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(Summary Report)

A STUDY OF THE

ZIRCONIA-HAFNIA SYSTEM

Aerospace Research Laboratories  
Wright-Patterson Air Force Base, Ohio  
Attention: Dr. Robert Ruh

Contract No. AF 33(616)-7074

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IITRI-B194-23  
(Summary Report)  
May 1, 1963 - April 30, 1964

for

Aerospace Research Laboratories  
Office of Aerospace Research  
Wright-Patterson Air Force Base, Ohio  
Attention: Dr. Robert Ruh

April, 1964

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## A STUDY OF THE ZIRCONIA-HAFNIA SYSTEM

### ABSTRACT

A definitive study of phase relationships in the  $ZrO_2$ - $HfO_2$  system was conducted in this the fourth year of work on metal-oxygen systems. Metallographic, X-ray, differential-thermal, and microprobe analyses were applied to annealed and quenched specimens of arc-melted compositions. The system forms a continuous series of solid solutions in the low-temperature monoclinic structure as well as the high-temperature tetragonal structure. There is a relatively small intervening monoclinic plus tetragonal two-phase solid solution field. This field lies approximately on a straight line connecting the inversion temperatures of the two oxides. The melting points of  $ZrO_2$ - $HfO_2$  compositions likewise lie roughly on a line connecting the melting point of each oxide. There are no intervening complex oxides.

As a facet of this program, additional effort was directed toward a better definition of the high-temperature, high-hafnium region of the Hf-O system. This study was brought to a conclusion and a final Hf-O diagram is presented.

Finally, tasks of a service nature were conducted for cognizant personnel at ARL.

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## A STUDY OF THE ZIRCONIA-HAFNIA SYSTEM

### 1. INTRODUCTION

This is the twenty-third report issued on the subject contract, and the sixth and final report on the study of phase relationships in the zirconia-hafnia ( $ZrO_2$ - $HfO_2$ ) system. Earlier efforts were concentrated on an examination of the Ti-Zr-O system and on a delineation of the Hf-O binary diagram. Some work on the Hf-O system was done during the period covered by this report. The new investigation covered by this report is a logical extension of metal oxide studies. In this instance, the phase relationships in the  $ZrO_2$ - $HfO_2$  vertical section of the Zr-Hf-O system have been investigated.

### II. MATERIALS AND EXPERIMENTAL PROCEDURES

The oxides employed in this study were available from earlier work on the subject contract. Additional quantities of  $ZrO_2$  and  $HfO_2$  were obtained from the previous sources in order to insure an adequate supply of materials of uniform composition and purity. The oxide powders were cold-compacted into wafers, segmented, and stored for use. Table I lists the suppliers and purity of the several oxides used in this work.

All compositions used for experimental work were prepared by conventional arc-melting techniques. A modified approach to arc melting was investigated but found to be of no advantage. This point is discussed further in Section III.

The principal technique employed for delineating phase boundaries was the metallographic analysis of heat-treated and quenched specimens. Heat treatments discussed in this report were performed in one of two ways. Specimens annealed at temperatures up to  $1000^\circ C$  were sealed in evacuated Vycor bulbs, held for an appropriate time at a given temperature to within  $\pm 3^\circ C$ , and rapidly quenched at the conclusion of the anneal by breaking the bulb under water. Specimens treated at temperatures between  $1000^\circ$  and  $1200^\circ C$  were processed in a similar manner, except that quartz bulbs were employed and a reduced pressure of argon was admitted to the bulb before sealing. In all cases, individual specimens were wrapped in tantalum foil to preserve integrity and identity. For treatments at  $1400^\circ C$  and higher, an NRC Model 2914 high-temperature vacuum resistance furnace was used, or a platinum (air) furnace which was employed for several of the  $ZrO_2$ - $HfO_2$  anneals.

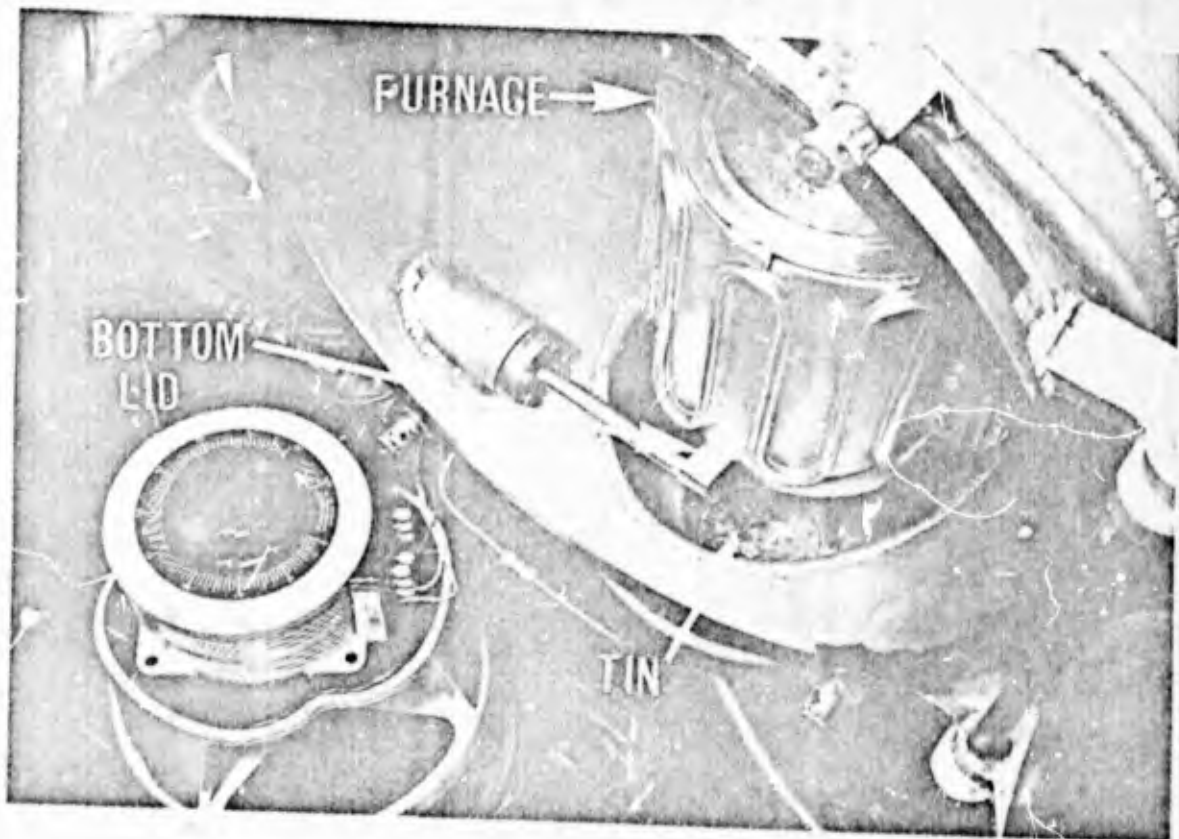
In order to effect a better quench for samples annealed in the NRC high-temperature resistance furnace, a liquid tin quenching bath was designed, constructed, and adapted to the furnace. The furnace with quench bath is shown in Figure 1. Specimens are annealed by suspending them within the heating zone enclosed by the water-cooled copper chamber visible in the photo. At the conclusion of the anneal, the bottom lid is swung open, automatically releasing the specimen suspension wire permitting the specimen to drop into the liquid tin bath. The tin, meanwhile, has been heated to just above its melting point ( $232^\circ C$ ) by an externally mounted resistance heater.

