Zirconium and Hafnium

By Robert F. Griffith

ZIRCONIUM

Zirconium is a comparatively new metal, which promises greatly expanded usefulness. Interest in zirconium metal increased in 1952 as industry became more aware of its unusual combination of properties. Because it has good structural properties and excellent corrosion resistance, and because it readily allows the passage of slow neutrons (low thermal neutron absorption cross section), zirconium is used as a material of construction for nuclear-reactor plants. One of the significant developments in 1952 was the execution of a contract by the Atomic Energy Commission with Carborundum Metals Co., Akron, N. Y., for the production of 150,000 pounds of zirconium sponge annually for 5 years at less than $15 a pound. As an alloy constituent, zirconium imparts highly desirable properties to steel, magnesium, and other metals. The production of corrosion-resistant zirconium alloys received considerable attention in 1952.

Although over 80 percent of the United States zircon supply is used in refractories, ceramics, and foundry applications, the most spectacular use of zircon (the principal source mineral of zirconium) during the past 2 years has been in the production of metallic zirconium. Zircon reserves are large, and mine-production capacity in the United States is more than ample to satisfy demands. The supply of zirconium metal, however, is limited by existing processing capacities and resultant high price of the metal.

Government controls on quantities of zirconium used in steel production were relaxed on August 27, 1952, by an amendment to National Production Authority Order M–80.

As a result of hafnium-free zirconium produced at the Electrodevelopment Laboratory of the Bureau of Mines, Albany, Oreg., larger quantities of hafnium were available for research. Additional information on hafnium has been confined to the concluding section of the chapter.

DOMESTIC PRODUCTION

Mine Production.—Domestic production of zircon decreased 5 percent in 1952 compared with the record high production in 1951. This slight decrease reflected market conditions rather than production capacity. Three operating companies in Florida marketed zircon in 1952: Rutile Mining Co. of Florida, South Jacksonville; Humphreys Gold Corp., Starke (operating for E. I. duPont de Nemours & Co.

1 Commodity-industry analyst.
on a contract basis); and Florida Ore Processing Co., Melbourne. Quantitative data are not available for publication.

Zircon produced as a result of monazite-dredging operations in Idaho was not marketed because of unfavorable freight rates and market conditions.

**Refinery Production.**—The principal producers of materials containing zirconium are listed below:

<table>
<thead>
<tr>
<th>Producer and plant location</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>F. W. Berk &amp; Co., Woodbridge, N. J.</td>
<td>Zirconium compounds.</td>
</tr>
<tr>
<td>Corhart Refractories Co., Louisville, Ky.</td>
<td>Refractories.</td>
</tr>
<tr>
<td>De Rewal International Rare Metals Co., Philadelphia 5, Pa.</td>
<td>Low-hafnium zirconium oxide and metal powder; zirconium compounds.</td>
</tr>
<tr>
<td>The Massillon Refractories Co., Massillon, Ohio</td>
<td>Zircon crucibles, brick, and special shapes.</td>
</tr>
<tr>
<td>Metal &amp; Thermit Corp., New York 17, N. Y.</td>
<td>Zirconium compounds for ceramics, refractories, etc.</td>
</tr>
<tr>
<td>Stauffer Chemical Co., New York 17, N. Y.</td>
<td>Zirconium tetrachloride.</td>
</tr>
<tr>
<td>Titanium Alloy Manufacturing Division (TAM) of National Lead Co., Niagara Falls, N. Y.</td>
<td>Zirconium metal sponge, briquets, ingots and shapes; alloys; compounds; ground zircon; and stabilized zirconia refractories.</td>
</tr>
</tbody>
</table>

The Carborundum Metals Co., Inc., a subsidiary of the Carborundum Co., Niagara Falls, N. Y., began constructing a plant at Akron, N. Y., to produce zirconium and hafnium metals for the Atomic Energy Commission. The Rust Process Design Co., Pittsburgh, Pa., designed the plant, which will cost an estimated $2.5 million and will produce 150,000 pounds of sponge metal annually. Production was scheduled to begin in July 1953. Zircon sands from Florida will be treated in an electric furnace to make carbide. This phase of the process will be handled by Carborundum Co. in existing facilities. The zirconium carbide will be processed to zirconium chloride; the chloride will be purified, then reduced to metal. The process is a modification of the Kroll process developed at the Bureau
of Mines station at Albany, Oreg. The Titanium Alloy Manufacturing Division of National Lead Co. produced Kroll process zirconium metal for general industrial use.

