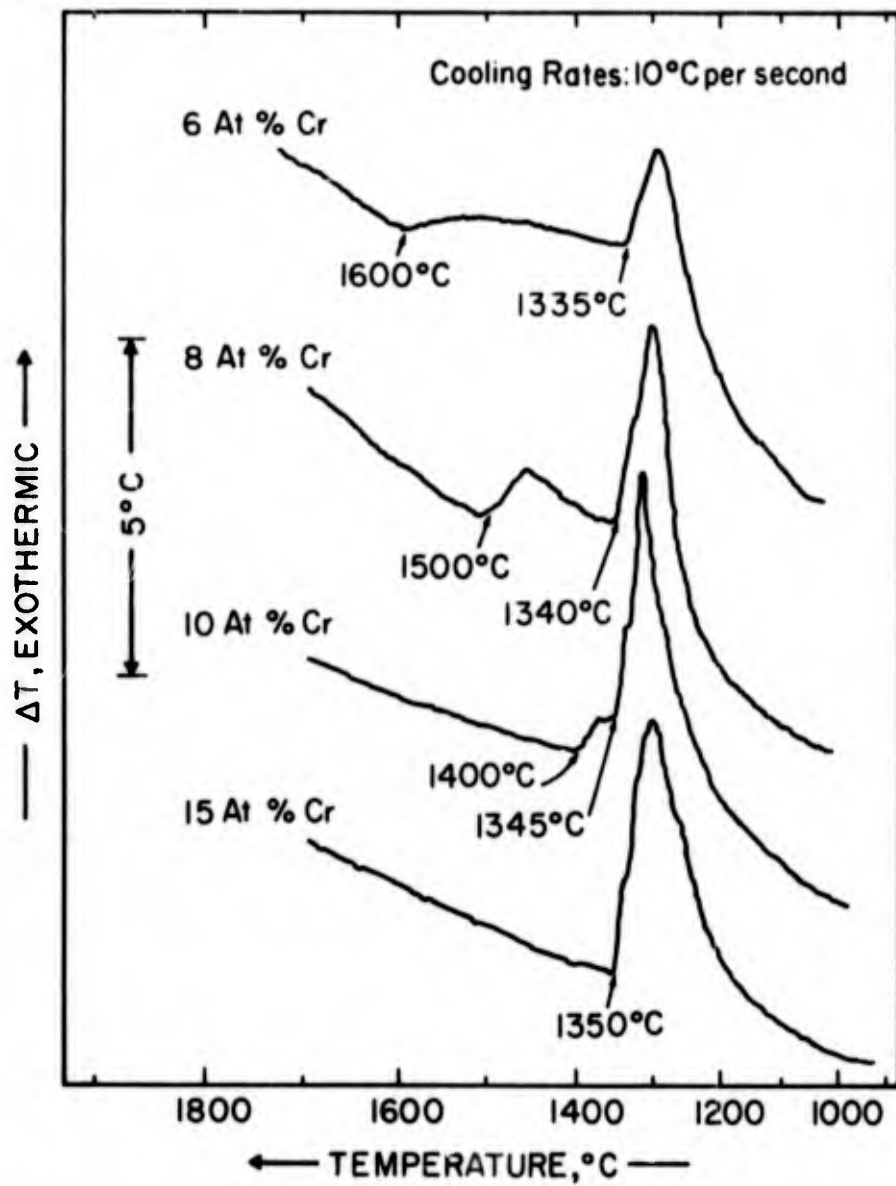


Figure 13. DTA-Thermograms (Cooling) of Hafnium-Rich Hf-Cr Alloys.

