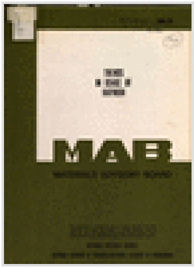

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TRENDS IN USAGE OF HAFNIUM

REPORT

of the

COMMITTEE ON TECHNICAL ASPECTS OF CRITICAL AND STRATEGIC MATERIALS

MATERIALS ADVISORY BOARD
DIVISION OF ENGINEERING - NATIONAL RESEARCH COUNCIL

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ABSTRACT

Hafnium has important applications as a nuclear control rod material, as a base material for oxidation-resistant alloys (with columbium or tantalum), and as a minor constituent in tantalum- , columbium- , tungsten- and nickel-base alloys. The metal is obtained in amounts of 1-6% as a by-product of zirconium purification. Other applications, and the prospects for replacing hafnium with other metals, are mentioned in the report.

HAFNIUM

Background

Hafnium was discovered in 1922 but only minor activity occurred on the characterization, application, and production of this metal until the early 1950's. This is evidenced by the production figures on hafnium shown in Table 1. Hafnium is normally found with zirconium in the mineral zircon as an associated element in the amount of about 2 weight % Hf.

The estimated 1968 hafnium crystal bar yield is about 1% of zirconium output compared to the 2% hafnium in mineral zircon, while the 1964 yield is 4.25%. This anomaly is not fully explained by available data. However, it should be noted that zirconium producers have been processing some high-Hf zircon (about 6% Hf) from Kennecott's Nigerian pyrochlore (Nb) mining operation. This would have been a factor in changing the yield data.

Because of its strong tendency to absorb neutrons, hafnium must be removed from the zirconium before the zirconium can be used in nuclear reactors. In 1951 the Naval Reactors Branch of the Atomic Energy Commission initiated a program for the development of hafnium as a high-reliability control rod material for nuclear reactors used in submarine propulsion.

Applications

Table 2 itemizes those applications of hafnium, its alloys, and its compounds that have been identified. Discussion of some of the key uses follows.

1. Control Rod

Experimental data on hafnium after long exposures in the Shippingport PWR have shown excellent service in respect to neutron absorbing characteristics, hot water corrosion resistance, and mechanical properties. In metallic form it does not have to be clad for use in water cooled reactors, resulting in economic and

TABLE 1

PRODUCTION OF ZIRCONIUM AND HAFNIUM

Calendar Year	Pounds of Reactor Grade Zirconium	Price per Pound of Zirconium	Pounds of Hafnium Crystal Bar	Price per Pound of Hafnium Crystal Bar**
1949	3,000	$150.00*	----	$ ----
1950	30,000	110.00*	----	----
1951	140,000	50.00*	----	----
1952	210,000	40.00*	3,100	93.00
1953	200,000	12.00	5,000	70.00
1954	310,000	13.00	7,700	53.00
1955	425,000	13.00	4,800	46.00
1956	475,000	11.00	6,900	57.00
1957	1,250,000	9.00	12,700	52.00
1958	2,200,000	7.50	18,200	40.00
1959	2,400,000	6.50	19,500	40.00
1960	2,600,000	6.00	44,000	40.00
1961	2,900,000	5.50	50,200	40.00
1962	2,400,000	5.50	44,100	35.00
1963	2,000,000	5.00	42,600	35.00
1964	1,500,000	5.00	63,600	30.00
1965	1,000,000	4.50	32,100	85.00
1966	1,250,000	5.00	32,500	85.00
1967	2,000,000	5.00	27,000	85.00
1968	3,500,000(est)	5.00	36,000(est)	85.00

*This price based on zirconium crystal bar; reactor grade was as high as $1000/lb. The Mark I Nautilus Prototype core used crystal bar metal but the Naval Reactors program on sponge metal improvement raised the purity to the point where the crystal bar purification was not required to make the new Zircaloy core alloy.

