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BIBLIOGRAPHY OF HAFNIUM OXIDE, HAFNIUM SILICATE AND HAFNIUM CARBIDE

C. E. Curtis

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HAFNIUM OXIDE

HISTORY

1. D. Coster, H. Hevesy
   Missing Element of Atomic Weight 72
   Nature 111, 79 (1923)

Dauvillier's X-ray spectrum of this element is questioned because: (1) The lines are faint and differ from the wave length calculated by interpolation in the measurements of Hjalmar and Coster; (2) According to the Bohr theory, element 72 should not be a rare earth but a homolog of zirconium; (3) General views based on the periodic system agree with the foregoing.

C. and D. find lines in the spectrum of Zr preparations with Lambda equal to 1565.5, 1576, 1371.4, 1323.7; estimated that 1% Hf was present in a Zr mineral from Norway.

Hafnium was given the Latin name for Copenhagen.

* *

2. D. Coster, G. Hevesy
   The New Element Hafnium
   Nature 111, 252 (1923)

The main reasons for believing that Urbain's celtium is not hafnium are: (1) C. & H. purified Hf from rare earths easily while U. had difficulty in case of celtium; (2) Concentrated Hf preparations do not have the Ct spectrum; (3) U. obtained only weak X-ray lines from concentrated solutions; C. & H. found Hf lines in abundance in Zr minerals.

Hafnium content of earth's crust is estimated to be over 10^{-5}%.

* *

3. G. Hevesy
   Discovery and Properties of Hafnium
   Chem. Reviews 2, 1-41 (1925)

The discovery stemmed from Bohr's theory which showed (from the quantum theory) that the new element 72 should resemble, not the rare earths as Urbain thought, but Zr (#40) as shown below:

	1	$2_1 2_2$	$3_1 3_2 3_3$	$4_1 4_2 4_3 4_4$	$5_1 5_2 5_3 5_4 5_5$	$6_1 6_2 6_3 6_4 6_5 6_6$
Zr(40)	2	8	18	8 2	(2)	
Lu(71)	2	8	18	32	8	1
Hf(72)	2	8	18	32	8	2

* *

4. V. M. Goldschmidt, L. Thomassen
The Occurrence of Element 72 (Hafnium) in Malacon
Norskr. Saertryk 7, No. 1, 61-8 (1923)

From its position in the periodic table 72 would be expected in the Zr and Th minerals. Roentgen spectrographic lines identified Hf lines in 2 varieties of zircon.

* *

5. G. Urbain, D. Dauvillier
The New Element 72
Nature 111, 218 (1923)

A reaffirmation of their discovery of element 72 denied by Coster and Hevesy. They claim that their spectrums of Zr minerals show lines identical with celtium lines previously reported.

* *

6. H. M. Hansen, S. Werner
The Optical Spectrum of Hafnium
Nature 111, 322 (1923)

Fifty-two lines ascribed to Hf are reported with wave lengths to hundredths of an angstrom unit and with relative intensities; all lines are between 2500 and 3500. Not the slightest trace was found of lines reported by Urbain for "Celtium". Preparations initially contaminated with rare earths were obtained spectroscopically free of all except Hf, Zr and Ti. Many of the Hf lines had been originally ascribed to Zr.

* *

7. M. Bodenstein, O. Hahn, O. Hönigschmid
Fourth Report of German Atomic Weight Commission
Ber. 57B, I-XXVI (1924)

Preference is expressed for hafnium as the name of the new element 72 with Coster and Hevesy as discoverers.

* *

8. E. Cattelain
Celtium or Hafnium? Brief Monograph of
the New Element, Atomic Weight 72.
J. Pharm. Chem. 6, 515-22, 563-7 (1927)

A review of the controversy and a detailed account of the new element.

PHYSICAL PROPERTIES

Density

9. G. Hevesy, V. Berglund
Density of Oxides of Zirconium and Hafnium
J. Chem. Soc. 125, 2372-5 (1924)

The oxides were prepared from the sulfates by heating at 400° and at 20°:

ZrO_2 density 5.73

HfO_2 density 9.67

The density of the oxides when prepared from basic sulfates or from oxychlorides was lower by as much as 0.2. The Hf content of Zr samples can be found with a fair degree of accuracy from the density of the oxide prepared from the normal sulfate.