(Temperature Figures Shown on Curves are Pyrometric Control Measurements)

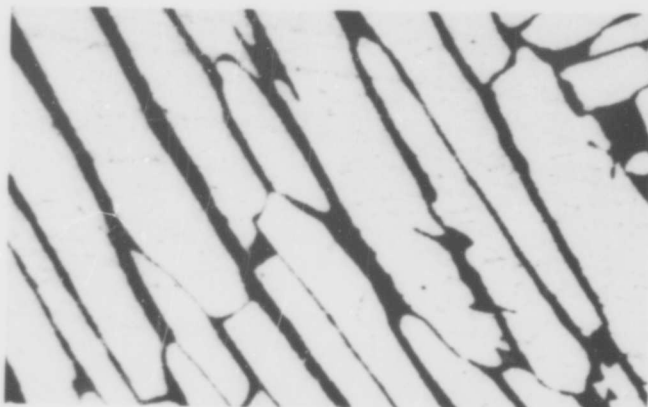


Figure 14(a): X720  
Hf-Cr (96-4 At%), Cooled at  
4°C per Second from 1700°C.  
Proeutectoid  $\alpha$ -Hf (bright-  
grains) and Small Amounts  
of Eutectoid.



Figure 14(b). X375  
Hf-Cr (90-10 At%), Cooled  
at 3°C per Second from 1550°C.  
Slightly Hypo-Eutectoid  
Composition.  
Eutectoid Not Resolved.

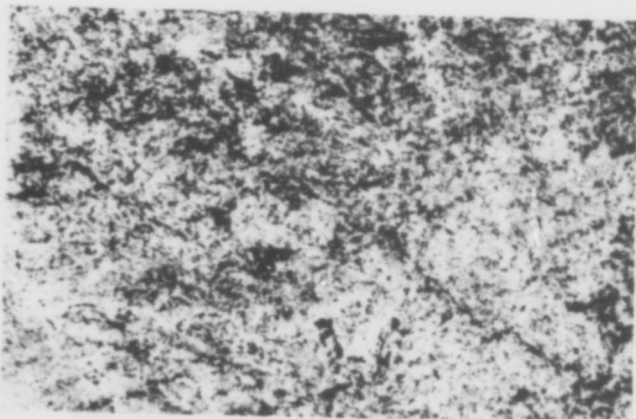


Figure 14 (c). X1000  
Hf-Cr (88.5-11.5 At%),  
Cooled at 9°C per Second  
from 1400°C.  
 $\alpha$ -Hf + HfCr<sub>2</sub> Eutectoid,  
Lamellar Structure not  
Resolved.

Figures 14(a) through 14(c):  
Micrographs of Hafnium-Rich Hf-Cr Alloys.

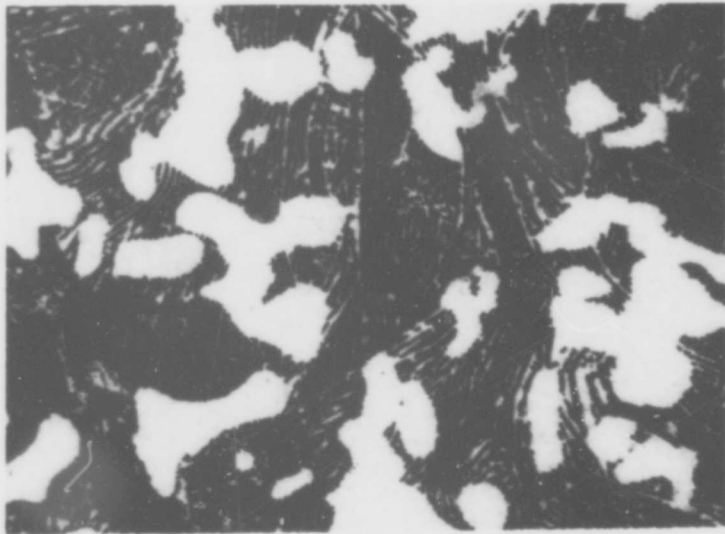


Figure 15. Hf-Cr (63-37 At%), Rapidly Cooled from 1530°C. X1000  
Primary  $\beta$ -Hf in a Matrix of  $\beta$ -Hf +  $\text{HfCr}_2$  Eutectic.



