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THE PROPERTIES OF ZIRCONIUM
AND

ITS POSSIBILITIES FOR THERMAL REACTORS

BY

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of the

Power Pile Division

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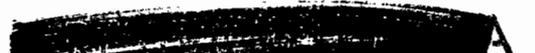
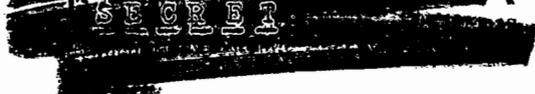

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INTRODUCTION

Up until about a year ago, zirconium had not been seriously considered for reactor uses because of an apparently high absorption cross section to thermal neutrons. New cross section measurements on pure zirconium made during the winter of 1947-48, however, showed that the apparently high cross section of zirconium was not due to zirconium, but to the element hafnium, which co-exists with zirconium and is so similar to zirconium in chemical properties that it cannot be separated by ordinary chemical methods.

Since this discovery, great interest has been taken by various laboratories operated for the Atomic Energy Commission throughout the country in the development of the metallurgy of a ductile zirconium and in the development of processes for the separation of the undesirable element, hafnium.

The Power Pile Division of the Oak Ridge National Laboratory has completed a study of the water-cooled and water-moderated power reactor for the propulsion of naval craft, viz. submarines (see ORNL-133). As was anticipated, many problems in the design of a water-cooled reactor became apparent, among which one of the greatest of these was the choice of a structural material which would resist the corrosive effect of high temperature, high pressure water containing dissolved oxygen, hydrogen, and perhaps hydrogen peroxide.

Therefore, since zirconium was known to have good corrosion resistance to aqueous solutions and had just been discovered to be desirable from a nuclear viewpoint, a study of the possibilities of this metal as a structural material for a water-cooled reactor was undertaken. This investigation included 1) the collecting of many facts concerning zirconium beginning with the history of the metal, 2) the compiling of information relative to its properties, its production, and its fabrications, hafnium separation processes, and corrosion studies. This report was prepared as a convenient reference for those who may be interested in any or all of these branches of investigations concerning zirconium.

CHAPTER I

THE HISTORY OF ZIRCONIUM¹

The recorded discovery of zirconium dates back to 1789 when Klaproth, in analyzing a precious stone known as jargon from Ceylon discovered what he thought to be a new earth and called "Zirconerde". Other investigators confirmed this discovery in the minerals now known as zirconium ores. However, it was not until 1824 that anyone was able to reduce the metal from the oxide. Berzelius accomplished this, producing the first known zirconium metal, though quite impure.

Other "elements" such as sonorium, jargonium, nigrium, euxenium were reported to exist in zirconium oxide but only the element hafnium really proved to exist. Bohr predicted in 1922 in conclusion from his theory of atomic structure that zirconium was not an earth as Klaproth had thought and did not belong to the rare earth group but that it was quadrivalent and therefore the direct homologue of zirconium.

Since the X-ray spectrum of zirconium could be predicted, Coster and van Hevesy investigated various zirconium ores by X-ray spectroscopy and substantiated Bohr's conclusion. Coster and van Hevesy also discovered the presence in the zirconium ores of the new element hafnium suggested by the Latin name Hafnia, for Copenhagen, where the discovery of the element was made following its earlier production there.

Chapter II

THE ABUNDANCE OF ZIRCONIUM^{1,2,3}

The earth's crust has been estimated to contain 0.028 per cent zirconium, a figure which indicates that zirconium is more abundant than the common metals nickel (.020 per cent), copper (.010 per cent), zinc (.004 per cent) and lead (.002 per cent). Zirconium has been known as a rare metal because of the difficulty of extracting the pure metal from the ores just as aluminum was considered rare before the days of the development of the electrolytic method now used in its production.

The most abundant zirconium bearing mineral is the ore "zircon", $ZrSiO_4$, which crystallizes in the tetragonal system and is isomorphous with rutile, TiO_2 . The transparent yellowish or reddish varieties of the silicate are known as the precious stone hyacinth, and the colorless silicate as jargon. Other zirconium silicate bearing ores are alvite, malacone and cyrtolite.

Zirconium is not only found as the silicate but as the oxide. The Brazilian mineral, baddeleyite, is a fairly pure oxide. Some silicate is often found with the oxide. Commercially the Brazilian mineral is called "zirkite".

Zirconium ores contain varying amounts of hafnium, an element which is almost identical to zirconium in all its chemical properties but differs in its nuclear properties in that it has a very high cross section to thermal neutrons, a high atomic weight and high density. The hafnium/zirconium ratio by weight of the many zirconium bearing ores range from less than 1 per cent in the Brazilian baddeleyite to 54 per cent in the cyrtolite found in some localities in the United States, probably the feldspar mine in Bedford, N. Y., and 54 per cent in the alvite minerals of Kraero. Three per cent is a more average figure, however. In the western hemisphere, the zircon sands of Florida contains about 3.3 per cent hafnium and the zirkite of Brazil about 0.7 per cent.

CHAPTER III

THE PHYSICAL AND ATOMIC CONSTANTS OF ZIRCONIUM INCLUDING
PROPERTIES OTHER THAN MECHANICAL*

The element zirconium is the fortieth element in the periodic table and has been assigned the atomic weight of 91.22 by the International Union of Chemists in 1935. It has a grain structure of hexagonal close-packed crystal below 865° C** in the α phase and a body-centered cubic crystal structure above 865° C in the β phase.^{4,5}

In the α phase, zirconium has the lattice constants of $a = 3.22A^{***}$ and $c = 5.13A^{***}$ and in the β phase $a = 3.61A$.⁵

W. Hume-Rothery in his book "The Structure of Metals and Alloys" (Inst. of Metals, 1936)⁶ gives the interatomic distances of $d_1 = 3.16(6)$ and $d_2 = 3.22(3)$ in the α phase with $d_1 = 3.12(6)$ in the β phase. Also given are Goldsmidt's atomic diameter for coordination No. 12 as 3.19 for the α phase and 3.22 for the β phase zirconium.

W. Hume-Rothery also shows the electrons in the shells in the order of 2, 8, 18, 10, and 2.

The density of zirconium has been reported from 6.4 to 6.54 as is seen in the following list of literature values:

6.4^{56,82}

6.48⁴

6.49¹⁰

6.50^{11,57}

6.51⁵

6.52¹

6.54⁵³

*Acknowledgement is made here for the assistance of the data compiled by R. I. Jaffee and I. E. Campbell of Batelle Memorial Institute in their report "Properties of Zirconium".

**Donald B. Alnutt and Charles L. Scheer claim this temperature to be 860° C Zeitschrift für anorganische und allgemeine Chemie, Vol. 202, 1931, p.293 as 862 ± 5° C.

***a = 3.228, b = 5.140, and c/a = 1.59 according to W. G. Burgers in private communication to A. E. van Arkel ("Reine Metalle", J. Springer, Berlin, 1939, p. 198). and a = 3.23 and b = 5.14 according to A. W. Hull (Ref. 10)

The melting point of zirconium has also been reported over a wide range which is given below:

1700° C (3090° F)^{56,82}

1800° C (private communication Foote Mineral Co. to
Batelle Memorial Institute)

1857° C¹

1860° C (3870° F)^{5,53}

1900° C¹⁴

The boiling point has been determined as over 2900° C as given in the International Critical Tables¹² and assigned a definite value of 5050° C in the A.S.M. Handbook of 1939.¹⁶

Values for the linear coefficient of thermal expansion are reported as follows:

Temperature Range °C	Value
RT (21)	$6.3 \times 10^{-6}/^{\circ}\text{C}$ ($3.5 \times 10^{-6}/^{\circ}\text{F}$) ^{1,56}
100-600	$4.7 \times 10^{-6}/^{\circ}\text{C}^4$
20-600	$4.96 \times 10^{-6}/^{\circ}\text{C}^{52}$
20-200	$5.4 \times 10^{-6}/^{\circ}\text{C}^{15}$
200-300	$6.4 \times 10^{-6}/^{\circ}\text{C}^{15}$
300-400	$6.9 \times 10^{-6}/^{\circ}\text{C}^{15}$
400-500	$7.9 \times 10^{-6}/^{\circ}\text{C}^{15}$
500-600	$8.4 \times 10^{-6}/^{\circ}\text{C}^{15}$
600-700	$8.9 \times 10^{-6}/^{\circ}\text{C}^{15}$
0-100	$10.4 \times 10^{-6}/^{\circ}\text{C}^7$
75-1112	$4.96 \times 10^{-6}/^{\circ}\text{C}^{18}$
230	$4.26 \times 10^{-6}/^{\circ}\text{C}^{18}$
387	$9.53 \times 10^{-6}/^{\circ}\text{C}^{18}$
572	$13.89 \times 10^{-6}/^{\circ}\text{C}^{18}$
765	$19.24 \times 10^{-6}/^{\circ}\text{C}^{18}$
956	$24.38 \times 10^{-6}/^{\circ}\text{C}^{18}$
1137	$29.85 \times 10^{-6}/^{\circ}\text{C}^{18}$

The specific heat of zirconium is given as follows:

R.T.	0.066 cal/gram ¹⁶
0-100°C	0.068 cal/gram ¹⁴
-253 to -196° C	0.0262 cal/gram ¹⁷

TABLE I¹⁹Heat Capacity of Zr

T, °K	C _p , cal./mole/deg.	T, °K.	C _p , cal./mole/deg.
53.2	2.393	166.1	5.454
56.8	2.613	176.0	5.549
60.8	2.844	186.2	5.614
65.6	3.102	196.1	5.679
70.6	3.349	206.3	5.743
75.4	3.572	216.4	5.801
79.8	3.750	226.2	5.845
84.1	3.905	236.4	5.887
94.9	4.252	246.0	5.920
104.5	4.515	256.7	5.980
115.0	4.747	266.4	6.021
124.1	4.920	276.4	6.065
136.1	5.119	286.6	6.086
146.2	5.239	296.8	6.105
156.0	5.354		

TABLE II¹⁹Heat Capacity of Zirconium (smooth values)

T, °K	C _p , cal./mole/deg.	T, °K	C _p , cal./mole/deg.
50	2.190	200	5.706
75	3.550	225	5.840
100	4.398	250	5.952
125	4.932	275	6.050
150	5.286	298.16(25.16°C)	6.123(.0671 cal/g/°C)
175	5.530		

Entropy calculations made at the Pacific Experimental Station, U. S. Bureau of Mines, gave the following:¹⁹

0-51° K (extrapolation)	0.992
51-298.16° K (measured)	<u>8.193</u>
S° _{298.16}	9.18 ± 0.08 cal./mole/°K

The thermal conductivity values reported for zirconium are:

0-100° C	$\sim .067 + 30\% \text{ cal/s/g/}^\circ\text{C}^7$
32-212° F	$\sim 16.2 \text{ BTU/hr/}^\circ\text{F}^7$

The electrical resistivity values known are given as follows:

Temperature °C	Ohms/cm.
0	4.9×10^{-5} (Ref. 20)
0	3.9×10^{-5} (Ref. 5, 21)
0	4.1×10^{-5} (Ref. 1, 22)
877 (1150° A)	1.44×10^{-4} (Ref. 21)
1157 (1430° A)	1.26×10^{-4} (Ref. 21)
20	4.9×10^{-5} (Ref. 5)
——(Probably R. T.)	1.7×10^{-4} (ref. 82)

The temperature coefficient of electrical resistivity has been stated as follows:

Temp. Range °C	Coef.	Remarks
0-100	.0044 ^{1,23}	
——	.0041 ⁷	
0-100	.0044	As deposited by "hot wire" method.
0-100	.0039 ²¹	Cold swaged rod
0-100	.0042 ²¹	Cold-swaged and annealed in vacuo 1 hr. at 600° C.

Certain metals such as thallium, mercury, tin, and lead exhibit properties of superconductivity or a sudden and rapid decrease in the electrical resistance at very low temperatures. Zirconium, however, at temperatures to 1.1° C showed no superconductivity according to W. Meissner²⁴ and still no superconductivity down to 3° K as declared by N. Kurti and F. Simon. Simon and Kurti, however, found a discontinuity in the conductivity-temperature relationship at 0.7° K.

With diamagnetic magnetism, the magnetic susceptibility of zirconium is given as -0.45×10^{-6} in cgs units in the Handbook of Chemistry and Physics. A. R. Kaufman and C. F. Squire plotted the magnetic susceptibility of zirconium as a function of temperature as determined by the method of measuring the force which a non-homogeneous magnetic field exerts on a specimen.²⁶ The graph of this work is shown in Fig. 1 at the end of this chapter.

The rapid change in the magnetic susceptibility of zirconium should be noted to be coincidental with the transition phase change of close-packed hexagon to body-centered cubic at 865° C (1138° K).

The photoelectric threshold is given as 3,220 angstroms by R. Schulze in Z. Phys. vol. 34, 1933, p. 185, and as 3,200 by H. C. Rentschler and D. E. Henry in the Electrochemical Society Preprint No. 87-14, 1945.

The work function, ϕ , is reported as follows:

eV

4.13²⁷

3.28²⁸

3.84²⁹

4.1³⁰

The electron emission is expressed by the formula¹

$$i = AT^2 \frac{eb}{T} \text{ Amp/cm}^2$$

and when the filament is new, $A = 37200$ and $b = 60600$. When the filament has glowed for a certain time, however, the constants change to $A = 330$ and $b = 47,900$ and the electron emission is increased.²⁷ According to H. H. Potter in Proc. Phys. Soc. 53, 1941, p. 695, the thermoelectric power is expressed by

$$Q = A + B\mu v \text{ per } ^\circ \text{C}$$

and in the temperature range of 100-400° C, the constants are $A = 11.3$ and $B = -0.033$.

The coefficient of spectral emissivity is presented in a table arranged by R. I. Jaffee and F. E. Campbell as follows:

Wave Length Angstroms	α Zirconium	β Zirconium	References
6520	0.48	0.43	C. Zwicker Physics, 6 1926, P. 361.
5410	0.50	0.46	Roeser and Wensel.
	(Solid Zr)	(Liquid Zr)	
6500	0.32	0.30	Temp. and Its Measure- ment, Reinhold.

J. H. de Boer and J. D. Fast have determined the vapor pressure formula for zirconium to be

$$\log p = \frac{-1300}{T} + 0.77$$

where T is in degrees absolute.²² Most metals have a B value for the following formula

$$\log p \text{ (mm Hg)} = \frac{-A}{T} + B$$

of about 9.3 but the value of 0.77 for zirconium is abnormal. C. Zwicker believes the oxide layer holds back the vapor pressure and attributes the abnormal B value to this factor.

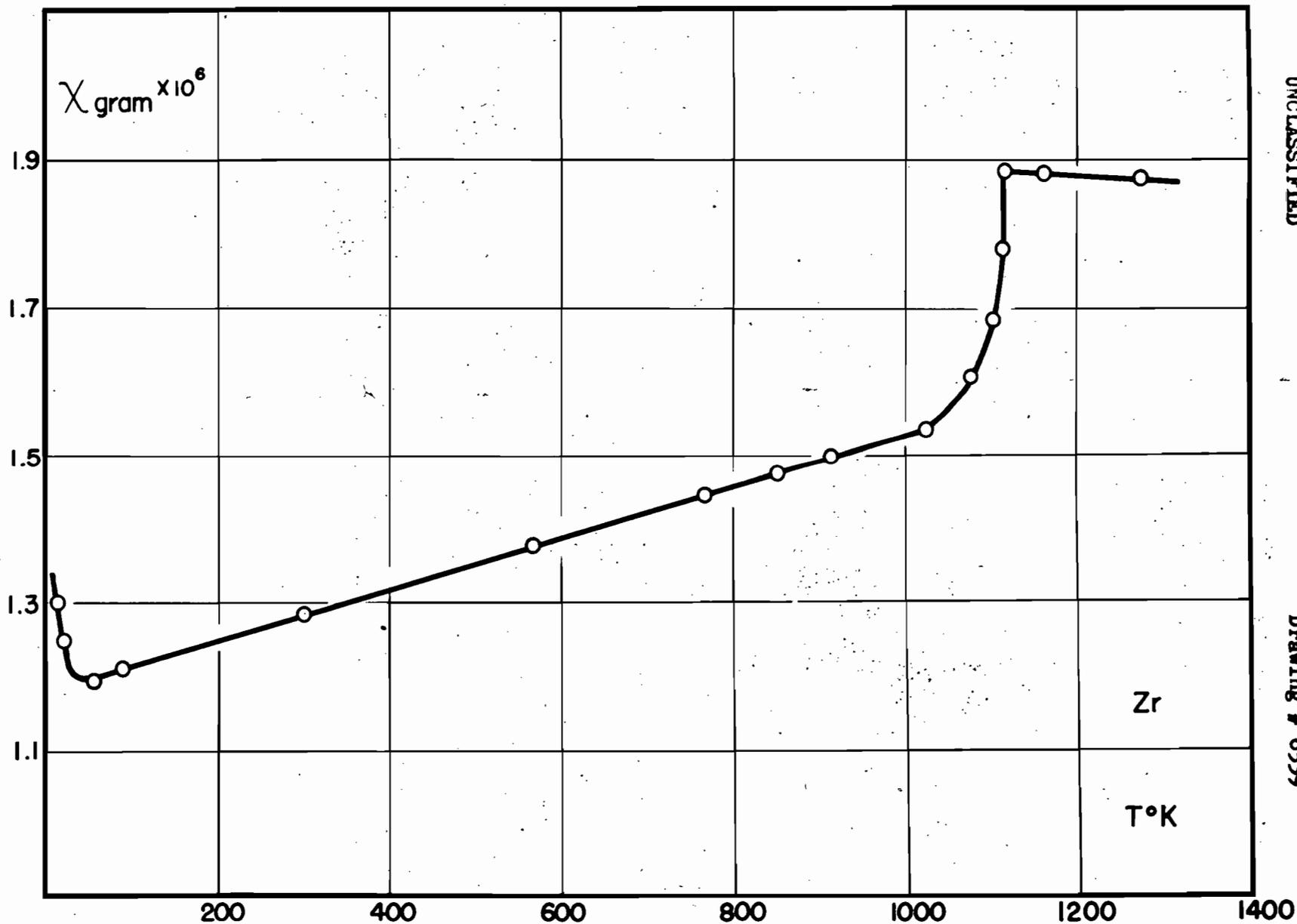


FIG. 1

PARAMAGNETIC SUSCEPTIBILITY OF ZIRCONIUM AS A FUNCTION OF TEMPERATURE.²⁶

Chapter IV

THE MECHANICAL PROPERTIES OF ZIRCONIUM

Unlike one would suspect, there is almost a phlethora of data on the mechanical properties of zirconium. The magnitude of this data is the reason for separating the mechanical properties of zirconium from those reported in the previous section.

Not only is there an abundance of data concerning the mechanical properties of zirconium, but there is also a wide disagreement on the values themselves. There are valid reasons for the divergence of numerical values when considering the history of the test specimens themselves, viz. the purity, the degree of cold working, and the amount of heat treatment (whether purposive or "accidental"). For example, the ultimate tensile strength values reported begin at 30,000 psi and extend to as high as 142,000 psi.

The ratio of unit stress to unit deformation, or the modulus of elasticity is often taken as a basic criterion for important engineering materials. Such is true of zirconium as well as, for example, steel and aluminum. A partial list of values known are presented below.

Table I

Modulus of Elasticity Values

Description of Zirconium	Modulus of Elasticity $\times 10^7$ psi
Bureau of Mines Mg reduced Zirconium (condition unknown)	~13.57
Presumably iodide deposited	10.75 ¹⁶
Foote Mineral "Zirmet" (iodide deposited)	9.5 - 12 ⁵³
Bureau of Mines Mg reduced	
a) Drawn (hence cold worked) .010 wire	10.7 ³²
b) 76.9% cold reduced swaged bar	14.5 ³²
c) 76.9% cold reduced swaged bar tempered at 850° F	14.0 ³²
d) 76.9% cold reduced swaged bar tempered at 1450° F	11.35 ³²

Other values of the modulus of elasticity are given in tables II, IV, and V at the end of this chapter.

To date only three commercially feasible processes have been developed for producing ductile zirconium. One is by the thermal decomposition of the tetraiodide, or the so-called "hot wire method", a second is by magnesium reduction and sometimes called the "Kroll" or Bureau of Mines method, and the third is by calcium reduction and is today generally referred to as the "Westinghouse method".

These three processes give varying purity, with the iodide process giving the highest purity. An attempt to compare the purity of zirconium by the three methods is shown in the following table:

Table I³¹

Comparison of Purity of Zirconium Produced by Three Methods

	O ₂	N ₂	C	Fe	Si	Al	Mn	Ca	Mg	Cu
Footc Mineral										
Iodide Deposited	.03*(.04) ⁹⁶	.01*	(.01-.05)*	.04	.05	Tr.	Tr.	—	—	Tr.
Bureau of Mines Mg Reduced	.08*, ⁹⁶	.04*	.08(.15)*	.2	—	Tr.	Tr.	Tr.	Tr.	Tr.
Westinghouse Co. Ca. Reduced	.13*, ⁹⁶	.06*	—	—	—	—	—	—	—	—

* Data from R. I. Jaffee, Battelle Memorial Institute, presented at Brookhaven Information meeting, April 28, 1948.

The Footc Mineral Company has released the following information included in Tables II, III, IV, and V (at the end of the chapter) for iodide deposited zirconium.

The Bureau of Mines, Northwest Electrodevelopment Laboratory furnished the following comparison of its Mg reduced zirconium in the cold worked and annealed condition showing the effect of heat treatment by annealing.⁷

Table VI

The Effect of Annealing of Bureau Zirconium on Mechanical Properties

	(Yield strength) psi	(Ult. Tensile) Str. psi	(% Elong.)	(% Red in Area)
Cold worked Zr.	60,000	102,000	3	32
Annealed Zr	20,000	57,000	16	31

The effect of heat treatment on the tensile strength is shown in the table below.³²

Table VII

The Effect of Vacuum Heat Treatment of Zirconium on Tensile Strength⁵

<u>Condition</u>	<u>Tensile Strength</u> psi	<u>Elongation</u> %*
0.525 mm wire cold swaged	115,000	3
400° C, 3 hour (vac.)	101,000	2.5
500° C, 3 hour (vac.)	56,000	12
600° C, 1 hour (vac.)	51,000	12.5
700° C, 1 hour (vac.)	44,000	12.5

Table VII (Cont'd)

Condition	Tensile Strength psi	Elongation %*
800° C, 1 hour (vac.)	38,500	11
900 1 hour (vac.)	43,000	15.5
1000 15 min.(vac.)	44,000	15

* On 15 cm gauge length

The effect of tempering and annealing of $\frac{1}{4}$ " turned bar (iodide deposited zirconium) rolled and swaged to $\frac{1}{8}$ " dia. gave the following values:³²

Table VIII

The Effect of Tempering and Annealing on the Mechanical Properties of a Rolled and Swaged Zirconium Bar

	Hard Drawn	Tempered at 850° F	Annealed at 1450° F
Ult. strength, psi	88,300	81,600	35,900
Yield at 0.2% offset, psi	69,700	55,200	15,900
Yield at 0.1% offset, psi	63,300	48,300	13,800
Proportional limit (.01%), psi	32,100	29,100	8,350
Reduction in area, %	40.6	26.0	32.2
Elongation in 4 diameters	18.0	20.0	31.0
Elongation in 8 diameters	8.5	12.0	25.5

The effects of tempering and annealing on a hard drawn wire (iodide deposited) is given below:³⁵

Table IX

The Effect of Tempering and Annealing on Mechanical Properties of Hard Drawn Zirconium Wire

Condition	Tensile Strength psi	Elongation %
0.017" dia. wire hard drawn	128,800	2
0.017" tempered at 850 F	93,500	5.5
0.017" annealed at 1450 F	61,000	14

The effect of extrusion and vacuum heating and quenching of U. S. Bureau of Mines magnesium reduced zirconium on the ultimate tensile and yield strengths is shown below:^{9,52}

Table X

The Effect of Extrusion and Heat Treatment on the
Mechanical Properties of the Bureau of Mines Zirconium

Condition	Ultimate Tensile Str. psi	Yield 0.1% Offset psi	Elonga- tion %	Red. in Area %
As received (no treatment)	70,400	45,200	14.9	27.8
Extruded at 1060° C with 14:1 red.	79,500	47,700	19.9	43.7
Extruded at 800° C with 14:1 red.	80,200	42,700	15.3	43.8
Extruded at 1060° C, heated to 1,000° C in vacuum and water quenched.*	89,700	59,800	9.6	37.3
Extruded at 800° C, heated to 1,000° C in vacuum and cooled slowly	70,600	34,100	16.5	38.7

* Sample sealed in quartz tube under high vacuum, heated for 1/2 hr., then quenched.

The effect of vacuum heating to 1,000° C followed by water quenching a Bureau of Mines zirconium sample on the ultimate tensile and yield strengths is shown below:⁵²

Table XI

The Effect of Water Quenching on the Mechanical
Properties of Bureau of Mines Zirconium

	Ult. Tensile Str. Psi	Yield Str. 0.1% Offset psi	Elonga- tion %	Red in Area %
Bureau of Mines Zr as received	65,700	42,000	12.5	34.9
Heated to 1,000° C in vacuum and water quenched*	95,000	71,000	9.1	29.4

* Sample sealed in quartz tube at high vacuum, heated for 1/2 hours and then quenched.

A comparison of various extrusion conditions on iodide deposited zirconium is given below:^{9,52}

Table XII

Room Temperature Tests of Foote Zirconium

	Ultimate Tensile Strength psi	Yield Point psi	Elongation %	Reduction in area %
A. Foote Mineral Co. crystal bar as received.	40,700	18,800	13.6	est. 40
B. Foote Mineral Co. crystal bar melted and extruded at 800°				
Spec. No. 1	63,600		21.4	39.8
Spec. No. 2	66,100		26.0	39.6
C. Foote Mineral Co. crystal bar chips compressed and extruded at 1060° C	77,500	36,600	23.2	44.7
D. Foote Mineral Co. crystal bar cast in graphite and extruded at 1000° C in steel can.				
Spec. No. 1	56,400	34,100	23.0	47.2
Spec. No. 2	56,400	36,000	20.0	45.2
E. Several Foote Mineral Co. crystal bars packed side by side in steel can and extruded at 1060° C.				
Spec. No. 1	55,100	31,600	24.8	49.1
Spec. No. 2	55,700	29,000	24.3	49.7

The hot strengths of iodide deposited zirconium in atmospheres of helium and nitrogen are given below:^{9,52}

Table XIII

The Hot Strength of Zirconium in Helium and Nitrogen Atmosphere

Temperature °C	In Helium Atm. X10 ³ psi	In Nitrogen Atm. X10 ³ psi
500	24	15
700	10	7.0
800	6.6	0.5

Elevated temperature tests in argon gas at MIT made with iodide deposited zirconium melted and extruded at 800° C with 11.4:1 reduction reveal the following:^{9,52}

Table XIV

Elevated Temperature Tests on Melted and Extruded Zirconium

<u>Temp. Degrees C</u>	<u>Ultimate Tensile Strength psi</u>	<u>Elongation %</u>	<u>Reduction in Area %</u>
Room	63,600	21.4	39.8
250	40,100	32.7	55.1
500	28,500	39.7	68.0
750	7,950	99.6	97.8

One value for the shear strength of an unworked Foote Mineral Company rod is reported by R. I. Jaffee of Battelle Memorial Institute as 45,000 psi.