The Bureau of Mines station, Albany, Oreg., was the principal producer of zirconium metal in 1952; over 200,000 pounds of clean zirconium sponge was produced. A plant fire on October 22, 1952, which began in a dust collector on a sand-blasting machine, caused considerable damage and curtailed production to some extent.

CONSUMPTION AND USES

Consumption of zircon in the United States in 1952 is estimated to have been about 40,000 tons. The largest use was in the manufacture of refractories, followed in order by foundry facings, foundry sand, and blasting grain; porcelains; miscellaneous compounds; metal and alloys; pottery; and glass.

Zircon is used commercially with and without processing; for foundry and some ceramic applications it is only sized and possibly ground. Zircon refractories are desirable because of their resistance to abrasion, low thermal expansion, and resistance to certain molten metals, acidic chemicals, slags, and glasses. Conversion of zirconia (ZrO₂) from the monoclinic to the cubic form has produced a super-refractory with excellent resistance to thermal shock. Among zirconium chemicals, the sulfate is probably the largest tonnage item. Used in tanning white leather, white zirconium oxide is precipitated in the leather fibers. Zircronyl acetate and ammonium zirconyl carbonate are used to render textiles water repellant. Zirconium carbonate is used in salves and ointments and as an antiperspirant. A new-type electric light has, as its light source, a film of molten zirconium metal at the end of a small tube packed with zirconium oxide. This molten film radiates relatively little heat, yet the lamp has over 10 times the brightness of ordinary tungsten lamps.

The current largest use of metallic zirconium is as a material of construction for nuclear-reactor plants. The low absorption cross section of zirconium, which allows the passage of slow neutrons, thus conserving them for their primary function of maintaining a chain reaction, is exceeded among the metals only by beryllium, bismuth, and magnesium. The structural performance and other desirable properties of these metals are inferior to zirconium. High-purity zirconium, "zirmet," is used in power, transmitting, and long-life receiving tubes. Other uses for ductile metallic zirconium are based for the most part on its excellent corrosion resistance. Use of zirconium in ferrous and nonferrous alloys is increasing. Zirconium can be substituted for manganese in steel. Additions of zirconium to sand-cast magnesium-thorium alloys have a beneficial effect on strength at elevated temperatures.

---

2 Metal Progress, vol. 62, No. 6, December 1952, p. 68.
7 Metal Progress (abst.), Zr and Ti Substitutions for Manganese in Steel: Vol. 61, No. 2, February 1952, pp. 162-164.
STOCKS

Industry stocks of zircon concentrates (plus 65 percent ZrO₂) were about 9,000 tons at the close of 1952, down about 1,500 tons from 1951 year-end stocks. Approximately 25 percent of annual consumption was available from stocks. This apparent shortage caused little concern because ample supplies of zircon continued to be readily available. Stocks of other zirconium minerals were insignificant.

Zircon is acquired for the National Stockpile only through transfer of Government-owned stocks. Stockpile quantitative data are not available for publication.

PRICES

E&MJ Metal and Mineral Markets quoted zircon concentrates (65 percent ZrO₂), c. i. f. Atlantic ports, at $47–$50 per long ton in January 1952; $42–$45, April 10; and $42–$43, September 18. These prices were largely nominal, and individual transactions and contracts were negotiated.

