Zirconium and Hafnium

By Horace T. Reno

ZIRCONIUM metal, produced in the past almost entirely by the Government, was produced in appreciable quantity in 1954 by private enterprise. Carborundum Metals Co., Inc., using a slight modification of the Kroll process developed in the laboratories of the Bureau of Mines, achieved full output at its Akron, N. Y., plant and filled the company's commitments to the Atomic Energy Commission for zirconium, with excess metal available for sale on the commercial market. National Lead Co. formed a subsidiary, Zirconium Metals Corp. of America, to handle production and sale of zirconium; the new corporation used the Kroll process to make ductile zirconium but did not extract the hafnium content to make a product suitable for use in nuclear reactors. The Bureau of Mines, by virtue of operations at its Albany, Oreg., plant, continued as the principal supplier of zirconium in 1954.

The U. S. S. Nautilus, the atomic-powered submarine in which zirconium was an important material of powerplant construction, completed its trial runs in 1954. Successful performance of the powerplant intensified interest in zirconium and established it as one of the new metals of the atomic age. Low neutron-absorption factor was the property that led to development of improved methods for recovering zirconium; but the additional qualities of high strength, easy formability, and corrosion resistance were the properties that won it final acceptance in the construction of nuclear powerplants. These properties also increased interest in the metal for other uses.

Zirconium, when used for other than nuclear purposes, does not need to be free of hafnium because the presence of a small quantity does not significantly change its physical and chemical properties. Such impure zirconium can be produced for about a third less than hafnium-free zirconium and therefore competes in a broader market. It was used in corrosion-resistant equipment in 1954 and apparently will be an important material in this field. The Bureau of Mines laboratories at Albany, Oreg., used zirconium to make 24 items that required strength and corrosion resistance and found that when they were exposed to corrosive liquids, fumes, and mists the lower maintenance costs involved would more than offset the relatively high cost of the zirconium.

Zircon, the mineral source of most zirconium, was used principally in refractories, foundry sands and facings, and ceramics.

1 Commodity-industry analyst.
DOMESTIC PRODUCTION

Mine Production.—Domestic mine production of zircon decreased from 23,900 short tons valued at $894,900 in 1953 to 16,300 short tons valued at $745,300 in 1954, a decrease of 32 percent in quantity and 17 percent in value. Mine shipments exceeded mine production by 10 percent and decreased mine stocks by 61 percent. All marketed zircon of domestic origin was produced in Florida as a coproduct in the placer mining of monazite and titanium minerals. Zircon produced in Idaho as a byproduct of monazite dredging was not marketed because of unfavorable freight rates and is not included in domestic production figures.

Refinery Production.—The Kroll-process zirconium-hafnium plant of Carborundum Metals Co., Inc., placed in operation late in 1953, achieved full production in 1954, and the company began to actively seek new markets for its zirconium products when production exceeded the quantity required to fill AEC contract commitments. The Bureau of Mines zirconium-hafnium production plant at Albany, Oreg., however, continued to be the major United States producer, with an output of more than 310,000 pounds of zirconium sponge and over 7,000 pounds of hafnium sponge for the AEC.

The zirconium oxide plant of Zirconium Corp. of America, Solon, Ohio, began production in 1954. At full capacity the plant will produce 8,000 pounds of pure zirconium oxide a day. Firth Sterling Corp., Trafford, Pa., installed consumable-electrode arc-melting equipment with a capacity to melt 10,000 pounds of zirconium metal sponge a month. Zirconium Metals Corp. of America, a subsidiary of National Lead Co., began production of wrought zirconium-metal products.