Proportional limit values for zirconium not already given in tables II, III, IV, and V are as follows:⁵⁴

	<u>psi</u>
U. S. Bureau of Mines ingot as received	33,700
U. S. Bureau of Mines ingot extruded at 1950° F with 14:1 red. in area	31,800
Foote Mineral Company iodide dep. crystal bar	12,500

A compilation of all known hardness determinations on zirconium is shown in the following table:

Table XV

Compilation of Hardness Data on Zirconium

<u>Description of Conditions</u>	<u>Rockwell B</u>	<u>Rockwell C</u>	<u>Brinell</u>	<u>Vickers</u>
Iodide deposited (as deposited)	----	----	----	82 with 10 kg load.
Iodide deposited (as deposited)	38 ⁹	----	----	----
Iodide deposited (as deposited)	50 ⁴	----	----	----
Iodide deposited (as deposited)	26-35 ⁹⁹	----	----	----
Cold worked crystalline bar	90-100 ⁴	9-23*	183-241*	183-241*
Iodide deposited cold rolled to 33% reduction	79 ⁵²	----	143*	143*
Iodide deposited cold rolled to 56% reduction	90 ⁵²	9*	183*	183*
Cold reduced from 1/4" dia. turned annealed bar of Foote Mineral iodide deposited "Zirmet"	35-52 ⁵³	----	----	----
Iodide deposited melted bars (as melted)	76 ⁵²	----	134*	134*

Table XV (cont'd)

<u>Description of Conditions</u>	<u>Rockwell B</u>	<u>Rockwell C</u>	<u>Brinell</u>	<u>Vickers</u>
Above ingot cold rolled to 33% reduction	89 ⁵²	.8*	179*	179*
Above ingot cold rolled to 56% reduction	92 ⁵²	12*	192*	192*
Bureau of Mines Mg reduced as rec'd	84 ⁵²	2*	159*	159*
Above cold rolled to 33% reduction	97 ⁵²	20*	223*	223*
Above cold rolled to 56% reduction	101 ⁵²	18 ⁵² (23*)	245*	245*
Vacuum arc melted Mg reduced	94*	15*	200 ³³	200*
Bureau of Mines				
Sintered from Ca reduced	91*	10*	188*	188 ³⁴
"Westinghouse" Process				
Induction melted from "Westinghouse" Process	104*	29*	277*	280 ³⁴
Iodide deposited rod turned to 1/2" dia. and swaged to 1/8" dia. with 77% reduction in area	85-86.5 ⁹⁹	3-5*	163-164*	163-164*
Above specimen annealed	38-44 ⁹⁹	----	----	----
Cold-swaged 1/8" dia. iodide dep. rod 76.9% reduced in area	87.4 ³⁵	6*	172*	172*
Above tempered at 850°F	87.7 ³⁵	7*	173*	173*
Above annealed at 1450°F	30.3 ³⁵	----	----	----
Iodide deposited rod heated to 1000°C in vacuum and quenched in oil bath	114-115*	44-46 ⁹	415-444*	427-472*
Iodide deposited rod heated to 1000°C in vacuum and cooled slowly	90*	9 ⁹	183*	183*

* Converted value as per Hardness Conversion Table, P. 127, Metals Handbook, American Society for Metals, 1939 edition.

The oxygen content has an effect upon the hardness as is illustrated in the list below: ³⁹

<u>Description of Zirconium</u>	<u>Brinell Hardness 3,000kg. 10 mm, 60 sec.</u>
"Pure" Bureau of Mines Mg reduced ingot	< 135
Ingot with 0.1% O ₂	190-200
Ingot with 0.2% O ₂	~ 250
Ingot with 0.3% O ₂	~ 300

The values for the mechanical properties of zirconium presented in this section are dependent on many variables. For example, a comparison of the hot strengths of zirconium in helium and argon atmospheres show considerable difference in values. This is not due entirely to the surrounding gas medium but mainly to the difference in the previous history of the samples. Both were iodide deposited zirconium but one was melted and extruded, the other not.

TABLE II

PHYSICAL PROPERTIES OF IODIDE DEPOSITED ZIRCONIUM

Test	<u>Zirconium Rods (Range of Results)</u>		
	As Deposited Zr Rod	Zr Rod App. 3/16" turned to 1/2" swaged to 1/8" dia.; 77% reduction (:. cold worked)	Zr Rod, cold worked as in Column "2" then vacuum annealed
Ultimate Strength	30,000 to 36,000 psi*	81,000 to 86,500 psi	37,500 to 41,000 psi
Yield Strength (0.2% off-set)	13,000 to 16,000 psi	67,000 psi (extrapolated value)	13,000 to 16,000 psi
Proportional Limit (0.01% off-set)	7,800 to 8,400 psi	25,000 to 38,000 psi	6,000 to 8,200 psi
Elongation (4 dia.-gauge length)	25 to 32%	12 to 18%	30 to 38%
Reduction in area	20 to 36%	30 to 40%	27.5 to 40.5%
Modulus of Elasticity	9.0 to 12.5 x 10 ⁶ psi	12.5 to 14.2 x 10 ⁶ psi	10.0 to 11.6 x 10 ⁶ psi
Hardness (Rockwell B)	26 to 35	85 to 86.5	38 to 44

* A test at MIT reported in Progress Report MIT-1001 for the months of October, 1947 - January, 1948 reveals a value of 40,700 psi ultimate strength with 13.6% elongation and an estimated 40% reduction in area.

TABLE III

PHYSICAL PROPERTIES OF IODIDE DEPOSITED ZIRCONIUMZirconium Wire 0.017 to 0.002 Diameter (Range of Results)

Test	Annealed	Hard drawn, stress relieved 1/2 hour 800° F.	Hard Drawn
Ultimate Strength	54,300 to 61,000 psi	82,800 to 115,500 psi	100,000 to 142,000
Yield Strength (0.2% off-set)	32,500 to 48,300 psi	---	---
Elongation, 10 in.	9 to 18%	1 to 5.5%	1 to 2.5%

TABLE IV

PHYSICAL PROPERTIES OF IODIDE DEPOSITED ZIRCONIUMCold Rolled Zr Strip 0.005 to 0.035" thick, 1/2" wide Std. Strip Specimen

Test	Annealed, cut paral- lel to direction of rolling	Annealed, cut perpen- dicular to direction of rolling	Annealed, with inter- mediate annealing during rolling, cut parallel to direc- tion of rolling
Ultimate Strength	36,000 to 42,000 psi	27,000 to 42,000 psi	34,000 to 38,000 psi
Yield Strength (0.2% off-set)	16,000 to 24,000 psi	15,000 to 30,000 psi	16,000 to 20,000 psi
Proportional Limit (0.01% off-set)	11,000 (one value)	6,000 to 16,000 psi	8,500 to 10,000 psi
Elongation, 2 in.	16 to 40%	14 to 32%	22.5 to 43.4%
Modulus of Elasticity	10 to 14.6 x 10 ⁶ psi	7.2 to 16.4 x 10 ⁶ psi	11 to 14.5 x 10 ⁶ psi

TABLE V

PHYSICAL PROPERTIES OF IODIDE DEPOSITED ZIRCONIUM

Cold Rolled Zr Strip 0.005 to 0.035" thick, 1/2" wide Strip Std. Specimen

Test	Hard Rolled, cut parallel to direction of rolling	Hard Rolled, cut perpendicular to direction of rolling	Hard Rolled, with intermediate, annealing during rolling, cut parallel to direction of rolling
Ultimate Strength	85,000 to 107,000 psi	76,000 to 108,000 psi	54,000 to 63,000 psi
Yield Strength (0.2% off-set)	68,000 to 93,000 psi	61,000 to 73,000 psi	46,000 to 54,000 psi
Proportional Limit (0.01% off-set)	41,000 to 47,500 psi	34,000 and 37,500 psi (2 values)	22,000 to 26,000
Elongation, 2 in.	1 to 8.6%	0.5 to 6%	5 to 13%
Modulus of Elasticity	11.3 to 13.5 x 10 ⁶ psi	10.1 to 13.5 x 10 ⁶ psi	11.2 to 15.3 x 10 ⁶ psi
Test	Hard Rolled, with intermediate annealing during rolling, cut perpendicular to direction of rolling	Half hard, 2 Brown and Sharp numbers reduction, stress relieved 1/2 hr. 800° F, cut parallel to direction of rolling	Half hard, 2 Brown and Sharp numbers reduction, stress relieved 1/2 hr. 800° F, cut perpendicular to direction of rolling
Ultimate Strength	49,000 to 67,000 psi	52,000 to 58,000 psi	51,000 to 66,000 psi
Yield Strength (0.01% off-set)	39,000 to 55,000 psi	40,000 to 47,000 psi	44,000 to 54,000 psi
Proportional Limit (0.01% off-set)	21,000 to 26,000 psi (4 values)	25,000 and 27,000 psi (2 values)	26,000 to 34,000 psi (4 values)
Elongation, 2 in.	3.5 to 12%	7 to 15%	3.5 to 12%
Modulus of Elasticity	9 to 14.8 x 10 ⁶ psi	11.5 to 14.8 x 10 ⁶ psi	10 to 15.2 x 10 ⁶ psi

Chapter V

THE NUCLEAR PHYSICS PROPERTIES AND THE EFFECT OF HAFNIUM IN ZIRCONIUM

It was the co-existence of zirconium and hafnium and the great similarity of their chemical properties with consequent difficulty in isolating pure zirconium that delayed an active interest in zirconium as a structural material in reactors. Pure hafnium has an absorption cross section to thermal neutrons of 101 barns⁷ and a total cross section of ~2000 barns at about 1 ev⁷⁵. Therefore, a trace of hafnium could account for an apparently high cross section for zirconium. Until about the middle of 1947, no very serious considerations for the use of zirconium as a structural material in thermal reactors were contemplated because of the reported high cross section measurements, one being 2.8 barns.

The insistence and determination of A. R. Kaufmann of MIT brought about the recheck of several cross section measurements and spectrographic analyses on zirconium and in the late summer of 1947, H. Pomerance and J. I. Hoover believed the absorption cross section to be not greater than 0.4 barns. By the end of the month of March, 1948, a sufficiently pure sample of zirconium oxide, ZrO_2 , was made available by the fractional phosphate precipitation method of hafnium separation to determine a more reliable value for σ_a . The new value assigned to σ_a for zirconium was determined to be 0.4 barns and not 2.8 barns as had been previously reported. This sample, prepared by the U. S. Bureau of Standards was believed to contain 350 ppm of hafnium. Furthermore, it was thought that the sample contained traces of the rare earths, gadolinium and samarium which might be responsible for the value of $\sigma_a = 0.4$ being as high as it was. Gadolinium has a total cross section of 48,000 barns to thermal neutrons of 0.025 ev.

More exacting checks on the spectrographic analysis of the Bureau of Standards sample made by Dr. Scribner of the Bureau indicated that the sample had <200 ppm of hafnium and <2 ppm of the rare earths. Therefore, the value of 0.4 barns was taken as authoritative for the thermal neutron absorption cross section for zirconium.*

When it seemed certain that the cross section of zirconium to thermal neutrons was as low as 0.4 barns, a great surge of interest in the metallurgy of zirconium developed within various reactor study groups of the AEC.

Previous to the above investigations of zirconium, only the following elements and materials were being considered for structural purposes in thermal reactors:

Aluminum
Beryllium
Beryllium oxide
Carbon (graphite)
Columbium
Steel

The above all have various limitations. Aluminum is limited to low temperatures because of its melting point, 1220.4° F. (Marks Handbook) and its low high temperature strength. Beryllium as produced today is brittle and difficult to fabricate. Beryllium oxide has only moderately good resistance to thermal shock (much inferior to zirconia for example). Furthermore, it suffers from radiation damage. Graphite is exceedingly affected by neutron

* See footnote, Chapter XI, p. 80.

bombardment, changing the thermal conductivity to nearly $1/30$ its original value. It is also brittle. Columbium has a higher cross section (1.2 barns for σ_a) than one would desire and furthermore is not as corrosion resistant as Beryllium. Steel has a cross section too high for a breeder pile (2.5 - 2.7 barns for σ_a) and would necessitate the use of even more fissionable material for a reactor to reach criticality.

Zirconium has a lower absorption cross section than columbium and steel, twice that of aluminum and forty times that of beryllium. However, it is extremely ductile compared to beryllium and has even better corrosion resistance to water. The operating temperature of a zirconium pile, however, is limited to the region of less than $\sim 750^\circ\text{F}^9$ because of the high gas absorption by zirconium at higher temperatures. If zirconium could be coated with silicon by the thermal decomposition of SiCl_4 (such as is done with molybdenum ribbon for oxidation protection of molybdenum up to 1700°C) then the limiting operation temperature would be much higher.⁷

The water cooled reactor studied by the Power Pile Division of the ORNL is not designed as a breeder pile and hence a cross section of 0.4 barns is tolerable. Furthermore, the design of the fuel elements involves the use of high surface area, high heat transfer, thin curved plates and a supporting web, all of which would be much more readily and easily fabricated from zirconium than beryllium.

A table of densities, tensile strength and absorption cross section to thermal neutrons for various materials is reproduced below:

Table I 3,8

Material	Mass M	Density ρ	Cross Section	
			σ_s	σ_a
Al	26.97	2.7	1.33	0.24
Be	9.02	1.85	4	0.01
BeO	25.02	2.85	8.1	0.011
C	12.01	1.65	4.8	0.0045
Cb	92.91	8.4	6	1.2
Fe	55.84	7.8	11	2.5
Zr	91.22	6.4	8.2	0.4

Resonance peaks formerly attributed to Zirconium have been established as Hafnium resonance peaks and the first is reported (going from low to high

energy levels) by L.J. Rainwater of Columbia at 1.04 ev. The slow neutron transmission graphs prepared by W. W. Havens, Jr., and L. J. Rainwater showing the resonance peaks in hafnium and unpurified ZrO_2 are shown on the following two pages. (See also Havens et al, Phy. Rev., 71, 165, 1947). Zirconium has a resonance cross section also but its value is considerable below that of hafnium.

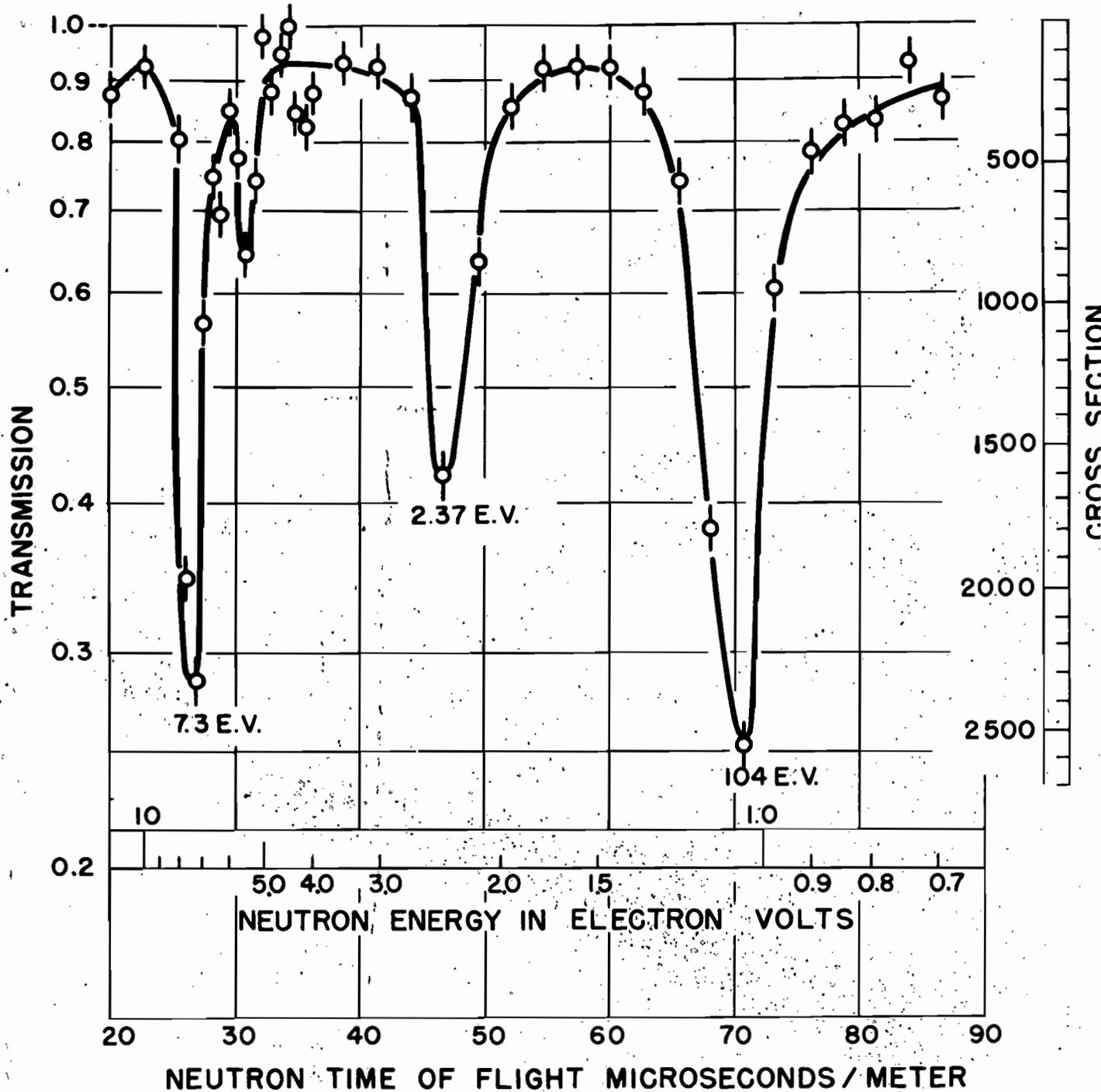
The resonance integral, $\int \frac{\sigma dE}{E}$ for zirconium has been calculated to have an upper limit of 4 barns by measurement of the epi-cadmium capture cross section.* Since the resonance integral is $\int \frac{\sigma dE}{E}$ for the range of E from thermal neutrons (.025 ev) through the fast neutrons (at least 1 Mev) and the predominance of this absorption lies in the lower or thermal regions, zirconium appears more useful to fast piles or to power reactors where a sacrifice in neutron economy is not so important. For the high flux pile or a breeder pile, the resonance integral of 4 barns is an important factor.

* Communication from A. S. Langsdorf, Jr., ANL, dated July 7, 1948.

UNCLASSIFIED

Drawing # 6540

FIG. 2 GRAPH BY L.J. RAINWATER AND W.W. HAVENS, JR. SHOWING SLOW NEUTRON TRANSMISSION OF 0.16 gm./cm² OF HAFNIUM



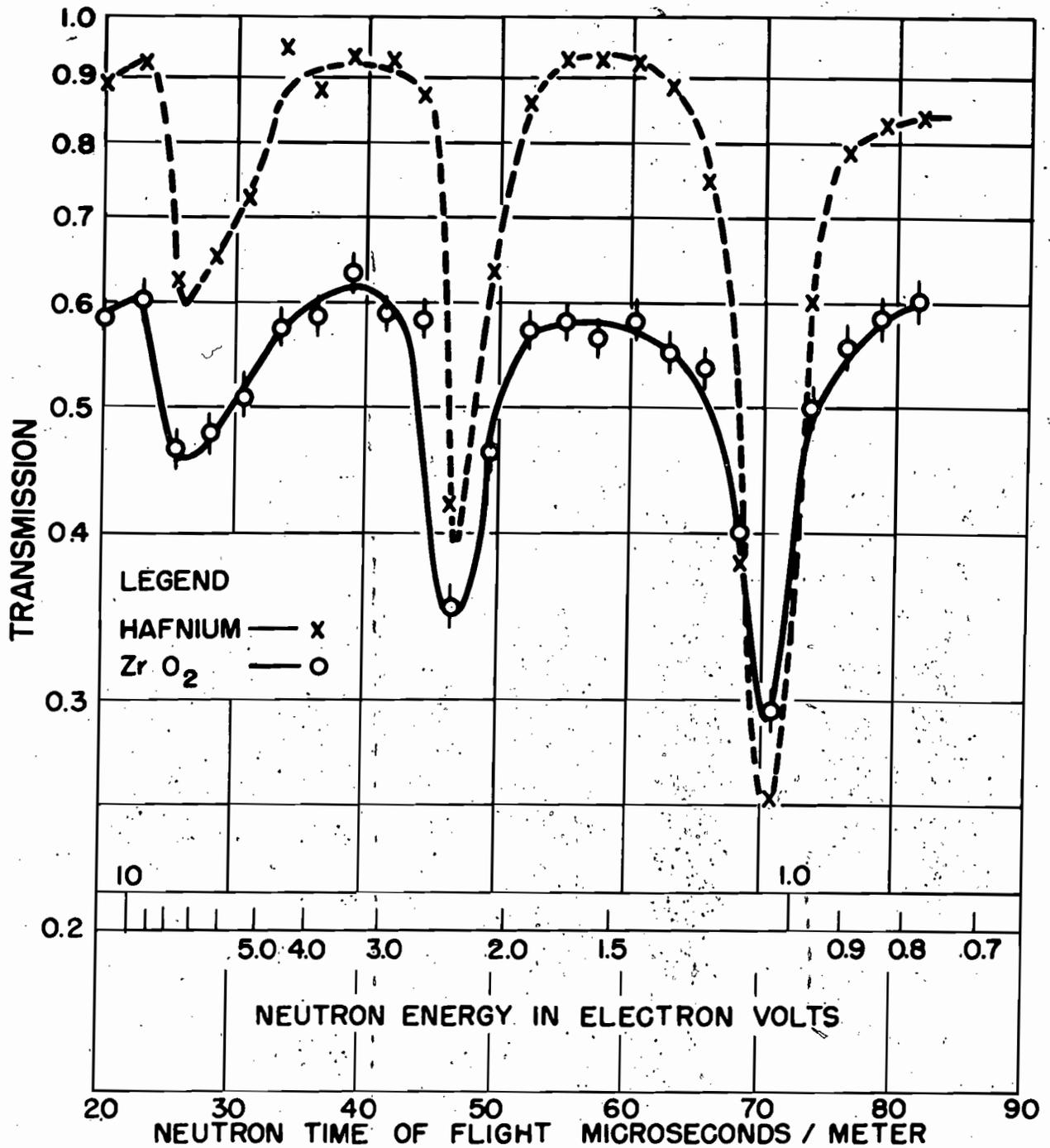


FIG. 3

GRAPH BY L.J. RAINWATER AND W.W. HAVENS JR. SHOWING SLOW NEUTRON TRANSMISSION OF 6.45 gm/cm² OF Zr O₂ AND .16 gm/cm² OF HAFNIUM

CHAPTER VI

THE PRODUCTION OF THE DUCTILE ZIRCONIUM METAL

The preparation of zirconium metal in various degrees of ductility has been achieved by the reduction of the following:³⁷

- (a) Halides by the "hot-wire" dissociation method
- (b) Chlorides or double chloride with sodium, calcium, or magnesium
- (c) Oxide with calcium, magnesium, or aluminum
- (d) Double alkali fluoride with sodium or aluminum
- (e) Oxide with carbon or the carbide with oxide
- (f) Double fluoride or double chloride by fusion electrolysis
- (g) Aqueous solutions by electrolysis

Of the above methods only the hot-wire dissociation of the tetra-iodide, the calcium reduction of the oxide, and magnesium reduction of the chloride are commercially practical today. The thermal decomposition of zirconium tetra-iodide is the most expensive of the three but also gives the highest purity, disregarding the element hafnium. No one of the three methods apparently has an advantage over any of the other for hafnium removal (see Chapter XI concerning hafnium separation)

The relative purity of the zirconium produced by these three methods has been discussed in Chapter IV (see page 16).

Tetra-iodide Decomposition

The iodide dissociation method for producing ductile zirconium by deposition of zirconium for the decomposition of the tetra-chloride can be carried out in the apparatus shown in Figure 4 at the end of this chapter. A complete description of this method follows:³⁸

The preparation of ductile zirconium is accomplished in a pyrex glass apparatus in which the vacuum is maintained at about 10^{-4} mm. of mercury. The raw materials are zirconium powder and iodine. The zirconium powder should be thoroughly degassed by heating in vacuum before the iodine is admitted. A tungsten or zirconium filament is used as the core of the deposited crystalline rod. This filament is maintained at $1400 - 1500^{\circ} \text{C}$, and the zirconium powder in the neighborhood of 300°C . The iodine acts as a carrier and very little is required. It reacts with the zirconium forming the tetra-iodide vapor which deposits the metallic zirconium by thermal decomposition of the iodide on the hot filament. The current in the filament may be increased from about $1/4$ amp to $100 - 200$ amps before a zirconium rod of $1/4$ inch diameter is deposited.

The cost of producing ductile Zr by the iodide method set a commercial price of \$235.00/lb in the spring of 1948.

Magnesium Reduction of Chloride^{58,74,87,*}

The Kroll or magnesium reduction of the chloride method (or also referred to as the Bureau of Mines method) involves a somewhat complicated but ingenious process. Zircon sand is converted into a carbide by heating with carbon in an electric furnace (see figure 5). The resulting carbide is then converted into the chloride by chlorination and the raw zirconium chloride which is then purified (see figure 6). The chloride is subsequently vaporized in a specially designed reduction furnace and reacted with molten magnesium metal in an atmosphere of helium. The residual salts are then removed by vacuum distillation and the spongy mass of zirconium which remains is melted in an arc furnace under purified helium. A process diagram is shown in figure 7.

The Bureau of Mines laboratory at Albany, Oregon estimates the cost of production at \$10.00/lb.