* *

10. G. Hevesy
Discovery and Properties of Hafnium
Chem. Rev. 2, 1-41 (1926)

Redetermination of density by pycnometer method gave:

ZrO_2 density 5.73
HfO_2 density 9.68

* *

Melting Point

11. F. von Henning
Melting Points of Ceramic Ores
Naturwissenschaften 13, 661 (1925)

Determined melting points of ZrO_2 and of ZrO_2-HfO_2 mixtures and extrapolated for m. p. of HfO_2.

	M.P.
ZrO_2 pure	2960 ± 20°A
0.49 ZrO_2 plus 0.51 HfO_2	3026 ± 20
0.07 ZrO_2 plus 0.92 HfO_2	3072 ± 20
pure HfO_2 (extrapolated)	3085 ± 25° (2812 ± 25°C)

* *

12. P. Clausing
Melting Points of Zirconia and Hafnia
Z. anorg. allgem. Chem 204, 30-39 (1932)

With probable error of $\pm$ 20°K

HfO_2 plus 1% ZrO_2	3047°K (2774°C)
ZrO_2 plus 1% HfO_2	2950°K (2677°C)

Only HfO_2 and ZrO_2 were present. The method used was similar to that used by M. Pirani and H. Alterum for metals. The difference between the m.p. of HfO_2 and ZrO_2 was 98 $\pm$ 10° as compared with Henning's 125°.

* *

13. Lange's Handbook of Chemistry
1944-1949

HfO_2 m.p.	2812°C
ZrO_2 m.p.	2700

* *

Boiling Point

14. David Richardson
Boiling Points by Spectroscopy
Spectroscopy in Science and Industry
Proceedings of Fifth Summer Conference (M.I.T)
on Spectroscopy and its Applications
John M. Wiley & Sons (1938)

In the carbon arc it is uncertain whether the b.p. of the oxide or carbide is obtained. Detns. on materials including HfO_2 ranged from 3550 to 6100°C.

* *

Magnetic Susceptibility

15. G. Hevesy
Investigations of Properties of Hf
Danske Videnskarbenus Silskab. Medd. VII (1925)

HfO_2	0.112×10^{-6}	- Magnetic susceptibility
ZrO_2	0.110×10^{-6}	- Magnetic susceptibility

That is, both are diamagnetic.

* *

Spectroscopic Analysis

16. R. Wm. Shaw, Henry G. Kitcham
Vibrational analysis of the HfO_2 Band Spectrum
Phys. Rev. 43, 753 (1935)

No data concerning HfO_2 in Chem. Abstracts but considerable data is given under the subject of "Hafnium".

* *

Crystal Lattice Data

17. L. Passerini
Isomorphism Among the Oxides of the Quadrivalent Metals
Gazz. chem. ital. 60, 762-76 (1930)

Besides the problem of isomorphism of the oxides, P. studied the cubic form of HfO_2 and ZrO_2. The existence of the monometric form was established for ZrO_2 but not for HfO_2 except by analogy in similar chemical behavior.

Cubic solid solutions between ZrO_2 and HfO_2 were obtained in which a greater proportion of one oxide dissolved in the other; it was possible to determine the dimensions of the cubic cell of HfO_2 and to estimate the diameter of the Hf^{++++} ion. The oxides were prepared by calcination at approximately 800°C of solid solutions of the hydroxides previously pptd. from nitrates of sulfates by KOH. For the cubic forms:

	HfO_2	ZrO_2
a	5.115 ± 0.01 A. U.	5.065
V	133.82 x 10^{-24} cc.	129.94
d	10.43	6.27
diam. (calcd.)	1.79 A. U.	****
lattice	fluorite	fluorite

* *

X-Ray Analysis

18. A. C. Richardson, D. W. Scott, J. F. Shea
The Sepn. of Zr. and Hf
AECD 2979

Page 84 - X-ray diffraction photograms of 99% and 92.5% pure HfO_2 showed them to be isomorphous with monoclinic ZrO_2 but the diffraction lines were too diffuse for detg. their lattice constants. Both X-ray and petrographic methods failed to show any difference between the two samples.