TABLE I

## FORM, PURITY, AND SUPPLIERS OF ALLOYING INGREDIENTS

Form	Zirconium Oxide		Hafnium Oxide	
	Reactor Grade	Spectrographic Grade	Reactor Grade	Spectrographic Grade
Supplier	Titanium Alloy Mfg. Div. National Lead Co., Niagara Falls, N. Y.		Wah Chang Corp. Albany, Oregon	
Typical Analysis (a)	B <sub>2</sub> O <sub>3</sub> nd	V <sub>2</sub> O <sub>5</sub> nd	Al 35	Pb 10
	SiO <sub>2</sub> 0.15 w/o	CuO 0.002 w/o	B 35	Si 600
	P <sub>2</sub> O <sub>5</sub> nd	ZnO nd	Cd <1	Ti 2000
	Sb <sub>2</sub> O <sub>5</sub> nd	BaO nd	Co <5	V 15
	Fe <sub>2</sub> O <sub>3</sub> 0.003 w/o	SiO nd	Cr <75	W <50
	Cr <sub>2</sub> O <sub>3</sub> nd	Na <sub>2</sub> O nd	Cu <40	
	MnO <sub>2</sub> nd	Li <sub>2</sub> O nd	Fe 2100	
	PbO nd	K <sub>2</sub> O nd	Mg 50	
	MgO 0.03 w/o	BeO nd	Mn 15	
	SnO nd	Ni <sub>2</sub> O <sub>3</sub> nd	Mo 10	
	Cb <sub>2</sub> O <sub>5</sub> nd	HfO <sub>2</sub> <0.02 w/o	Ni 40	
	TiO <sub>2</sub> 0.005 w/o	Al <sub>2</sub> O <sub>3</sub> 0.005 w/o		
		CaO nd	Zr	2.2 w/o
			Loss on ignition	0.03 w/o

(a) Values for ZrO<sub>2</sub> given as weight per cent (w/o) or not detected (nd).Values for HfO<sub>2</sub> given as parts per million except w/o as noted.



Neg. No. 26023

Fig. 1 - High Temperature Vacuum Resistance Furnace with Liquid Tin Quench Bath.

As soon as the samples plunge into the bath, the power to the heater is turned off and a water cooling coil of several turns of copper tubing is turned on. In this way, the specimens are rapidly cooled from, say, 2150° to 232°C and then cooled at a somewhat slower rate to room temperature.

After the furnace proper has cooled to a safe temperature, the chamber is opened, the tin is reheated to its melting point, and the specimens are removed. It was expected that there would be no noticeable effect on microstructure due to the comparatively slow cool from 232°C to room temperature and the need to reheat the specimens in order to remove them from the quench bath.

Specimens are individually wrapped in tantalum packets, each packet being identified with a stamp. There have been no problems in establishing the identity of each packet after removal from the molten tin; it has been possible to process eight or ten samples at a time without difficulty.

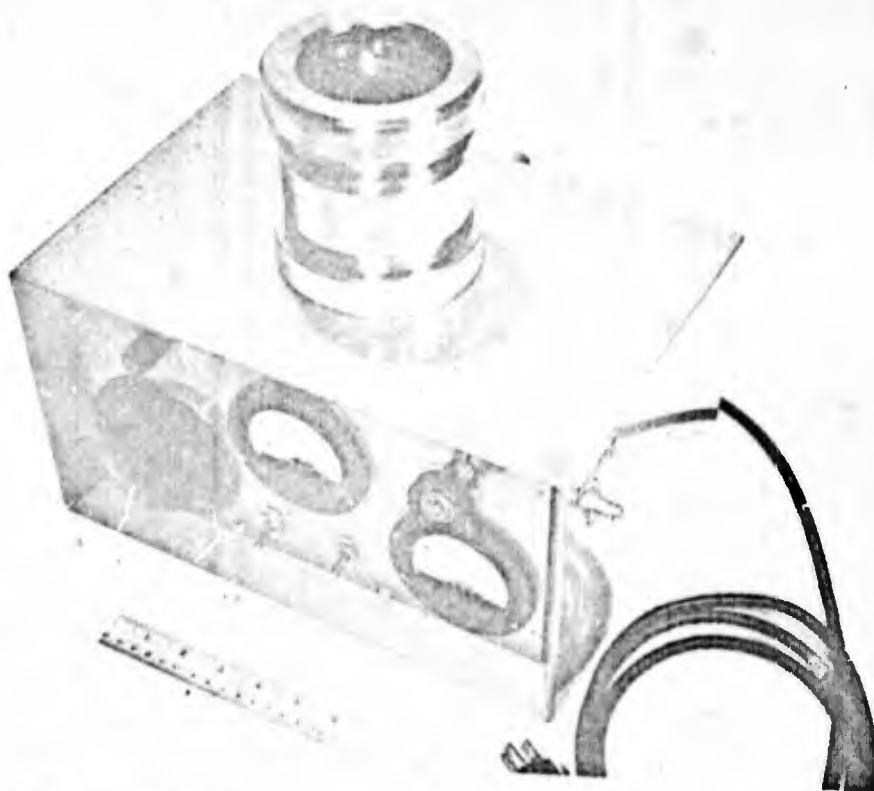
The melting point vs. composition studies described in this report were conducted using a furnace designed and constructed specifically for this purpose. After a reassessment of the equipment available for melting point determinations and a consideration of the requirements for work of this nature in the  $ZrO_2$ - $HfO_2$  system, it was deemed advisable to construct a new device for this work. The design requirements include the following:

1. Expendable heating element since the molten specimens inevitably attack the element.
2. Easily controlled heating and cooling rates.
3. Provisions for optical temperature measurement.
4. Ability to operate in vacuum or inert atmosphere.
5. High-temperature capability up to 3000°C.
6. Simple design.