Figure 16. Hf-Cr (59-41 At%), Rapidly Cooled from 1510°C. X1000  
 $\beta$ -Hf +  $\text{HfCr}_2$  Eutectic

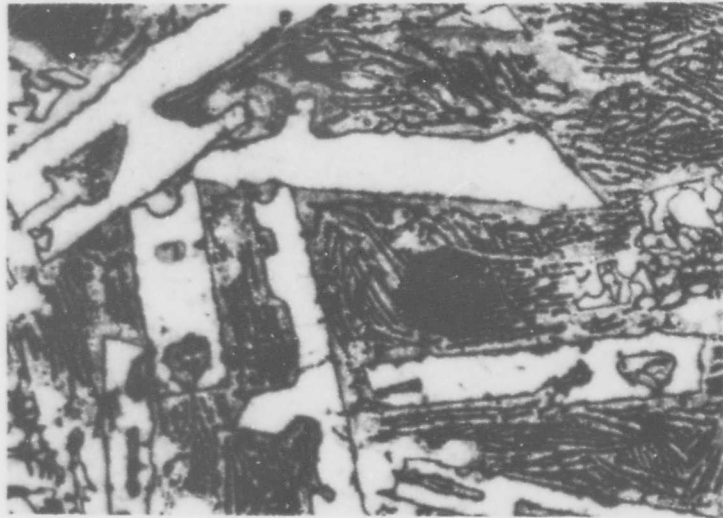


Figure 17. Hf-Cr (50-50 At%), Rapidly Cooled from 1650°C. X1000  
Primary HfCr<sub>2</sub> in a Eutectic Matrix.

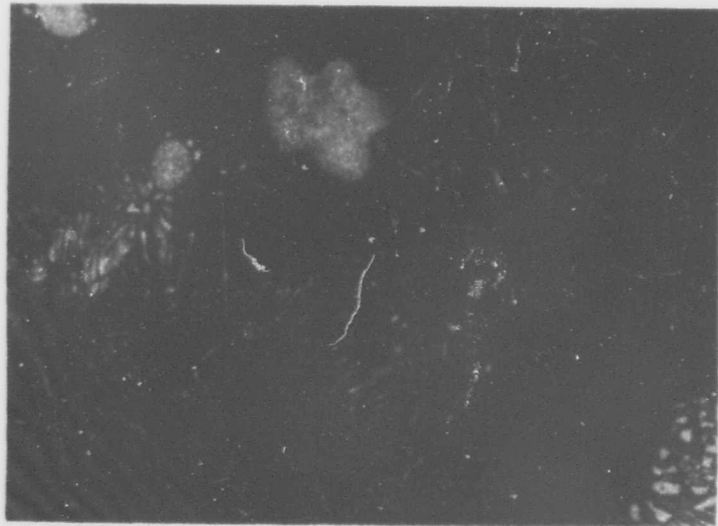


Figure 18. Hf-Cr (13-87 At%), Rapidly Cooled from 1700°C. X1000  
Isolated Grains of Primary Chromium in a Predominantly  
Eutectic Structure.