Calcium Reduction of the Oxide⁵⁸

Oxide reduction with the alkaline earth metals has been accomplished in heavy-walled closed vessels known as "bombs". Such a reduction involves a closed system and no control is possible for the gas impurities particularly. Since the ductility of zirconium is very dependent upon the control of gaseous impurities, Lilliendahl and Rentschler of Westinghouse improved the bomb method of oxide reduction through the use of very pure calcium and improved techniques which allow the reactions to be controlled and effected in vacuo or in an inert atmosphere (see Figure 8). This development of the process made it possible to produce pure zirconium by reducing the oxide with calcium or magnesium contained in a molybdenum crucible in an atmosphere of argon. A special glass bulb possessing the high temperature resistance qualities of quartz was placed around the assembly and the crucible heated by high frequency to 1000 - 1200° C. An excessive vaporization of calcium or magnesium at these temperatures was suppressed by the inert gas filling. The metal obtained by this reduction method is produced in powder form with the average analysis as follows:

C	0.02%
SiO	0.02%
Fe	0.05%
Ca	0.10%
Ti	0.01%

The powder is compressed in hardened steel dies into compacts involving pressures of 40 - 50 psi. These compacts are strong and can be handled. They are either sintered or melted in high vacuums of at least 10⁻³ mm of Hg or better in a suitable refractory (see figure 9).

* For the most recent publication of the Bureau of Mines ductile zirconium program, see reference 87.

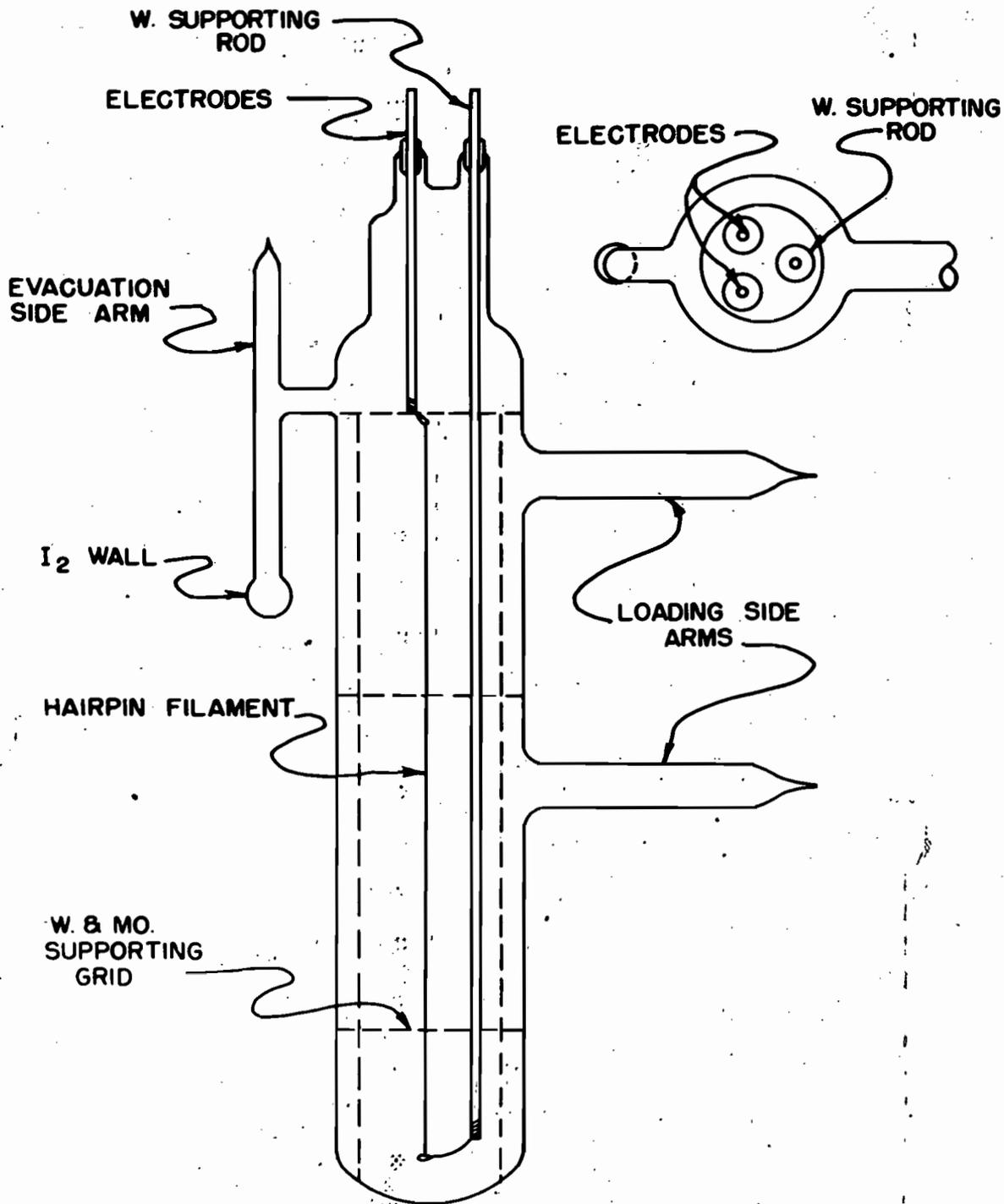


FIG. 4 PYREX GLASS APPARATUS FOR THE PREPARATION OF IODIDE DEPOSITED ZIRCONIUM.

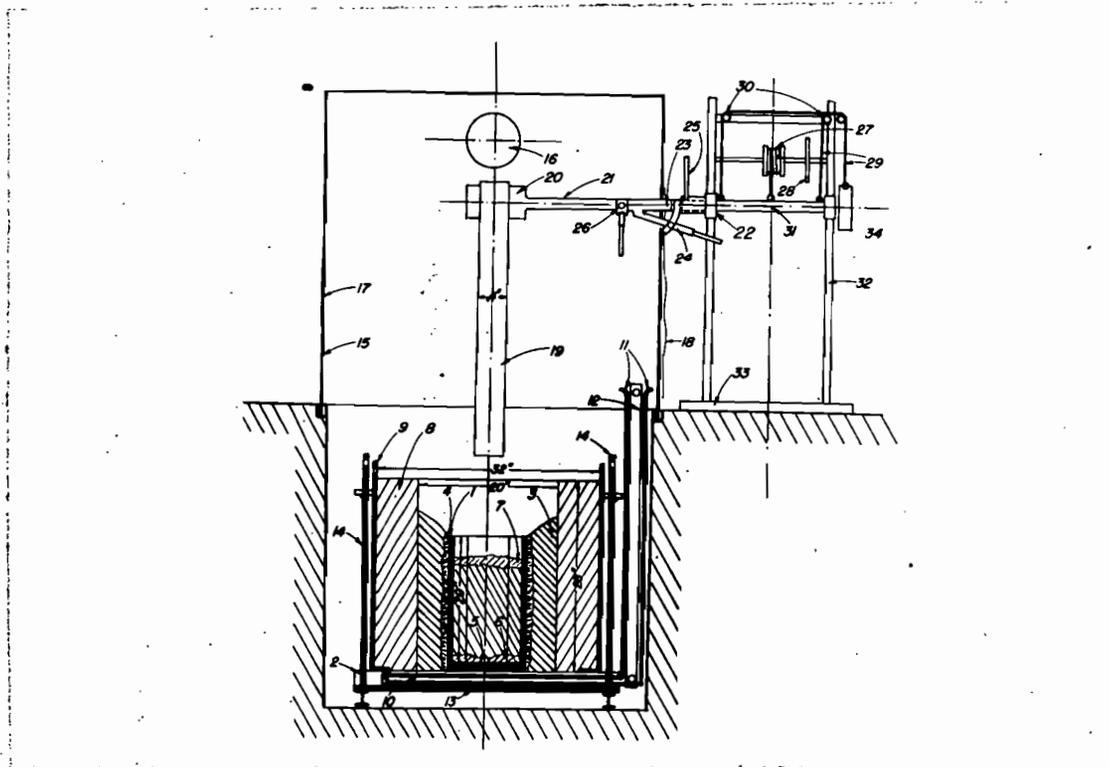


Fig. 5 Arc furnace for the production of zirconium carbide.⁷⁴

1. Graphite plate crucible.
2. Graphite plate bottom.
3. Charcoal filling.
4. Old batch filling.
5. Graphite bottom of crucible.
6. Graphite powder seal of bottom.
7. Graphite powder top seal.
8. Refractory lining.
9. Iron shell.
10. Water-cooled contact plate.
11. Water cooling.
12. Bus bar to bottom.
13. Iron bottom plate.
14. Vertical furnace columns.
15. Hood
16. Exhaust duct.
17. Window opening for feed.
18. Asbestos cloth.
19. Graphite electrode.
20. Electrode holder, water-cooled.
21. Electrode arm.
22. Guide.
23. Hollow shaft.
24. Arm for horizontal movement in picture plant.
25. Arm for horizontal movement perpendicular to picture plane.
26. Cable contact.
27. Drum.
28. Hand wheel.
29. Counterweight and cables.
30. Rolls.
31. Cross bar for vertical electrode movement.
32. Vertical columns of electrode lift.
33. Base plate.

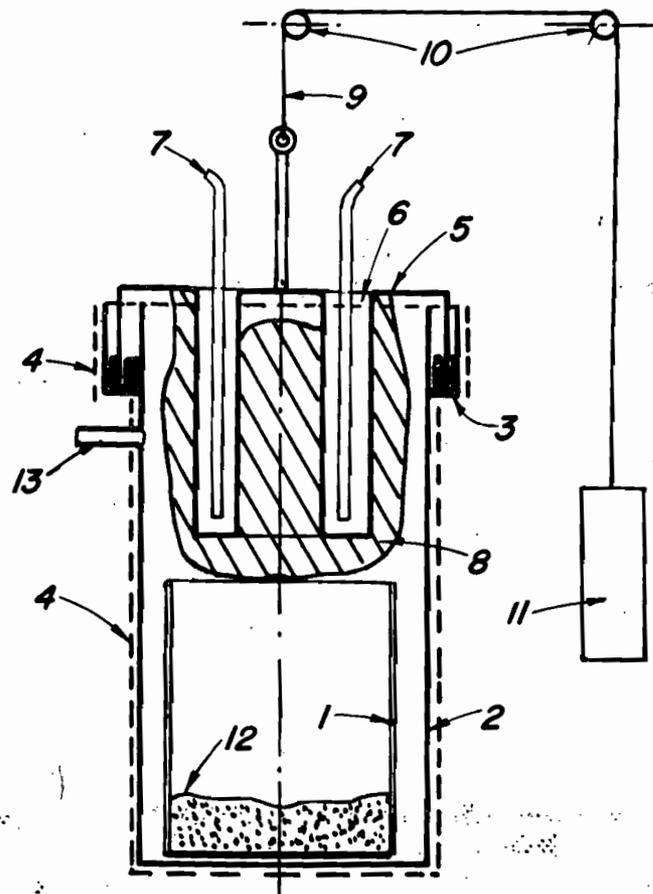


Fig. 6 Apparatus for producing dense zirconium chloride. 74
 1. Crucible. 2. Reduction furnace. 3. Fusible metal seal. 4. Heating coil. 5. Floating top. 6. Condenser. 7. Compressed air. 8. Zirconium chloride ingot. 9. Steel wire suspension. 10. Pulleys. 11. Counterweight. 12. Oxide residue. 13. Needle valve stem.

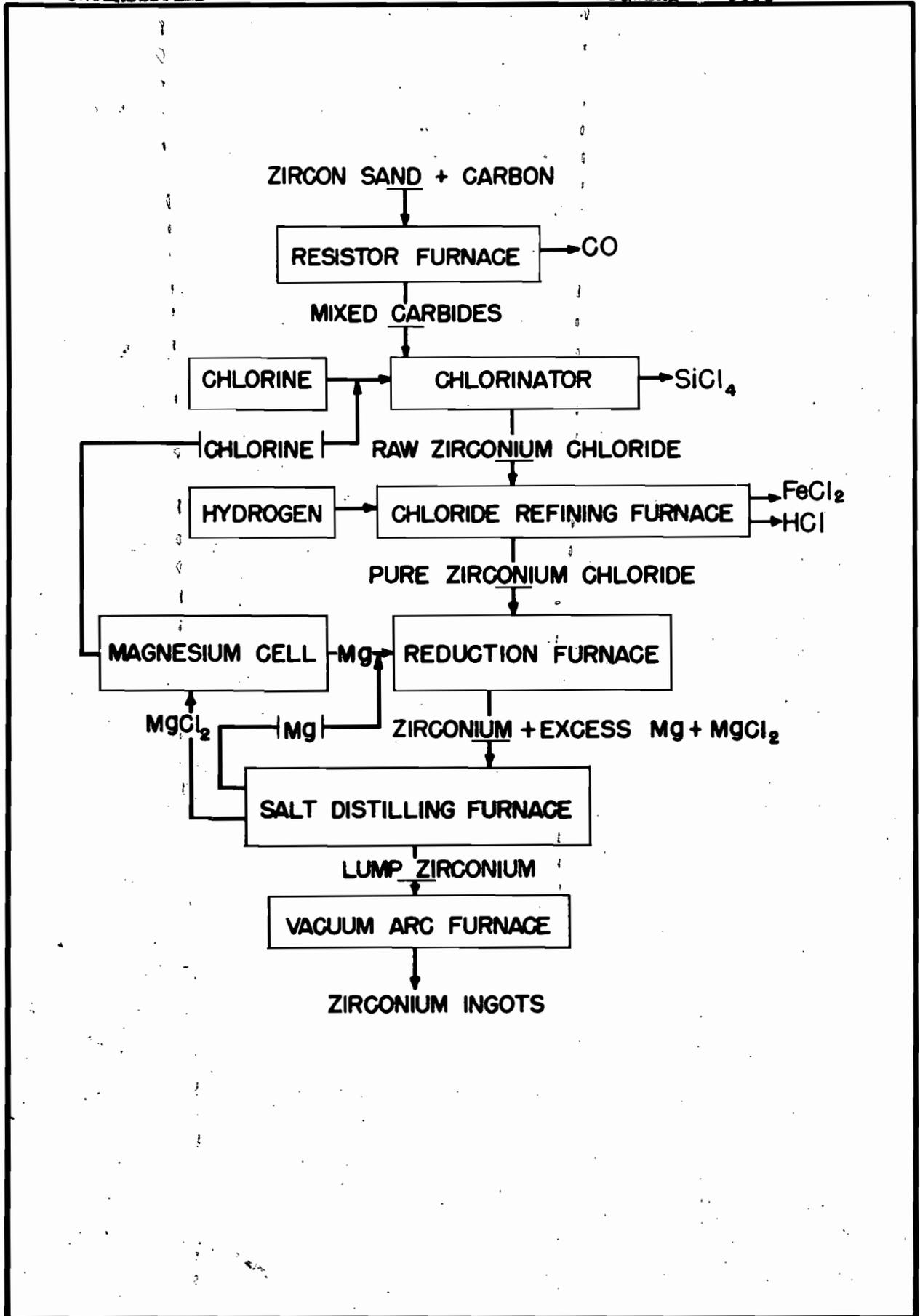


FIG. 7 . FLOW SHEET OF PROCESS FOR PREPARING PURE ZIRCONIUM
IN BUREAU OF MINES.⁵⁸

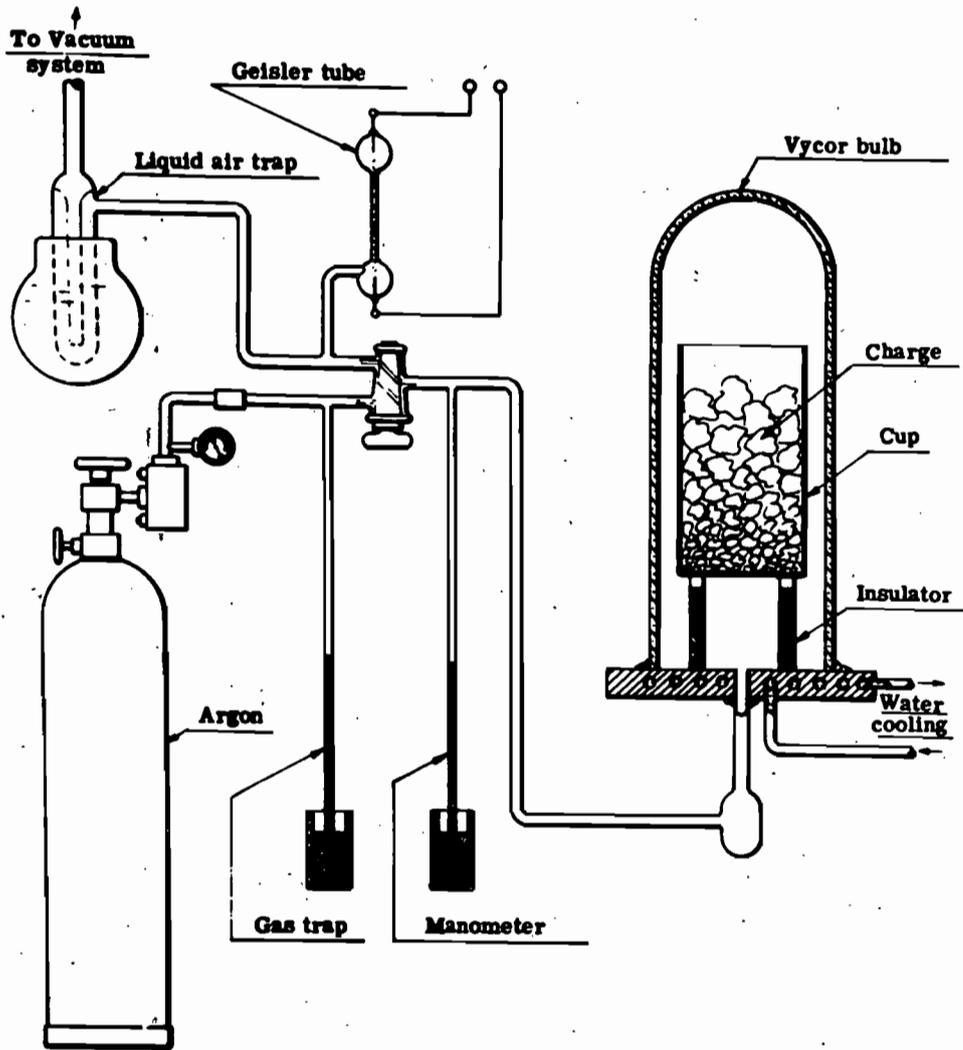


Fig. 8. Apparatus used by Lilliendahl and Rentschler to produce pure zirconium. ⁵⁸

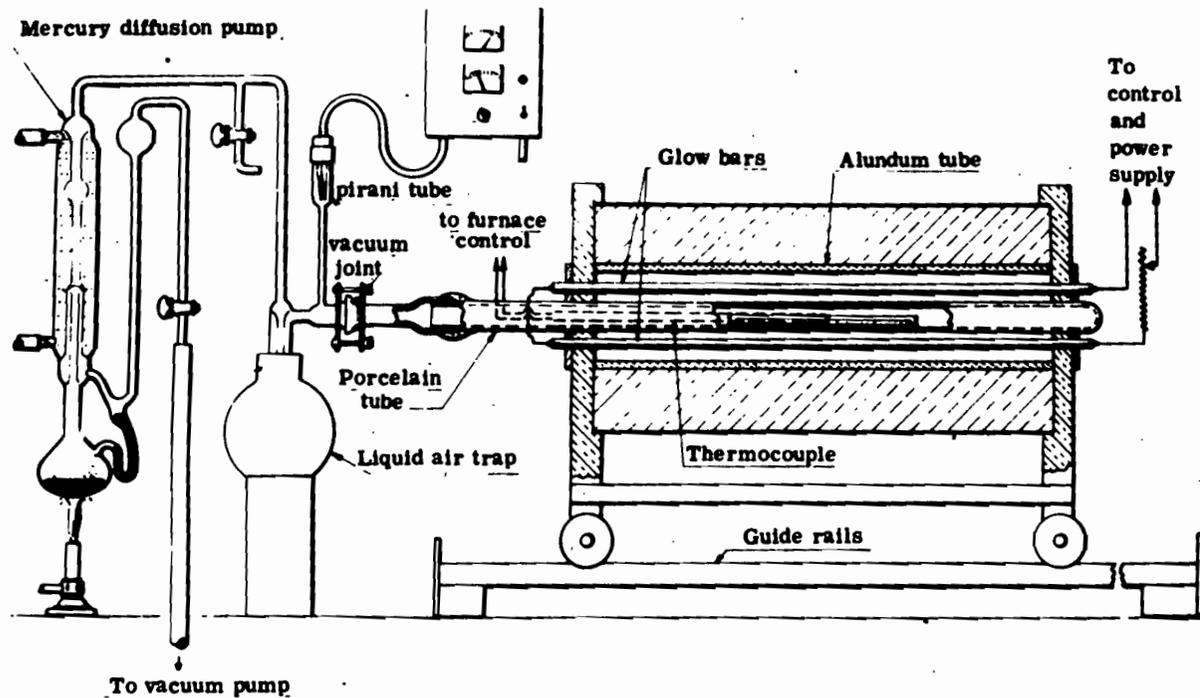


Fig. 9. Vacuum sintering furnace for zirconium.⁵⁸

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CHAPTER VII

THE PRODUCTION OF ZIRCONIUM POWDER

Berzelius first prepared zirconium as a powder in 1824 by reducing potassium-fluozirconate with potassium.³⁶ Zirconium powder cannot be made by the reduction of the oxide by hydrogen⁴². It can however be made by a thermit reaction in steel bombs through the reduction of the oxide with sodium, magnesium, aluminum, or calcium.^{1,42,58} Such a powder is used in the iodide deposition method for producing ductile zirconium.

DeBoer states that a very good crude zirconium powder is prepared using a mixture of calcium and sodium in a vacuum. De Boer also reports that the reduction of the oxide with a mixture of magnesium and sodium gives good results.

The reduction of zirconium oxide by calcium is done in specially designed vessels which are resistant to both high temperatures and pressures. The reduction product is digested in hydrochloric acid to remove the acid soluble salts. A typical analysis of the zirconium metal powder produced by the calcium reduction of the oxide followed by the hydrochloric acid wash is as follows: total zirconium, 98.3%; Ca, 0.02%; Fe, 0.008%; Al, 0.008% and Si, 0.002%. The balance of about 1.7% is probably combined oxygen and nitrogen. The average particle size of this metal powder is about 5 microns.⁴

The ignition point of zirconium powder of this size is about 190° C. It is extremely pyrophoric and must be handled with precautions in shipping. The hazards of handling are considerably reduced by shipping the metal wet or in paste form running about 25% moisture content.⁴

CHAPTER VIII

THE FABRICATION OF ZIRCONIUM

Zirconium produced by the thermal decomposition of the tetra-iodide or by magnesium reduction of the purified chloride is termed "malleable" or "ductile" and can therefore be fabricated in many ways. Zirconium produced by powder metallurgy from the powder cannot be either hot or cold worked to any relative degree and is therefore not ductile.¹

Since zirconium like many metals, can be much more satisfactorily hot worked than cold worked because of work hardening in the cold state, it presents a problem unique to itself and to a few other metals that have great affinity to gas absorption at elevated temperatures. Even the annealing of zirconium cannot be done in hydrogen or other reducing gases such as carbon monoxide because of the great affinity of zirconium for all gases, excepting the rare and noble gases at elevated temperatures. The annealing of zirconium is generally accomplished in purified helium, argon, or krypton.

Since the hot rolling of zirconium would be extremely difficult and burdensome in the presence of a controlled atmosphere, an iron cladding can be placed around zirconium for hot rolling or extrusion in much the same manner as is done with beryllium. Copper can also be used for cladding.²¹

Rolling Zirconium

Zirconium sheet with a bright smooth finish produced by cold rolling in polished ground rolls is commercially available in thicknesses as small as 0.001 inch. The volume of metal for any one sheet had previously been limited to the volume of one crystal bar deposited by the iodide method until the magnesium reduction method was perfected.

The size of the crystal bar itself is limited to the size of the apparatus which determines not only the volume of the charge and the vacuum problems, but most importantly the electric current limitations. In the tetra-iodide decomposition method of ductile zirconium production the current must be increased as the diameter of the crystal bar increased in order to maintain decomposition temperatures.

Vacuum melting of several crystal bars to obtain a large ductile ingot has always resulted in some small gas absorption (most likely from the crucible itself) with the best attainable vacuums and with resultant loss in ductility through slight embrittlement.

Now, however, zirconium can be produced in 10 lb ingots by the vacuum casting of the "spongy" metal produced by magnesium reduction of the purified chloride. Also, an experiment at MIT has indicated that a large billet of ductile zirconium can be produced by the hot extrusion of a bundle of crystal bars which are encased in an iron can for protection against rapid gas absorption. This same experiment gave an extruded billet which possessed strength and ductility superior to those of the crystal bar itself.

When hot rolling zirconium, W. J. Kroll, et al., state that 50% reduction can be achieved between reheating of the iron clad billets.

Heavy billets can be hot rolled without cladding by heating to 700° C if one wishes to sacrifice some of the surface of the billet in conversion to an oxide scale. This scale is yellow to brown in color on the hot rolled magnesium reduced zirconium. The yellow is probably due to the presence of iron.⁷⁴ The scale is soft and can be removed with ordinary abrasives. The rolling of iron clad billets at temperatures above 950° C should be avoided because the iron and zirconium unite between 800-1000° C. In a trial run at the Electrodevelopment Laboratory at Albany, Oregon, a zirconium sheet which was sheathed in iron and rolled at 1,025° C suddenly ignited and burned vigorously.⁷⁴

Zirconium hot rolled to nearly the finished size and then cold rolled as a polished sheet to 0.010 inch thick can be bent sharply at an angle of 180° without cracking.⁷⁴ Fully annealed 0.005 inch thick zirconium sheet can be readily bent through 180° on a 0.010 inch radius without cracking.⁴

Without special highly polished roll mills, zirconium can be rolled from 0.002 inch to 0.001 inch thick by inserting the zirconium sheet between clean dry sheets of nickel. It has been observed that softer metals have a tendency to tear the zirconium.⁴

Drawing

Zirconium wire is produced commercially today in diameters of 0.002 inches to 0.040 inches. The greatest difficulty in drawing zirconium has been the seizing of the zirconium to the die during the drawing operation. The Phillips Laboratory at Eindhoven, Holland, and the Foote Mineral Company in Philadelphia, have both observed that this seizing can be reduced considerably by the presence of an oxide film on the slug. A short time treatment in air at 650-700° C gives the zirconium slug an oxide scale which apparently acts as a die lubricant.³² Alnutt and Scheer claim that no other die lubricant which they tested could withstand the pressures that the oxide film could. The oxide film is hard, about 7 on the Mohs scale⁴, and the life of the die is limited.

Welding

Spot welding and electric arc butt welding of zirconium can be achieved without much difficulty if the current time is properly controlled by maintaining the current just sufficient to cause a weld and limiting the time of weld to a minimum.^{4,32}

Heliarc welding of zirconium has been successfully carried out.^{7,31}

Riveting, Crimping, and Slotting

Sheet metal parts made of zirconium are most readily fabricated by riveting, crimping, and slotting according to Scheer and Alnutt.

Spinning and Bending

As has already been mentioned, a fully annealed 0.005 inch zirconium sheet can readily be bent 180° on a 0.010 inch radius without cracking.