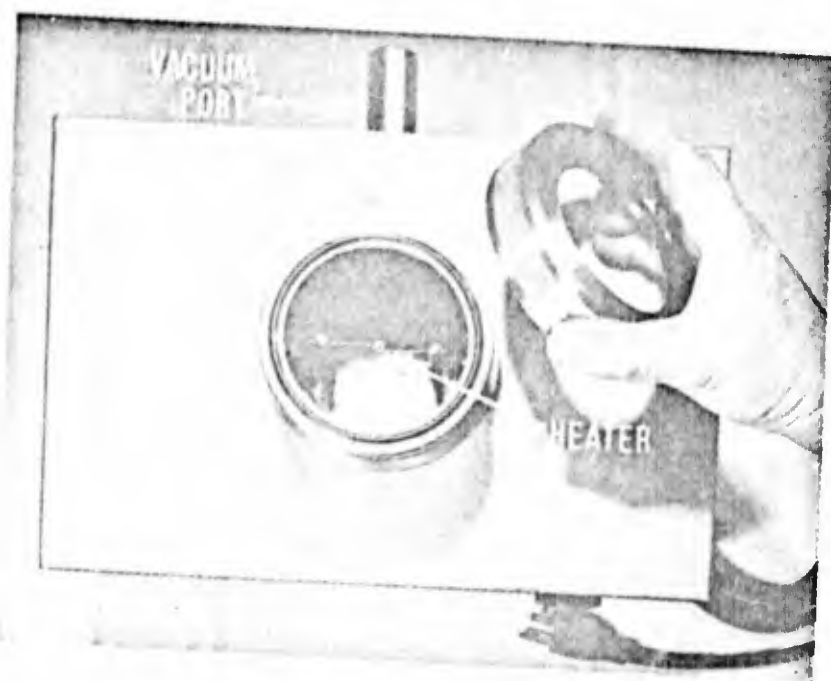
The furnace designed and built to fulfill these requirements is shown in Figure 2. It requires only vacuum and electrical connections (no water), has an expendable tungsten wire basket as a heater, and can be used for either vacuum or inert gas determinations.

The tungsten wire baskets used to support and contain the specimen are preformed and are available commercially from E. Fullam, Inc., Schenectady, N. Y. The baskets are relatively inexpensive (about 30 cents each) and are discarded after each run. Inasmuch as the specimen wets the tungsten after melting, it is of course impossible to reuse the baskets.

A small sample is placed within the conical basket, the cover is placed on and the unit is evacuated. Power is supplied to the heater (basket) through two uncooled copper posts in the chamber. The posts pass into the chamber through electrically insulated and vacuum-tight feed-troughs. The variable transformer seen at the left in the top photo of Figure 2 is connected to a step-down transformer, which in turn delivers power to the heater at 0-20



Neg. No. 26259



Neg. No. 26260

Fig. 2 - Two Views of the Melting Point Furnace

volts. The total power consumption is less than 500 watts. The temperature is raised by increasing the power output from the variable transformer. Thus, the basket and sample are heated at any desired rate. The sample is observed through a Leeds and Northrup optical pyrometer. Temperature measurements are taken with the optical pyrometer on the tungsten wire adjacent to the specimen. Indications of melting are manually recorded together with temperatures.

The raw melting point data are treated in the following manner. The observed temperatures read on the tungsten wire basket are converted to "true" temperature based on emissivity corrections for tungsten readily available in the literature. The correction then does not require a knowledge of the emissivity of the alloy specimen, often not available or else not accurately known.

### III. RESULTS AND DISCUSSION

A total of 35 ingots of compositions varying from  $ZrO_2$  to  $HfO_2$  were prepared for use in this study. Ten of the ingots were preliminary melts prepared in the interest of determining if a modified approach to the arc-melting procedure might be beneficial.

A series of five compositions containing 0, 25, 50, 75, and 100 w/o  $HfO_2$  (0, 16.3, 36.9, 63.7 and 100 m/o) were selected. For the first set, calculated amounts of the pressed powders of the two oxides were weighed and arc-melted together. For the second set, the appropriate amounts of loose powders were weighed, blended, and compacted into aspirin size tablets (several tablets were produced for each composition). These tablets were then wrapped in tantalum tubes and sintered at  $1500^\circ C$  for two hours. The sintered tablets were then arc-melted to yield a series of five compositions the same as the first. Comparisons of ease of arc-melting, weight losses, and structure were made to determine if any benefit was derived from the second procedure. Fundamentally, the object of the pressing and sintering prior to arc-melting was to preclude the main problem (blowing) attendant on melting powder material.

A comparison of the microstructures of the arc-melted and the pressed, sintered, and arc-melted materials indicated that the sintering operation was in fact detrimental. Metal phase (alpha solid solution, Zr-Hf-O) was evident in certain of the ingots prepared from the sintered oxides. No metal phase was seen in the conventionally arc-melted materials. Weight losses were considerably greater in the sintered and melted ingots. The larger weight losses are attributed to the loss of fragments during the extra handling operations and the loss of oxygen during the sintering process. The pressure was seen to rise in the vacuum furnace employed for sintering, and the tantalum tubes were severely embrittled. As a result of this study, all compositions used in experimental work were produced by conventional arc-melting procedures.

In addition to the ingots prepared with the reactor grade of  $HfO_2$  (~2 w/o Zr), four ingots were arc-melted utilizing the spectrographic grade of  $HfO_2$  containing only 180 ppm  $ZrO_2$ . These four compositions were



Neg. No. 25615

Fig. 3

X500

$ZrO_2 + 10$  w/o  $HfO_2$  (6.1 m/o) specimen in the as arc-cast condition. This polarized light photo illustrates a typical martensitic structure.

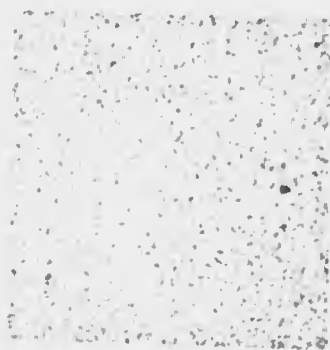


Neg. No. 25616

Fig. 4

X500

$ZrO_2 + 50$  w/o  $HfO_2$  (36.9 m/o) specimen in the as arc-cast condition. This is also a polarized light photomicrograph and is similar to the structure shown in Fig. 3.

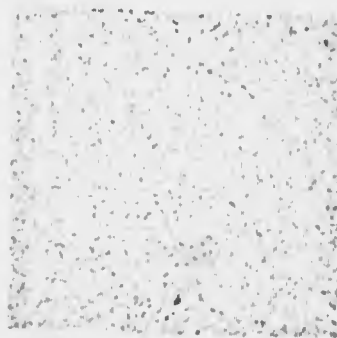


Neg. No. MP 507

Fig. 5

X165

Zr X-ray image of the specimen shown in Fig. 4. The uniform brightness of a uniform distribution of Zr.