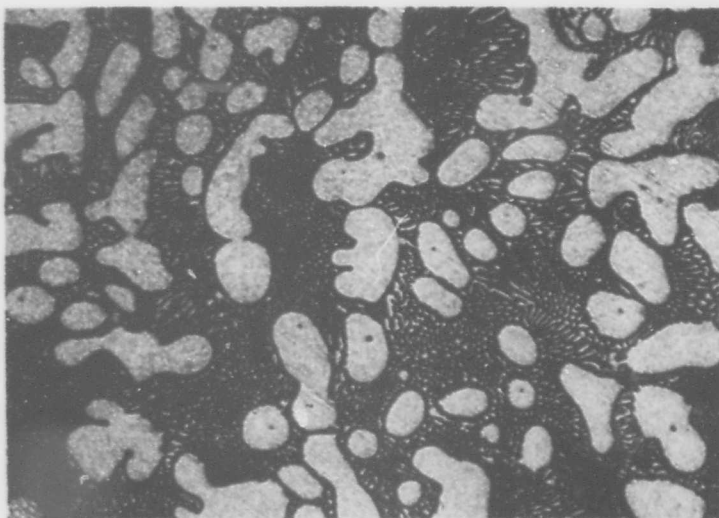


Figure 19. Hf-Cr (10-90 At%), Cooled at 30°C per Second from 1730°C. X760

Primary Chromium and  $\text{HfCr}_2 + \text{Cr}$  Eutectic.

The eutectoid reaction in this system also occurs with high speed and the  $\beta$ -hafnium phase could not be retained by tin-quenching the alloys from temperatures above 1360°C. X-ray patterns of alloys from the concentration region Hf +  $\text{HfCr}_2$ , regardless of the heat treatment, therefore always showed the pattern of  $\alpha$ -Hf beside the equivalent amount of  $\text{HfCr}_2$ .

Melted and quenched alloys, as well as samples annealed at subsolidus temperature, invariably showed the presence of only the hexagonal, C14-type modification of  $\text{HfCr}_2$ ; no signs of a transition could be detected in the DTA-runs. At high temperatures ( $\sim 1500^\circ\text{C}$ ), the phase was found to exhibit a noticeable range of homogeneity, extending from approximately 64 At% Cr ( $a = 5.090 \text{ \AA}$ ;  $c = 8.25 \text{ \AA}$ ), to 67 At% Cr ( $a = 5.056 \text{ \AA}$ ;  $c = 8.21 \text{ \AA}$ ), as verified independently by metallographic inspection of the alloys. In disagreement with the earlier findings by Elliott<sup>(6)</sup> and by Alisova et al.<sup>(8)</sup>, we were unable to detect the cubic, C15-type, modification in any of the heat-treated