* *

CHEMICAL PROPERTIES

Molecular Weight and Volume

19. G. Hevesy
Discovery and Properties of Hafnium
Chem. Revs. 2, 1-41 (1925)

	Molecular Wt.	Molecular Vol.
HfO_2	178.6	21.76
ZrO_2	91.3	21.50

* *

Preparation

20. J. H. deBoer (to N. V. Philip's Gloeilampen Fabrieken)
Hafnium and Zirconium Compounds
U. S. 1, 771, 557 (July 29, 1930)

A mixture of Hf and Zr salts such as can be derived from the "at least tervalent oxides of the elements of the second column of the fifth group with the exception of N and Bi"; for example, a mixture of Zr and Hf phosphates is treated with a soln. contg. Hf to produce soluble Hf and Zr compounds which may be treated with aq. soln. of ammonia for pptn. of the said oxides.

* *

21. J. H. deBoer, J. D. Fast
Prepn. of Pure Metals of the Ti group by the Thermal Decompn. of their Iodides; III-Hafnium
Z anorg. allgem. Chem. 187, 192-208 (1930) (Cf. C.A. 20, 2627)

Discusses the difficulty in obtaining Hf metal pure by the chloride or iodide attack methods. Pure HfO_2 was converted to metal by Ca and Na reduction.

* *

22. Imperial Chemical Industries, Lts., and F. L. Clark
Dioxides of Ti, Zr, Hf, Th
British Pat. 339, 608 (Sept. 7, 1929)

Electrolytic sepn. of a suspension contg. a compound of Hf, preferably under 20 atmospheres of H or air at 90 to 120° with insoluble anode of C, Ni, Cr, or steel.

23. Heraeus-Vacuum Schmelze A. G. and Wilhelm Rohn
Reduction of Oxides
German pat. 600, 369 (Sept. 29, 1934)

Hf is derived from the reaction of HfC with HfO_2 in a bath of fused Hf under reduced pressure.

* *

24. E. M. Larsen, W. C. Fernelius, L. L. Quill
Concentration of Hf; Preparation of Hf-Free Zr
Ind. Eng. Chem., Anal Ed. 15, 512-15 (1943) (Cf C.A. 36,4051)

By repeated phosphate pptns. HfO_2 concentrations were changed from 13 to 93% in 7 fractionations.

* *

Heat of Reduction

25. I. I. Iskol'dikii, T. G. Shokhor
Metallurgy in the Light of Electrochemical Series
J. Applied Chem. (USSR) 19, 693-704 (1946) (in Russian)

The heats of reduction of 25 oxides (including HfO_2) by 14 elements (Li, Ca, Mg, Th, et al) are compared with the electromotive potentials of the latter; parrallelism is shown.

* *

Heat of Formation

26. W. A. Roth
Ordinal Number and Heat of Formation
Naturwissenschoften 19, 860 (1931)

Heats of formation determined by bomb combustion

HfO_2 271 ($\pm$ 5) kg. cals
ZrO_2 257.4 ($\pm$ 0.6)

In curve of heat versus atomic number value for Hf falls below expected value.

* *

27. W. A. Roth, G. Becker
Atomic Number and the Heat of Formation
Z. Physik Chem. A159, 1-26 (1932)

At constant pressure and 20°, heat of formation of HfO_2 is 271; Quartz (alpha) 207; ZrO_2 258.1; ThO_2 292.6

(Normally there is no connection between atomic number and heat of formation)

28. A. F. Kapustinskii
Thermochemistry and Atomic Structure; I-Rule of Thermochemical Logarithmiscity and Heats of Formation of the Halides
Izvest. Akad. Nauk. U.S.S.R.
Otdel. Khim. Nauk. 1948, 568-80 (1949)

A plot of the heats of formation of the oxides of the elements of the fourth group shows some deviation in the cases of HfO_2, CO_2, and ThO_2.