Zirconium-metal powder was quoted January through November at $7–$8 per pound, depending on quantity; and December 11, $7 per pound, no reference to quantity. Ductile zirconium metal made by the iodide-reduction process and fabricated forms from that stock produced by Foote Mineral Co. were quoted as follows: Zirconium crystal bar, $70 per pound for 100 pounds and up, $90 per pound for quantities less than 100 pounds; zirconium wire (annealed), 0.070–0.003-inch diameter, $327 to $793 per kilogram; zirconium swaged rod (unannealed), ⅛ to ⅛-inch diameter, $200 to $210 per kilogram; and zirconium sheet, 0.015- to 0.002-inch thick, $289 to $450 per kilogram. Prices for ductile zirconium produced by the Titanium Alloy Manufacturing Division, National Lead Co., and forms fabricated from that stock remained unchanged in 1952. Prices quoted were as follows: Zirconium-metal sponge and briquets, $10 per pound; hot-rolled plate and bars, base price, $27 per pound; hot-rolled strip, base price, $28 per pound; cold-rolled strip, base price, $35 per pound; cold-drawn wire, 0.060- to 0.375-inch diameter, $42.50 to $32.50 per pound, 0.015- to 0.030-inch diameter, $0.08 to $0.15 per foot, respectively. Zirconium tetrachloride was quoted at $0.34 per pound, f. o. b. Niagara Falls, N. Y., in lots of 1 ton to a carload.

Zirconium alloys, contract price, were quoted by Electro Metallurgical Co., Division of Union Carbide & Carbon Co. f. o. b. railroad freight cars at destination as follows: Zirconium-ferrosilicon, 12–15 percent Zr, $0.08 to $0.1075, 35–40 percent Zr, $0.2025 to $0.2525, depending on quantity and size; zirconium briquets (11 percent Zr, 38 percent Si), $0.075 to $0.10 per pound, depending on quantity; and nickel-zirconium (40–50 percent Ni, 25–30 percent Zr) $1.25 to $1.35 per pound, depending on quantity.

The Oil, Paint and Drug Reporter quoted zirconium compounds, per pound, in large lots, f. o. b. New York, as follows: Acetate, January $0.265, June $0.23; carbonate, $0.305; hydride, January $12, June $7.50 to $10, December $7.25 to $11.50; nitrate, $4.50 to $7; and oxide, $1.50.

FOREIGN TRADE

Australia continued to be the principal source of zirconium ore imported for consumption in the United States during 1952. A small quantity, less than 10 percent of the total, came from Brazil. Imports from Australia have been in the form of clean zircon concentrates containing 66 percent ZrO₂ and in mixed zircon-rutile concentrates containing 65 percent zircon, or 43 percent ZrO₂. Since 1949 the trend has been toward separating the heavy minerals before shipment. In 1952, 80 percent of the zircon imported from Australia was in the form of clean zircon concentrates. Twenty-seven pounds of special quality zirconium metal, valued at $500, was imported from the United Kingdom and France.

Exports of zircon concentrates in 1952, principally to Canada, totaled 554 short tons valued at $42,221; 20 tons were exported to Mexico and 1 ton to France. Exports of zirconium metal, alloys, and primary forms totaled 51,151 pounds, valued at $42,677. Canada was the major recipient. Zirconium powder, metal, alloys, and primary forms were retained on the positive list of products requiring export licenses to foreign destinations (except Canada).

**TABLE 1.—Zirconium ore (concentrates)¹ imported for consumption in the United States, 1948–52, by countries, in short tons**

[U. S. Department of Commerce]

<table>
<thead>
<tr>
<th>Year</th>
<th>Australia ²</th>
<th>Brazil</th>
<th>Canada</th>
<th>India</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Short tons</td>
<td></td>
<td></td>
<td></td>
<td>Value</td>
</tr>
<tr>
<td>1948</td>
<td>14,320</td>
<td>3,553</td>
<td>2</td>
<td>279</td>
<td>18,154</td>
</tr>
<tr>
<td>1949</td>
<td>18,839</td>
<td>1,994</td>
<td></td>
<td></td>
<td>20,833</td>
</tr>
<tr>
<td>1950</td>
<td>15,988</td>
<td>697</td>
<td>141</td>
<td></td>
<td>16,936</td>
</tr>
<tr>
<td>1951</td>
<td>25,208</td>
<td>2,084</td>
<td></td>
<td></td>
<td>27,292</td>
</tr>
<tr>
<td>1952</td>
<td>21,935</td>
<td>1,972</td>
<td></td>
<td></td>
<td>23,907</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$571,161</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$636,539</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$431,107</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$644,428</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$630,559</td>
</tr>
</tbody>
</table>

¹ Concentrates from Australia are zircon or mixed zircon-rutile-ilmenite, and those from Brazil are baddeleyite or zircon. All other imports are zircon.