Neg. No. MP 506

Fig. 6

X165

Hf X-ray image of the specimen shown in Fig. 4. This image confirms a uniform distribution of Hf.

prepared in order to study an effect observed in the X-ray patterns of certain compositions in the  $\text{HfO}_2$ -rich region of the system.

Table II summarizes the compositions of all ingots prepared for this study.

As-cast microstructures were studied metallographically; the structures were remarkably similar immediately suggesting that  $\text{ZrO}_2$  and  $\text{HfO}_2$  form a continuous series of solid solutions. Typical structures are shown in Figures 3 and 4. The serrated or martensitic appearance of these structures must be attributed to the fact that the specimens have gone through a tetragonal to monoclinic inversion on cooling in the arc furnace. In an attempt to verify this hypothesis, an as-cast specimen of the 50 w/o  $\text{HfO}_2$  (36.9 m/o) composition was subjected to microprobe analysis. The results shown in Figures 5 and 6 illustrate that there is neither an enrichment nor a depletion of either zirconium or hafnium in any area. The two metallic elements are uniformly distributed, as would be the case in a system with mutual solid solubility.

Samples of selected compositions were then annealed at 800°, 1000°, 1200°, 1400°, 1600°, and 1800°C. These annealed specimens were subjected to X-ray and metallographic study.

The metallographic studies supported the concept of complete mutual solubility between the two oxides. There was no discernible difference between any of these specimens or specimens annealed at any of the temperatures. Even when samples were quenched from above the monoclinic to tetragonal inversion temperature they were no different from specimens annealed below (in the monoclinic field). Annealing at the lower temperatures had little, if any, effect on the type of structure initially developed during the solidification and the cool to room temperature within the arc-melting furnace.

It was hoped that a metallographic study of annealed and quenched specimens would provide some unequivocal sign that a given sample had been annealed in the tetragonal, monoclinic, or monoclinic plus tetragonal field. Such evidence was not identified.

X-ray procedures were applied to annealed and quenched specimens, in the hope that powder patterns might provide evidence for delineating the two-phase field. It was hoped that some criterion would be evident for determining whether a specimen had been annealed above, below, or within the monoclinic to tetragonal region. This was not the case. The specimens all displayed lines corresponding to the monoclinic structure. There was a smooth transition in crystal lattice d-spacing as the composition varied from  $\text{ZrO}_2$  to  $\text{HfO}_2$ , but there was no line broadening or similar feature which could be identified as evidence of the specimen having undergone the tetragonal to monoclinic inversion during the quench.

For the X-ray analysis work powder patterns were prepared using a 114.6 mm camera and copper  $K_\alpha$  radiation. The diffraction patterns were measured, and interplanar d-spacing were determined. This work included studies of diffraction patterns of the as-received oxides plus the arc-melted oxides as well as annealed and quenched specimens of various compositions.

TABLE II  
SUMMARY OF ZIRCONIA-HAFNIA COMPOSITIONS<sup>+</sup>

Alloy Code No.	Weight Per Cent Hafnia (w/o HfO <sub>2</sub> )	Mole Per Cent Hafnia (m/o HfO <sub>2</sub> )
Z-0H	0	0
Z-5H	5	3.0
Z-10H	10	6.1
Z-15H	15	9.4
Z-20H	20	12.8
Z-25H	25	16.3
Z-30H	30	20.0
Z-35H	35	24.0
Z-40H	40	28.1
Z-45H	45	32.4
Z-50H <sup>(*)</sup>	50	36.9
Z-55H	55	41.7
Z-60H	60	46.7
Z-65H	65	52.1
Z-70H <sup>(*)</sup>	70	57.7
Z-75H	75	63.7
Z-80H	80	69.8
Z-85H	85	76.8
Z-90H <sup>(*)</sup>	90	84.0
Z-95H	95	91.7
Z-100H <sup>(*)</sup>	100	100

<sup>+</sup> All compositions were prepared with reactor grade HfO<sub>2</sub>. In addition, the compositions marked (\*) were also prepared with spectrographic grade HfO<sub>2</sub>.

A tabulation of selected results is presented in Table III. All specimens exhibited a monoclinic pattern; d-spacings varied within the range of experimental error. It is interesting to note that in the case of the as-received  $ZrO_2$ , at least one line corresponding to a cubic structure was present which was not detected in any arc-melted  $ZrO_2$  as  $ZrC_2$ -rich compositions.

One unanticipated feature was observed in some X-ray patterns. An "extra" line at d-spacing of  $2.92 + 0.01$  A was evident in nearly all the specimens containing more than 50 w/o  $HfO_2$  (36.9 m/o). This line was observed irrespective of the temperature at which the sample was annealed. The presence of the line was composition-sensitive, and can be attributed to the degree of purity of the reactor-grade  $HfO_2$  employed for these melts. As proof, four compositions at 50, 70, 90, and 100 w/o  $HfO_2$  (36.9, 57.7, 84.0, and 100 m/o) were prepared using the spectrographic grade of  $HfO_2$ . Specimens were annealed at and quenched from selected temperatures, above and below the monoclinic plus tetragonal region. The results of the X-ray studies of these samples clearly indicate that the presence of the extra line is attributable to impurities in the reactor-grade  $HfO_2$  since none of the high-purity oxide specimens exhibited this line.

In order to define the monoclinic plus tetragonal phase field in this system, differential thermal analysis was the next logical step. One sample of  $ZrO_2 + 50$  w/o  $HfO_2$  (36.9 m/o) was forwarded to ARL for study in a new piece of DTA equipment available there. The results of this study are summarized in Table IV. As anticipated, there is a hysteresis effect on heating and cooling. The values determined lie very close to a straight line drawn between the monoclinic to tetragonal inversion temperature for  $ZrO_2$  ( $\sim 1100^\circ C$ ) and  $HfO_2$  ( $\sim 700^\circ C$ ). Additional differential thermal analysis work was then conducted at this laboratory, and these data are likewise presented in Table IV.

Thus, all experimental evidence indicates that the two oxides form a continuous series of solid solutions in the monoclinic as well as the tetragonal structures. There must be a small monoclinic plus tetragonal two-phase field between these areas of complete miscibility. A continuous series of solid solutions in this system was, in fact, suggested by C. E. Curtis et al. (1)

Finally, melting point vs. composition studies were conducted. The furnace described in an earlier section of this report was used for this work. The melting points of  $ZrO_2$  and  $HfO_2$  were measured as were data for  $ZrO_2$ - $HfO_2$  compositions at 10 w/o  $HfO_2$  increments. In the treatment of the data, the melting points of  $ZrO_2$  and  $HfO_2$  ( $2680^\circ$  and  $2900^\circ C$ ) were accepted as base points from which the observed melting points of the  $ZrO_2$ - $HfO_2$  compositions were corrected. The results are shown in Table V. Whereas the melting points of the binary oxides are fixed, the ternary solid solutions must have both solidus and liquidus points. The observed melting temperature for a given composition has been assumed to lie somewhere between these two points.