* *

Catalytic Properties

29. S. B. Anisimov, G. I. Khaidarov
Catalytic Properties of HfO_2 and ZrO_2
Zhur. Obshchii Khim. (Jour. of Gen. Chem.) 18, 40-42 (1948) (Russian)

A catalyst is prepared by fusing 99.5% of HfO_2 with Na_2CO_3 at 800°, dissolving in H_2SO_4, pptg. Fe with NH_4CNS and ether, pptg. $Hf(OH)_4$ with NH_4OH.

HfO_2 and ZrO_2 cause dehydration and dehydrogenation of EtOH, their activities being identical.

* *

30. Howard D. Hartough, Alvin I. Kosak (to Socony-Vacuum Oil Co., Inc.)
Hafnium Oxide Catalyst
U. S. 2, 458, 512 (January 11, 1949)

Thiophene is acylated with anhydride or chloride of a carboxylic acid in the presence of silica gel impregnated with an oxide of Ti, Zr, Hf, Th, Fe, Ni, or Co. Thus, to 1 mol of thiophene and 1 mol of Ac_2O(95%) was added 10 g. of 90% SiO_2 and 10% of ZrO_2 and the mixture heated at 106-114°C in 4 hours and filtered to yield 44 g. of 2-acetylthiophene. (Describes use of ThO_2 also).

* *

SUB-ATOMIC PHENOMENA

Cross section

31. K. Heinz Lauterjung
Effective Cross Section of Certain Elements for Slow Neutrons
Ann. Physik 41; 177-92 (1942)

Neutrons from a D-D source were slowed down in paraffin, restricted to a beam by Cd and after passing through a scattering foil were counted

in a BF_3 chamber. The following total (scattering plus absorption) areas ($X\ 10^{-24}$ sq. cm.) were measured. The substance bombarded is in parentheses.

Hf (HfO_2)	175.4 ± 29.0
Ga (Ga)	18.5 ± 7.6
Ge (GeO_2)	24.3 ± 7.3
Rb (RbI)	11.8 ± 1.9
In (In)	198.6 ± 11.3
Cs (CsCl)	50.5 ± 3.8
Zr (Zr)*	15.0 ± 10.0

*Value corrected with the aid of above Hf value

* *

Radio Activity

32. A. Flammerfeld (Kaiser Wilhelm Ins. Chem., Berlin)
Isomers of Stable Nuclei by (Mu, Lambda) Processes of Dysprosium and hafnium
Naturwissenschaften 32, 68-9 (1944)

With 97% HfO_2 slow neutrons gave an intensive activity of 19 seconds half period, with energy of 190 e. kv. The material formed was probably Hf^{179} or Hf^{177}.

* *

USES

HfO_2 Refractory

33. R. Reichmann, and H. Kohl (Siemans and Halske A. G.)
Method of Molding of Nonplastic Metallic Oxides
U. S. Pat. 1,934,091 (Nov. 7, 1933)

Nonplastic oxides are molded into refractory articles by special treatment of the oxide previous to molding. The oxide is first calcined until it begins to crystallize, is then ground to 2 to 15 microns; 100 parts are made into as perfect a suspension as possible by addition of dilute HCl (6 to 8 parts), heated and mixed. Excess water is removed by filtration, leaving a crumbly mass containing 5% moisture. This is molded by pressing, ramming and shaking without binders. Body is sintered at 1750°.

* *

34. Siemans & Halske A. G.
Refractory Compositions
Brit pat. 410,988 (July 14, 1933)
also French pat. 757,864,(Jan. 5, 1934)

Sintered bodies are prepared from metal oxides, e.g., Al, Be, Cr, Mn, or Hf, which are free of impurities, especially of clay and silica, by casting a paste which has been activated with acid, the concentration of the acid being regulated according to the grain size of the oxide. Dilute acid is added to fine material and a stronger acid to coarser material. After molding the products are fired above 1600°.