A limited amount of drawing and spinning, perhaps with 10% deformation, can be accomplished before the metal must be annealed before further cold working can be done. Cold working causes embrittlement through work hardening and frequent annealing at temperatures in the range of 800 to 1,000° C. in purified helium or argon gas will restore nearly all of the original ductility.

Annealing can be done in air only on large pieces, and should be done quickly and not repeated more than two or three times.

Machinability

Experience at Eindhoven in the Phillips Laboratories, in Philadelphia at the Foote Mineral Company, and at various AEC installations indicates that the ductile zirconium can be easily machined. Experience at ORNL has shown that it machines with as little difficulty as a low grade carbon steel.

CHAPTER IX

THE CHEMICAL REACTIVITY OF ZIRCONIUM

(This section is concerned mainly with the chemical reactivity of zirconium with other elements, especially the gases, at room and elevated temperatures. A separate section concerns the corrosion of zirconium in aqueous solutions.)

Although powdered zirconium is pyrophoric and reacts with air at temperatures of 190-210° C., massive zirconium is quite stable to all gases at room temperatures. Zirconium has a heat of formation of 129.5 Kcal. per gram atom of oxygen, a value second to aluminum among the corrosion resistant metals. The reaction of zirconium and oxygen can take place at low temperatures and when the exposed surface area of each particle of zirconium is large, such as in the case of powdered zirconium, the reaction proceeds almost violently.

In the case of the compact or massive metal however, the oxide film forms immediately upon exposure to oxygen and aids as protection against further corrosion. At moderate temperatures the oxygen ions, molecules, or atoms probably do not diffuse interstitially through the oxide layers. One would expect this oxide layer not to exceed 50A as is the case for aluminum and chromium at moderate temperatures.²

At higher temperatures, however, zirconium will absorb many different gases with the exception of the rare and noble gases. Oxygen, nitrogen, carbon monoxide, carbon dioxide, hydrogen, and water vapor are particularly reactive at high temperatures where the surface film offers less protection against the interstitial diffusion of at least one of the reacting substances through the film itself. It appears that considerable quantities of the reactive gases mentioned above can be absorbed without the formation of a new phase. However, de Boer says that oxygen free zirconium has a sharp transition point (or phase change) at 862.5° C. which can be shifted to 1150°C. or more by the presence of oxygen.⁴⁶

Because zirconium is such a good absorber of gases at high temperatures, its first principal commercial use was in the coating of elements in electron tubes for the purpose of gas absorption. These remarkable "getter" properties make zirconium difficult to heat even in the best vacuums without absorbing some even minute quantities of gas.

The absorption of gases in vacuum at 1000° C. for 24 hours is shown below:⁹

TABLE I

Pressure, mm Hg	Weight gain, %
3.0×10^{-5}	~ 0.5
3.5×10^{-4}	~ 1.25
1.5×10^{-2}	~ 2.9
5.0×10^{-2}	~ 3.5

A. R. Kaufmann and P. Kulin of MIT have found that the only way to attempt a heat treatment of zirconium such as annealing without a change in chemical purity is to do it in the best vacuum possible and surround the specimen itself with a zirconium envelope.³¹

Oxygen Absorption and Oxidation

Various and somewhat conflicting data are available concerning oxygen absorption. J. D. Fast states that oxygen is absorbed at temperatures above 700° C. whereas Ehrke and Slack⁴⁰ believe the minimum temperature to be 885° C. Furthermore, S. Hukagawa and J. Nambo⁴¹ show that oxygen is absorbed at temperatures as low as 180° C. with optimum absorption at 650-700° C.

Figure 10 at the end of this chapter shows the work of Hukagawa and Nambo and indicates that after the first rapid absorption at 180° to 230° C. a stable condition exists until further oxygen absorption occurs at 450° C. W. M. Raynor theorizes that the first reaction at 200° C. may be a formation of a "solid solution" with oxygen and that the second absorption interval of 450-600° is the result of the formation of the oxide.

Another more generally accepted theory is that the protective oxide film that forms even at room temperatures becomes thick enough to stop absorption at 230° C., but becomes dissolved in the metal at around 450°C. allowing further absorption.

De Boer states that a piece of zirconium covered with an oxide film becomes lustrous when heated in vacuum. His belief is that the oxide dissolves into the metal. Several properties of the metal are noticeably affected by this absorption of oxygen and a comparison of these properties with those of the pure gas free ductile metal offers a quick determination of relative gas content. The electrical resistivity is increased, the melting point is raised, the temperature coefficient of the electrical resistivity is decreased, and the atomic distance is somewhat increased. Obviously the ductility is also decreased.⁴³

Some of the lack of agreement in the work of Fast's and also of Ehrke and Slack as compared with that of Hukagawa and Nambo may be due to the fact that the former three used massive ductile metal whereas the latter used molybdenum ribbon sprayed with zirconium powder. It is quite likely that the greater surface areas of exposure of the powder may be responsible for the absorption of gases at lower temperatures than with the massive or compact metal. Actual electron tube production and research shows that Hukagawa and Nambo are correct in the absorption temperatures of the powder.⁴²

W. M. Raynor of the Foote Mineral Company states that the oxide film does not dissolve rapidly until temperatures above 865° C. However, tests at MIT on the oxidation of iodide produced zirconium indicate that temperatures in the neighborhood of 400° C. would be the maximum safe operating temperatures of massive zirconium metal for long periods of operation (say 2,000 hrs.) in air. (See figure 11.).

The only recent data on oxygen absorption of iodide deposited zirconium for three different elevated temperature runs are given below:⁹

@ 516° C. a weight gain of 0.023% was experienced in 1½ hours and 0.0849% in 17½ hours.

@ 700° C. a weight gain of 0.235% in 164 hours was noted

@ 1,000° C. a weight gain of 3.46% in only 3½ hours followed by rapid oxidation was experienced.

The data shown in Table II below are indicative of not only the oxygen absorption but the nitrogen absorption, both which can be loosely termed "corrosion" in a gaseous medium. The effect of the presence of larger amounts of impurities in the magnesium reduced zirconium on the corrosion of Zirconium in air is also graphically represented in figure 11.

Table II⁹

Corrosion Data of Foote Zirconium in Air at Elevated Temperatures

°C	Surface area of sample tested cm ²	Original Weight of sample gm	Weight gain/unit surface area, gm/m ²					
			47 hours	162½ hours	487 hours	555 hours	1029 hours	2312 hours
200	5.8130	5.3228	1.548					1.720
300	5.5943	5.0787		0.894				1.787
400	5.7207	5.2729	1.223	2.272		4.370		6.293
500	5.6544	5.1274	6.720	10.081			27.235	78.670

NOTE: Samples were held in porcelain boats.

Table III⁹

Corrosion Data of Bureau Zirconium in Air at Elevated Temperatures

°C	Surface area of sample ₂ tested cm	Original Weight of sample gm	Weight gain/unit surface area, gm/m ²					
			70 hours	142 hours	237 Hours	451 hours	759 hours	
200	5.7258	5.3777		.175		.524	.175*	
300	5.7258	5.3063	.349	.524		.349	1.397	
400	5.7258	5.3129	1.921	2.969	3.493	4.541	6.462	
500	5.7562	5.3397	9.902	13.029	17.199	28.491	49.338	

* Inaccuracies in weighing may account for this drop.

As to the liberation of absorbed oxygen at elevated temperatures, oxygen is retained even at temperatures exceeding 1500° C.⁴² According to de Boer, however, the oxygen can be shifted from one end of a zirconium rod to the other by passing direct current through the rod at 1500°C. The oxide is believed to migrate to the anode as in electrolysis.⁴⁷ Albutt and Scheer claim that the ductility can be restored to the cathode end of a zirconium bar containing the oxide by passing a DC current through the bar allowing it to reach 900. They also concur on the migration of oxygen to the anode.⁴ Such experiments have recently been tried on the removal of oxygen from beryllium but met with no success in removing the oxygen.

As to the quantity of oxygen absorbed, J. D. Fast⁴⁵ claims that up to 40 atomic per cent of O_2 can be dissolved without X-ray evidence of the presence of a compound. Hall, Martin, and Rees (in Trans. Faraday, Sec. 41, 1945, p. 306) report as high as 50 atomic percent absorption of oxygen in what they term "true solid solutions". W. G. Guldner and L. A. Wooten claim 38 atomic per cent of oxygen can be dissolved into ductile zirconium strip without the formation of a new phase.⁹⁵

The measurement of oxygen in zirconium is a difficult problem. Fast reports the pressure of oxygen in equilibrium with the saturated solution of oxygen in zirconium was too low for direct measurement - even less than 10^{-8} atm. at $2700^\circ F.$ ⁵ Kroll, Schlechton, et al., investigated a method of oxygen determination that depends on the chlorination of the metal with purified chlorine that is especially free of oxygen, nitrogen, and carbon dioxide. The purification of the chlorine is performed by condensing the cylinder chlorine with dry ice. This causes the oxide bearing materials to become a residue. The method is limited to zirconium which is free of carbon, tungsten, and the metals of the fifth group of the periodic table as these elements form volatile oxychlorides. (See appendix for Dr. Knoll's own description of the test procedure.)

W. C. Lilliendahl, et al.⁸⁶, have also developed a quantitative method of evaluating oxygen in zirconium by the direct determination of the zirconium oxide content by vaporization of the method in chlorine gas. This method is essentially the same as that proposed by Kroll but higher temperatures are involved, i.e., $800^\circ C.$ instead of $500^\circ C.$ for the chlorination of the zirconium. The zirconium oxide residue must be corrected for side reactions with carbon. They claim a precision of approximately 0.02 per cent with 2.0 g. samples.

Reactivity with Water Vapor⁹⁵

Guldner and Wooten in their experiments for determining the gettering properties of zirconium for application to electron tubes, noted a water vapor absorption nearly at the same rate as oxygen for the temperature range of $200-350^\circ$. A specimen thus treated was observed to liberate hydrogen when the temperature was raised. It was further noted on exposing a zirconium coated plate to water vapor in the temperature range of $700-800^\circ C.$ that hydrogen was formed and liberated in the system.

Nitrogen Absorption

Nitrogen, according to Fast, is absorbed at temperatures exceeding $1,000^\circ C.$ and again we have conflicting data of Hukagawa and Nambo who claim that nitrogen is completely absorbed at $600^\circ C.$ ⁴¹ Their curves (Figure 12) indicate that some of the nitrogen may be released at higher temperatures. W. M. Raynor believes this is probably hydrogen present in the zirconium, however, which would account for the increase in pressure shown above $650^\circ C.$

Guldner and Wooten state that the reaction of nitrogen with zirconium does not occur at room temperature but begins slowly at $400^\circ C.$ ⁹⁵ At $800^\circ C.$ they further note that "the gas is cleared up very rapidly".

Again it should be reiterated that some of the differences in the results of Fast and Hukagawa and Nambo are due to the facts mentioned under "Oxygen Absorption and Oxidation" (see p.43). Table XIII in the chapter entitled "The Mechanical Properties of Zirconium" shows the effect of a nitrogen atmosphere on the hot properties of zirconium.

Zwicker believes that nitrogen also shifts the transformation point similarly as does oxygen.⁴⁸

Fast, in his studies of the influence of nitrogen gas on zirconium, claims that it is not released upon heating. However, van Arkel relates that at least small amounts of nitrogen are released at elevated temperatures.¹¹

Guldner and Wooten observed on heating a sample that had "sorbed" 13 atomic per cent of nitrogen to 1300° C. that no gas was liberated and therefore concluded that a very stable compound had been formed.

The effect of nitrogen absorption on the physical properties of zirconium is similar to oxygen. The hardness, tensile strength, and electrical resistivity are raised and the ductility decreased. The nitride is a better metallic conductor than the metal itself. Because of this fact, there must be a point where the resistivity reaches a maximum, after which the resistivity will be diminished again. P. Clausing found such a point.¹

Nitrogen diffuses more slowly than oxygen in zirconium which permits the longer hot working of the metal in a nitrogen atmosphere before embrittlement became too great.

The solid solution range of nitrogen in zirconium is smaller than that of oxygen and is estimated to be in excess of 20 atomic per cent.^{32,42} J. D. Fast claims that up to 20 atomic per cent nitrogen can be dissolved without X-ray evidence of the presence of a compound.⁴² Recent work with X-ray diffraction patterns by Guldner and Wooten of the Bell Telephone Laboratories evidences a compound formation of zirconium nitride.⁹⁵

Absorbed nitrogen, like oxygen, can not be completely reversibly released after absorption.^{39,42} It can readily be determined, however, by the Kjeldahl method.³⁹ Kroll observes that the compound of zirconium, zirconium nitride, starts to dissociate in vacuum at 500°, but feels that complete dissociation would be only problematic. Kroll further relates that a dissociation of the nitride, produced by the reaction of pure sublimed zirconium chloride and ammonia gas, may take place at the melting point of zirconium since a slight gas evolution is sometimes perceptible. He finally adds however, that it is questionable whether or not even prolonged heating of molten zirconium would remove all of the nitrogen.

Hydrogen Absorption

The use of hydrogen gas as a reducing agent in cleaning the oxide film from many metals at high temperatures is not applicable to zirconium. Zirconium being in the fourth group of elements in the periodic table, has a high affinity for hydrogen, as well as the halides, sulfur, nitrogen and carbon.

The hydrogen absorption curves of J. D. Fast and Hukagawa and Nambo are shown in figures 13 and 14 at the end of this chapter.

The graph of Fast's work shows that the hydrogen is absorbed from 300 to 400° C. and again liberated between 500 and 850° C, reabsorbed at 862° C., and again released above 862° C.

Guldner and Wooten found the optimum temperature for hydrogen absorption to be 300° C.⁹⁵

Hukagawa and Nambo's work reveals a reversible cycle but also shows that a certain quantity of hydrogen can be permanently removed by heating to 600° C. or over and following through with one complete cycle of heating and cooling (see figure 14).⁴² W. M. Raynor states that there must have been some hydrogen present (as in the nitrogen curves of Hukagawa and Nambo) because the pressure increases with the temperature and does not show that hydrogen is absorbed at 300 to 400° C., which J. D. Fast found to be the case with pure zirconium.⁴² A spread between the curves indicating that a proportion of the hydrogen has been permanently absorbed after one complete cycle of heating and cooling is difficult to explain since although a hydride is formed at lower temperatures, this hydride breaks down at approximately 400° C. The hydrogen must be retained in solid solution according to this thinking. However, the work of Hukagawa and Nambo was done below 800° C., and therefore they did not experience the phenomenon of the transition temperature of 862° C., and its effect upon hydrogen absorption. The solubility of hydrogen increases suddenly at this point.

Van Arkel¹¹ states that all the absorbed hydrogen can be removed in vacuum at 1500° C., therefore agreeing with J. D. Fast⁴² on the reversibility of hydrogen absorption. Guldner and Wooten note the reversibility of hydrogen gas absorption and claim a temperature of only 800° C as sufficiently low enough for complete gas liberation.⁹⁵

The effect of hydrogen gas in solid solution in zirconium is to lower rather than raise the transition temperature between the α and β phases. Hydrogen is more soluble in the α phase than the β phase, whereas oxygen is more soluble in the α phase zirconium.³²

G. Hagg has shown by X-ray analysis that up to 5 atomic per cent of hydrogen dissolves into zirconium to give a true solid solution. He further reveals that two phases, both expanded zirconium lattices, are present in compositions ranging from 5 to 33 atomic per cent of hydrogen.⁴⁹

Carbon Dioxide Absorption⁹⁵

Guldner and Wooten have studied the "sorption" of carbon dioxide and observed a 0.45 cc. mm (pressure) carbon dioxide /mg of zirconium at 400° C. At 800° C. they state the rate of uptake to be rapid. No gas was given off when this sample was heated to 1300° C.

X-ray diffraction analysis indicated the presence of zirconium oxide, ZrO_2 , and zirconium carbide, ZrC . Both chemical and X-ray investigations reveal stable chemical compounds are formed when zirconium absorbs carbon dioxide at temperatures in the neighborhood of 800° C.

Carbon Monoxide Absorption⁹⁵

Guldner and Wooten observed that the behavior of carbon monoxide with zirconium was very similar to that of carbon dioxide. Both chemical and X-ray examinations reveal the compound formation of zirconium dioxide and zirconium carbide.

Absorption of the Rare and Noble Gases

As has been previously stated, the rare and noble gases are not absorbed by zirconium. Thus for example the heat treatment of zirconium such as annealing at 1000° C. is usually done in helium or argon gases.

An experiment on iodide deposited zirconium at 1,000° C. in unpurified argon gas resulted in a 1.3073 gram sample gaining only 0.0075 grams in 3 hours. This was a weight gain of 0.575% in 3 hours in argon gas as compared to 3.46% gain in 3½ hours in oxygen which furthermore was followed by rapid oxidation.⁹ A test of 100 hours would probably have found the oxygen surrounded specimen completely gone and the argon gas enclosed specimen still absorbing any impurities in the unpurified gas itself, but not however, disintegrating, as would be the case in oxygen. Zirconium shavings have been suggested as purifiers for the rare and noble gases; viz. helium, neon, argon, and krypton.⁴²

Reactivity with the Halogens

Zirconium is known to react readily with all of the halogens at moderate temperatures (200-400° C) to form the volatile tetrahalides. It is also known that under certain conditions, the less volatile dihalides, which offer some protection to further attack, may be formed. This fact particularly apparent in the iodine reaction for it has been noted at all temperatures above 500-600° C. the di-iodide is sufficiently volatile to prevent the formation of an effective protective film.

The sublimation of the iodide without decomposition in vacuo makes it possible to produce zirconium by the thermal decomposition of the sublimed iodide. A complete treatise on this preparation of the ductile zirconium by thermal decomposition of the tetra-iodide under the chapter entitled "Production of the Ductile Zirconium Metal".

The reactivity of the halogens towards zirconium decreases with increasing atomic number and the iodide is the least stable of the halides. This factor determines the choice of the halogen, iodine, as the carrier for zirconium in the halide thermal decomposition method of zirconium production.

Experiments have shown that oxidized zirconium is apparently not attacked, at least not readily, by iodine.¹ This is probably true of the other halogens also.

Chlorine is also reactive with zirconium. The temperature at which this takes place however, has been described as a "dull red heat" by de Boer. The tetra-chloride has also been employed in the production of ductile zirconium by the thermal decomposition of the tetra-chloride. However, the "hot wire" must

be maintained at a higher temperature than with the tetra-iodide since the decomposition of the tetra-chloride proceeds at higher temperatures. Tungsten wire cannot be used as the "hot wire" in the thermal decomposition of the tetra-chloride because tungsten forms a low melting point eutectic with zirconium at temperatures required for the tetra-chloride decomposition.¹¹

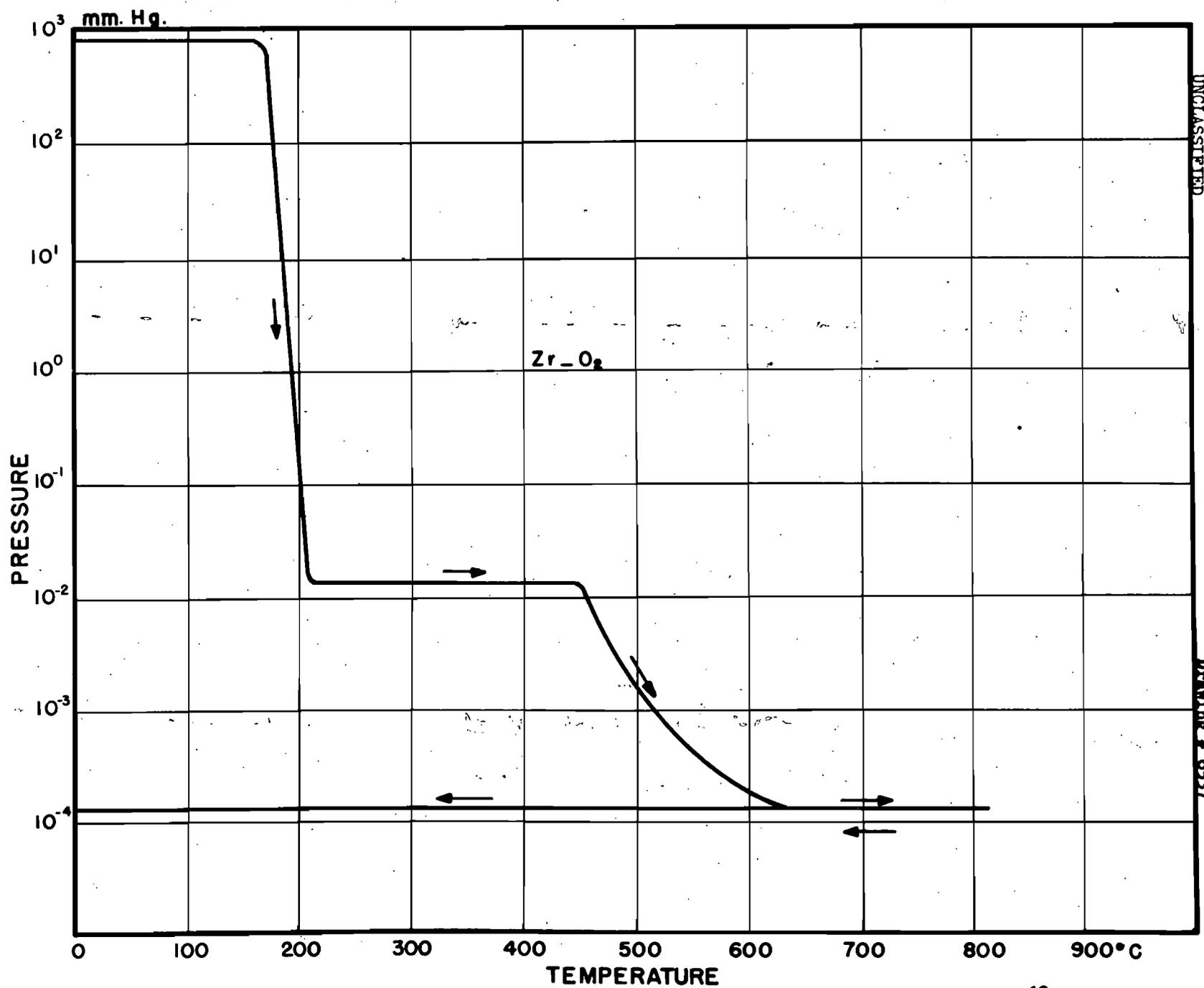
Reactivity with Carbon, Silicon, Boron, and Sulfur³²

Each of the elements carbon, silicon, boron, and sulfur reacts with zirconium at temperatures in the neighborhood of 1400° C. However, at low temperatures the reactions proceed slowly.

Finely powdered carbon in the form of graphite reacts readily with zirconium at high temperatures. However, molten zirconium is reported not to react with massive graphite but is known to wet graphite very well.³

Reactivity with Ammonia³²

Zirconium is quite stable to ammonia at moderate temperatures but at higher temperature (1000° C.), Zr_3N_2 is formed.