² Imports of zircon, rutile, and ilmenite from Australia until early 1948 were largely in the form of mixed concentrates. These mixed concentrates are classified by the U. S. Department of Commerce arbitrarily as “zirconium ore,” “rutile,” or “ilmenite.” Total zircon content of the zirconium ore (as shown in this table) and of the rutile and ilmenite concentrates (see Titanium chapter) are estimated as follows: 1948 15,573 tons; 1949, 14,023 tons; 1950, 15,098 tons; 1951, 24,577 tons; and 1952, 21,500 tons.

TECHNOLOGY

The specific gravity of zircon (4.7) enables it to be concentrated with other heavy minerals by gravity methods. Clean zircon is produced from heavy-mineral concentrates by a combination of drying, screening, electrostatic, and electro-magnetic processes. Zircon, in contrast to ilmenite, rutile, garnet, and many other heavy minerals, is nonconductive and can be separated, with monazite, by electrostatic methods. Monazite, which is slightly magnetic, can be separated from zircon by electromagnets. To obtain clean zircon, the zircon-rich tailings from the electrostatic-electromagnetic processes are again subjected to gravity concentration (spirals or tables) to eliminate light, nonconductive minerals, such as quartz and feldspar. The enriched product is then usually dried at 1,200° F. to remove organic stainings and treated in high tension separators and induced roll magnetic separators to remove residual conductive and magnetic minerals. A 99-percent zircon product is usually obtained by these methods.

Anhydrous zirconium tetrachloride, the starting material in the magnesium-reduction (Kroll) process for production of ductile zirconium, is now produced by direct chlorination of a zirconium oxide-carbon mixture. The zirconium oxide used in this process is obtained from crude ZrCl₄, which has been processed to remove the hafnium. Crude ZrCl₄ is prepared by smelting zircon sand with an excess of carbon, followed by chlorination of the resultant zirconium carbide.

Zirconium metal is also produced by reduction of ZrCl₄ by sodium (Hunter process), by reduction of ZrO₂ by metallic calcium (developed by the Westinghouse Corp.), and by the iodide process (Van-Arkel-de Boer, used by the Foote Mineral Co.).

High-temperature experiments with zirconium and zirconium compounds conducted by the Bureau of Mines were described, and a report on the mechanical properties of zirconium was published by Sylvania Electric Products, Inc., Atomic Energy Div., December 9, 1952.

Zirconium alloy investigations received considerable attention in 1952. A patent was issued for a pyrophoric alloy of lead and zirconium, which alloy when subjected to a sudden heavy impact is pulverized and set afire. Applications in ammunition as a tracer, as a means for igniting an incendiary mixture, and as an aid to spotting bullet impacts are reported.

---

12 Frost, F. D., Zirconium-Cerium Master Alloys for Magnesium: Battelle Memorial Inst., Columbus, Ohio (Contract No(s(s) 51-001-c), July 1952, 2 pp.
Increased interest in zirconium metal, alloys, and compounds resulted in the description of several zirconium analytical methods.\textsuperscript{13}

**RESERVES**

Zircon is unique among rare-metal minerals in that deposits from which zircon can be extracted economically are plentiful. Zirconium is classed as a rare metal not because of its relative scarcity in the earth's crust (0.02 to 0.03 percent), but because of the difficulty in extracting the metal from its ores. Zirconium is the ninth most common metal in the earth's crust and thus more abundant than copper, lead, zinc, nickel, and some other familiar metals. A fortunate aspect of zircon is that its specific gravity and resistance to abrasion enable it to be concentrated in placer deposits from which it may be extracted cheaply.

Known placer deposits in Florida, California, Idaho, and Oregon are estimated to contain 15 million tons of zircon. These reserves could be increased substantially if the demand for zircon warranted intensive, exploratory campaigns.