Other processors of zircon and manufacturers of zirconium and hafnium products were:

<table>
<thead>
<tr>
<th>Producer and plant location</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bureau of Mines, Northwest Electrodevelopment Experiment Station, Albany, Oreg.</td>
<td>Hafnium-free zirconium sponge, zirconium-alloy ingots, and hafnium sponge.</td>
</tr>
<tr>
<td>Carborundum Metals Co., Inc., Akron, N. Y.</td>
<td>Hafnium-free zirconium sponge and zirconium compounds.</td>
</tr>
<tr>
<td>Corhart Refractories Co., Louisville, Ky.</td>
<td>Refractories.</td>
</tr>
<tr>
<td>DeRewal International Rare Metals Co., Philadelphia 5, Pa.</td>
<td>High-purity zirconium-metal powder, oxide, and compounds.</td>
</tr>
<tr>
<td>Electro Metallurgical Division, Union Carbide &amp; Carbon Corp., New York 17, N. Y. (Plants at Niagara Falls, N. Y., Sheffield, Ala., and Alloy, W. Va.)</td>
<td>Hafnium-metal powder, oxide, and compounds.</td>
</tr>
<tr>
<td>Kawecki Chemical Co., New York 17, N. Y.</td>
<td>Iodide-process zirconium crystal bar, hafnium crystal bar, and zirconium-metal shapes.</td>
</tr>
</tbody>
</table>

Refractories.
Producers and plant locations:

- Metal & Thermite Corp., New York 17, N. Y.
- Pacific Graphite Co., Inc., 40th and Linden, Oakland, Calif.
- Shieldalloy Corp., New York 17, N. Y.
- Stauffer Chemical Co., New York 17, N. Y.
- Chas. Taylor & Sons (subsidiary of National Lead Co.) Cincinnati, Ohio.
- Titanium Alloy Mfg. Division of National Lead Co., New York 6, N. Y.
- Titanium Zirconium Co., Inc., Fleming, N. J.
- Zirconium Corp. of America, Solon, Ohio.
- Zirconium Metals Corp. of America (subsidiary of National Lead Co.) New York 6, N. Y.

Products:

- Zirconium compounds for pottery industry.
- Zirconium-metal powder, zirconium hydride, and zirconium alloys.
- Fused, stabilized zirconia refractories and granular zirconia.
- Granular and milled zirconium silicate and zirconium porcelain, enamels, refractories, glass, and pottery.
- Foundry facings.
- Zirconium sulfate solution (tanning agent).
- Milled and granular zircon.
- Zirconium tetrachloride (custom chlorination).
- Refractories.
- Stabilized zirconia refractories and ground zircon.
- Zirconium salts and compounds.
- Zirconium crystal bars and metal shapes.
- Stabilized zirconia and zirconium compounds.
- Ductile zirconium and zirconium compounds.

Consumption and uses:

Zircon consumption in the United States in 1954 was estimated at 42,000 tons, a decrease of 3,000 tons compared with consumption in 1953. By far the largest quantity was used in refractories, foundry sand and facings, and ceramics. According to information furnished by principal dealers and consumers, about 7 percent of the zircon consumed was used in metals and alloys and less than 2 percent in chemicals and salts.

Zircon sand is superior to silica sand for foundry purposes because it has uniform grain size, is a better heat conductor, and is not wetted by molten metals. It is replacing metal shot as a chilling medium in magnesium castings. Zircon and zirconium compounds were widely used in ceramics, ceramic enamels, and glazes. A zircon-cordierite ceramic body that has near zero porosity (preventing infiltration of molten metal or other liquids) and high resistance to heat shock was developed. The protective-coatings industry used zirconium complex of a synthetic acid as a drier catalyst. Hydrous zirconium dioxide, both alone and with carbonate, was used to cure dermatitis resulting from poison ivy and zirconium compounds, including hydrous zirconia and zirconium lactate, were used as personal deodorants. Combinations of zirconium acetate, zirconyl carbonate, and wax emulsion were used to render textiles water repellent. Pure zirconium oxide was used as an opacifier in antimony and sheet-steel enamels.