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Drawing # 6537

FIG.10 ABSORPTION OF OXYGEN BY ZIRCONIUM (HUKAGAWA & NAMBO)⁴²

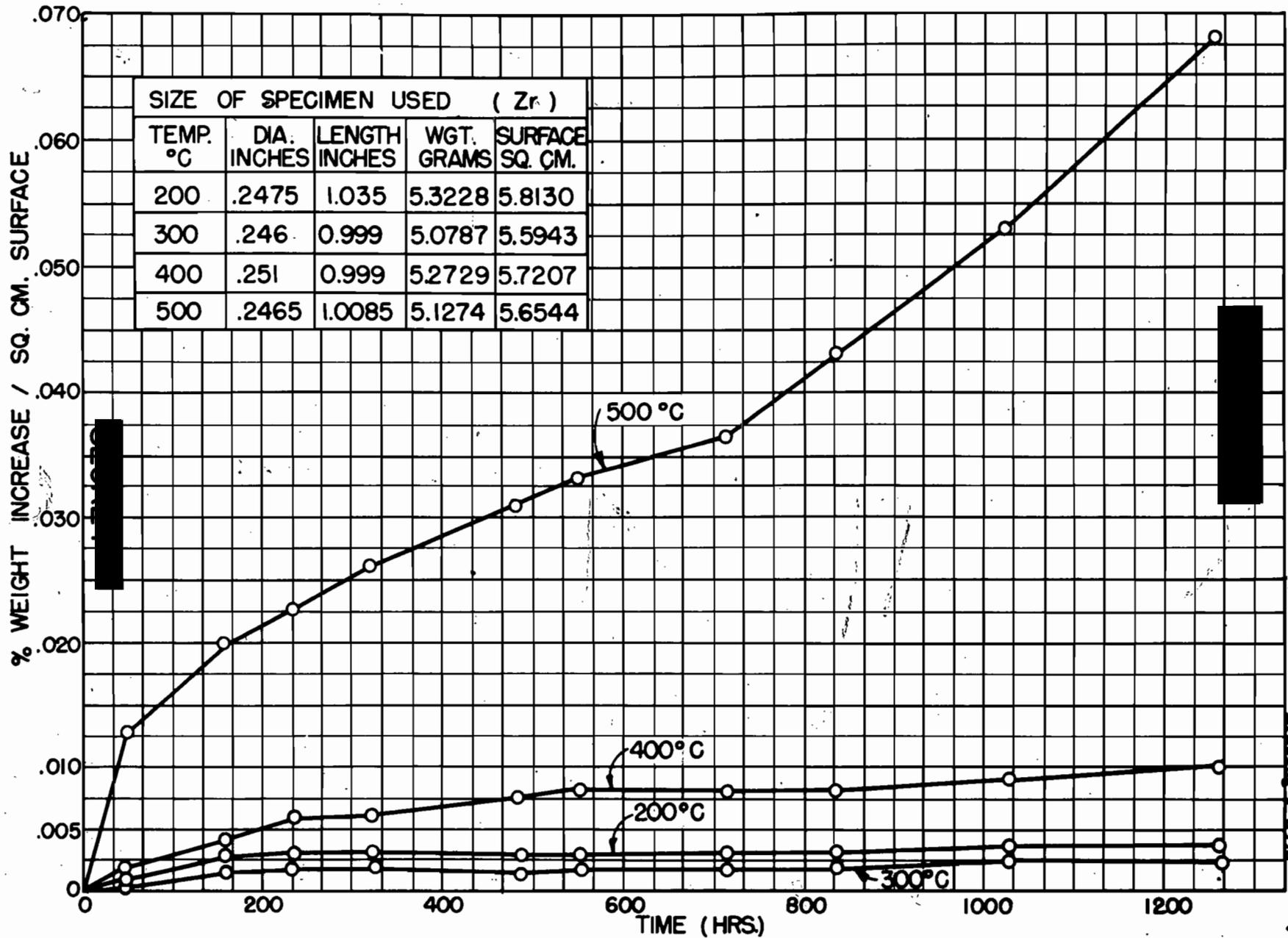


FIG. 11
GAIN IN WEIGHT OF ZIRCONIUM ON HEATING IN AIR (FOOTE CRYSTAL BAR)⁵²

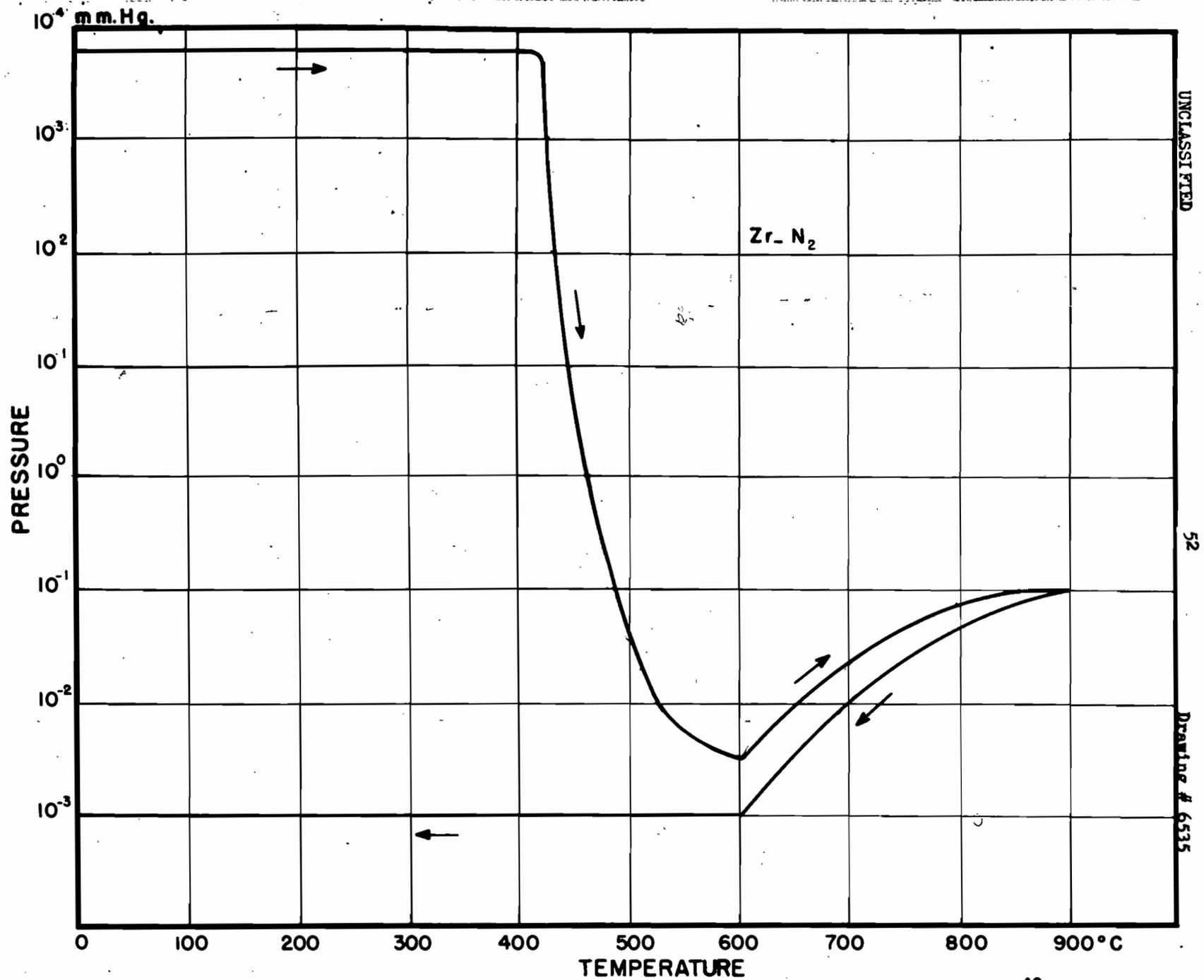


FIG.12 ABSORPTION OF NITROGEN BY ZIRCONIUM (HUKAGAWA & NAMBO)⁴²

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Drawing # 6535

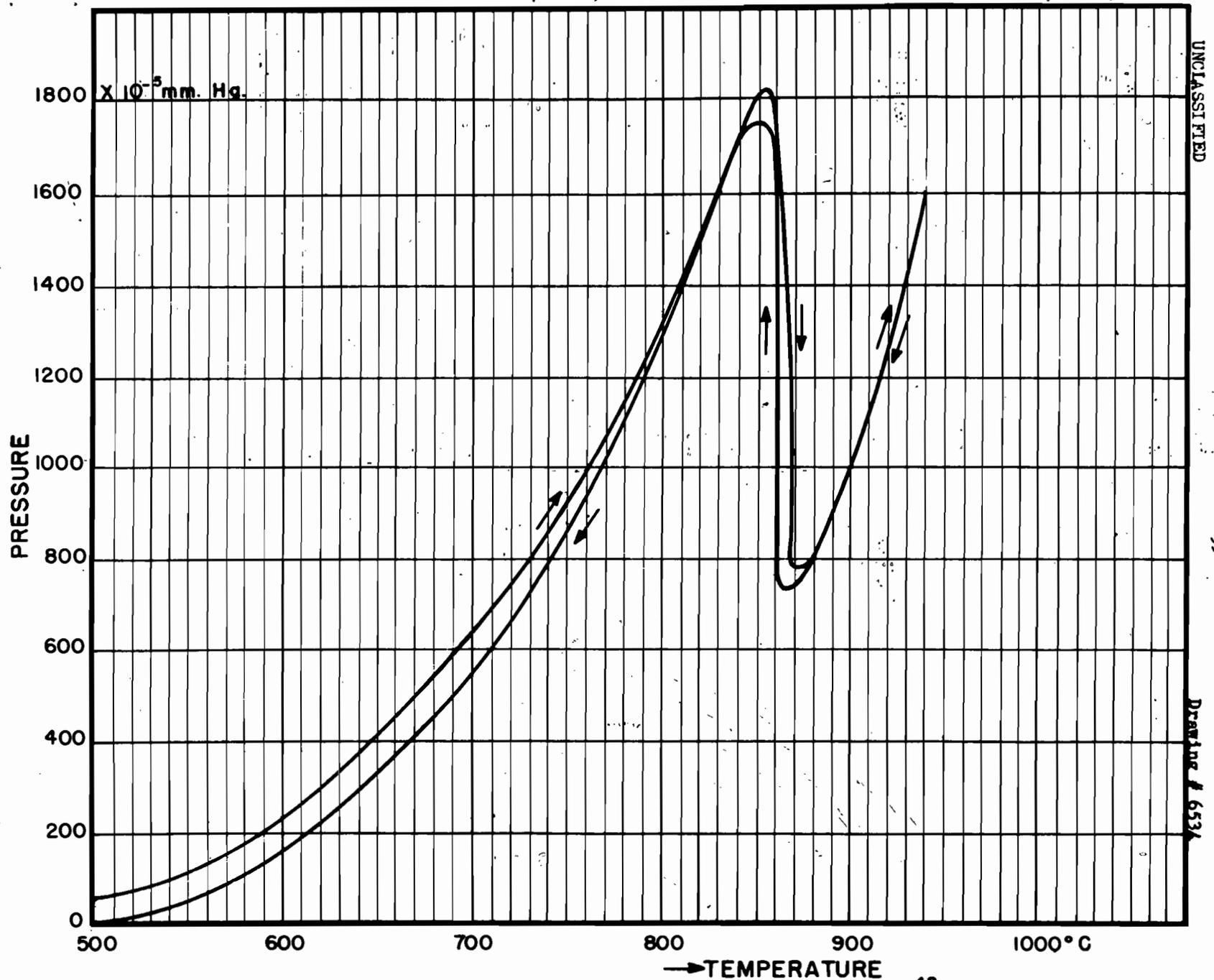


FIG.13 ABSORPTION OF HYDROGEN BY ZIRCONIUM (J.D. FAST)⁴²

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Drawing # 6531

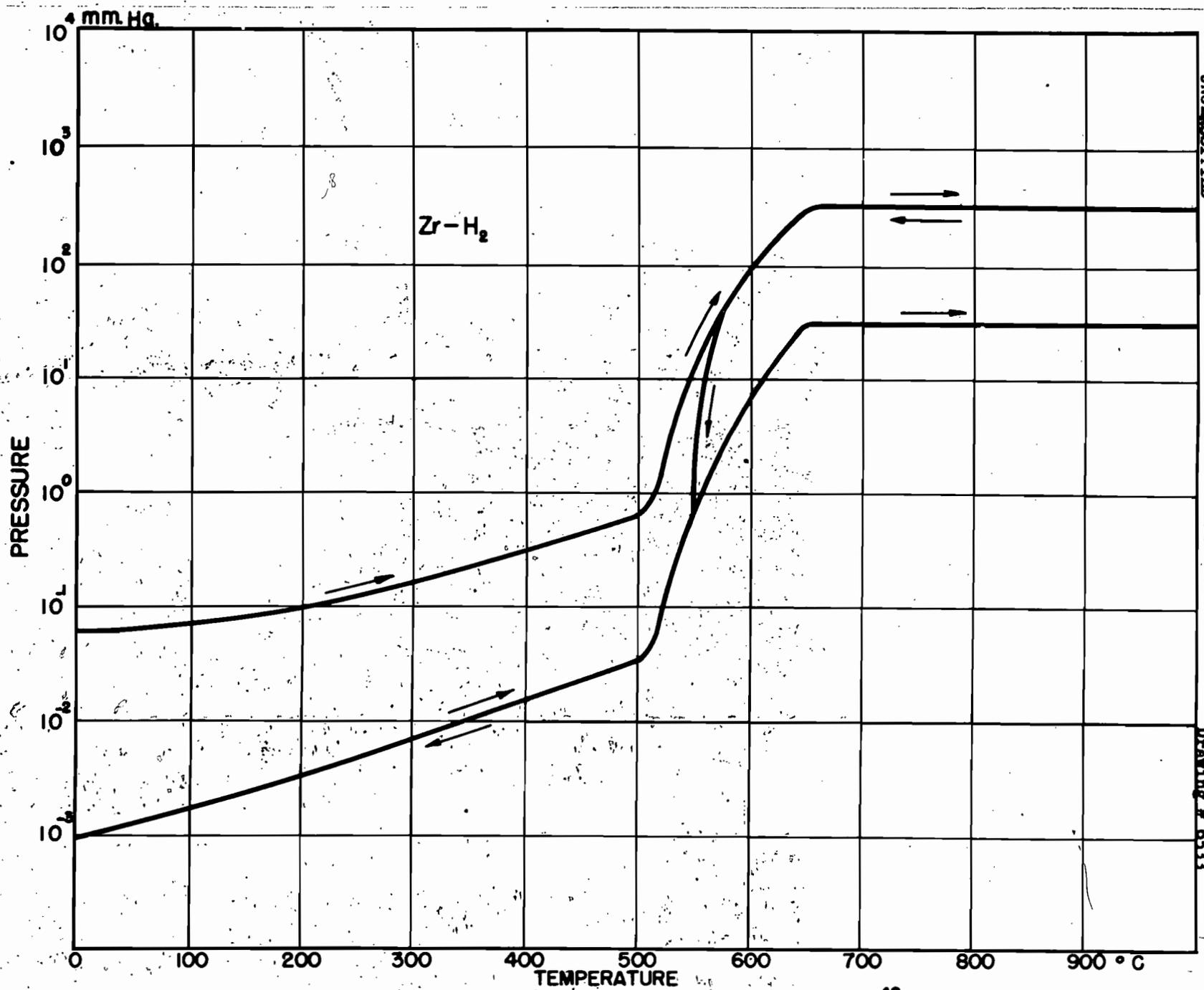


FIG.14 ABSORPTION OF HYDROGEN BY ZIRCONIUM (HUKAGAWA & NAMBO)⁴²

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Drawing # 6533

CHAPTER X

THE CORROSION RESISTANCE OF ZIRCONIUM

Zirconium has been observed to have high corrosion resistance to many aqueous media. It is, in general, even more resistant to acid corrosion than the metal titanium but not quite as good as tantalum which is used widely in the chemical industry because of its good acid corrosion resistance. Zirconium, however, has superior alkali resistance to tantalum. Uhlig states that zirconium is resistant to strong alkalies and molten caustics.⁵⁴

Acids and Bases

Specific data concerning the corrosion of zirconium in various acids and bases are given in the two following tables compiled from tests at the Foote Mineral Company on iodide deposited zirconium:

Table I⁵⁴

The Effect of Various Common Corrosive Agents on Ductile Zirconium at Room Temperature

Size of specimen -- 6.2 x 1.3 x 0.13 mm (2.5 x 0.5 x 0.005 in.).
Surface preparation - degreased.

Agent	Concentration	Time, days	Corrosion rate, ipy
HF	All dilutions	---	Rapid attack
H ₂ SiF ₆	Conc.	---	Rapid attack
AgNO ₃	0.8%	3	No attack*
H ₂ SO ₄	10%	14	0.0002
HCl	Conc.	14	0.0001
HCl	5%	14	No attack*
HNO ₃	Conc.	14	0.00001
HNO ₃	10%	14	0.00001
H ₃ PO ₄	Conc.	14	0.00004
H ₃ PO ₄	10%	14	0.00002
Citric acid	10%	14	No attack*
Oxalic acid	10%	14	No attack*
NaOH	10%	14	No attack*
KOH	10%	14	0.00002
NH ₄ OH	28%	14	0.00003
NaF	10%	14	0.0003
I ₂ in KI	0.1%	14	No attack*
Atmosphere	---	Years	No attack*

* No attack = loss less than 0.1 mg.

* Research Laboratory, Foote Mineral Co., Philadelphia, Pa.

Table II⁵⁴The Effect of Various Common Corrosive Agents on Ductile Zirconium at 100° C.

Size of specimen - 6.2 x 1.3 x 0.13 mm (2.5 x 0.5 x 0.005 in.).
Surface preparation - degreased.

Agent	Concentration	Time, days	Corrosion rate, ipy
H ₂ SO ₄	10%	14	0.0007
HCl	Conc.	14	0.0002
HCl	5%	14	No attack*
HNO ₃	Conc.	14	0.00005
HNO ₃	10%	14	0.00003
H ₃ PO ₄	10%	14	0.00005
Citric acid	10%	14	0.00002
Oxalic acid	10%	14	0.00004
NaOH	10%	14	0.00002
NaOH	50%	4	0.00017
KOH	10%	14	No attack*
NH ₄ OH	28%	14	Gained weight
HgCl ₂	Sat. soln.	14	No attack*
NaCl	20%	5	Slight tarnish

* No attack = loss less than 0.1 mg.

* Research Laboratory, Foote Mineral Co., Philadelphia, Pa.

Discrepancies in the results of isolated corrosion studies have been noted by various investigators and these have been attributed to the presence of very small amounts of impurities. For example, early reports indicate that zirconium is readily attacked by hydrochloric and dilute sulfuric acid but other more recent tests show differently. This can be explained by the presence of aluminum and other impurities. Another example is shown by comparing some early work at the Battelle Memorial Institute with some more recent work at the Foote Mineral Company. Battelle reported zirconium as quite resistant to attack by aqua regia. Foote, however, found that the metal was severely attacked even at room temperatures and that boiling aqua regia completely dissolved a thin strip in a few hours. Both samples were reported as the iodide deposited zirconium but there must be some difference in the impurities present which would have an affect on the corrosion resistance of the protective film.³²

The importance of impurities in the corrosion attack of water at elevated temperatures is strikingly shown in a later part of this chapter which is concerned specifically with water corrosion.

Resume of Acid and Base Corrosion

Reviewing tables I and II and the literature, one observes that zirconium resists nitric acid in all concentrations, even at 100° C., and even the oxidizing solutions, concentrated hydrochloric acid up to 100° C., hot 20% sulfuric acid, chlorine gas either dry or wet, hot 10% and 50% sodium hydroxide, fused sodium hydroxide, 20% sodium chloride solution at 100° C., acetic and oxalic acids, hydrogen sulfide gas, and cold dilute silver nitrate.²

Potassium hydroxide only slightly attacks zirconium. Zirconium is attacked more by concentrated sulfuric acid at 100° C., and also by ferric chloride, 75% phosphoric acid, nascent chloride, bromine, fluorine in water, and hydrofluor-silicic acid. Zirconium dissolves rapidly in hydrofluoric acid.

Alkalies

The corrosion resistance of zirconium to alkalies is definitely superior to that of both tantalum and titanium as well as that of 18-8 stainless.³² It is also resistant to molten caustic as well as strong alkalies.⁵⁴

Tests at the Argonne National Laboratory have shown that zirconium holds up well in hot (600° C.) NaK.⁷

Water Corrosion Tests

Various corrosion tests both static and dynamic have been run on zirconium in moderately high temperature water under high pressure.

A 500 hour dynamic erosion-corrosion test run by the Detroit Edison Company gave the following comparative results:⁵⁵

Table III

Summary of Detroit Edison Erosion-Corrosion Test

	Avg. Water Temp Deg F	Avg. Pressure Differential, psi	Avg. pH	Average Conductivity Micromhos	Weight Loss, grams
Carbon steel	401.3	300	7.3	0.59	0.5610
18 chromium - 8 nickel					0.0062
Zirconium*					0.0003
Beryllium					0.4713
Aluminum ^o					2.1211
Columbium					0.04+

*Slotted half lost 0.0007, plain half gained 0.0004.

^oRemoved after 65 hours test.

+Gained instead of lost.

Results of 163 Hour Dynamic Corrosion Test at ORNL

A photograph of the specimens used in the Detroit Edison test is included as Figure 15 at the end of this chapter.

A dynamic corrosion test at ORNL operated for 163 hours and with water at a temperature of 250° C., and 1250 psi and moving at a rate of approximately 43 fps (based on 1 gpm flow of water through a 0.094 inch hold for the zirconium specimen only) gave the following results:⁷

Table IV

Material	Weight (Initial) grams	Weight (Final) grams	% Weight Gain
Foote Mineral Co. Zr	8.9000	8.9046	0.052
Bureau of Mines Zr.	11.1141	11.1309	0.151
Fansteel Columbium	4.5591	4.6041	0.987*

***NOTE:** The ratio of surface area to volume for the columbium sample was considerably higher than for the two zirconium specimens and hence a comparison of corrosion rates of zirconium and columbium based upon per cent weight gained is meaningless.

One of the first recorded elevated temperature high pressure water tests in an autoclave or pressure bomb is reported in MIT-1001.⁶ Reference is made there to iodide deposited (Foote Mineral Company) zirconium which has been tested 1613 hours in distilled water at 250° C. A fairly constant weight was maintained indicating no corrosion. A magnesium reduced (Bureau of Mines) zirconium specimen also tested for corrosion under identical conditions showed an increasing weight gain with time. The Bureau of Mines zirconium specimen in 213 hours gained three to four times the weight gained by the Foote zirconium specimen in 1613 hours and also had not reached a constant weight as had the Foote zirconium specimen.

The graph in Figure 16 at the end of this chapter shows the comparison of the corrosion resistance of Foote and Bureau zirconium showing the constant weight, or zero weight gain per unit of time achieved by the Foote zirconium. ORNL tests run in 315° C., distilled H₂O in autoclaves graphically illustrate the comparative corrosion resistance of iodide deposited Foote zirconium and magnesium reduced (Bureau of Mines) zirconium. Here again the increasing corrosion rate of the magnesium reduced (and impure) zirconium is shown as is reported in MIT-1001.

Three additional and simultaneously run tests at ORNL on iodide deposited zirconium made in air saturated demineralized water at 315° C. (600° F.) for 64 hours show that the rate of corrosion is negligible after the initial 16 hours period. The graph, figure 17, further substantiates the MIT tests, and previous ORNL tests, figure 16.

The corrosion data of nine zirconium specimens with various histories for each group of three appears in the table below:⁹

TABLE V
Corrosion Data of Nine Zirconium Specimens

Sample No.	Surface Area cm ²	Weight gain per surface area gm/m ²				
		24 hrs.	48 hrs.	111 hrs.	251 hrs.	
Foote Mineral Company Crystal Bar Zirconium	1	1.0447	1.436	1.532	1.436	2.585
	2	1.1199	1.429	2.054	1.518	2.679
	3	1.2479	1.683	1.923	2.003	2.885
Bureau of Mines Zirconium	1	.966	7.143	11.387	19.772	36.128
	2	1.247	6.175	8.821	17.322	32.879
	3	1.398	7.296	10.515	17.668	32.690
Foote Mineral Co. Crystal bar melted in graphite crucible 10-15 minutes between 1830-60°C.* Graphite machined off and sample taken from center.	1	.907	43.109	97.133	261.521	884.344
	2	.985	48.731	106.802	279.695	883.046
	3	1.366	65.081	145.461	380.600	1027.598

A comparison of the corrosion resistance of zirconium, beryllium, Carpenter #20 stainless steel is given in the table VI at the end of this chapter.

Although beryllium appears poor in comparison to zirconium, Carpenter Stainless Steel #20, and the GT-45 alloy, and has in some tests practically disintegrated at 300°C. in 24 hours (see ORNL-48-8-57, p.4), the effect of the presence of gaseous and other impurities in beryllium upon corrosion may be as compelling a factor as in zirconium corrosion. As no appreciable quantity of truly gas-free and ductile beryllium has ever been produced, such a test has obviously been impossible to substantiate this belief. The effect of electrolytic corrosion and pH value of the beryllium corrosion testing medium is also of prime importance for investigation.

This section has included corrosion data on three widely considered coolants for thermal reactors, water and the liquid metal, NaK as well as corrosion data obtained from other common corroding agents. Information on the third important reactor coolant, the gases, is given in the section entitled "Chemical Reactivity of Zirconium".

Table VI

Comparison of Corrosion Test Results for Zirconium,
Beryllium, Carpenter #20, Stainless Steel* & GT-45 Alloy Steel**

Conditions: Samples inserted into 50 ml air saturated demineralized water in 100 ml. autoclave and held at 315° C.

<u>Material</u>	<u>Initial weight Grams</u>	<u>Final weight Grams</u>	<u>Area Cm²</u>	<u>Gain Cm/Cm²</u>	<u>Total Time Hours</u>	<u>pH</u>	<u>Remarks</u>
Zr	1.8062	1.8073	20	0.6	64	6.16	Lost original lustre but smooth. Had few white streaks that do not wipe off.
Be	3.7044	3.7070	16	1.62	57 ~ 6.2		Sample had bluish cast and white spots
Carp.#20	15.0472	15.0484	16	0.75	57 ~ 6.2		Sample had very light orange rusty color on surface
GT-45	19.1677	19.1677	20	0.	126½ ~ 6.2		Sample tarnished a little.

* Typical chemical analysis: 29.0% Ni, 20% Cr, 2.0% mo. min., 3% Cu. min., 0.07% C max., 0.75% Mn, and 1.00% Si.

** ARM Co's. gas turbine alloy with typical chemical analysis of 14.0% Ni, 17.25% Cr, 2.87% Mo, 3.14% Cu, 0.076% C, 1.45% Mn, 0.49% Si, 0.026% P, 0.009% S, 0.22% Ti and 0.36% Co.



Zirconium
(Focote Mineral Co.)



Columbium
(Fansteel Corp.)



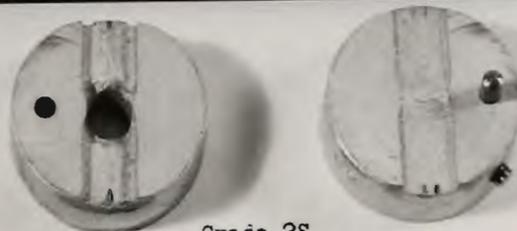
Low
Carbon Steel
(Control Sample)



Type #347
Stainless Steel
(18% Cr-8% Ni
Cb stabilized)



Beryllium



Grade 2S
Aluminum

A COMPARISON OF THE CORROSION AND CORROSION RATES FOR TWO KINDS OF ZIRCONIUM IN DEMINERALIZED (AND PROBABLY AIR SATURATED) WATER AT 315°C⁵⁵

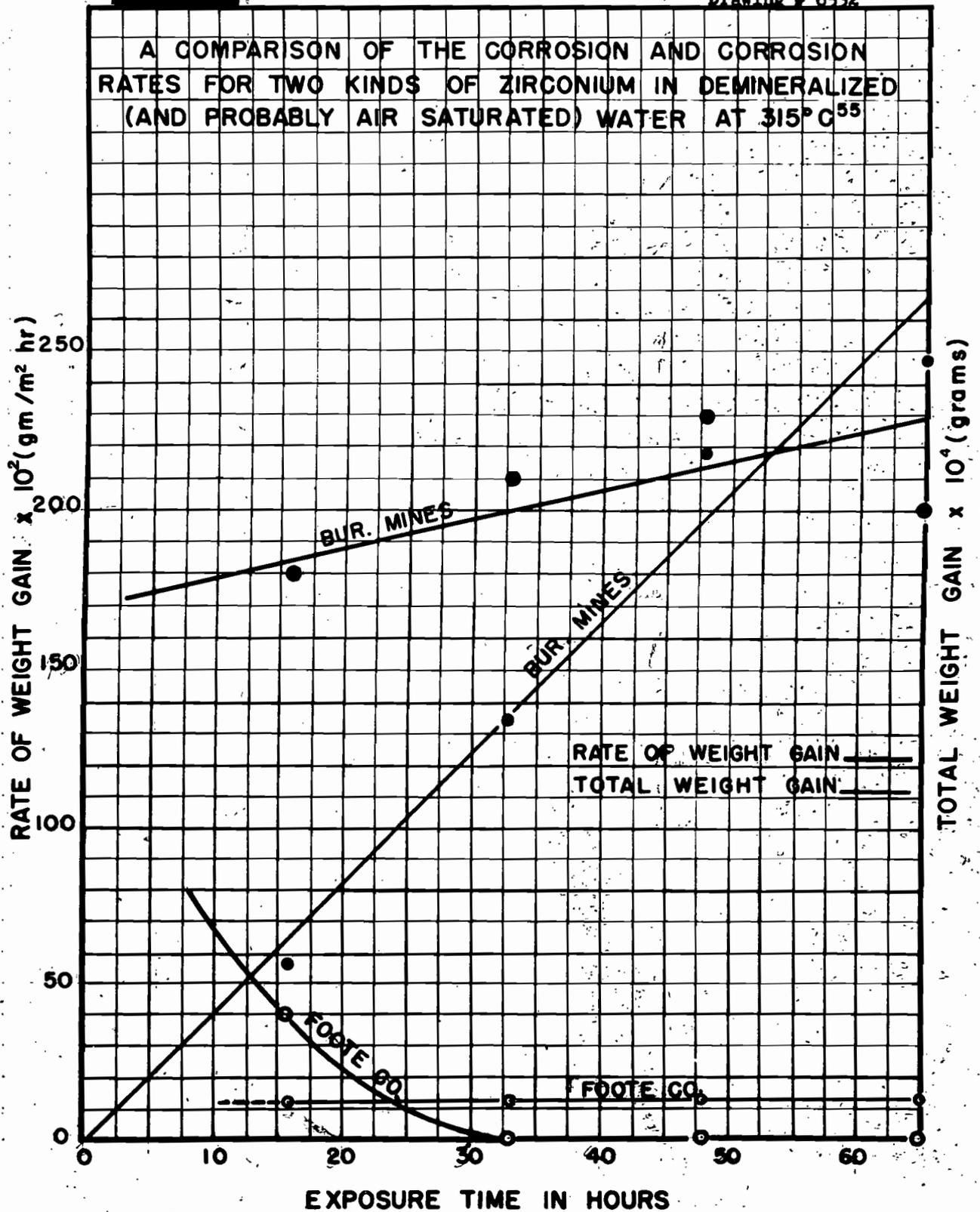


FIG. 16

NOTE 1: THE SLOPE OF THE CURVE BETWEEN 0 & 16 HRS. IS NOT KNOWN.
 THE VALUE OF WEIGHT GAINED IN 16 HRS. MAY BE THE SAME FOR
 A MUCH SHORTER PERIOD OF TIME.