* *

35. R. Reichmann (Siemans & Halske A.G.)
Method of Making Bodies Consisting of Metallic Oxides
U. S. Pat. 2,2021,520 (November 19, 1950)

Preparation and forming of porous bodies consisting of oxides of Al, Be, Mn, Zr, Hf, Mg and combinations of these, is described.

* *

36. R. Reichmann, (Siemans & Halske A.-G.)
Method of Making Shaped Bodies of Nonplastic Metallic Oxides
U. S. Pat. 2,031,129 (February 18, 1936)

Finely grind the oxide, add a binding agent under pressure and extrude through dies, calcine to 1600°.

* *

37. N. V. Philip's Gloeilampen Fabrieken
HfO_2 in Electric Lamp Filaments
Brit. Pat. 220, 301 (August 9, 1923)

W, Mo, Ta, etc. used in electric lamp filaments are improved by the addition of 0.1-3% of HfO_2 which retards the crystallozation of the metal.

* *

38. Ioana Manescu
L spectra and Characteristic Levels of Hf (72) and Feeble L Emissions of Hf and Ta
Compt. Rend. 215, 104-6 (1942)

Used an absorbing screen of HfO_2 to find discontinuities in emission spectrum of Hf.

39. L. Passerini
Isomorphism Among the Oxides of Quadrivalent Metals:
The System CeO_2-HfO_2
Gazz. chim. ital. 60,762-766 (1930)

The CeO_2-HfO_2 system was studied by the X-ray powder method. Cubic solid solutions of the fluorite type were formed; the solution is only partial, 25% CeO_2 in HfO_2 and 32% HfO_2 in CeO_2 being the maximum.

HAFNIUM SILICATE

PHYSICAL PROPERTIES

X-ray Analysis

1. A. C. Richardson, D. W. Scott, J. F. Shea
   The Separation of Zr and Hf
   AECD 2979

(Preparation as per previous abstract, same authors; HfO_2 (92.5% pure plus SiO_2 99% pure, mol to mol) heated to 2660°F, cooled, fused in an arc, reheated from 0 to 120 hours at 2660°F).

Major phase was isomorphous with monoclinic* zirconium silicate and minor phase of HfO_2.

Differences in crystal lattice constants for Hf silicate and Zr silicate could not be determined because the former contained both HfO_2 and ZrO_2, possibly in solid solution and the Zr silicate contained an unknown amount of Hf** which could have been in solid solution. The implication is that Hf silicate is isomorphous with Zr silicate and the Hf oxide is isomorphous with Zr oxide.

* *

2. P. D. Zemany, E. H. Winslow, G. S. Poelmetz, H. A. Biebhofsky
   X-ray Absorption Measurments: Comparative Method
   Based on Measurements with Multiplier Phototube
   Anal. Chem. 21, 493-7 (1949)

X-ray beam after passing through known thickness of control was picked up by the photomultiplier tube, keeping the voltage and amperage across the X-ray tube constant. Known weight of this material was pivoted into position and output of multiplier tube was measured. They found that the results (in microamperes) were additive in the case of all oxide mixtures tested with the exception of ZrO_2-HfO_2 mixtures. This shows that a single measurement of X-ray absorption with a phototube cannot establish the composition in high HfO_2 compositions.

The current output of the tube varied as the 24th power of the primary voltage across the X-ray tube and as the 5th power of the voltage across the multiplier phototube.

* *

*Probably a typographical error since zircon is tetragonal (CEC).
**Probably meant to be HfO_2.