---

(1) C. E. Curtis, L. M. Doney and J. R. Johnson, J. Am. Ceram. Soc., 37, 1954, 458-465.

TABLE III

## INTERPLANAR SPACINGS\*

ZrO <sub>2</sub> As Rec'd. d I	ZrO <sub>2</sub> Arc Melted d I	HfO <sub>2</sub> As Rec'd. d I	HfO <sub>2</sub> Arc Melted d I	ZrO <sub>2</sub> 50w/o HfO <sub>2</sub> Arc Melted d I	ZrO <sub>2</sub> 50w/o HfO <sub>2</sub> 1000°C-100 hr d I
5.06 vw	5.10 w	5.03 vw	5.046 vw	5.06 vvw	5.04 vvw
3.64 m	3.67 m	3.65 w	3.66 vw	3.63 m	3.65 vw
3.15 vs	3.67 vw	3.59 vw	3.60 vw	3.13 s	3.59 vvw
2.94 ms**	3.147 vs	3.128 vs	3.134 s		3.134 s
2.82 ms	2.83 ms	2.81 s	2.91 vvw**		
2.62 w	2.61 m		2.82 ms	2.81 ms	2.81 ms
2.58 w		2.588 m	2.61 vw	2.60 m	2.59 m
	2.537 w	2.52 mw	2.58 vw		
2.53 m	2.47 vw	2.477 vw	2.52 w		2.52 w
	2.45 vva		2.47 vvw	2.53 w	2.47 vvw
2.31 vw	2.33 vw	2.31 w	2.316 vw	2.32 vw	2.31 vw
	2.33 w				
2.198 mw	2.20 vw	2.188 mw	2.194 w	2.20 vw	2.199 vw
	2.17 vw	2.168 vw	2.169 vvw	2.188 vvw	
2.00 vw	2.016 vw	2.168 vw	2.008 vvw	2.02 vvw	2.00 vvw

TABLE III (continued)

ZrO <sub>2</sub> As Rec'd. d	ZrO <sub>2</sub>		HfO <sub>2</sub>		ZrO <sub>2</sub>		ZrO <sub>2</sub>	
	As Rec'd. d	Arc Melted I	As Rec'd. d	Arc Melted I	As Rec'd. d	Arc Melted I	As Rec'd. d	50w/o HfO <sub>2</sub> Arc Melted I
1.98 vw	1.98 vw	1.977 vw	1.998 vw	1.977 vw	1.989 vw	1.977 vw	1.977 vw	1.977 vw
1.84 w	1.84 w	1.833 w	1.977 vw	1.833 w	1.85 w	1.833 w	1.833 w	1.835 vw
	1.81 m							
1.80 ms	1.80 vw	1.803 w	1.30 mw	1.803 w	1.80 mw	1.803 w	1.803 w	1.805 mw
1.79 w	1.778 vw	1.786 vw	1.789 vw	1.786 vw	1.778 vw	1.786 vw	1.778 vw	1.795 vw
			1.76 vv	1.77 vw		1.77 vw		1.765 vw
1.69 vw	1.69 w	1.68 w	1.678 w	1.68 w	1.69 vw	1.68 w	1.69 vw	1.68 w
1.648 vw	1.65 m	1.645 vw	1.647 w	1.645 vw	1.65 vw	1.645 vw	1.65 vw	1.64 vw
					1.64 vv	1.64 vv	1.64 vv	1.626 vw
1.63 vv		1.62 vv	1.63 vw	1.62 vv	1.61 vv	1.62 vv	1.61 vv	
1.60 vv	1.60 vw	1.597 vw	1.597 w	1.597 vw	1.58 vw	1.597 vw	1.58 vw	1.60 vw
1.578 vv	1.58 vw	1.573 vw	1.57 vw	1.573 vw		1.573 vw		1.57 vw
1.549 vv					1.54 m		1.54 m	
1.53 m	1.539 w	1.531 w	1.53 w	1.531 w		1.531 w		1.53 mw
1.50 vv	1.51 vw	1.501 vw	1.499 vw	1.501 vw	1.508 vw	1.501 vw	1.508 vw	1.50 vw
					1.49 vw		1.49 vw	
1.487 vv	1.49 vw	1.487 vw	1.48 vw	1.487 vw		1.487 vw		1.485 vw
1.47 w	1.476 mw	1.467 w	1.46 w	1.467 w	1.475 vw	1.467 w	1.475 vw	1.467 vw

TABLE III (continued)

ZrO <sub>2</sub> As Rec'd. $\frac{I}{d}$	ZrO <sub>2</sub> Arc Melted $\frac{I}{d}$	HfO <sub>2</sub> As Rec'd. $\frac{I}{d}$	HfO <sub>2</sub> Arc Melted $\frac{I}{d}$	ZrO <sub>2</sub> 50w/o HfO <sub>2</sub> Arc Melted $\frac{I}{d}$	ZrO <sub>2</sub> 50w/o HfO <sub>2</sub> 1000°C-100 hr $\frac{I}{d}$
1.44 vvw	1.447 vw	1.438 vw	1.443 vvw 1.435 vvw	1.44 vvw	1.439 vvw
1.415 vw	1.416 w	1.41 m	1.41 w	1.419 w	1.41 mw
1.359 vvw	1.358 vvw	1.35 vw	1.35 vvw	1.357 vvw	1.35 vvw
1.319 vvw	1.32 vw	1.31 w	1.316 vw	1.32 vvw	1.33 vvw
1.29 vvw	1.287 vw	1.29 vvw	1.294 vvw		1.29 vvw
1.267 vvw	1.276 vw			1.26 vvw	
1.257 vvw		1.25 vw	1.255 vvw		1.25 vvw
1.207 vvw				1.208 vvw	
1.17 vw					

\* d = spacing in angstroms

Relative intensity: vw = very weak  
w = weak  
m = moderate  
s = strong  
ms = moderately strong  
vvw = very very weak

\*\* This line corresponds to a cubic pattern.