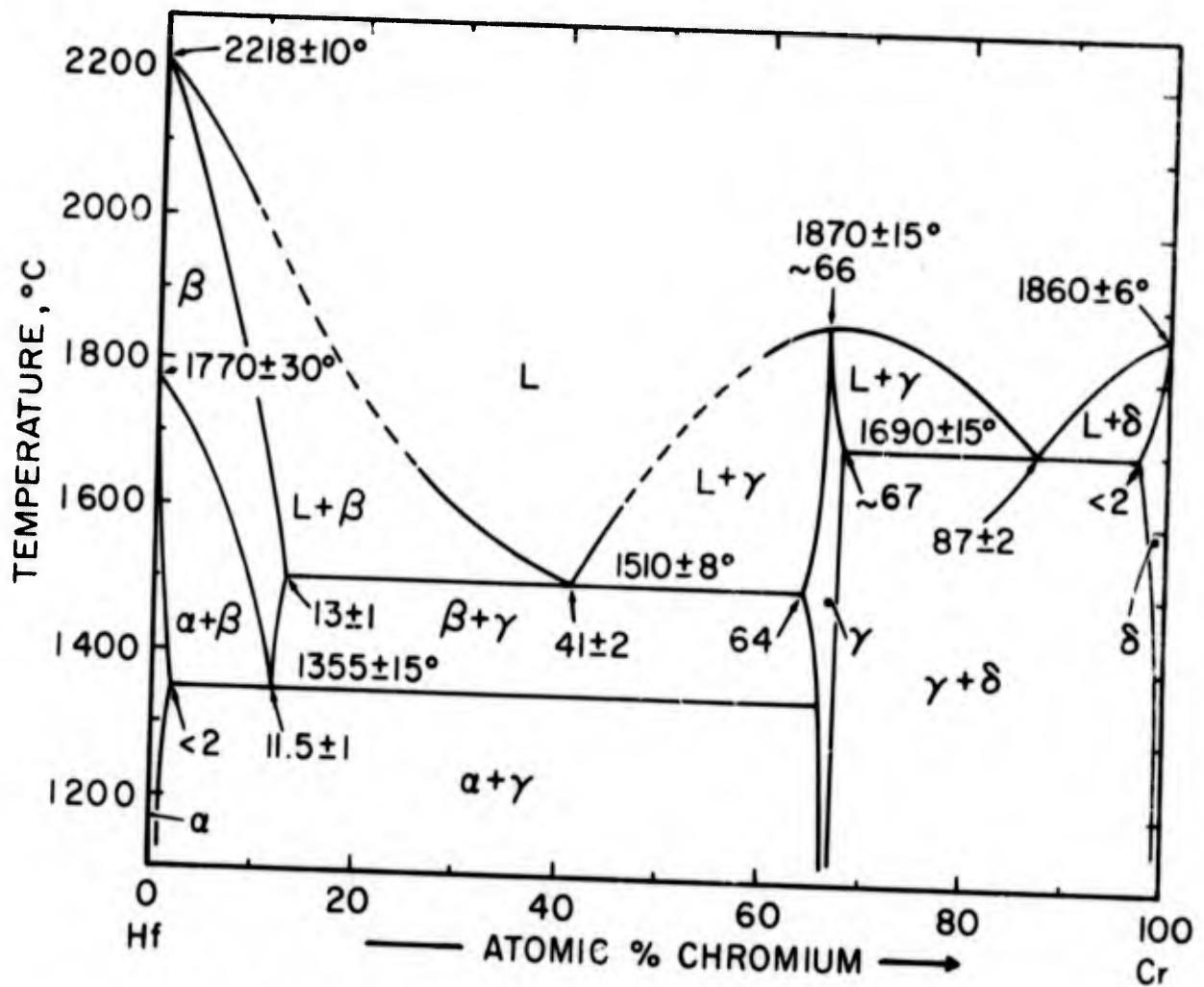


Figure 20. Proposed Phase Diagram for the Hafnium-Chromium System.

(Temperature Figures Refer to Mean Value and Estimated Overall Uncertainty).

alloys, which included a sample series which was heat treated for 220 hrs at 900°C. Alisova et al. (8) state in their paper, however, that the transformation occurs rather sluggishly; one therefore may argue that equilibrium was not attained in our experiments. Nevertheless, regardless of whether or not a transition of the  $\text{HfCr}_2$ -phase does occur at some lower temperature, our experiments do ascertain that the hexagonal is the stable form above 1100°C.

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DOCUMENT CONTROL DATA - R&D		
<i>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</i>		
1. ORIGINATING ACTIVITY (Corporate author) Aerojet-General Corporation Materials Research Laboratory Sacramento, California		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP N.A.
3. REPORT TITLE Ternary Phase Equilibria in Transition Metal-Boron-Carbon-Silicon Systems Part I. Binary Systems. Vol. XIV. Constitution of the Hafnium-Vanadium and Hafnium-Chromium Systems.		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)		
5. AUTHOR(S) (Last name, first name, initial) Rudy E. Windisch, S.		
6. REPORT DATE May 1968	7a. TOTAL NO. OF PAGES 22	7b. NO. OF REFS 12
8a. CONTRACT OR GRANT NO. AF 33(615)-1249	8a. ORIGINATOR'S REPORT NUMBER(S)	
b. PROJECT NO. 7350		
c. Task No. 735001		
d.	8b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFML-TR-65-2, Part I, Volume XIV.	
10. AVAILABILITY/LIMITATION NOTICES This document has been approved for public release and sale; its distribution is unlimited.		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY AFML (MAMC) Wright-Patterson AFB, Ohio 45433	
13. ABSTRACT  The binary systems hafnium-vanadium and hafnium-chromium were investigated by means of X-ray, melting point, DTA, and metallographic techniques. Phase diagrams of both systems from approximately 1100°C through the melting range were established.		



14	KEY WORDS	LINK A		LINK B		LINK C	
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