2. Gregg, G. W., Zirconium Metal as a Drier Catalyst: Paint Ind. Mag., vol. 1, No. 4, April 1954, pp. 17-19.
Zirconium in the form of zirconium-ferrosilicon found wide application as a deoxidizer and scavenger of nitrogen and sulfur in the manufacture of steel. Zirconium tetrachloride and zirconium tetrafluoride with alkali chlorides were used to refine the grain and increase the strength of magnesium castings.\(^5\)

Zirconium was employed more extensively in 1954 as a corrosion-resistant material. The Bureau of Mines published descriptions of some useful applications of zirconium, including a list of 24 specialized items ranging from a zirconium-lined tank to proportioning pump parts and laboratory apparatus.\(^6\)

**STOCKS**

Industrial stocks of zircon concentrate (plus 65 percent ZrO\(_2\)) totaled about 9,600 tons at the close of 1954. National stockpile data cannot be published.

**PRICES**

E&MJ Metal and Mineral Markets quoted zircon concentrate (65 percent ZrO\(_2\)), c. i. f. Atlantic ports, at $42–$43 per long ton to January 21, $45–$46 per long ton to May 13, $47–$48 per long ton to December 16, and $48–$49 to the end of the year.

Zirconium-metal powder was quoted in E&MJ Metal and Mineral Markets throughout 1954 at $7 per pound. Zirconium alloy, 12–15 percent Zr, 39–43 percent Si, bulk, carload lots, was quoted at 7¢ per pound to March 18 and 8¢ per pound to the end of the year; and 35–40 percent Zr, 47–52 percent Si, was quoted at 20.25¢ per pound throughout the year.

Commercial quotations were as follows:

**Zirconium Metals Corp. of America (subsidiary of National Lead Co.), late 1954**

- Zirconium-metal sponge and briquets, per pound: $10.00
- Zirconium hot-rolled plate and bars, per pound, base price: 27.00
- Zirconium cold-rolled strip, per pound, base price: 35.00
- Zirconium cold-drawn wire 0.060–0.375 inch in diameter, per pound: 42.50–32.50

**Foote Mineral Co., late 1954**

Iodide-process ductile zirconium metal:
- Zirconium crystal bar, lots over 100 pound, per pound: $70.00
- Zirconium wire annealed, 0.050–0.005 inch diameter, per kilogram: 450.00–600.00
- Zirconium sheet, 0.010–0.002 inch thick, per kilogram: 425.00–750.00
- Zirconium powder, pyrotechnic grade, 100-pound lots or over, per pound: 10.50

**Electro Metallurgical Division of Union Carbide & Carbon Co., late 1954, f. o. b. railroad freight cars at destination**

Zirconium-ferrosilicon:
- 12–15 percent Zr per pound, depending on quantity and quality: $0.08 – 0.1075
- 35–40 percent Zr per pound, depending on quantity and quality: 0.2525–0.3025

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\(^5\) Work cited in footnote 4.

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Electro Metallurgical Division of Union Carbide & Carbon Co., late 1954, f. o. b. railroad freight cars at destination—Continued

Zirconium briquets (11 percent Zr, 38 percent Si) per pound, depending on quantity ......................................................... $0.075 -0.10
Nickel-zirconium (40-50 percent Ni, 25-30 percent Zr) per pound, depending on quantity ........................................... 1.25 -1.35

DeRewal International Rare Metals Co., late 1954

Hafnium-metal powder (99.3 percent), per gram ........................................ $25.00
Hafnium oxide (99.5 percent), per gram ............................................ 17.00
Hafnium tetrachloride (99 percent), per gram ...................................... 16.00
Hafnlyl sulfate, nitrate, and chloride (99 percent), per gram ............... 15.00

FOREIGN TRADE

Although domestic capacity to produce zirconium concentrate was reported to be adequate to supply United States requirements, a substantial quantity was imported from Australia and Brazil. Australian imports were in the form of zircon concentrate; Brazilian imports were predominately baddeleyite. The average declared value of zircon imported from Australia in 1954 was $20.32 per short ton. The average declared value of zirconium ore concentrate imported from Brazil was $96.70 per short ton.

Exports of zirconium ore and concentrate to Canada and Mexico in 1954 totaled 692 short tons valued at $42,725. Exports of zirconium metals and alloys in crude form and scrap to Canada and Austria totaled 39,678 pounds valued at $5,254. Two pounds of semifabricated zirconium forms valued at $593 was exported to Japan.