ZrO<sub>2</sub>

1107	1165	1224
1147	1175	1195
1142	1163	1183
1012	1007	990
1010	1008	992
1012	1008	998

TABLE IV

SUMMARY OF DTA WORK ON ZrO<sub>2</sub>-HfO<sub>2</sub> COMPOSITIONS

Composition	Cycle	Transformation, °C		
		Initiation	Peak	Completion
ZrO <sub>2</sub>	Heating	1130	1180	1210
ZrO <sub>2</sub> + 15 w/o HfO <sub>2</sub> (9.4 m/o HfO <sub>2</sub> )	Heating	1210	1270	1330
ZrO <sub>2</sub> + 25 w/o HfO <sub>2</sub> (16.3 m/o HfO <sub>2</sub> )	Heating	1240	1300	1330
ZrO <sub>2</sub> + 50 w/o HfO <sub>2</sub> * (36.9 m/o HfO <sub>2</sub> )	Heating	1385	1405	1420
		1397	1406	1423
	Cooling	1320	1307	1284
		1306	1293	1280

1391-1406-1402

1312-1300-1282

\* This specimen run at ARL. Other DTA work was performed at ITRI.

ZrO <sub>2</sub> + 70% HfO <sub>2</sub>	Heating	1500	1537	1550
		1510	1540	1555
		1505	1545	1570
	Cooling	1348	1332	1312
		1355	1340	1323

100-200  
800 2056

TABLE V  
SUMMARY OF MELTING POINT DATA  
ON ZrO<sub>2</sub>-HfO<sub>2</sub> COMPOSITIONS

<u>Composition</u>	<u>Avg Corrected Melting Point, °C</u>
ZrO <sub>2</sub>	2680
ZrO <sub>2</sub> + 10 w/o HfO <sub>2</sub>	2730
ZrO <sub>2</sub> + 20 w/o HfO <sub>2</sub>	2745
ZrO <sub>2</sub> + 30 w/o HfO <sub>2</sub>	2735
ZrO <sub>2</sub> + 40 w/o HfO <sub>2</sub>	2750
ZrO <sub>2</sub> + 50 w/o HfO <sub>2</sub>	2780
ZrO <sub>2</sub> + 60 w/o HfO <sub>2</sub>	2790
ZrO <sub>2</sub> + 70 w/o HfO <sub>2</sub>	2810
ZrO <sub>2</sub> + 80 w/o HfO <sub>2</sub>	2825
ZrO <sub>2</sub> + 90 w/o HfO <sub>2</sub>	2860
HfO <sub>2</sub>	2900

The results of this investigation are summarized in Figure 7, a plot of the  $ZrO_2$ - $HfO_2$  system. The diagram is characterized by its simplicity, having continuous monoclinic as well as tetragonal one-phase fields with an intervening small two-phase field. The melting point data likewise indicate a narrow range of liquid plus solid. No evidence of a cubic phase field was found in this study. Inasmuch as the existence of a cubic modification of  $ZrO_2$  is still in a state of flux and since a cubic modification of  $HfO_2$  has never been reported, the diagram shown here makes no reference to this point.

#### IV. OTHER WORK

##### A. Hf-O System

Experiments with a new series of binary hafnium-oxygen alloys were conducted since some additional effort was deemed necessary to resolve the phase relationships in the low-oxygen, high-temperature region of this system which had been studied during the preceding year.

Seven compositions were prepared by arc melting. Portions of these alloys were annealed at and quenched (liquid Sn) from elevated temperatures, and studied metallographically. Typical structures of a 6.3 w/o (0.6 a/o) oxygen alloy, quenched from 2000° and 2150°, are shown in Figures 8 and 9, respectively. These photos are typical of all-alpha and alpha-plus-transformed beta structures observed in specimens quenched in the liquid tin bath. These and other specimens, similarly treated, were used to delineate the boundaries shown in Figure 10.

Figure 10 represents the best approximation of phase relationships in the high-temperature, hafnium-rich region of the system. Data points based on a metallographic study of annealed and quenched specimens are shown, as well as data points determined in the new furnace for melting point determination. The remaining portion of the system has not been altered, and the phase relationships over the entire diagram from Hf to  $HfO_2$  are shown in Figure 11.

Some discussion of the melting point-composition data is in order. This work was done in the furnace constructed specifically for this purpose as described in an earlier section of this report. Specimens were contained in a tungsten wire basket and heated at a fairly rapid rate until melting was observed. The raw melting point data were converted to "true" temperature based on emissivity corrections for tungsten available in the literature. In this work, eleven determinations of the melting point of hafnium yielded an average figure of 2290°C. This value is approximately 68°C above the most acceptable melting point given in the literature. Therefore, 68°C was subtracted from the average melting point of hafnium determined in this new furnace and from the average "melting point" of the alloys. Thus, in a sense, all data are semiquantitative and have been normalized to agree with the accepted melting point of hafnium. As experience is gained in using this new tool, it is hoped that truly quantitative data may be obtained. For now, however, it is felt that this treatment is justified.