Zircon reserves in other parts of the world are known to be extensive. Quantitative data, however, are lacking. In Australia, a 75-mile stretch of beach between Stradbroke Island, Queensland, to Lennox Head, New South Wales, is reported to contain 1 million tons of zircon in high-grade deposits containing more than 300 pounds of heavy minerals per ton.\textsuperscript{14} Extremely large reserves of lower-grade material are known to exist.

Reserves of baddeleyite (ZrO\textsubscript{2}), in Brazil are estimated to be on the order of 2 million tons. Large deposits of zircon are also known in the States of Baia, Espírito Santo, and Rio de Janeiro. Deposits have been found in British, Dutch, and French Guiana and other countries of South America but have not been developed.

Large deposits of zircon are known to occur in India, at the mouth of the Nile River in Egypt, and in beach sands in French West Africa.

**WORLD REVIEW**

**Australia.—** Plans to exploit large, low-grade (2–3 percent heavy minerals) sand deposits at Stradbroke Island, Queensland, by dredging were initiated by the Zinc Corp., 95 Collins St., Melbourne.\textsuperscript{15} The deposits are estimated to contain 10 to 15 pounds each of zircon and rutile per ton of sand.

**Belgian Congo.—** An abundance of zircon has been found in certain alluvials of the following rivers: Yebu, Aruwimi, Ituri, Lowa, Ulindi, Zalya, Luizi, Kalasangashi, Musele, Mayama, and the Lulua. These deposits have not been exploited.\textsuperscript{16}

---


\textsuperscript{16} Mining Journal (London), vol. 239, No. 6118, Nov. 21, 1952, p. 569.

Brazil.—Baddeleyite (ZrO₂) occurs in the Pocos de Caldas district, a mountainous plateau of acidic, igneous rocks at about 3,600 feet elevation. The principal deposits are in an elliptical area about 20 by 15 miles in the States of São Paulo and Minas Gerais approximately 130 miles north of the city of São Paulo. About 3,000 tons are exported annually to the United States, England, Norway, and Germany. About 200 tons are consumed annually in São Paulo, Brazil, by the refractory and ceramic industry.

Egypt.—About 1,200 tons of zircon concentrates (64 percent ZrO₂) are produced annually from large black sand deposits at the mouth of the Nile River.

French West Africa.—Zircon is produced as a coproduct with ilmenite from beach deposits of Senegal and Casamance.

United Kingdom.—An estimated 10,000 tons of zircon was consumed by the refractory industry in England in 1952. Murex, Ltd., Rainham, England, installed facilities to produce zirconium sheet up to 22 inches wide by 5 feet long for use in the chemical industry.17 A plant for the production of zirconium compounds for use in the ceramic and refractory industries was completed at Newcastle-upon-Tyne by Goodlass Wall & Lead Industries, Ltd.18

HAFNIUM

Hafnium, a metallic element discovered in 1923, was little more than a laboratory curiosity until 1951. The metallurgical development of processes to produce hafnium-free zirconium metal has resulted in the availability of larger quantities of hafnium for experimental purposes.

Source.—Hafnium and zirconium have many similar properties and occur together in ore minerals. Known Zr-Hf minerals generally contain much more zirconium than hafnium. Recent studies of zircon from many parts of the world indicate that zircon usually contains 1–1.5 percent hafnium. Altered zircon (for example, the mineral cyrtolite) may contain as much as 17 percent hafnium. There are no known commercial deposits of altered zircon minerals; however, unaltered zircon reserves represent a substantial potential source of hafnium. The hafnium content of the crust of the earth has been estimated to be greater than mercury, columbium, tantalum, or silver. Many high-hafnium minerals exhibit marked radioactivity; the relationship, however, between uranium-thorium and hafnium is not clearly understood.

Properties.—The specific gravity of hafnium (13.3) and atomic weight (178.6) are approximately twice those of zirconium. Hafnium resembles zirconium closely but has a higher melting point (3,590° F.), less ductility, higher electron emission, and a very strong tendency to absorb slow neutrons. This latter property makes hafnium an objectionable impurity in zirconium metal used in nuclear-reactor plant design. The probability that a hafnium nucleus will capture a thermal neutron is approximately 550 times over that of a zirconium nucleus.