Reexports of ore and concentrate to Canada and Japan in 1954 totaled 1,347 short tons valued at $65,317.

TABLE 1.—Zirconium ore (concentrates) 1 imported for consumption in the United States, 1945-49 (average) and 1950-54, by countries, in short tons

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</thead>
<tbody>
<tr>
<td>North America: Canada</td>
<td>1</td>
<td>141</td>
<td></td>
<td>2,084</td>
<td>1,972</td>
<td>1,206</td>
</tr>
<tr>
<td>South America: Brazil</td>
<td>2,678</td>
<td>697</td>
<td></td>
<td>2,084</td>
<td>1,972</td>
<td>1,206</td>
</tr>
<tr>
<td>Asia: India</td>
<td>862</td>
<td></td>
<td></td>
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<tr>
<td>Africa: French West Africa</td>
<td>1</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Oceanica: Australia 2</td>
<td>19,021</td>
<td>15,588</td>
<td>25,208</td>
<td>21,655</td>
<td>22,461</td>
<td>17,249</td>
</tr>
<tr>
<td>Total: Short tons</td>
<td>22,593</td>
<td>16,826</td>
<td>27,292</td>
<td>23,907</td>
<td>24,667</td>
<td>18,657</td>
</tr>
<tr>
<td>Value</td>
<td>$621,342</td>
<td>$431,107</td>
<td>$664,428</td>
<td>$630,599</td>
<td>$717,783</td>
<td>$486,555</td>
</tr>
</tbody>
</table>

1 Concentrates from Australia are zircon or mixed zircon-rutile-limonite, and those from Brazil are baddeleyite or zircon. All other imports are zircon.
2 Imports of zircon, rutile, and limonite 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 "limonite." Total zircon content of the "zirconium ore" (as shown in this table) and of the "rutile" and "limonite" concentrates (see Titanium chapter) are estimated as follows: 1949, 14,623 tons; 1950, 14,098 tons; 1951, 24,877 tons; 1952, 21,600 tons; 1953, 22,200 tons; and 1954, 16,300 tons.
3 Owing to changes and tabulating procedures by the U. S. Department of Commerce data are not comparable to earlier years.

4 Figures on imports and exports compiled by Mae B. Price and Elsie D. Page, Division of Foreign Activities, Bureau of Mines, from records of the U. S. Department of Commerce.
TECHNOLOGY

Until 1954 many of the properties reported for zirconium were actually properties of zirconium containing some hafnium. Hafnium is intimately associated with zirconium in ores, and owing to the chemical similarity of the two elements separation is difficult. Investigators recognized the need for specifying both the chemical analysis and purification methods used when reporting results of physical tests of zirconium. Consequently, in 1954 more or less agreement was achieved on the fundamental properties of zirconium.

The Kroll process and the iodide process for making ductile, malleable, hafnium-free zirconium have been refined during the past few years so that purer metals can now be produced on a large scale. Some of the mechanical properties of these purer metals were investigated.8

Zirconium has relatively poor mechanical properties at elevated temperatures. It was found that binary additions of tungsten, chromium, vanadium, columbium, tantalum, and molybdenum strengthen zirconium at 1,800° to 2,200° F. but that all except tantalum and vanadium markedly reduce the workability. Molybdenum, tungsten, and chromium proved most effective.9 A study was made of tensile properties, hot hardness, and impact strength of arc-melted binary alloys of iodide-process zirconium containing up to 1 weight-percent chromium, iron, or nickel in the annealed condition.10

Because zirconium mineral concentrates have high melting points, a large part of the cost of producing the metal is in the expense of fusing its ores. Caustic fusion processes for treating zirconium minerals were investigated.11

The problem of separating hafnium from zirconium on a commercial scale was solved in 1953, but the details of the process were classified and remained classified through 1954. However, results were published on investigations of liquid-liquid extraction of zirconium and hafnium and on the behavior of the elements in cation-exchange resin.12