Indices of Refraction

3. A. C. Richardson, D. W. Scott, J. F. Shea,
The Sepn. of Zr and Hf Quarterly Report
AECD 2979

Due to deterioration of phosphorus oils the previously reported indices were incorrect. The corrected values are as follows:

	N_o	N_e
Hafnium Silicate	1.89	1.94-1.95
Hafnium Oxide (starting material)	1.98-2.02	
Hafnium Oxide pptd. in silicate matrix	2.02-2.04	
Zirconium Silicate	1.92	1.97
Zirconium Oxide	2.2	

* *

Use as Catalyst

4. Dominion Tar and Chemical Co., Ltd.
Styrenes and Other Aromatic Compounds
British 609,825 (Oct. 7, 1948)

Silicates of Zr, Ti, Hf and Th are catalysts for the decomposition of $ArAr'CHCH_2R$ to $ArCH{:}CHR$ and $Ar'H$ at temperatures above 350° in the presence of a diluent such as H_2O with a contact time of 0.004 to 0.4 sec.

HAFNIUM CARBIDE

Preparation

1. C. Agte, K. Moess
   Methods of Preparation of Pure High Melting Carbides and Borides and Description of their Properties;
   I-Preparation of Carbides and Nitrides (Sinter Method)
   Z. anorg. allgem. Chem. 198, 233-43 (1931)

I. Carbides are prepared by heating the metal or pure oxide with lampblack in a gastight tube furnace; 1/2 hour at 1700-2100°C is generally enough; use of 15-25% less carbon than theoretical was found sufficient.

II. Preparation by growth: Vapor of the carbide (or nitride or boride) is deposited on a heated filament. In the case of the boride the reaction is

$$HfCl_4 + 2BBr_3 + 5H_2 \longrightarrow HfB_2 + 4HCl + 6HBr$$

HfC grows rapidly and is porous and coarsely crystalline at higher filament temperatures.

* *

2. C. Agte, H. Alterthum
   Systems of High Melting Point: Contributions to the Problem of Carbon Fusion
   Z. Tech. Physik 11, 182-91 (1930)

Carbides of Hf, Zr, and others are usually prepared by ignition of the metals or oxides with carbon in a carbon tube furnace. For testing melting points, etc. the carbides were pressed into rods and sintered at high temperatures.

* *

3. Karl Becker
   Physical Characteristics of High Melting Compounds
   Physik. Z. 34, 185 (1933)

In most cases the necessary amounts of the metal and carbon form the carbide in ½ hour at 2200°C. Little volatilization is encountered. The carbides (nitrides and borides also) were pressed into shape, then sintered at 2500-3000°C, in a carbon rod resistance furnace in hydrogen atmosphere or inert gas or vacuum.

* *

4. J. S. Anderson
Interstitial and "Berthollide" Compounds
Chem. and Indus. 15, 766-9 (1937)

The general method of preparation of the carbides in powdered form is by direct union of the metal (powdered) with C (B and N also) at approximately 2200°C. They are purified by volatilizing out the impurities. Carbides can be deposited on a hot filament of Pt, C, etc., from volatilized chloride mixed with a hydrocarbon.

* *

PHYSICAL PROPERTIES

Structure

5. Karl Becker
Physical Characteristics of High Melting Compounds
Physik. Z. 34, 185-98 (1933)

Crystal form of HfC is cubic. Lattice constant aA = 4.69; (ZrC= 4.76)

* *

6. H. J. Goldschmidt
Crystal Structure of the Carbides
Iron and Steel 22, 239-46 (1949); also see Jour. Iron Steel Inst. (London) 160, 345-62 (1949)

The article deals principally with iron-alloying elements including Cr, W, Mo, Ni, Cu, Ti, Mn, Zr, Ta, and Hf.

HfC probably has the highest m.p. among all simple carbides; probably has the NaCl type of structure; the only evidence for this is that Agte and Alterthum reported a continuous series of solid solutions between TaC (cubic) and HfC.

* *

7. J. S. Anderson
Interstitial and "Berthollide" Compounds
Chem. & Indus. 15, 766-9 (1937)

In the refractory carbides and nitrides the cations (metallic constituents) being larger, determine the structure which is the reverse of ionic compounds. The other components must be present not as ions but as neutral atoms in order for the relative radii of metal and nonmetal to fit together, the nonmetal entering the interstices between the metal atoms. They are called "interstitial" compounds and the composition is determined by the number of geometrically equivalent positions between the close-packed metal ions. The tendency is to form 1:1 compounds regardless of the usual valency.