Pure hafnium, produced under controlled conditions, is a bright, ductile metal. Although somewhat more difficult to work than duc-

---

17 Metal Industry, Rare-Metal Fabrication: Vol. 80, No. 4, Jan. 25, 1962, p. 66.
tile zirconium because of its greater tendency to absorb gases, hafnium can be bent, deep-drawn, formed, and cold-worked to a maximum reduction of 30 percent between anneals. It can be hammered cold, drawn into wire, and rolled into sheet. Hafnium has excellent resistance to oxidation in still air and has corrosion resistance to certain acids and bases comparable to zirconium.

**Production.**—Several tons of hafnium metal containing less than 2 percent zirconium have been produced by the Bureau of Mines at Albany, Oreg. De Rewal International Rare Metals Co., Philadelphia, Pa., is a pioneer in the production of hafnium metal and compounds. Fairmount Chemical Co., Newark, N. J., reportedly produces hafnium oxide; Metal Hydrides, Inc., Beverly, Mass., has experimented with a hafnium-nickel alloy; Zirconium Co., Flemington, N. J., produces hafnium oxychloride; F. W. Berk & Co., Woodridge, N. J., produces the oxide; and Foote Mineral Co., Philadelphia, Pa., produces iodide crystal bar hafnium from hafnium sponge produced by the Bureau of Mines, Albany, Oreg.

**Uses.**—Most of the hafnium produced to date has been consigned to the Atomic Energy Commission; specific applications have not been revealed. The small quantities of metal and compounds available for experimental industrial applications have been used in chemical and physical research to determine their properties. The oxide and carbide of hafnium are among the most refractory compounds, with melting points of 2,664° and 3,787° C., respectively. Hafnium boride is an extremely hard material. The oxide and salts of hafnium exhibit catalytic properties similar to their zirconium homologues. The high melting point of hafnium and its high degree of electron emission suggest uses in radio tubes, incandescent lamps, and rectifiers and cathodes for X-ray tubes. The high thermal neutron absorption cross-section suggests use for shielding against radioactivity. As a metal for jewelry, hafnium is heavy, probably as tarnish resisting as gold, and can be formed and polished beautifully.

**Prices.**—In 1952, De Rewal International Rare Metals Co. quoted hafnium metal (99.5 percent Hf) and hafnium oxide (99 percent HfO₂) at $22 per gram (100-gram lots). This company announced plans to expand production with expectations of offering hafnium metal at $150 per pound.

**Technology.**—Hafnium can be separated from zirconium by fractional crystallization, fractional precipitation, by the use of ion exchange resins, or by liquid-liquid separation. In the processing of zirconium, commercial zirconium tetrachloride containing hafnium is processed to effect the hafnium separation. Details of this process are not available for publication. The resultant hafnium hydroxide is calcined to hafnium oxide, which is then processed in the same manner as zirconium oxide, with only slight operational changes, to produce hafnium sponge metal. Ductile hafnium metal produced from hafnium sponge by the iodide process (Foote Mineral Co.) contains less than 1 percent zirconium. The high reactivity and sensitivity of hafnium (and zirconium) to the effects of oxygen, nitrogen, and other contaminating elements poses special problems in the production of usefully ductile metal.

Hafnium analyses are usually performed by making a chemical separation and extracting hafnium and zirconium in the form of com-
bined oxide. The oxide is weighed and the percentage determined. The ratio of hafnium to zirconium plus hafnium is determined by X-ray spectroscopy. Results are usually reported in terms of this ratio because, regardless of the purity of the ore sample or the purity of the chloride, oxide, or metal, from that ore, the ratio of hafnium to hafnium plus zirconium is numerically the same. If desired, however, the hafnium content of the original sample can be calculated.

Outlook.—The availability of enough hafnium metal and compounds for industrial purposes may depend upon expanded production of hafnium-free zirconium. If hafnium is not an objectionable impurity in zirconium used for nonreactor applications or unless a strong demand develops for hafnium and its compounds, the large-scale separation of the two metals probably will be undertaken only if a low-cost process is developed.

SELECTED BIBLIOGRAPHY

KROLL, W. J. Production and Uses of Rare Metals. Min. and Met., vol. 27, No. 473, May 1946, p. 262.