NOTE 2: ALL SAMPLES HAD APPROXIMATELY THE SAME AREA OF EXPOSURE (20cm²)

NOTE 3: 50 ml H₂O IN 100 ml CAPACITY AUTOCLAVE.

TABLE OF WEIGHT g SAMPLE AT GIVEN TIME			
TIME	EXP. 17	EXP. 18	EXP. 19
0 HRS.	1.6947g	1.7156 g	1.8062 g
16	1.6970	1.7168	1.8075
32	1.6969	1.7167	1.8072
48	1.6971	1.7168	1.8072
64	1.6972	1.7169	1.8073

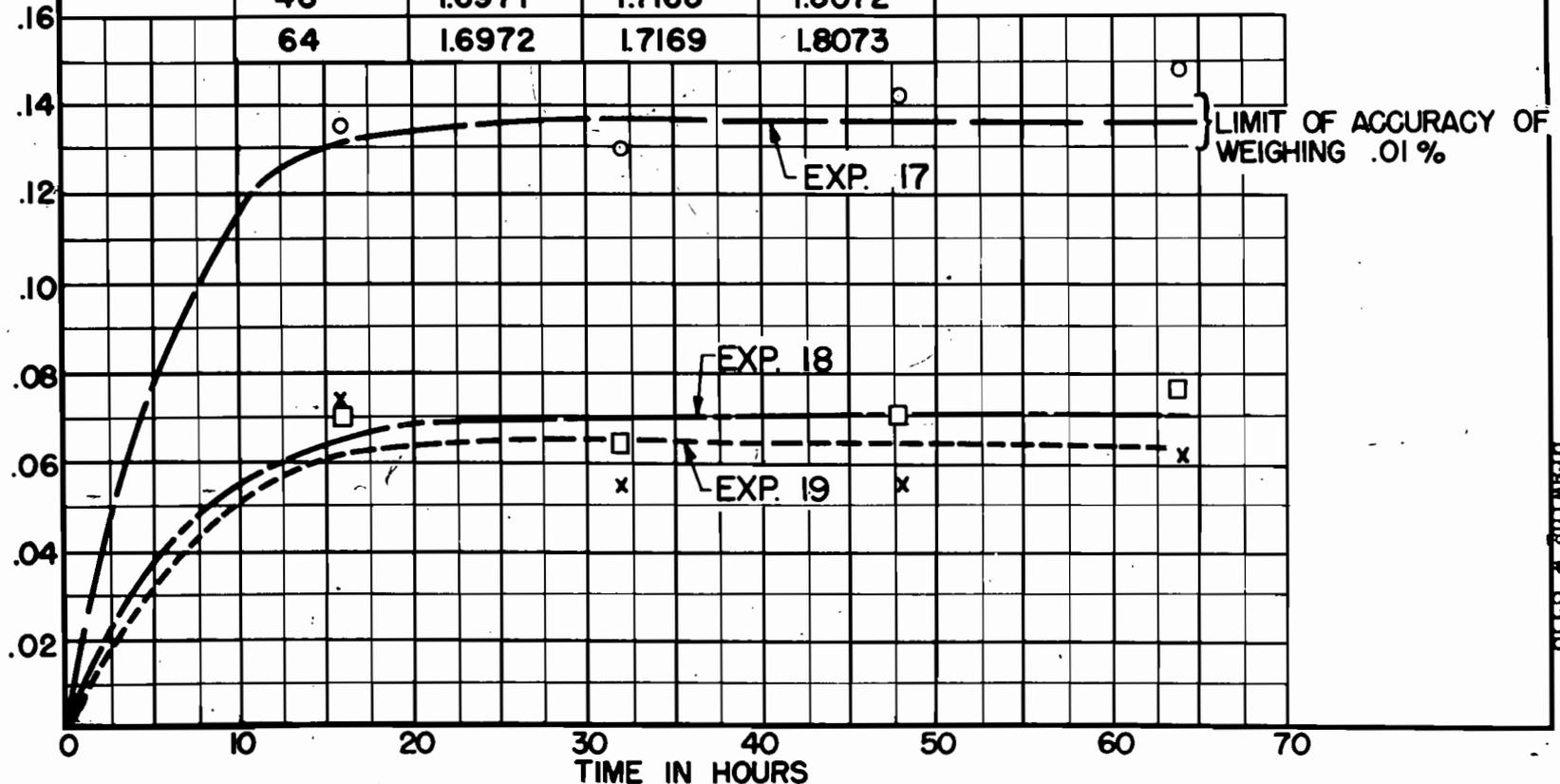


FIG.17 GRAPH SHOWING CORROSION OF THREE SPECIMENS OF FOOTE MINERAL (IODIDE DEPOSITED) ZIRCONIUM AT 315°C IN AIR SATURATED DEMINERALIZED WATER.

Drawing # 6530

Chapter XI

THE SEPARATION OF HAFNIUM FROM ZIRCONIUM

Both zirconium and hafnium occur in the fourth group in the periodic table, have the same valence, possess nearly the same ionic diameters, and are very similar in chemical affinity to other elements or compounds which are commonly used for separating various metallic elements. In fact the degree of resemblance of hafnium to zirconium far exceeds that of niobium (columbium) to tantalum or of molybdenum to tungsten.⁶⁸

These factors make separation of the two extremely difficult. Nowhere in the periodic table are there greater resemblances between the chemical similarity of elements than in the two horizontal rows which include zirconium and hafnium.

Several physical and chemical differences no matter how slight have been studied by many investigators for the possible separation of hafnium from zirconium. These differences are listed below:

1. Vapor pressure of the two metals and their salts.
2. Solubility of hafnium and zirconium salts leading to fractional crystallization.
3. Rate of fractional precipitation
4. Mass
5. Ionic diameters
6. Distribution ratios of metal chelates
7. Decomposition temperatures of some of the compounds.
8. Electrochemical potentials of the zirconyl and hafnium ions.

Separation by Vacuum Distillation

The speed of evaporation and vapor pressures for zirconium and hafnium differ appreciably. De Boer and Fast have determined the vapor pressure from the basic formula

$$\log p(\text{mm Hg}) = \frac{-A}{T} + B$$

to be

$$\log p = \frac{-30200}{T} + 9.46$$

for hafnium and

$$\log p = \frac{-13000}{T} + 0.77$$

for zirconium.²² C. Zevikker (Physica, Vol.8, 1928, p.241) attributes this abnormal behavior to the oxide layer on zirconium which holds back the vapor pressure. Zirconium is much better protected by the oxide layer than hafnium against the action of iodine.²²

This difference in the vapor pressure of various salts of zirconium and hafnium makes it practical to separate the two by vacuum distillation. R. A. Stauffer of the National Research Corporation suggests centrifugal fractional distillation of ammonium zirconium fluoride. Equipment for separating solutions whose boiling points differ by only 2-3° C. by centrifugal vacuum fractional distillation has been developed and good separation is reported.⁷

Van Arkel and De Boer found that by heating a mixture of $ZrCl_4$ and PCl_5 , a compound of $2ZrCl_4 \cdot PCl_5$ was formed which could be distilled quite readily. The distillation temperature they observed was 416° C. On cooling it crystallized to a hard compact mass.⁵⁹

Further experimentation of theirs revealed that a compound between $ZrCl_4$ and $POCl_3$ corresponding to the formula $2ZrCl_4 \cdot POCl_3$ had even a lower boiling point, viz. 363 or 364° C. and on cooling congealed to a glassy viscous mass. Zirconium fully free of hafnium, silicon, iron, titanium and thorium can be successfully produced through the distillation of this compound. They observed that two distillations removed the iron and another the hafnium. All fractionations revealed that hafnium distilled off as a volatile compound before zirconium.⁵⁹

Separation by Fractional Crystallization of Salts by Difference in Solubility

The separation of not more than two closely related elements is fairly rapid even where the differences in solubilities are not great. For fractional crystallization in aqueous solution, the salt used must yield an anion containing zirconium, because it has been found that salts containing a cation bearing this element are too easily hydrolyzed.³⁹

One method of separation of hafnium from zirconium by fractional crystallization is by the preparation of potassium hexafluoride of the mixture of the two metals. Potassium hafnium hexafluoride, K_2HfF_6 is 1.5 times as soluble as K_2ZrF_6 and hafnium can be collected from the soluble end of the series leaving zirconium at the less soluble end.³⁹ Sulfuric acid can be added to give the sulfates which are ignited and K_2SO_4 is extracted with hot water. Zirconium oxide is finally converted to the oxychloride and recrystallized from hydrochloric acid.

Ammonium hexafluorides can also be used but the ratio of their solubilities is not as favorable. However, they are more soluble than the potassium compounds and consequently require less volume of solution.

Zirconium citrate, contrary to what might be expected from the literature, was found by D. H. Drophy and W. P. Davey of the General Electric Company to be relatively insoluble in pure water, while hafnium citrate is quite soluble.*

* W. M. Latimer and J. H. Hildebrand⁸² also offer an exception to most literature agreement concerning the solubility of the zirconium citrate. They state that there exists a great difference in the solubilities of the citrate compounds of zirconium and hafnium.

Zirconium citrate is also soluble in ammonium hydroxide or in an excess of citric acid. By adding a limited amount of an aqueous solution of citric acid to a solution of crude zirconium nitrate, a precipitate of pure zirconium citrate is obtained which they identified by its X-ray absorption spectrum. The conditions of the separation are, however, such that although the precipitate is free from hafnium, the soluble portions also contains some zirconium.⁶⁰

In addition to the above differences in the solubility of zirconium and hafnium compounds, hafnium oxalate is known to be soluble in excess oxalic acid and its oxychloride is less soluble than that of zirconium.³⁹

Separation by Fractional Precipitation

Perhaps the only separation method tried thus far on a nearly commercial and economically practical basis has been the fractional phosphate precipitation method. Work has been done on this at the Foote Mineral Company since the winter of 1947-48. With yields in the neighborhood of 70-80%, the following results were reported from a series of precipitations:⁷²

Table I

Results of Fractional Phosphate Precipitations at Foote Mineral Co.

<u>Sample No.</u>	<u>Hf x 100/Zr</u>	<u>Sample No.</u>	<u>Hf x 100/Zr</u>
A	2.34	12-0	0.81
B	2.25	12-A	0.73
C	2.17	12-B	0.59
D	2.07	12-C	0.51
E	1.95	12-D	0.49
F	1.72	12-E	0.45
G	1.41	12-F	0.36
		12-G	0.34
		12-H	0.33
		12-I	0.34
		12-L	0.33
		12-L ₂	0.30
		12-M	0.27
		12-N	0.23
		12-O	0.20

Progress resulting from improved techniques has since netted separation under 0.1% ratio and a pilot plant is now being set up at the Foote Mineral Co. to produce the oxide with this percentage ratio of Hf/Zr. It is estimated that it will be early in 1949 before the ductile zirconium metal is produced with Hf/Zr ratio of less than 0.10%.

The preparation of the eight gram sample by Dr. Edward Wickers group at the U. S. Bureau of Standards for cross-section determination at ORNL gave the lowest recorded hafnium and zirconium. Fifteen or more precipitations with a

low yield of about 3% finally gave a sample with 200 ppm of hafnium. It was with this sample that H. Pomerance of ORNL established the presently accepted value of 0.4* barns for the thermal neutron absorption cross-section.

Another fractional precipitation method was reported by Prandtl (Z. anorg. allgem. Chem., Vol. 208, 1932, p. 420ff.) which depends upon the fractional precipitation of the ferrocyanides of zirconium and hafnium from a solution containing oxalate and sulfate ions, the purpose of which is to form complex ions of different stability. The hafnium is enriched in the precipitates. Prandtl's early work described a procedure for yielding a product containing 90% hafnium oxide and 10% zirconium oxide starting with a material containing about 1% hafnium oxide.⁶²

Schumb and Pittman⁶² in further developing and checking Prandtl's process also improved the chemical analysis method of Claassen (Z. anal. Chem. Vol. 117, 1939, p. 252ff.) for hafnium and zirconium determination which is reported in the chapter of this work entitled "Methods of Analysis for Hafnium". Schumb and Pittman also found ambiguity to the description by Prandtl of his own work but eventually were able to take a mixture containing 12% Hafnium oxide and 88% zirconium oxide and convert it in four operations by the ferrocyanide method to yield an oxide mixture containing 80% hafnium oxide and 20% zirconium oxide.

Separation by Electromagnetic Methods

Zirconium and hafnium could feasibly be separated on an isotope separation scale such as is used in the electro-magnetic separation of the uranium isotopes from the chloride. The mass difference of zirconium and hafnium, atomic weights 91.22 and 178.6 respectively, is much more favorable than in the case of the uranium isotopes, U²³⁵ and U²³⁸.

Such an isotope separation of hafnium and zirconium is reported by Mr. Boyd Weaver at Y-12 in Oak Ridge to be on their schedule early in 1949 mainly for the purpose of obtaining pure zirconium for further cross-section determinations at ORNL and separating each of the hafnium isotopes for similar nuclear measurements.

Here again, as in the analysis of hafnium in zirconium by the mass spectrometer, (see chapter XII) the contamination of Zr⁹⁰ by the doubly charged Hf¹⁸⁰ ions is a problem. Although the isotope separating calutrons are but large scale duplicates of the mass spectrometers in principle, the problems of the chemical preparation of the chloride and the difference in vapor pressures of zirconium and hafnium chlorides are actually not problems at all but factors aiding in the separation of the two metals.

* The value of 0.27 given in C. E. Winters memorandum on the Minutes of the First Meeting of the Zirconium Committee of ORNL, dated August 10, 1948. (ORNL - Central Files 48-3-360) has since been considered doubtful and H. Pomerance has recently calculated a value of 0.32 barns based on the summation of measured cross-sections for each of the 5 isotopes and taking into account the abundance of each of the isotopes.

The chlorination of the Zr-Hf alloy for the preparation of the raw materials for the calutrons and mass spectrometers results in a partial separation of hafnium from zirconium which of course, changes the original ratio of hafnium to zirconium in the raw materials unless the chlorination procedure is precisely controlled under certain equilibrium conditions.

It is in the "source" (the ionization and ion beam focusing chamber) of the mass spectrometer that the ionization of the vaporized chloride occurs. This process is affected by the difference in the rate of vaporization and the difference in the temperatures of vaporization of the zirconium and hafnium chlorides and a true relationship of the Hf/Zr ratio is not obtained.

Separation by Thermal Diffusion

The separation of uranium isotopes by thermal diffusion of the liquid uranium hexafluoride was achieved during the war. Although such a method was found inefficient for separating uranium isotopes, it seemed advisable to undertake such a study for hafnium and zirconium in order to explore all possible means of separating the two. J. I. Hoover⁹⁴ of the Naval Research Laboratory (where a uranium hexafluoride thermal diffusion pilot plant was operated early in the war) was assigned the problem to determine the feasibility of such a method.

The gaseous or liquid thermal diffusion separation is possible because of the fact that when a temperature gradient exists in a gas or liquid, the heavier molecules concentrate at the colder end and the lighter ones at the hotter end. Thermal diffusion processes also take advantage of the fact that thermal convection currents arise in gases and liquids when the molecules are at different temperatures. The thermal convection currents set up counter current flow and thermal diffusion causes the preferential flow of the heavy molecular outward across the interface between the two currents.

Preliminary results at the Naval Research Laboratory indicated a large change in the WF_6 and UF_6 ratio by liquid thermal diffusion of solutions of UF_6 and WF_6 . In one 95 hour run the ratio of WF_6/UF_6 at the top of a thermal diffusion column changed from 0.05 to 19.⁽⁹⁴⁾ Such promising results stimulated the investigation of hafnium separation from zirconium by liquid thermal diffusion.

Three organic compounds was considered: zirconyl stearate, zirconium tetra isoamylate, and zirconium tetra 2-ethylhexylate. The last of these three was chosen because it had the best over-all physical and chemical properties.

The results of several runs using zirconium tetra 2-ethylhexylate containing $\sim 97\%$ $Zr(OC_8H_{17})_4$ and $\sim 3\%$ $Hf(OC_8H_{17})_4$ are given below:

Table 94

Results of Thermal Diffusion Experiments of Hf-Zr
Separation at USNR Laboratory

Run #	Temperature Gradient c/cm	Length of run (continuous) hours	Hf/Zr		Remarks
			Bottom	Top	
1	~ 5500	198	1		The temperature gradients were achieved by changing hot & cold wall temperatures and/or spacing
2	~ 2500	140	1		
3	~ 1450	140	1		
4	~ 3750	190	1		
5	~ 2240	95	1		

The expected change in ratio however, did not take place. J. I. Hoover relates that decomposition of the 2-ethylhexylate occurred in each case and that such a decomposition possibly explains such a lack of separation. Hoover further postulates that the products of decomposition were separated according to molecular weights but since there was no preferential decomposition of either the $\text{Hf}(\text{OC}_8\text{H}_{17})_4$ or $\text{Zr}(\text{OC}_8\text{H}_{12})_4$ in the original salt, then each group of molecules of equal molecular weight would contain the same hafnium to zirconium ratio.

Hoover concludes that regardless of the explanation for the lack of separation, the results indicate that the use of the zirconium tetra 2-ethylhexylate compound is not applicable to such a separation but that a more ideal compound of zirconium might be used successfully, however.

(The complete communication from Mr. Hoover is given in the Appendix. Further details may be found there.)

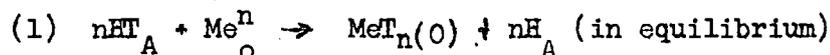
Separation by the Ion Exchange Method

Even though hafnium has more neutrons, protons, and electrons than zirconium, it lies at the bottom of the Lanthanide contraction and has an ionic diameter smaller than that of zirconium. Elements whose valences are identical can be separated by ion exchange methods by virtue of differences in ionic diameters and the ion exchange rates.

Since the ionic diameters of zirconium and hafnium are within 1% of each other, such a method, although practical, would be most difficult and even the preparation of a 10 mg. sample of pure zirconium by ion exchange would be no simple task.

Separation by Preferential Extraction of Metal Chelates^{*,7,66,67,69,93}

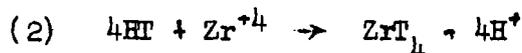
The separation of zirconium from hafnium by the preferential extraction of zirconium from an acidic aqueous solution into an organic solution containing TTA has generally been referred to as the TTA method. TTA is the abbreviation used for the solid compound, thenoyltrifluoroacetone.** The reaction of this compound with various metals is as follows:



where Me refers to a metal of valence n and HT refers to the acidic enol form of the TTA molecule, and the subscripts A and O refer to aqueous and organic phases. The mechanism of the reaction is a combination of hydrogen replacement and coordinate bonding.

The TTA method of separation is the basic chelating method used in the separation of the radioactive zirconium from the fission products of uranium fission. It involves the mixing of an aqueous solution of the metallic salts with an organic solution (such as benzene, toluene, or carbon tetrachloride) of the TTA compound. The chelating agent gradually complexes with the zirconium with resultant extraction of the zirconium chelate into the organic solution.

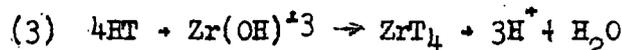
The reaction for zirconium in solutions of very high acidity is probably as follows:



but R. E. Connick and W. H. McVery⁶⁷ postulate the following for solutions as acidic as 2 molar perchloric acid:

1. $\text{Zr}(\text{OH})^{+3}$ is the predominating species (not Zr^{+4});
2. Extraction has a third power H^+ dependence; and
3. A fourth power TTA dependence.

Assuming these conditions, the simplest expression of the extraction would be



E. H. Huffman and L. J. Beaufait⁹³ found a similar TTA dependence for hafnium. Therefore the same extraction expression probably holds for hafnium because of its chemical similarity to zirconium.

* The author gratefully acknowledges the assistance of Mr. J. P. McBride of ORNL in preparing this section of Chapter XI.

** For preparation of the thenoyltrifluoroacetone compound, see Reid, J. C. and Calvin, M. I. MDDC-1405 (BC-75) dated August 13, 1947.

The equilibrium constant would then be represented by the formula

$$(4) K_{Zr} = \frac{(ZrTl_4)(H^+)^3}{(HT)^4[Zr(OH)^{+3}]} = D.R_{Zr} \frac{O(H^+)^3}{A(HT)^4}$$

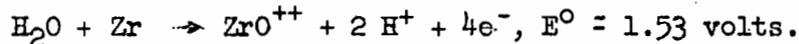
For the extraction of Zr from perchloric acid, Connick and McVey⁶⁷ calculate a K_{Zr} of 7.6×10^8 . A constant calculated for the extraction of hafnium according to the above expression (3) would have a value of 3.3×10^7 . Hence, a preferential extraction ratio of zirconium over hafnium of about 20:1 is to be expected at constant TTA concentration and constant acidity.

Separation by Electrochemical Means

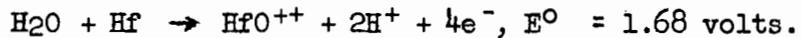
If a great enough difference in the oxidation potential of the zirconyl and hafnyl ions existed or if either of the two could be separated by electrolysis from a solution containing them, it would be possible to separate one from the other by controlled cathode potential.

W. M. Latimer in his text, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution", reports a difference in the oxidation potential for the zirconyl ion, ZrO^{++} , and the hafnyl ion, HfO^{++} , of about 0.15 volts.⁸³

Latimer gives the free energy of formation of the zirconyl ion, ZrO^{++} , to be -198,100 cal. and the oxidation potential as follows:



Although Latimer found no value in literature for the free energy of formation of the hafnyl ion, HfO^{++} , he assumed the free energy of hydration of the oxide the same as for ZrO_2 and also notes that HfO_2 is slightly more basic than ZrO_2 . By the assumption of the identity of the free energies of hydration between the zirconium and hafnium oxides, he calculates the free energy of formation of the hafnyl ion to be -212,100 cal. The oxidation potential (i.e. the Hf- HfO^{++} couple) of the hafnyl ion, HfO^{++} , follows:



This difference in oxidation potential (1.68-1.53 or 0.15 volts) between the hafnyl and zirconyl ions stimulated an investigation by J. C. Griess of ORNL to see if it was possible to develop an electrochemical method of separating hafnium from zirconium. He made polarographic studies and observed no intermediate valences for hafnium. In fact he found no polarographic waves for hafnium. Consequently, this element will not plate by electrolysis of aqueous solutions. He did observe that it was possible to get polarographic waves for zirconium from relatively simple salts of zirconium, viz. the chloride and the perchlorate, but he was not able to electroplate any appreciable amount of zirconium (see Chapter XV).⁷⁶

Latimer⁸³ and Laubengayer and Eaton⁸¹ also found that the quadrivalent zirconium unlike its neighbors in the periodic table cannot be reduced to a state of intermediate valence by electrolysis of solutions of zirconium. The latter two observed that the quadrivalent zirconium can be reduced under some conditions to the metal (see also Chapter XV on the plating of zirconium).

Laubengayer and Eaton also state that zirconium is more like tantalum than its neighbors, or the rare earths, or the elements titanium, vanadium, and columbium, all of which exhibit step-wise reductions.

Since attempts to electro-deposit either hafnium or zirconium in any appreciable amount have met with failure, it would seem impossible to separate either from the other by electrochemical methods.

Separation by the Decomposition Temperatures of Hafnium and Zirconium Compounds

At least one further means of separating hafnium from zirconium is known. It has been determined that hafnium sulfate remains stable to nearly 500° C. whereas zirconium sulfate starts to decompose at temperatures slightly in excess of 400° C. 39

Chapter XII

THE METHODS OF ANALYSIS FOR DETERMINING HAFNIUM IN ZIRCONIUM

At least four methods of analysis have been tried in determining the amount of hafnium present in zirconium either quantitatively or qualitatively. Naturally, the chemical method is the oldest and probably the most thoroughly explored. However, it has great limitations and is not practicable for use in the range of low hafnium content below a few percent. This chapter reviews the chemical method as well as other work done to date on the other three methods.

Chemical Method of Analysis

Although much effort has been expended towards the separation of hafnium from zirconium, the various methods of separation such as, for example, the triethylphosphate fractional precipitation method, do not offer a suitable means for quantitatively determining the hafnium content in zirconium. Apparently the method involving the determination of the ignited oxides is the most satisfactory chemical means for evaluating the hafnium content.^{61,62}

By determining the density of the oxide mixture, one is able to calculate the percentage of hafnium oxide present because the molecular volumes of the two oxides are very nearly the same. The formula used for calculation is as follows:⁶¹

$$\% \text{HfO}_2 = \frac{d(\text{mixt.}) - d(\text{ZrO}_2)}{d(\text{HfO}_2) - d(\text{ZrO}_2)} \times \frac{d(\text{HfO}_2)}{d(\text{mixt.})} \times 100$$

The determination of the density of the finely powdered oxide, however, is attended with a certain amount of difficulty due to the absorption of gases by the finely divided material, and the accuracy of the result is always open to question because of the uncertainty concerning the density of pure hafnium oxide. Schumb and Pittman⁶² therefore discarded the density determination method and adopted a procedure basically worked out by Z. Claassen (Anal. Chem. Vol. 117, 1939, p.252). This method depended on the fact that zirconium and hafnium form selenites $[\text{Zr, Hf}(\text{SeO}_3)_2]$ of constant and definite composition which can be converted quantitatively to the oxides. The percentage of HfO_2 is calculated as follows:

$$\% \text{HfO}_2 = \frac{374.86 \text{ wt. of oxides} - 0.35702 (\text{wt. of selenites})}{\text{wt. of oxides}}$$

This method is claimed by Schumb and Pittman to have an accuracy of within 0.5% but is good only for a hafnium content of at least 25%.