**It should be noted that essentially all pricing through 1957 on zirconium and through 1964 on hafnium are actually cost figures of the Atomic Energy Commission. Further, these figures, particularly on hafnium crystal bar, are 'artifical' due to an arbitrary distribution of costs by the AEC between the basic products of the separations plant -- zirconium oxide and hafnium oxide. This assignment of costs, both at the U. S. Bureau of Mines (up until 1957) and during the later long-term contracts with non-Government producers (1957-1964), did not fully take into account an intrinsic distribution of separations costs or subsequent 'commercial risk' factors inherent in this relatively low volume metal. By 1965, full consideration of these factors resulted in costing on a more basic allocation between zirconium and hafnium oxide values as well as further processing costs and material yields through primary metal sponge and crystal bar refining.

TABLE 2

APPLICATIONS OF HAFNIUM AND ITS ALLOYS AND COMPOUNDS

Nuclear Energy

- control rods
- neutron flux depressors

Refractory

- insulators (HfO_2)
- high-temperature-high strength alloys
- oxidation resistance coatings
- filament in electric light bulbs (Hf and HfC)
- electrodes in x-ray, rectifier and high pressure tubes
- fibers in composite materials*
- heat-and wear-resistant parts (HfN)

Miscellaneous

- additive to refractory metal-base alloys
- getters in vacuum tubes*
- photographic flash bulbs*
- detonating caps and ammunition*
- cutting tools (HfB_2 and HfC)
- opacifier (HfO_2)
- optical glasses*

*Evaluated only

reliability advantages. It is unique in the extent to which it meets the requirements of a control rod material.

Hafnium is much more effective than is indicated by its thermal cross section of 105 barns because of its ability to absorb neutrons above thermal energies. This effect, known as resonance energy absorption, roughly doubles the effectiveness of hafnium as a neutron absorbing material and, in addition, this effectiveness changes relatively slowly with irradiation.

A family of hafnium-based ceramics for use as control rod material in commercial nuclear power reactors has recently been developed. Referred to as Rare Earth Pyrohafnates, these materials are compounds of hafnium oxide and oxides of selected rare earths such dysprosium, erbium, and holmium. Such control rods are competitive with silver-indium-cadmium in price and have a slightly greater worth. The Rare Earth Pyrohafnates are potential control rod candidates for commercial nuclear power control rod applications.

Few materials exist which meet all of the requirements for control rod material for the widely used water-cooled nuclear reactors. Materials which can be considered commercially are: Ag-In-Cd, boron stainless steel, and rare earth stainless steel. The final selection is based on individual nuclear design and economic trade-offs. A number of materials with high neutron absorption cross sections, compared in Table 3, have been considered as possible control rod materials.

2. Other Nuclear Uses

Hafnium has been considered for use as a burnable poison and as a neutron flux depressor. Neither of these application areas appears to have significant future requirements. The low burnout rate for hafnium as a poison tends to eliminate it for future consideration.

TABLE 3

MEASURED CONTROL WORTH OF VARIOUS MATERIALS*

Materials	*Amount of principal poisons (w/o)*	*Worth relative to hafnium*
Boron-stainless steel	3.0% B^{10}	1.13
Boron-stainless steel	2.0% B^{10}	1.08
Boron-titanium-hafnium	1.0% B^{10}	1.00
Hafnium		1.00
Silver-indium-cadmium	75% Ag, 20% In, 5% Cd.	1.03
Boron-stainless steel	0.97% B^{10}	0.97
Boron-titanium	1.0% B^{10}	0.96
Eu_2O_3-stainless steel	15% Eu_2O_3	0.94
Indium		0.93
Silver-cadmium	70% Ag, 30% Cd	0.92
Silver		0.88
Cadmium		0.88
Gadolinium-titanium	8.7% Gd	0.73
Eu_2O_3-stainless steel	4.1% Eu_2O_3	0.73
Sm_2O_3-stainless steel	2.7% Sm_2O_3	0.71
Haynes-25 alloy		0.66
Titanium		0.30
Stainless steel (Type 304)		0.24
Aluminum (Type 2S)		0.072
Zircaloy-2		0.049

Notes:

1. The control worth of any material is dependent upon the neutron spectrum of the reactor which, in turn, is a function of the reactor design parameters. The control worths given in the above table were measured in a critical assembly having a spectrum typical of many types of light water-moderated reactors containing highly-enriched uranium fuel.
2. Relative worths are based on 2 x 2 x 0.225 inch specimens.
3. Samples were measured in a slab critical assembly.