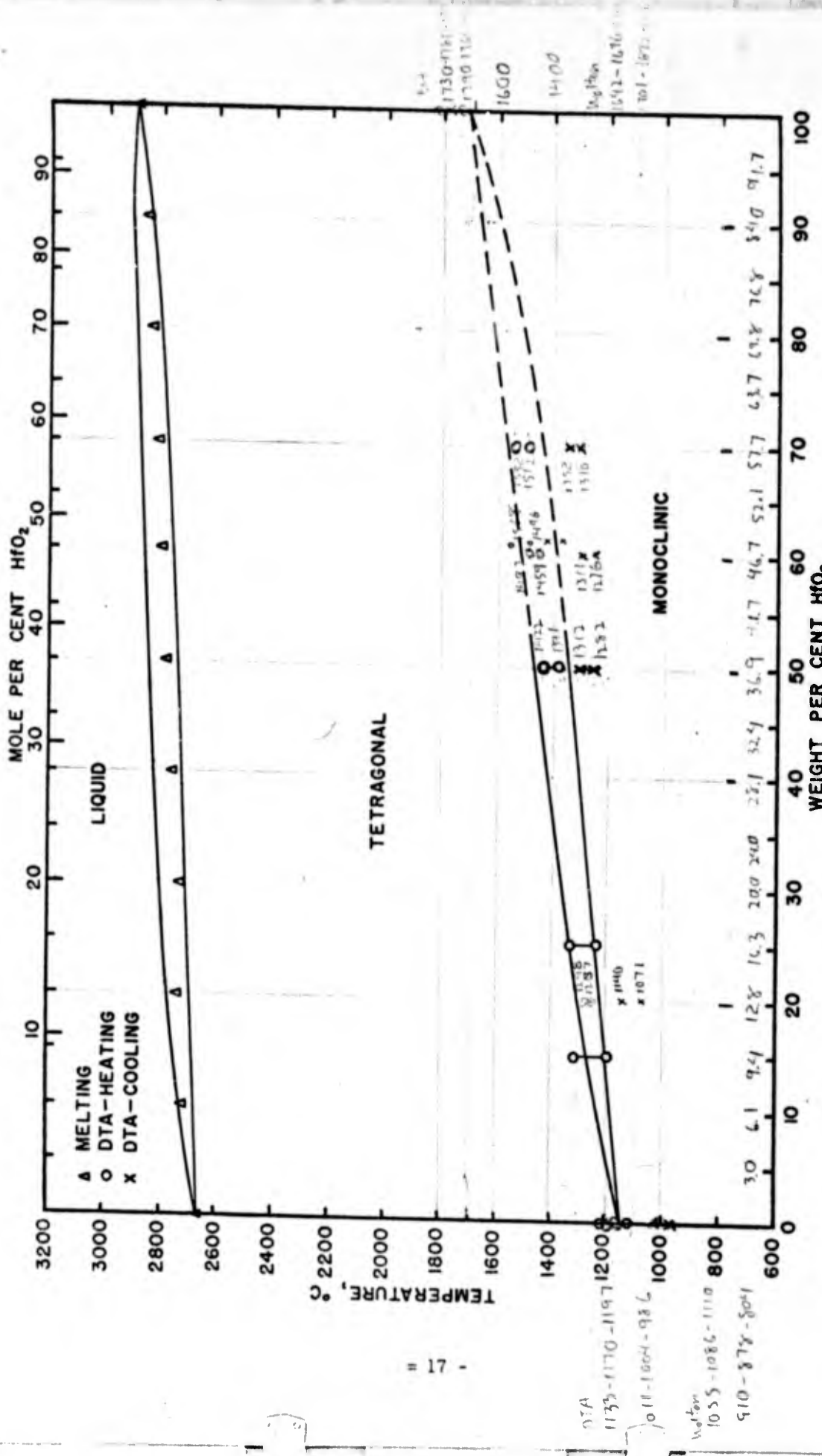
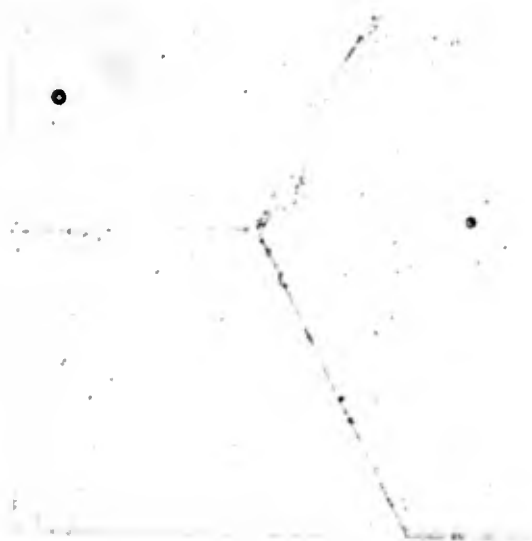


FIG. 7 THE ZIRCONIA-HAFNIA SYSTEM

1200°

100°

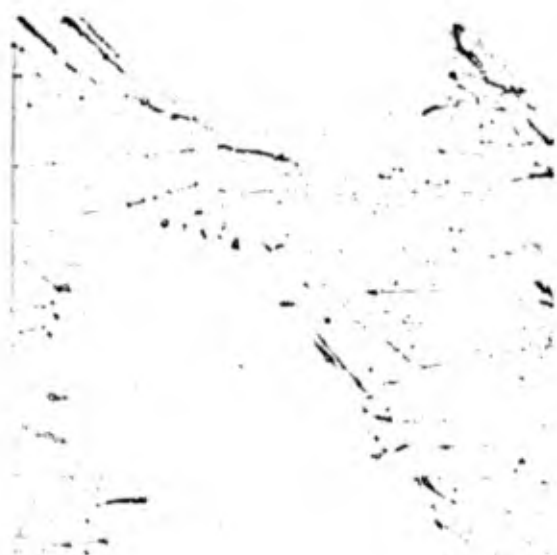


Neg. No. 26197

Fig. 8

X500

Hf + 6.3 a/o O (0.6 w/o) alloy  
quenched from 2000°C. Iso-  
thermal alpha.



Neg. No. 26196

Fig. 9

X500

Hf + 6.3 a/o O (0.6 w/o) alloy  
quenched from 2150°C. Iso-  
thermal alpha plus transformed  
beta.