Larsen, et al⁶¹ compared the results of the two methods above, the former of which depends upon the exact knowledge of the density of pure hafnium oxide and found agreement within the limits of the accuracy of the methods excepting in the hafnium oxide rich region.

Mass Spectrometer Analysis⁷

The analysis of hafnium in zirconium using the revised Nier mass spectrometer has been attempted at Y-12 in Oak Ridge under the guidance of Roger Hibbs. Various difficulties have been encountered and thus far this method is considerably unperfected.

The difference in vapor pressures of zirconium and hafnium chloride (a fact that makes vacuum distillation of the two metals possible by distillation of their salts) causes HfCl_4 to vaporize at a lower temperature* and more rapidly than the other and although the ionization potentials of the two chlorides are nearly the same, such a difference in vapor pressures causes considerably error to be introduced into mass spectrometric analysis.

Also adding to the difficulties involved is the fact that the doubly charged Hf^{180} ion appears coincidentally with singly charged Zr^{90} ion in the receiver of the instrument and it is necessary to compare the isotopes of zirconium, Zr^{90} and Zr^{92} for example, to determine the contribution of the doubly charged Hf^{180} ion to the apparently high Zr^{90} ion peak or use another isotope of zirconium for comparison.

Obstacles have also arisen in the chemistry of sample preparation by chlorination. Here again, the difference in the vapor pressures of ZrCl_4 and HfCl_4 acts in effect as a separation factor between the two metals and a procedure must yet be determined which will not change the Hf/Zr ratio during preparation of the sample for analysis.

Spectrochemical Analysis

Spectrochemical analysis of the hafnium content in zirconium is possible by at least two methods, the optical emission type, involving either the high voltage spark or the low voltage arc, and the x-ray emission type. The X-ray emission spectrography has certain advantages over the optical in that a hafnium free zirconium is not important as the X-ray emission system involves only the inner electrons of hafnium.⁷ Thus a pure zirconium matrix is not necessary. Much of the work has been done with X-ray emission analysis but it is time consuming and the necessary apparatus is not always available.

C. Feldman of ORNL has developed a technique for hafnium determination which uses a 10% sulfuric acid solution with a porous cup electrode and spark excitation.⁶⁵ A porous cup electrode of graphite 1/4" dia. x 1 1/2" long with a 1/8" dia. hole drilled along its axis to within 1.3 mm of the end serves as the upper electrode. A 1/8" dia. solid graphite rod serves as the lower electrode. The liquid feeds through by wick action constantly renewing the surface-film of liquid as it is dispersed by the spark. By this method Hf/Zr ratios in the range, $(\text{Hf} \times 100)/\text{Zr} = 0.073-9.28$ by weight, can be determined without the aid of Hf-free zirconium preparations. If the concentration of hafnium in a hafnium preparation is known, its concentrations in the zirconium preparation can be determined. The intensity ratio, $\text{Hf II } 2641.406/\text{Zr II } 2761.911$, is measured and the Hf/Zr ratio read from a standard curve.⁶⁵

*See footnote to chapter, p. 80.

Radiation-Activation Method of Analysis*

Following the discovery of artificial radioactivity, the possibility of detecting impurities quantitatively by the observance of the radioactivity in the artificially produced radioactive isotopes of the impurities became apparent. It has only been recently however, that fairly intense sources of either energetic charged particles or neutrons necessary for such a method of analysis have been available in various locations. The development of radiation detection instruments has advanced considerably and this new method of analysis is becoming important in certain fields. Although the radiation detection instruments are themselves not expensive, the sources of radiation are not cheap to construct and are not widely available at the present. Hence, the widespread use of this method of analysis is limited today.

Both hafnium and zirconium contain at least two radioactive isotopes after being subjected to neutron bombardment. Hf^{181} , Hf^{179} (**), Zr^{95} , and Zr^{97} are the four radioactive isotopes of importance.

Both Zr^{95} and Hf^{181} have decay β 's of nearly equal energy levels. However, their half-lives differ enough in length to make it feasible, although not practical, to compare the decay curves of these two isotopes for a quantitative analysis of one in the other.

The procedure followed in studying the decay curves of the radioactive isotopes for quantitative analysis is one which involves comparing both a sample of unknown Hf/Zr ratio to a sample of a known concentration or ratio. Both samples must be subjected to radiation simultaneously and under identical conditions. Simultaneous bombardment of the unknown sample with the known standard dispenses with inaccuracies arising from such variables as flux density, time of exposure, etc.

It is much more practical in the case of most elements, particularly those with long half-lives, to distinguish an impurity by virtue of the difference in the energy of β and γ rays found between the radioactive isotopes of the different elements. When an impurity such as hafnium is known, then by differential absorption or coincidence counting, a measure of the amount of the impurity can be established with the aid of a Geiger-Müller counter.

The most useful means of radio-activation analysis is probably the comparative method wherein a standard sample is subjected to the identical radiation as the unknown sample. This method has been developed for accuracy to diminish the dependence upon established decay schemes and uncertainties in

* The author gratefully acknowledges the assistance of Mr. H. Pomerance of ORNL in editing this section of Chapter XII.

**The 19 second radioactivity of Hafnium has been ascribed to Hf^{179} by E. Segre in MDDC 184 (A chart of Isotopes) dated May 15, 1945. Segre's reference for the hafnium isotopes was A. Flammersfeld⁹⁷ who in 1944 wrote "Es is also wahrscheinlich, dass die beobachtete Halbwertszeit von 19 Sek. ^{179}Hf order ^{177}Hf darstellt". Therefore it is apparent that the 19 second half-life isotope had not been definitely assigned to either Hf^{177} or Hf^{179} . Flammersfeld also gives the half-life length as $19 \pm 0,5$ seconds.

counting efficiencies which are likely to introduce appreciable limitations in the possibility of determining the absolute amounts of impurities. Caution must be taken in choosing standard samples which contain the same general impurities and no foreign constituents with large absorption cross sections and subsequent high counting rates such as boron, lithium, cadmium, and the rare earths for example.

To calculate the weight of the element hafnium, it is only a matter of comparing the counting rate of the unknown with that of the standard at the same time. Such a calculation is set up by the following formula:

$$\frac{(\text{Total activity of Hf in unknown})_t}{(\text{Total activity of Hf in standard})_t} = \frac{\text{Mass of Hf in unknown}}{\text{Mass of Hf in standard}}$$

G. E. Boyd of ORNL cautions that the chief source of uncertainty in the comparative method is the uncertainty in β counting, particularly in the low energy level.

In general, there are three methods of determining hafnium in zirconium and one method particularly adaptable for determining zirconium in hafnium. The first and most obvious method involves subjecting both the unknown sample and a known sample (both of very low Hf content, say $< 5\%$), and a pure zirconium specimen to identical radiation conditions. A quantitative analysis of the hafnium in the unknown sample can be achieved by ascribing the excess counts over and above those due to Zr^{95} to Hf^{181} . This is done after the samples have been removed from the source of radiation a couple of days, at which time the 17 hour Zr^{97} has decayed considerably. S. Reynolds of ORNL has developed this method, and results thus far agree with spectrochemical analyses.

A second hafnium analysis method utilizes the principle of delayed coincidence counting wherein the counting of both the decay electron from Hf^{181} (the < 0.45 Mev β) and the conversion electron of the 22 microsecond Tal^{181} is carried out. H. Pomerance and F. MacGowan of ORNL have employed this method.

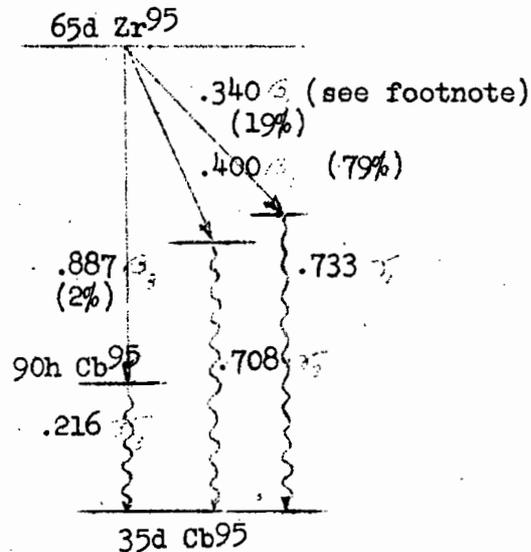
M. Goldhaber and E. Mateosian of ANL have developed a third hafnium analysis method which involves counting the 19 second hafnium isotope activity and comparing the activity of an unknown with a known sample.

For determining zirconium in hafnium where the percentage of hafnium is great in comparison with zirconium, the 17 hours Zr^{97} activity is counted. This method can be used for zirconium assay in most zirconium bearing materials.

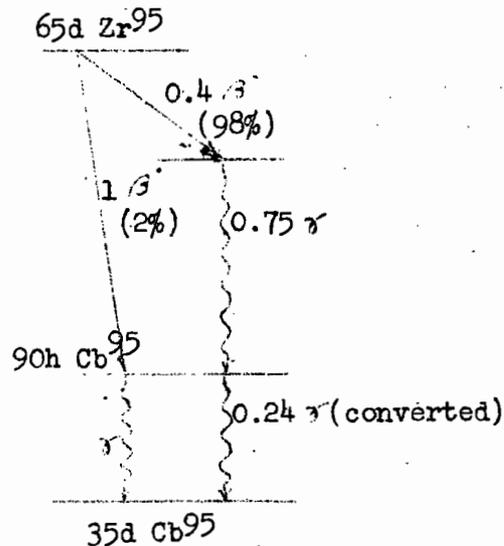
For reference convenience, the decay schemes of Hf^{181} and Zr^{95} are given at the end of this chapter on hafnium analyses methods.

DECAY SCHEMES FOR Zr^{95} AND Hf^{181}

The most recent scheme for the disintegration of 65 d $Zr^{95} \rightarrow$ 35 d Cb^{95} was proposed at ORNL by W. S. Lyon⁷ and J. E. Hudgens, Jr. It is as follows:

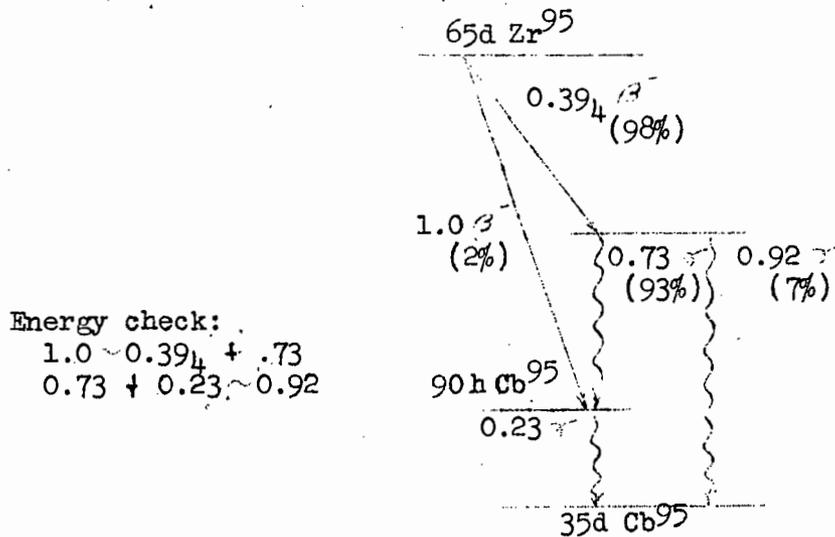


N. Sugarman in 1945 gave the following scheme as "plausible" for 65 day Zr^{65} decay to 35 day Cb^{95} . [Project Council - Information Meeting (Chemistry) February 21, 1945 CS-2745]:

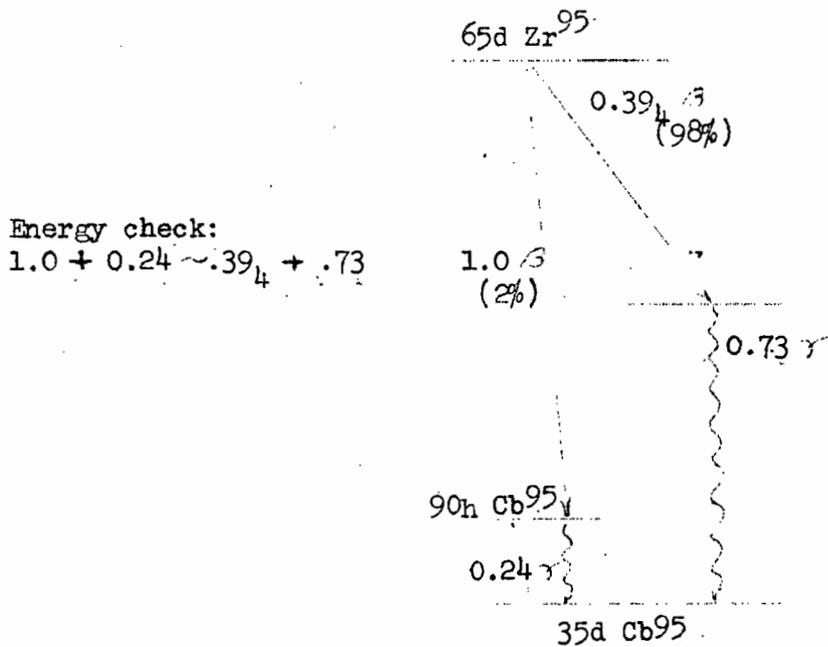


Note: All energy values given for the decay schemes of Zr^{95} and Hf^{181} are in Mev units.

J. S. Levinger in 1945 published a comparison of Nedzel's proposed disintegration of $^{65}\text{d Zr}^{95}$ as follows:

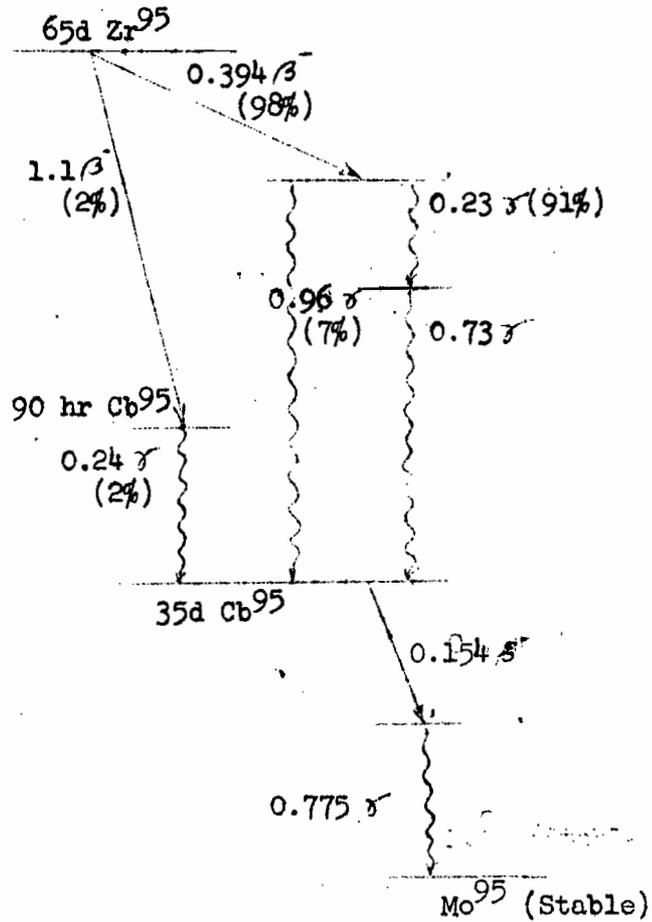


J. S. Levinger and Steinberg also published a possible variation with complete conversion of the 0.24 MeV γ assumed as follows:^{91,*}

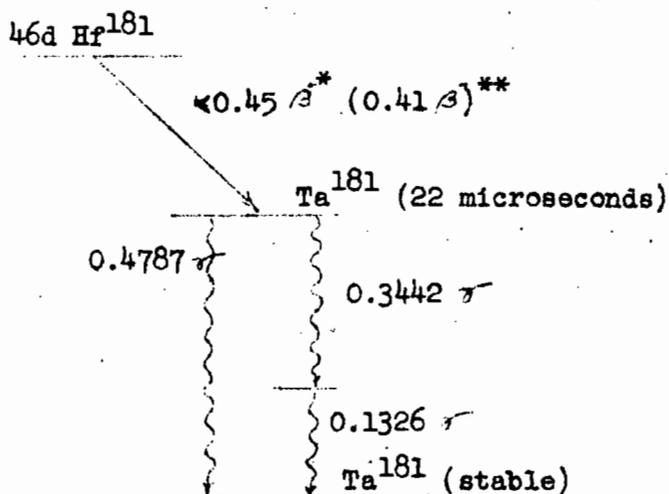


* Also given on page 6 of MUC-NS-3046 or PRR, Vol. 9B, 7-15-11

A fourth scheme is included by R. E. Connick and W. H. McVey⁶⁷ in their report "The Aqueous Chemistry of Zirconium". No reference to the author of the scheme is given in their report. It is presented below:



Cork, Shreffler, and Fowler⁹² give the generally accepted gamma values of Hf¹⁸¹ disintegration to Ta¹⁸¹ which can be arranged as in the scheme below:



Hedgran, A., et al,⁴⁵ have determined the half-life of Hf¹⁸¹ as 47 days. They have also given the β^- a value of .460 Mev and the three γ 's as 0.128, 0.342, and 0.472 Mev., all of which agree fairly closely with Cork, Shreffler, and Fowler.

* Ref. 8, p.167 (Also given are gammas of 0.52, 0.30, and 0.07 Mev).

** Private communication, Bruce Ketelle, ORNL.

Footnote to Chapter XII: This lower sublimation temperature of HfCl₄ compared to ZrCl₄ (referred to on page 74) was deduced during a mass spectrometer analysis at Y-12 in Oak Ridge when a change of the Hf/Zr ratio was observed to occur during this analysis. W. Fischer, et al¹⁰⁰ published a paper in 1939 stating that HfCl₄ appears to sublime at a lower temperature than ZrCl₄. C. Hall, H. R. Hoekstra, and J. J. Katz of ANL determined the vapor pressure of zirconium borohydride, Zr(BH₄)₄, to be 52.7 mm Hg and that of Hf(BH₄)₄ to be 56.9 mm Hg.¹⁰⁴ Van Arkel and de Boer⁵⁹ found in their experiments in separating zirconium from hafnium that hafnium was the first to distill off as a volatile compound in all their fractionations.

CHAPTER XIII

THE EFFECTS ON VARIOUS PROPERTIES OF ZIRCONIUM BY
A FEW MISCELLANEOUS IMPURITIES

In the chapter titled "The Chemical Reactivity of Zirconium" and in the chapter concerning the physical properties of zirconium, the effect of the gases on various properties of zirconium has been covered. Therefore, it is only within the scope of this chapter to include the effect of such impurities not generally assumed to be chemically reactive with zirconium, at least not at low temperatures. Such impurities are the elements carbon, silicon, aluminum, titanium, hafnium, and tin. The following can be written concerning these:

W. J. Kroll, et al³⁹ state that the inclusion of carbon and the carbides in small amounts has only slight effect upon the hardness and malleability of zirconium.

Aluminum does not detract from the malleability of zirconium according to van Arkel and titanium which forms a solid solution over the whole range hardens zirconium.

The presence of small percentages of hafnium (i.e., 2-3%) does not decrease the ductility of zirconium.^{7,37,*}

Tin, however, should be avoided according to Kroll and Schlechten as it has an adverse effect upon the ductility.³⁷

Silicon has a debatable effect on zirconium. De Boer⁵¹ finds it harmful and van Arkel¹¹ thinks small amounts of silicon as well as iron are tolerable.

*This fact also verified by E. G. Enck, Foote Mineral Co., Philadelphia, Pa., in discussion of paper given at the Annual Meeting of the Electrochemical Society at Louisville, Ky., on April 11, 1947. See p. 297, ref. 34.

CHAPTER XIV

THE SUITABILITY OF ZIRCONIUM FOR THERMAL REACTORS*

The selection of a structural material for thermal reactors depends upon many factors, the most important of which are as follows:

- a. Physical stability (viz. mechanical strength to withstand design load stresses, residual stresses, and thermal stresses).
- b. Radiation stability
- c. Chemical stability against the corrosive action of the reactor coolant.
- d. Minimum thermal neutron absorption.
- e. Good moderating properties to thermal neutrons.
- f. Ductility for fabrication and possession of the properties of fabrication such as machineability, weldability, the ability to be cold or hot worked without excess cracking, etc.
- g. Moderate cost.

Various metals and materials fulfill these prerequisites to different degrees. Table I on the following page lists those under consideration for thermal reactor construction and their various properties.

The radiation stability of zirconium and the other materials listed in Table I is apparently good with the exception of graphite and beryllium oxide, BeO. The former undergoes serious damage with accompanying loss in tensile strength and a tremendous loss in thermal conductivity.⁵¹ The latter, beryllium oxide, suffers a slight loss in thermal conductivity which reaches a plateau after a definite length of time.⁵¹

The chemical stability of zirconium is covered in detail in Chapter IX. A treatise on the chemical stability of the various other pile structural materials is not within the scope of this report on zirconium. However, a brief resume of the water corrosion work done at ORNL on the metals in Table I can be presented here.

All of the metals with the exception of iron show good corrosion resistance to water at low temperatures, i.e., below 200°C. However, in the

* It is not the purpose of this report to present the commercial and literature uses for zirconium and its compounds. Kroll and Schlechtenin their Information Circular IC 7341 entitled "Survey of Literature on the Metallurgy of Zirconium" give good references on pp. 10-21 to previous work in this aspect. W. M. Raynor in his article "Zirconium--an Abundant 'Rare' Metal" (Foote-Prints) and J. D. Fast in his article "Zirconium as a Getter" (Foote-Print Vol. 13, #1, 1940) elaborate on the greatest use of zirconium thus far -- as a gettering material in vacuum tube manufacturing.

TABLE I
Comparison of Nuclear, Physical, and Fabrication Properties of Various Thermal Reactor Structural Materials*

Material	M Mass	Density	Tensile Str. Room Temperature $\times 10^3$	Melting Point $^{\circ}\text{C}$	σ_a Barns	σ_s Barns	λ_a Absorption Mean Free Path, cm	Relative duct- ility (an indi- cation of cold forming, draw- ing, & stamping Properties)	General Welding Prop.	Relative Machinability
Al	26.97	2.7	12	660	0.24	1.33	80	Very ductile	Good	2S grade diffi- cult
Be	9.02	1.85	27	1350	0.01	4.	720	Brittle	Very dif.	Poor
BeO	25.02	2.85	14	2547	0.011	8.1	1317*****	Very brittle (must be molded or extruded)	-----	Must be ground
C	12.01	1.6	1	>3500	0.0045	4.8	2500	Brittle (must be molded or extruded)	-----	Easy
Cb	92.91	8.57	43	2415	1.2	6	15.0	Ductile	Good	Moderately diffi- cult
Fe	55.85	7.8	60	1375	2.5	11	4.2	Ductile	Good	Easy
Ti	47.90	4.5	120	1775	5.9***	14.2*****	2.98*****	Ductile	Good	Difficult
Zr	91.22	6.45	38	1860	0.4	8.2	62	Ductile	Good	Easy
Type #347 S.S.	----	---	185**	1385-1421	~2.7	---	---	Ductile	Good	Tough

*Note: The inclusion of the chemical properties of these materials in this table would make the table burdensome. Detailed chemical reactivity and corrosion studies of zirconium are given in Chapters IX and X respectively.

** Full hard thin gage sheet - Nordenholt, Kerr, and Sasso Handbook of Mechanical Design ©1942

*** Private communication of H. Pomerance, ORNL, dated July 26, 1948

**** Measurement of Goldhaber and Briggs for TiO_2 (Ref. 8)

***** Calculated from $\lambda_a = \frac{M}{\sigma_a \rho A}$ where M = molecular weight, σ_a = the absorption cross section to thermal neutrons, ρ = the density, and A = Avogadro's number, 6.06×10^{23} .

region of 300-315° C., 2 S, 17S, 24S, and 53S grades of aluminum do not hold up in distilled water. Tests at ORNL and MIT both indicate that the beryllium produced thus far is also questionable from a water corrosion standpoint at temperatures even as low as 300° C. Three machined beryllium samples placed in alundum crucibles in doubly distilled water at 300° C. showed decided disintegration in 24 hours in an MIT test.⁹ A beryllium specimen cracked and became white at the corners after 43 hours at 400° C. in distilled water in a stainless steel autoclave.⁷ Another beryllium specimen coupled with stainless steel at 650° F (343° C.) disintegrated in apparent stratified layers at 315° C. in some time less than 24 hours.⁷

Columbium was seriously corroded in less than 50 hours in pure distilled water at 315° C in a test at ORNL.⁵⁵ However, at a lower temperature a columbium specimen weighing about 125 grams gained only 0.025 grams in 500 hours during which time a stream of water averaging 205° C. (401.3° F) and moving at about 180 fps passed through a $\frac{1}{4}$ " dia. hole in the bottom half of the specimen striking a groove in the top half of the specimen. (See figure 15 p. 61)

Extensive tests by ORNL have shown titanium to possess remarkable corrosion resistance to pure distilled water, water containing dissolved oxygen, and water containing hydrogen peroxide at 300° C. (the H₂O₂ was in a 30% solution at room temperature).

Of the metals which show good corrosion resistance to high pressure water at 300° C. or lower, only zirconium has a low absorption cross section to thermal neutrons. Although the corrosion resistance of titanium is superior to zirconium, titanium has a σ_a value nearly fifteen times as great as zirconium.

High temperature applications of zirconium in gas cooled piles, however, would appear impractical because the metal has a maximum operating temperature for an oxidizing atmosphere of 400° C.⁹ (See also Figure 11 at the end of Chapter IX.) If the coolant is an inert gas and is exceedingly high in purity, then this maximum operating temperature could probably be revised upward but its use at 760° C. (1400° F.), the temperature of the outlet gas in the Daniels Pile, seems infeasible. Perhaps a metal coating can be developed for zirconium such as silicon, to protect the zirconium from embrittlement due to reactivity or absorption of the gas coolant or its impurities. Zirconium's low cross section compared to the stainless steels makes it still more desirable than the stainless steels as a structural material.

A comparison of the high temperature ultimate tensile strengths of the materials and metals under consideration in this chapter is given on the next page:

Table II 2,71

Ultimate Tensile Strength in PSI of Reactor Structural Materials*

Material	100°F	500°F	1,000° F.	1,500° F.
Al	12,000	3,500	(1,500 @700° F)	-----
Be	27,000	23,000	19,000	15,000
C	1,200	1,200	1,200	1,200
Cb	43,00	39,000**	32,000**	25,000**
Fe	43,000	40,000	18,800	6,000
Ti	90,000 ⁹⁸	60,000 ⁹⁸	35,000 ⁹⁸	-----
Zr	38,000	27,000**	15,000**	5,000**

* All materials fully annealed

** Estimated values

Since a reactor produces heat energy, which for power development must be converted into either mechanical or electrical energy, efficient heat transfer must exist between the reactor and the medium which carries away the heat. The thermal stresses set up within the fuel element within the reactor are a function of the heat flux and heat generation per unit volume.