*Metallurgy of Hafnium. Edited by D. E. Thomas and E. T. Hayes. U. S. Government Printing Office, Washington, 1960, X11 + 384 pp.

3. Non-Nuclear Uses

a) As a Base Metal

Hafnium has been used as a filament in gas-filled electric light bulbs, and also in rectifiers. It may be used as a component of flash powders, pyrotechnics, and primers. Like its sister metals titanium and zirconium, hafnium is effective as a "getter" in vacuum tubes to scavenge traces of oxygen and nitrogen. All of these historical applications were trial or short runs and should not enter into a consideration for future consumption requirements.

More recently some hafnium-based alloys using tantalum and/or columbium in the amount of 25% are in process of development.[1, 2] The objectives of the various government funded projects are to develop structural hafnium-base alloys for use in oxidizing environments of temperatures above 2000°F. Requirements are that alloys be fabricable, have a useful strength above 2200°F, have ductility as fabricated, as coated, and after air test, and be oxidation resistant in the bare metal state under both static and cyclic conditions to 2500°F and higher.

The Hf-20Ta-2Mo and the Hf-20Ta alloys have been evaluated as leading edge on ram-jet engines and hypersonic vehicles and have been considered to be quite attractive. The former alloy is available in both mill product and powder form. Sylvania reports good protection of columbium and tantalum-base alloys to 3600°F when coated with a member of this family of hafnium-tantalum alloys. All work in this area remains on an experimental or prototype basis. No significant production is projected for the Hf-Ta alloys unless a major redirection occurs in development of manned reentry vehicles.

Thin film capacitors made from hafnium have been evaluated. A hafnium film is deposited on a passive substrate by cathodic sputtering and the dielectric HfO_2 is subsequently produced by wet or plasma anodization. Life testing is underway at RCA. A potential for such capacitors exists if costs can be reduced. A study at Argonne National Laboratory shows almost identical polarization curves for tantalum and hafnium.

b) As an Alloying Element

In the period from 1964 to the present, studies by Westinghouse Astronuclear Laboratory and other companies engaged in research and development of air frame and propulsion units, as well as aerospace systems under Navy, NASA and Air Force funding, led to the development, as prime candidates, of several tantalum and columbium base alloys containing hafnium as a significant alloying element. These alloys are also important in space electric power applications, fuel cladding and isotope encapsulation.

Columbium alloys including

C-261	Cb-25%Ta-15%W-7%Hf-0.10%Y
C-103	Cb-10%Hf-1%Ti
C-129Y	Cb-10%Hf-10%W-0.10%Y

have been the most significant in structural applications and propulsion hardware. An example is C-103, in which over 50,000 pounds of vacuum arc metal ingot have been produced in the last five years (5,000 pounds of hafnium). This 'moderate' strength alloy, used primarily for its ease of fabricability, weldability, coatability and other favorable characteristics has had its highest volume use in the Apollo Project.

A relatively new columbium alloy, WC-3015, (Cb-28%Hf-2%Zr-15%W-4%Ta-0.10%C) is being investigated for gas turbine applications. Due to its oxidation resistance under operating temperatures in excess of 2000°F. The alloy develops a coating (.030"-.040" thick after 24 hours at 2400°F) upon exposure to the atmosphere which protects the core material from contaminants. Although the protective surface migrates toward the center with exposure time, the migration rate is easily within estimated maximum exposure times for turbine applications. This protection, due principally to the hafnium addition, is sufficient to allow mission completion in the event of primary coating failure. It is understood that optimization is under way to achieve improved mechanical properties. This development should be watched carefully, since a single stage of a turbine using WC-3015 blades could use 30-40 pounds of hafnium per engine. If 1000 engines were made employing this alloy, 30,000 to 40,000 pounds of hafnium could be consumed. This single application would consume this year's estimated production of hafnium as well as that associated with increased forecast of future zirconium production.