* *

Density

8. Karl Becker
Physical Characteristics of High Melting Compounds
Physik. Z. 34, 185-98 (1933)

Density calculated from lattice constant (= 4.69) is 12.20; (ZrC = 6.51). Measured density of HfC was not obtained; for ZrC it was 6.91.

* *

Tensile Strength

9. Karl Becker
Physical Characteristics of High Melting Compounds
Physik. Z. 34, 185-98 (1933)

Did not determine tensile strength of HfC but thinks it is close to that of TaC (= 2-3 kg./mm^2 at r.t.)

* *

Hardness

10. J. S. Anderson
Interstitial and "Berthollide" Compounds
Chem. and Indus. 15, 766-9 (1937)

Hf, Zr, Ti, Ta, Mo and W give rise to related groups of carbides, nitrides and borides all of which are very hard (hardness of W_2C is close to that of diamond).

* *

Color

11. C. Agte, K. Moess
Methods of Preparation of Pure High Melting Carbides and Borides and Description of their Properties;
I-Preparation of Carbides and Nitrides (Sinter Method)
Z. anorg. allgem. Chem. 198, 233-43 (1931)

The carbides and nitrides when pressed from powder into slugs at 2000 kg. per cm.^{2} and fired 2 to 4 times to 2500-3000°C were gray, brittle and hard.

* *

Melting Point

12. C. Agte, H. Alterthum
Systems of High Melting Point: Contributions to the Problem of Carbon Fusion
Z. Tech. Physik. 11, 182-91 (1930)

M. p. was determined by the method of Pirani and Alterthum by focussing a micropyrometer on a hole 0.3 mm. wide and 2 mm. deep which acts as a black body radiator. The carbides in rod form were heated by an electric current in 99% argon (the nitride was formed in a nitrogen atmosphere) using 10V. and 300 amps. Generally the composition and structure did not change in heating. Values determined:

HfC	4160 ≠ 150°C
ZrC	3805 ≠ 125°C

* *

13. Karl Becker
Physical Characteristics of High Melting Compounds
Physik. Z. 34, 185-98 (1933)

Specimens prepared as under abstract above (see Prepn.) M. p. of HfC 4160 ≠ 150 A; or ZrC 3805 ≠ 125 A. A composition of 4 Tac with 1 HfC melted at 4205 to 4215°Abs., the highest melting point of any known substance.

* *

14. J. S. Anderson
Interstitial and "Berthollide" Compounds
Chem. and Indus. 15, 766-9 (1937)

The carbides, nitrides and bories of Hf, Zr, Ti, Ta, Mo and W have extremely high melting points. HfC and TaC are solid at temperatures at which rhenium and tungsten melt and fused carbon volatilizes.

Compound	M. P. °K	Hardness (Moh)
HfC	4160	---
ZrC	3805	8-9
TiC	3410	8-9
TaC	4150	---
W_2C	3130	9-10
WC	3130 (decomposes)	---

An alloy of 20% ZrC plus 80% TaC has highest m.p. of any known substance (4215°K)

* *

15. R. W. K. Honeycombe
Metallic Carbides and Their Sintered Products
Australasian Engineer 4, No. 313, pp. 11-13, 25-29 (1942)