It was found that zirconia and zircon refractories may be more stable if they contain hafnium. Zirconium oxide for use in refractories must be stabilized to overcome crystal inversion because its monoclinic lattice is unstable at 1,100° C. The presence of hafnium probably would raise the inversion temperature because the lattice of hafnium

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oxide is stable at 1,700°C. A system of zirconium chemistry was suggested.14

RESERVES

Domestic zirconium-ore reserves have been estimated to contain 5 to 15 million tons of zirconium minerals. A slight increase in the value of zircon would make marginal deposits economic, doubling the present reserve figures. Florida beach deposits are believed to be adequate to supply domestic zirconium requirements at the present rate of consumption for more than 100 years.

Total free-world reserves of zirconium ore are unknown, but the known reserves, principally in Brazil, India, and Australia, are believed to be of the order of 10 million tons of contained zirconium minerals in deposits that are now being worked.

WORLD REVIEW

Australia.—Australia, the free world’s principal commercial source of zircon, produced 44,143 short tons of zircon in 1954, the largest quantity since 1951, when 47,006 short tons was produced. Australian zircon concentrates have been preferred by the molding and casting trade because they have a slightly larger grain size (between 80- and 100-mesh) than concentrates mined in India and the United States. About 1,000 tons has been consumed annually in Australia; the remainder was exported. Principal buyers of Australian zircon were United States, United Kingdom, and Japan.

Brazil.—Brazilian zirconium-mineral production apparently declined from a 7-year average (1946 to 1952) of 4,000 short tons to about 1,500 tons in 1953 and 1954. Probably the decrease was caused by the Government withdrawing radioactive lands on the Pocos de Caldes plateau from production.

Egypt.—Zircon was recovered at the mouth of the Nile River in Egypt as a coproduct in the mining of ilmenite, garnet, magnetite, and monazite. Mining was on a small scale, only 109 short tons of zircon concentrates being produced in 1954.

TABLE 2.—World production of zirconium ores and concentrates, by countries, 1945–54, in short tons

(Compiled by Pauline Roberts)

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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>17,002</td>
<td>13,891</td>
<td>24,165</td>
<td>25,017</td>
<td>23,488</td>
<td>24,120</td>
<td>47,006</td>
<td>32,893</td>
<td>31,655</td>
<td>44,143</td>
</tr>
<tr>
<td>Brazil</td>
<td>4,836</td>
<td>4,109</td>
<td>4,385</td>
<td>4,011</td>
<td>2,977</td>
<td>3,325</td>
<td>3,854</td>
<td>4,378</td>
<td>1,406</td>
<td>1,408</td>
</tr>
<tr>
<td>Egypt</td>
<td>11</td>
<td>4</td>
<td>104</td>
<td>141</td>
<td>105</td>
<td>4</td>
<td>133</td>
<td>263</td>
<td>109</td>
<td></td>
</tr>
<tr>
<td>French West Africa</td>
<td>43</td>
<td>211</td>
<td>270</td>
<td>243</td>
<td>2</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>India</td>
<td>1,142</td>
<td>522</td>
<td>( )</td>
<td>( )</td>
<td>( )</td>
<td>( )</td>
<td>( )</td>
<td>( )</td>
<td>1,047</td>
<td>1,012</td>
</tr>
<tr>
<td>United States</td>
<td>2,681</td>
<td>7,946</td>
<td>( )</td>
<td>( )</td>
<td>( )</td>
<td>( )</td>
<td>( )</td>
<td>( )</td>
<td>23,904</td>
<td>16,322</td>
</tr>
</tbody>
</table>

1 Estimated zircon contents of all zircon-bearing concentrates.
2 Chiefly baddeleyite.
3 Exports.
4 Imports into the United States.
5 Data not available for publication.

French West Africa.—French West Africa produced 1,012 short tons of zircon concentrate in 1954, which supposedly was exported to France.

India.—Zircon was produced in India as a coproduct in the mining of radioactive minerals. Production figures have not been published since 1946.