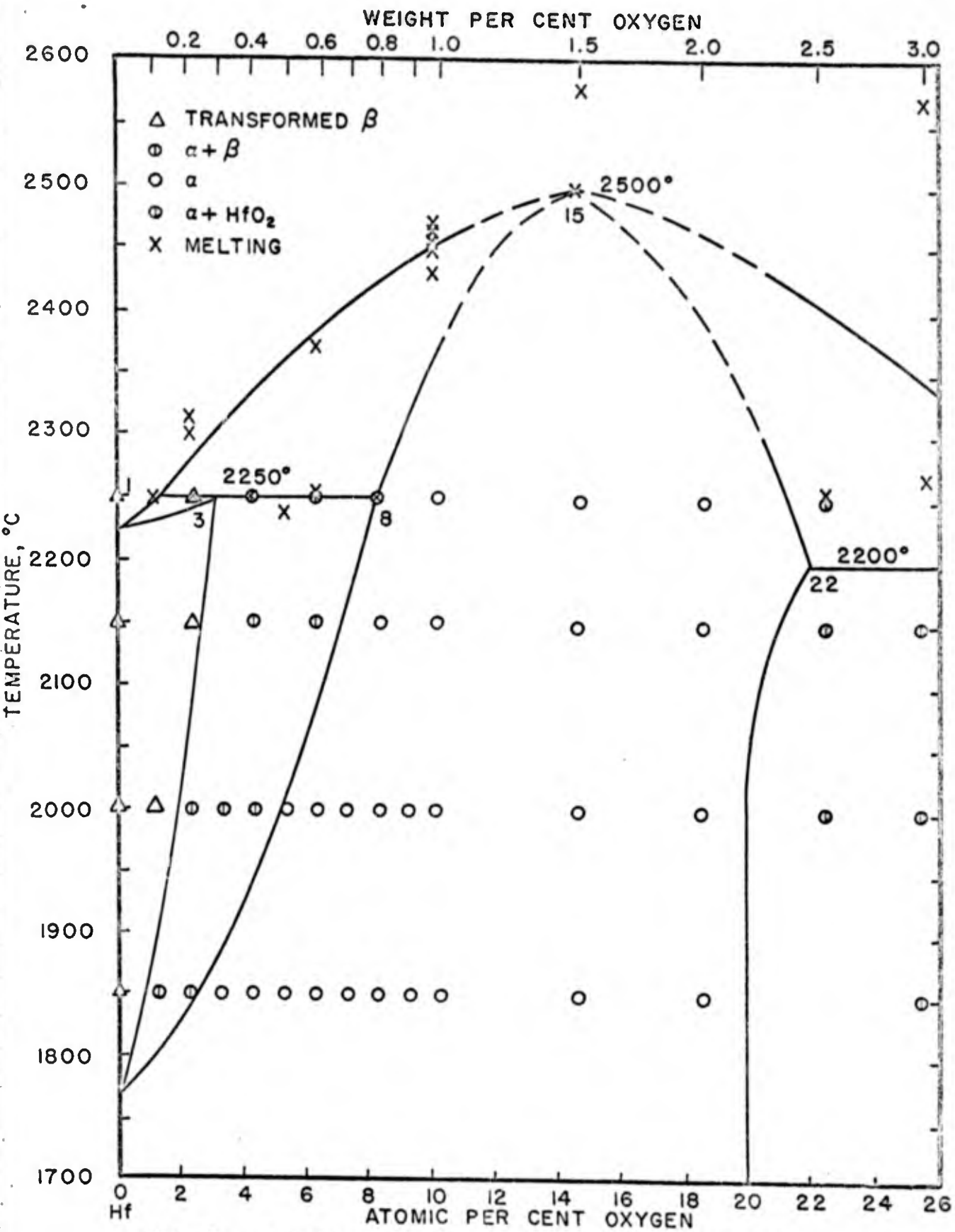


FIG. 10 THE Hf-RICH REGION OF THE Hf-O SYSTEM

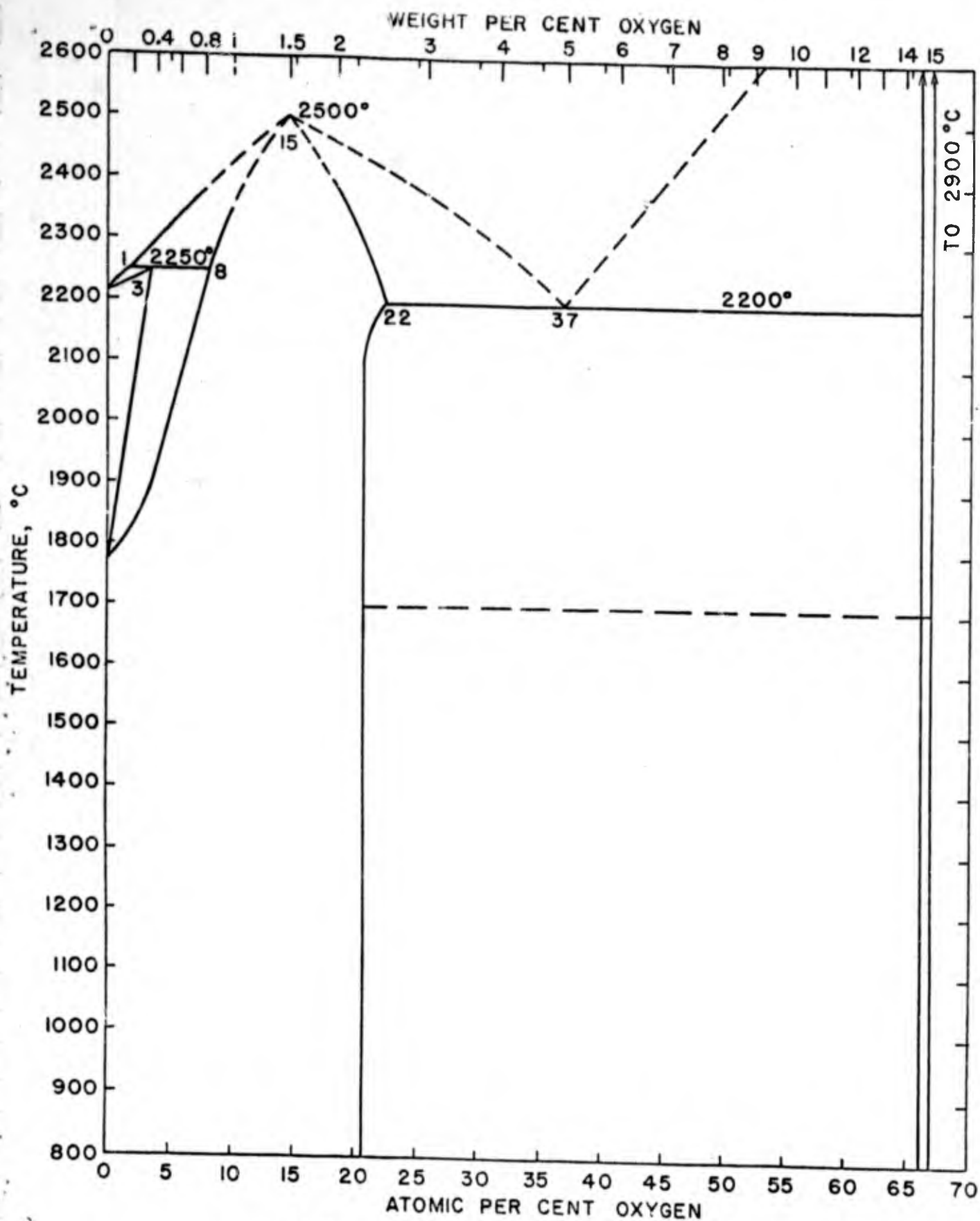


FIG.II THE HAFNIUM-OXYGEN SYSTEM

B. Service Tasks

During the period covered by this report a number of research services tasks were pursued for Dr. Robert Ruh of the Aerospace Research Laboratories. Such work included arc melting of oxide-metal compositions and microprobe analyses of specimens submitted. The arc-melted ingots were mailed to Dr. Ruh, and the results of the microprobe analyses have been detailed in separate correspondence and will not be repeated here.

V. CONTRIBUTING PERSONNEL AND LOGBOOKS

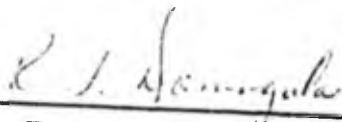
Personnel contributing to the work reported herein include:

W. A. Buknas	-	Heat Treatments
R. F. Domagala	-	Project Leader
G. W. Jarvis	-	Melting Point Studies
H. H. Nakamura	-	DTA Studies
D. C. Schell	-	X-ray and Technical Assistance
D. A. Stawarz	-	Arc Melting
C. E. Townsend	-	Project Technician

Data relating to this study are recorded in IITRI Logbook Nos. C-12602, C-13705, and C-14232.

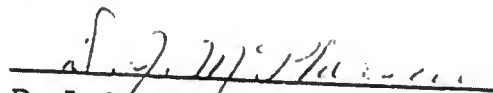
Respectfully submitted,

IIT RESEARCH INSTITUTE



R. F. Domagala, Manager  
Metallurgical Services

Approved by:



D. J. McPherson  
Director  
Metals and Ceramics Research