Dr. W. L. Sibbitt in his report entitled "An Evaluation of zirconium as a Structural Material for High Temperature Thermal Piles" (ORNL-11) writes that the critical thermal stress is proportional to a factor, F, which is given by the equation

$$\text{Eq. (1)} \quad F = \frac{S_u}{\frac{(E \alpha) l}{(1 - \mu) k}} \quad (1)$$

a basic thermal stress equation where

S_u = ultimate tensile strength

μ = Poisson's ratio

E = Young's modulus

α = Linear coefficient of thermal expansion

and k = Thermal conductivity.

A disputable assumption is made that perfect elasticity exists in these materials and that the stress-strain relationship of elasticity exists over the temperature range of 100-1500° F. It is this author's opinion that this relationship would hold nearly true for BeO only among the materials Al, Be, BeO, C., Cb, Fe, Ti, and Zr. However, first approximations can be

obtained with the above formula and for the reader's benefit two sets of calculations are presented below for comparison, one for zirconium and the other for beryllium:

TABLE III²

Thermal Stress Calculations for Zirconium
($\mu = 0.3$ est'd.)

Temperature °F.	S_u psi	$E \times 10^6$ psi	k (est'd) BTU/hr ft °F	$\alpha \times 10^6$ °F ⁻¹	$\frac{E \cdot \alpha}{(1 - \mu)k}$	F
100	38,000	10.7	34	3.6	1.615	23,600
500	27,000	9.4*	32	4.2	1.76	15,300
1,000	15,000	7.8*	30	5.0	1.86	8,060
1,500	5,000	6.0*	28	6.0	1.84	2,720

TABLE IV²

Thermal Stress Calculations for Beryllium ($\mu = 0.3$)

Temperature °F.	S_u psi	$E \times 10^6$ psi	k (est'd.) BTU/hr ft °F	$\alpha \times 10^6$ °F ⁻¹	$\frac{E \cdot \alpha}{(1 - \mu)k}$	F
100	27,000	38	80	6.0	4.07	6,640
500	23,000	31.5*	70	7.1	4.56	5,050
1,000	19,000	22.5*	56	8.5	4.87	3,900
1,500	15,000	15*	42*	10.0	5.10	2,940

* Estimated values

If the proper units are substituted into the denominator of equation (1) and multiplied by the heat flux in BTU/ft² and the heat flow distance in feet, both of which when combined are indicative of the power generation per unit volume, values for the thermal stress in psi are obtained.

Since F is a factor independent of the desired power generation per unit volume and dependent on characteristics of the material, the denominator does not include a factor which would be an arbitrary constant dependent on the reactor design. F can therefore be called a merit factor or an index to the thermal stress characteristics of materials.

In the region of 500° F (which is 32° F. over the coolant water outlet temperature for the proposed 66,00 KW water cooled naval reactor); zirconium has an F factor three times that of beryllium. This can be interpreted as indicating that for the same thermal stresses, zirconium can withstand higher temperature differentials than beryllium. This may appear surprising in lieu of the higher thermal conductivity and ultimate strength of beryllium over zirconium. However, the lower thermal expansion and lower modulus of elasticity (which indicates that for an identical strain or deformation per unit length a higher stress must exist in beryllium than in zirconium) contribute in equation (1) to make F higher for zirconium at

the two temperatures 500° and 1,000° F., but nearly the same at 1,500° F. principally because of the higher ultimate tensile strength of beryllium at this temperature.

The reader should be reminded again however, that these calculations are based upon the assumptions of the existence of perfectly elastic materials and of the validity of the stress-strain relationships of elasticity.

Chapter XV

THE PLATING OF ZIRCONIUM ON OTHER MATERIALS

The remarkable corrosion resistance of zirconium has naturally led to the desire to coat or plate other materials with an adherent, non-porous, uniform cladding of zirconium. Various methods of coating metals with zirconium have been attempted or considered such as electroplating, sputtering, vapor-deposition, and decomposition or reduction of the volatilized halides. An account of various attempts and successes of these methods is presented in this chapter.

Electroplating

Apparently the earliest record of attempts to electroplate zirconium was that of M. Becquerel⁷⁹ in 1831. Becquerel claimed the deposition of a 0.5 mm. film of a steel gray metal that tarnished in the presence of air. Others had previously tried deposition by electrolysis of fused salts. Becquerel however, used an aqueous chloride solution. His catholyte contained a high concentration of zirconyl chloride and a small amount of ferric chloride. The anolyte was a dilute solution of sodium chloride. After removing the iron from the steel gray deposit, the remaining zirconium was oxidized to give a small amount of ZrO_2 .

Kreman, Lorber, and Maas⁸⁰ in 1914 tried electrolysis of an alkaline tartrate solution but deposited no metallic zirconium. Apparently they had chosen this solution because it contained the zirconium as a complex ion, which they believed would deposit readily by electrolysis. However, this resulted in a poor hypothesis because such a solution has been found to have a low zirconium ion concentration.

Laubengayer and Eaton⁸¹ found in their polarographic experiments (see Chapter XI of this report) that high zirconium concentration and high pH favor electrodeposition. Bradt and Linford also agree to these findings.⁷⁷

Bradt and Linford succeeded in electroplating an exceedingly thin film of metallic zirconium by electrolysis of an aqueous solution of sodium and zirconyl sulfate. Their difficulties due to the hydrolysis of the zirconyl sulfate were partially avoided by the addition of Na_2SO_4 .⁷⁷

L. Troost reports that the electrolysis of molten potassium fluozirconate, or sodium chlorozirconate, furnished crystalline zirconium but E. Wedekind attempted this and obtained only an impure powder, greyish-black in color and easily oxidized.⁷⁸ J. W. Marden and M. M. Rich could obtain only the impure amorphous metal by L. Troost's process.⁷⁸

More recent work at Battelle Memorial Institute is reported by B. W. Gonser* to be also unsuccessful for electroplating zirconium by any methods including the electrolysis of aqueous solutions of the salts.

J. C. Griess of ORNL found it impossible to deposit an appreciable amount of zirconium by electrolysis either with a mercury or copper cathode.^{76,7}

All recent investigations concur that it is impossible to deposit metallic zirconium in sizable quantities electrolytically.

Deposition of Dissociated Volatile Halides

B. W. Gonser of Battelle reports that they have successfully coated other metals with zirconium by adapting the "hot-wire" method used in the crystal bar production to other shapes such as plates.⁸⁹ Messrs. Powell, Campbell, and Gonser⁸⁴ developed an apparatus and techniques for the deposition of tantalum and columbium by the hydrogen reduction of their pentachlorides. The advantage of hydrogen reduction over thermal decomposition of the halides is that the hydrogen reduction permits deposition at lower temperatures than are required for thermal decomposition of the halides and therefore is more suitable to a wider variety of base materials.

Dr. Gonser reports that zirconium can be deposited by the decomposition of the iodide, the chloride, or the bromide.⁸⁹ He adds that the iodide and bromide are more advantageous than the chloride because of the lower temperatures necessary for the thermal decomposition of the tetra-iodide and the tetra-bromide.

Battelle Memorial Institute has not only developed techniques for plating tantalum on iron, copper, nickel, steel, molybdenum, but have also applied coatings to such materials as quartz, alumina, and graphite.⁸⁴ These deposits were as thick as 0.030 inches or more and were adherent, ductile, and non-porous. The forms coated included wire, rod, sheet, block, tube, and crucible.

In the coating of tantalum and columbium at Battelle, certain variables were studied which are of applicable interest to zirconium coating.⁸⁴ One of these was the effect of specimen temperature which was found to increase the velocity of coating with increasing temperature. However, lower temperatures gave very fine grained, almost amorphous deposits, whereas higher deposition temperatures caused the formation of more coarsely grained deposits. Accompanying this tendency toward coarser grain at higher temperature existed the tendency to the formation of non-adherent powder deposits.

A second variable studied was the effect of hydrogen gas velocity over the specimen. The uniformity and efficiency of plating were found dependent upon the rate of flow as well as to whether or not it was a streamlined or turbulent flow. Low gas flow rates were noted to give higher plating efficiency but higher gas flow rates resulted in brighter, more uniform deposits, but with lowered plating efficiency.

Another cause of uneven plating is the edge effect which causes a faster deposit of the metal on sharp edges, points, or sharply curved surfaces. Powell, et al⁸⁴ claim that this results in "rough, macrocrystalline deposits (many times thicker than the plate on the plane surfaces) along the edges and corners of a specimen". When the specimen is uniform in cross-section and can be heated by resistance heating, a good control of plating thickness has been observed as being automatic. This is due to the fact that a heavy coating at

* Private communication of November 29, 1948 substantiating indirect communication in reference 31, page 2.

one point will cause the temperature to fall at that point thereby lowering the rate of deposition.

A third variable whose effects were observed at Battelle was the change in concentration of the chloride which was found (within certain limits) to increase the deposition rate with increased chloride concentration.

Plating by Sputtering

To the knowledge of the author, this method has not been tried but has been suggested by several metallurgists and investigators interested in the plating of zirconium on other materials.

B. W. Gonser⁸⁹ of Battelle and R. A. Noland⁹⁰ of ANL both agreed to the possibility of sputtering zirconium upon other metals in a tetra-iodide or other protective atmosphere providing the specimen was cooled sufficiently to keep it below the thermal decomposition temperature of the tetra-iodide vapor. Such an atmosphere would be necessary in view of the results of recent attempts to obtain a sufficiently good vacuum to prohibit gas pick-up by the zirconium ions and the deposited coating itself.^{7,88}

Plating by Vapor-deposition

R. A. Noland of ANL has informed the author that an apparently non-porous adherent but relatively thin coating of zirconium was deposited in the cooler portions of the ionization chamber of a mass spectrograph at Argonne.⁹⁰ A controlled procedure therefore seems likely whereby a coating of zirconium could be applied by vapor-deposition of evaporated zirconium.

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APPENDIX

APPENDIX

The original sketch for figure 18, the apparatus for the determination of oxygen in zirconium, shown on page 102 as well as the description of the experiment itself were supplied by Dr. W. J. Kroll of the Northwest Electrodevelopment Laboratory of the U. S. Bureau of Mines at Albany, Oregon. His communication to the writer is given as follows:

DEPARTMENT OF INTERIOR
Bureau of Mines

Northwest Electrodevelopment
Laboratory

Albany, Oregon
October 4, 1948

Mr. H. B. Fairchild
Staff Engineer
Power Pile Division
Oak Ridge National Laboratory
P. O. Box P
Oak Ridge, Tennessee

Dear Mr. Fairchild:

With reference to your letter of September 20, addressed to Dr. W. J. Kroll, we are giving you the available information on the analytical method used for some time at this laboratory for the determination of oxygen in zirconium.

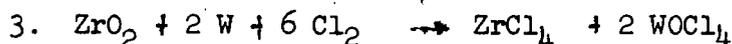
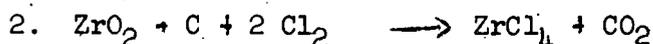
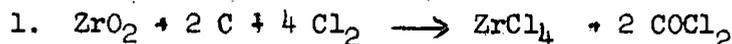
The use of iodine or bromine as reagents for the determination was abandoned because their reaction with zirconium is relatively slow. Experiments showed also that at 500° Centigrade ZrI_4 and $ZrBr_4$ break down to ZrI_3 , and $ZrBr_3$, respectively, which compounds are much less volatile than the tetrachlorides. Difficulty in purification of HCl discouraged its use as a chlorinating agent.

Chlorine was chosen for use in the procedure, so means of its purification were considered. Cylinder chlorine (Hooker Company) has the following upper limits of impurities, stated in percent by volume: CO_2 , 0.05; H_2 , 0.02-0.05; air, 1.0; $FeCl_3$, 0.002; and CO, trace. Air disappears after a short use of the cylinder. Information in the literature indicates that electrolytic chlorine may contain H_2O , C_6Cl_6 and ClO_2 .

The purification method used is that of Moser (L. Moser Zeitschrift für anorganische Chemie, Vol. 110 (1920) p. 140). According to this, the cylinder chlorine is condensed to a liquid in a flask with dry ice as a refrigerent. The condensed chlorine is boiled for a time by removing the dry ice to eliminate any foreign gases that might have dissolved in it, and the combustion equipment is purged with some of this waste chlorine. In this way, any CO_2 dissolved in the chlorine is probably driven off. The CO does not condense

in liquid chlorine since it boils at -192°C against -33.7°C for boiling chlorine. H_2O has too low a vapor pressure at -33.7°C to interfere seriously. The same holds true for ClO_2 (B.P. 9.9°C).

The chlorination method is not suitable for zirconium containing carbon, tungsten, molybdenum, vanadium, columbium, or other agents that form volatile oxychlorides, because the oxygen of the metal oxygen oxide is carried off as oxychloride or other oxygen compounds. Typical reactions are, for instance, these:



There is always about 0.02 percent carbon present even in the purest iodide zirconium made. This means that a minimum loss of 0.026 percent oxygen can be expected in the chlorination; however, this loss may be less, because of a lack of contact of oxide and carbon. If reaction No. 2 takes place, the oxygen losses would be twice as large as those shown in reaction No. 1.

Zirconium produced in this laboratory when remelted contains 0.1-0.2 percent C. making the use of this method of oxygen determination entirely useless, since all the oxygen, less than 0.1 percent, would be carried off as CO_2 or COCl_2 , presuming a good contact with the reagents exists. Reactions 3 and 4 were investigated and it was found that almost any amount of ZrO_2 could be driven off by mixing it with tungsten powder and heating in chlorine.

Tungsten may be introduced by melting the metal in the tungsten arc. Sometimes 0.2 percent W was found in the arc-fused metal. This amount of tungsten may carry off 0.06 percent O_2 or half of this amount, depending on the compound formed (equation 3 and 4.)

By-reactions may seriously interfere with the oxide determination. It is known that ZrCl_4 reacts with silica according to $\text{ZrCl}_4 + \text{SiO}_2 \longrightarrow \text{SiCl}_4 + \text{ZrO}_2$. As a matter of fact, the transparent silica boat used in the determination changed its weight slightly and became opaque.

Any attempt at using the chlorine method for the determination of oxygen in zirconium would have to consider the purification of the chlorine and the by-reactions in the chlorination causing oxychloride formation. As long as these points are not well under control, the chlorination method cannot be recommended. The method is probably entirely useless if low oxygen, high carbon, or tungsten materials are being analyzed. We mentioned these facts in a "Discussion" on the article by W. C. Lilliendahl, D. M. Wroughton and E. D. Gregory, published in the Journal of the Electrochemical Society, Vol. 93, No.6, June, 1948.

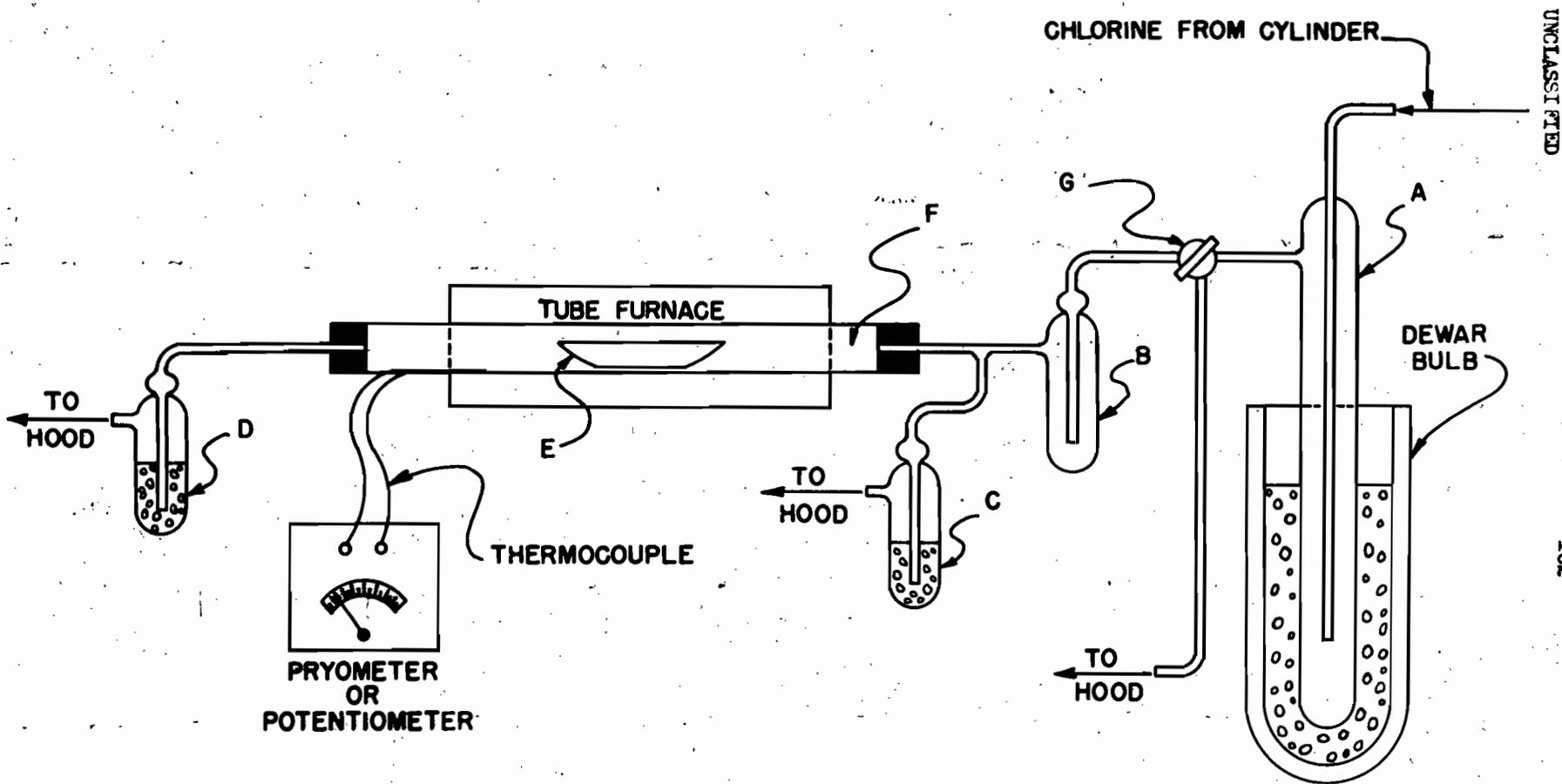


FIG.18 APPARATUS FOR THE DETERMINATION OF OXYGEN IN ZIRCONIUM

Drawing # 6531

Attached is a brief description of the chlorination apparatus and of the procedure used in its operation.

Yours sincerely,

/s/ W. J. KROLL

DETERMINATION OF OXYGEN IN ZIRCONIUM

Description of Apparatus: (Figure 18, previous page).

- A. Gas washing bottle used as trap for collection of liquid chlorine.
- B. Check valve used as trap.
- C. High Pressure check valve, H_2SO_4 filled.
- D. Low pressure check valve, H_2SO_4 filled.
- E. Quartz boat containing sample.
- F. Glass reaction tube (Vycor).
- G. Three-way stopcock.

Procedure:

"A quartz boat of sufficient size to hold 4-6 grams of sample is weighed after ignition to constant weight, a weighed amount of sample placed in the boat, and the boat and sample placed in the reaction tube, F. All connections are made tight and the stopcock, G, is turned so that A is connected to the hood. Chlorine is now admitted to A which is immersed in a cooling bath of dry ice in acetone contained in a Dewar bulb. Here the chlorine condenses and is simultaneously freed of carbon dioxide and oxygen which do not condense and are led to the hood along with any uncondensed chlorine. When 50-100 ml. of chlorine have been collected the cylinder valve is shut off and A is connected to the train by turning stopcock G. By lowering the Dewar bulb so as to warm the liquid chlorine, the vaporized chlorine is caused to flow through the train and its rate of flow is easily controlled by raising or lowering the cooling bath. By suitable adjustment of the level of sulfuric acid in C and D the chlorine will escape through C only if the path through the train, and thus through D, becomes plugged, which quite frequently happens. The bulb, B, serves merely as a trap to prevent sulfuric acid from being sucked back into the chlorine reservoir.

Chlorine is allowed to flow vigorously through all parts of the train for several minutes to insure displacement of air. The furnace is then turned on and brought to a temperature of $500^{\circ}C$ where it is held until the reaction is complete. The reaction begins at about $400^{\circ}C$ as evidenced by the evolution of zirconium chloride which vaporizes and then condenses in the cooler portions of the tube. The train must be watched carefully at this point for in the initial stages of the reaction, the rate of consumption of chlorine is so high in some instances that there is danger that some sulfuric

acid in D may be sucked into the reaction tube.

In the case of zirconium metal, the reaction is highly exothermic and the temperature of the sample undoubtedly exceeds considerably that of the furnace. The sample glows with a dull red heat as the reaction proceeds and the course of the reaction can be estimated by its appearance. When chlorination is complete, the sample no longer glows red and may even have disappeared entirely if no oxygen was present. After cessation of the reaction the flow of chlorine is continued for several minutes at 500° C. and then the furnace is shut off and the sample cooled to room temperature in a stream of chlorine. When the sample is cool, the flow of chlorine is shut off, and the sample placed in a dessicator and subsequently weighed.

From the weight of residue the amount of oxygen can be calculated if one assumes that the residue is pure zirconium oxide. If there is a possibility that there are other materials present, the residue should be analyzed for its zirconium content."

APPENDIX

Copy of the Communication, dated November 19, 1948, addressed to the author from:

J. I. Hoover, Nucleonics Division, Naval Research Laboratory,
Navy Department, Washington, D. C. Their reference: 3102(A)-123-49

SEPARATION OF HAFNIUM AND ZIRCONIUM

The large difference in mass of hafnium and zirconium has been utilized in an attempt to change the hafnium to zirconium ratio in a molten zirconium salt by liquid thermal diffusion. Preliminary results on liquid solutions of UF_6 and WF_6 indicate that large changes in the WF_6 to UF_6 ratio can be achieved by this method. The following table gives the results of tests on solutions of UF_6 and WF_6 :

		Time (Hours)		
		0	70	95
Run 1	$\left(\frac{WF_6}{UF_6}\right)$ Top	0.047	8.1	
Run 2	$\left(\frac{WF_6}{UF_6}\right)$ Top	0.05		19.

Although no ideal compound of zirconium was available, three organic compounds were considered: zirconyl stearate, zirconium tetra isocamylate, and zirconium tetra 2-ethylhexylate, the latter two being developed especially for the purpose.⁽¹⁾ Of the three compounds the 2-ethylhexylate was chosen to conduct the experiments since it had the best over-all physical and chemical properties. The stearate showed radical changes in physical properties after a few hours in the apparatus, where as the isocamylate decomposed slowly when heated in glass ware at 150° C. The 2-ethylhexylate withstood temperatures of 200° C in glass ware for extended periods (~ 200 hrs.) and showed only a slight tendency to decompose, The physical properties of the hexylate are as follows:

Composition of hexylate	MP	B.P.	Viscosity cp	Mol. Wgt.
			25° C	
97% $Zr(OC_8H_{17})_4$	0-20° C	decomposes	» 1	607
3% $Hf(OC_8H_{17})_4$				694

The results of several runs using zirconium tetra 2-ethylhexylate, are given in the following table.

(1) These compounds were developed in the Chemistry Division under the direction of Peter King.

Run #	Temperature (gradient)	Length of run (Continuous)	$\left(\frac{\text{Hf/Zr}}{\text{Hf/Zr}}\right)$	Bottom	Remarks
	C/cm	hours		Top	
1	~ 5500	198	1		The temperature gradients were achieved by changing hot & cold wall temperatures and/or annular spacing
2	~ 2500	140	1		
3	~ 1450	140	1		
4	~ 3750	190	1		
5	~ 2240	95	1		

In each case decomposition occurred in the apparatus; this was attributed to the catalytic action of the large metal surface in contact with the 2-ethylhexylate. There is a possible explanation for the lack of separation on the grounds of this decomposition. The products resulting from the decomposition, having a large difference in mass, were separated according to molecular weight; the compound with the highest molecular weight being concentrated at the bottom, and that with the lowest molecular weight concentrated at the top. Since there should be no preferential decomposition of either the $\text{Hf}(\text{OC}_8\text{H}_{17})_4$ or $\text{Zr}(\text{OC}_8\text{H}_{17})_4$ in the original salt then it might be expected that each group of molecules of equal molecular weight would contain the same hafnium to zirconium ratio. Since the test samples were of necessity taken from the separated compounds the results in the above table seem reasonable.

Regardless of the explanation for the lack of separation, the results indicate that the liquid thermal diffusion method is not applicable to separating hafnium and zirconium using liquid zirconium tetra 2-ethylhexylate. However, the method might be used successfully with a more ideal liquid compound of zirconium should such become available.

APPENDIX

(Because the author questions the accuracy and completeness of hydrogen embrittlement tests performed by the Sun Oil Company for the Foote Mineral Company, this information as given below has been inserted in the appendix.)

The Sun Oil Company has performed some hydrogen embrittlement tests for the Foote Mineral Company in a hydrogen atmosphere between 235 to 250 psi and at 400-420° F.

The results of tests on three samples are published here. Specimen #7 was welded across the center, specimen #8 was tested as received, and specimen #9 was oxidized in a gas flame prior to the test.

Table I¹⁹

Specimen #	Wt. Before Gms.	Wt. After Gms	Gain Gms
7	3.8371	3.8370	-0.0001
8	5.5905	5.5906	+0.0001
9	5.7884	5.7888	+0.0004

Results of the physical tests on the above specimens and two control samples are given in the table below:

Table II¹⁹

Description of Sample	Ult. Tensile St. psi	% Elongation in 2"
Sample #7	40,500	28
Control welded sample $\frac{1}{2}$ " wide	39,600	31
Control sample $\frac{3}{4}$ " wide 0.0105" thick	36,000	24
Sample #8	45,500	24
Sample #9	38,300	26 $\frac{1}{2}$

Interpretation of the above tables for corrosion data and physical properties data is difficult if not impossible because of the paucity of data. One would suspect an oxidized protective layer to offer some protection to specimen #9 but the available information on this specimen shows it to be the one to have the greatest corrosion.

Also one would expect an unwelded and thus unembrittled sample such as #7 and #9 to have more elongation before reaching the yield point than a welded sample. Table II indicates otherwise. Therefore it is the belief of the author that little value can be obtained from the results of this test.