	M. P. °C
HfC	3890
ZrC	3530
TiC	3150

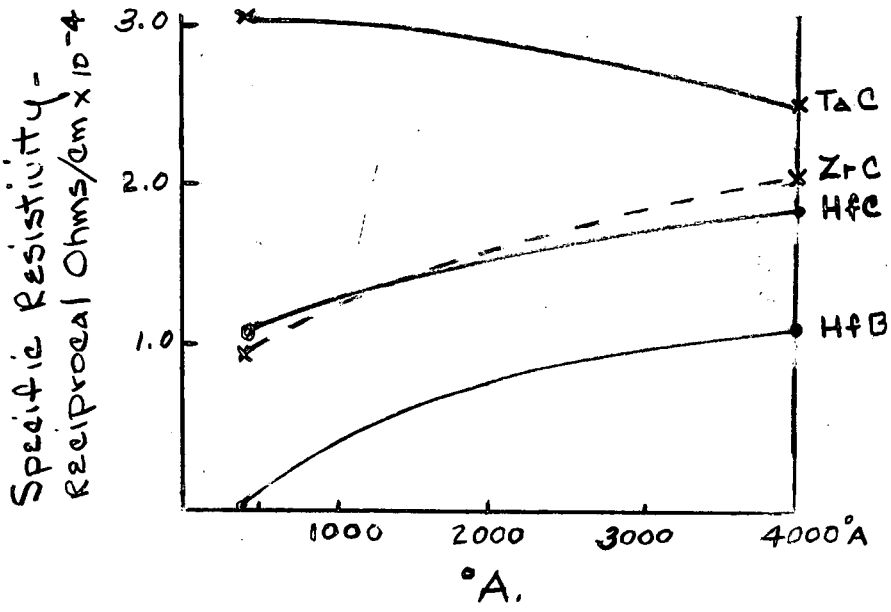
Bonding and forming of bonded carbides by hot-press method are discussed.

* *

Conductivity

16. Karl Becker
Physical Characteristics of High Melting Compounds
Physik. Z. 34, 185-98 (1933)

States that electrical conductivity is high and the temperature coefficient with increasing temperature is positive.



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Superconductivity

17. W. Meissner, H. Franz, H. Westerhoff
Measurement with the Help of Liquid Helium.
XVI-Investigation of Superconduction of Carbides
Z. Physik. 75, 521-30 (1932)

At liquid He temperatures HfC or HfB were not superconductive while the corresponding Zr compounds were superconductive.

18. Karl Becker
Physical Characteristics of High Melting Compounds
Physik. Z. 34, 185-98 (1933)

From r.t. to 1.28 A HfC was not superconductive. (HfB behaved similarly).

* *

Electron Emission

19. Karl Becker
Physical Characteristics of High Melting Compounds
Physik. Z. 34, 185-98 (1933)

Electron emission of the carbide is not known; that of HfN is less than that of pure metals.

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Metallic and Alloying Properties

20. J. S. Anderson
Interstitial and "Berthollide" Compounds
Chem. and Indus. 15, 766-9 (1937)

The carbides, nitrides and borides of Hf, Zr, Ta, Ti, Mo, and W have distinctly metallic properties, viz., they have a metallic luster, conductivity, the specific resistance increasing directly with the absolute temperature; they form alloys with metals, the alloys combining the high melting points and tensile strength necessary for high speed tools.

* *

Miscibility

21. Hans Nowotny, Richard Kieffer
X-ray Investigations of Carbide Systems
Metallforschung 2, 257-65 (1947)

The still-lacking pairs of carbide systems of the 4th and 5th principal groups of elements can be predicted to form uninterrupted mixed crystal series with the exception of HfC-VC.

* *

Heat of Formation

22. W. A. Roth, G. Becker
Atomic Number and Heat of Formation
Z. Physik. Chem. A 159, 1-26 (1932)

At constant pressure and at 20°C the heat of formation of HfC was calculated to be 45 (cals?). Normally there is no linear relation between atomic number and the heat of formation.

CHEMICAL PROPERTIES

23. J. S. Anderson
Interstitial and "Berthollide" Compounds
Chem. & Indus, 15, 766-9 (1937)

Chemically all of the high melting carbides are very inert. TaC is unaffected by water vapor or HCl at 600°C; VaC is attacked by S or Cl only at red heat; strongly oxidizing agents, e.g., HNO_3, react at lower temperatures.

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24. Heraeus-Vacuumschmelze A.-G. and Wilhelm Rohn
Reduction of Oxides
German Patent 600,369 (Sept. 29, 1934)

HfC reacts with HfO_2 in a bath of fused Hf under reduced pressure to form Hf.

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USES

25. Trenhard-Gas. Fur Elek. Gluhlampen M. B. H.
Electric Lamps
German 499,069 (May 24, 1928)

An HfC filament is used.