The NASA-Lewis Research Center developed in 1967 a tungsten alloy containing 4%Re, 0.35%Hf, 0.024%C. This alloy has exceptional high strength at elevated temperature with improved ductility at lower temperatures compared to pure tungsten.

The Canadian Ministry of Energy, Mines and Resources has reported on work they have under way in which hafnium of the order of 0.16-0.22% has been added to structural steels. Tensile tests at 205°C (400°F) on these steels in the as-rolled condition indicated that hafnium suppressed dynamic strain hardening and that, up to 0.22%, it had no effect on the 0.2% yield strength. Normalizing eliminated this effect.

In 1966 a nickel base cast superalloy was developed (TRW-NASA VI A) containing 0.43%Hf.[(4)] This alloy produced under NASA sponsorship for jet engine turbine bucket application represents a substantial improvement of about 50°F in use temperature over present day high strength nickel base superalloys. Experimental results have shown that hafnium is necessary in maintaining the high temperature properties of the alloy. TRW-NASA VI A is currently under intensive investigation by the turbine engine manufacturers; and as a result, is a large potential user of hafnium. If the alloy finds wide acceptance as a turbine engine material, it could conceivably use several thousand pounds of hafnium per year.

c) Hafnium as a Ceramic

Hafnium as contained in ZrO_2 has found a limited usage in the ceramic and glass industries. HfO_2, like ZrO_2, can be used as an opacifier in enamels and glazes. As a high temperature insulator, though highly competitive with ZrO_2 in properties; it has found only highly specialized applications. The natural content of HfO_2 in zirconia adds to its refractoriness because of its higher MP.

Hafnium silicate as a constituent of zirconium silicate improves the performance of zircon by raising the softening temperature.

Some limited work on HfC has been and is under way. The high melting point of 3890°C seemingly offers potential for high temperature applications but this is offset by poor mechanical properties. Wah Chang reports a columbium hafnium carbide that shows promise for application in the cutting tool industry.

Substitutability

The selection of hafnium as a control rod material in commercial reactors, although it possesses highly desirable properties, is based on economic factors. Currently the price of hafnium is about 2 to 2.5 times that of alternate materials. With the increasing price of silver, it has been estimated that hafnium could be competitive with the Ag-In-Cd alloy at Ag = $3.00/oz. In order to make a complete assessment of this aspect of the study, it is necessary to take into account such factors as fabrication costs, unit costs, life cycle, etc., which is beyond the scope of this memorandum. Further, much of the information is proprietary as it is based on design and economic trade-offs. This is a highly fluid area and one that is being constantly reviewed by the commercial reactor builders. A close watch should be maintained as the supply of hafnium could become quite tight.

Hafnium as an alloying element enjoys a secure position. For those applications where the refractory metal is employed as a containment material for alkali liquid metals, hafnium in tantalum is much superior to other getter-strengthener elements. For structural applications, hafnium as an additive element appears to be the most compatible constituent for additions of strength while retaining fabricability. In columbium base alloys, however, zirconium is the preferred element.

If it is necessary to increase the amount of hafnium available, increased production from the Nigerian deposits can possibly be obtained. Also, steps can be taken to remove hafnium from commercial zirconium chemicals (in which the accompanying hafnium is not objectionable and is not removed).

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CORRESPONDENCE

Specific and extremely helpful information was provided by Dr. Earl Hayes, Acting Director, Bureau of Mines (July 11, 1968); Mr. Stephen W. H. Yih, President, Wah Chang, Albany (July 17, 1968); Mr. J. D. Harsch, Sales Engineer, AMAX Specialty Metals (July 18, 1968); Dr. Mel Bleiberg, Westinghouse Advanced Reactors Division (July 8, 1968); Dr. W. A. Johnson, TRW, Cleveland (telecon July 17, 1968); Mr. M. Schussler, Technical Director, Fansteel (August 5, 1968); and, Mr. Frank Kerze, Jr., AEC (July 26, 1968). In particular, the contribution of Wah Chang Albany was well conceived and enabled this memorandum to be more meaningful.

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