# ZIRCONIUM AND HAFNIUM

### By Joseph Gambogi

Zirconium and hafnium are relatively abundant in the Earth's crust; however zircon (zirconium silicate) is the only naturally occurring mineral of commercial significance. Zirconium and hafnium are both contained in zircon at a ratio of about 50:1. Zircon is a byproduct of the mining and processing of heavy mineral sands for the titanium minerals rutile and ilmenite. The major end uses of zircon are refractories, foundry sands (including investment casting), and ceramic opacification.

World production of zirconium mineral concentrates was estimated to have increased slightly in 1995. Worldwide, zircon consumption was estimated to have increased by 2.8%.<sup>1</sup>

U.S. production and consumption of zircon concentrates were withheld to avoid disclosing company proprietary data. Domestic production of milled zircon increased 5% in 1995. According to U.S. Customs trade statistics, the United States was a net importer of zirconium ore and concentrates, and imports increased 14%.

With the exception of prices, all data in this report have been rounded to three significant digits. Totals and percentages were calculated from unrounded numbers.

#### Production

Data for zirconium and hafnium materials are developed by the U.S. Geological Survey from one voluntary survey of domestic operations. Of the 34 operations surveyed, 24 responded, representing 78% of the domestic production data in table 1. Data for nonrespondents were estimated based on prior-year levels. Domestic production and consumption of zircon concentrates were withheld to avoid disclosing company proprietary data. Milled zircon production increased 5% from that of 1994, while zirconium oxide production increased 17% from the 1994 level . (*See table 1.*)

U.S. mine producers of zircon in 1995 were RGC (USA) Mineral Sands, Inc. and E. I. du Pont de Nemours & Co. Inc. (Du Pont). Both producers mined heavy mineral sands deposits in Florida. U.S. producers of zirconium and hafnium metal were Teledyne Wah Chang (TWC), Albany, OR, and Western Zirconium, Ogden, UT. Primary zirconium chemicals were produced by TWC and Magnesium Electron Inc., Flemington, NJ. Secondary zirconium chemicals were produced by about 10 companies, and zirconia was produced from zircon sand at plants in Alabama, New Hampshire, New York, Ohio, and Oregon.

#### Consumption

Approximately 95% of all zirconium consumed is in the form

of zircon, zirconium oxide, or other zirconium chemicals. The remainder is consumed as zirconium metal and zirconium-containing alloys.

The mineral zircon is used for facings on foundry molds. Zircon facings increase resistance to metal penetration and afford a uniform finish to castings. Milled or ground zircon is used in refractory paints for coating the surfaces of molds. Zircon, in the form of refractory bricks and blocks, is used in furnaces and in hearths for containing molten metals. Zircon is also used in manufacturing fused cast and bonded aluminazirconia-silica-base (AZS) refractories for glass tank furnace use. The mineral baddeleyite is used principally in the manufacture of alumina-zirconia abrasives, but also is used in ceramic colors and refractories.

Stabilized zirconium oxide exhibits high light reflectivity and good thermal stability and is primarily used as an opacifier and pigment in glazes and colors for pottery and other ceramic products. Yttria-stabilized zirconia is used in the manufacture of sensors that control combustion in furnaces and automobile engines.

Because of its low thermal neutron absorption cross section, hafnium-free zirconium is used as cladding for nuclear fuel rods. Commercial-grade zirconium, unlike nuclear grade, contains hafnium and is used in the chemical process industries because of its excellent corrosion resistance. Hafnium is used in nuclear control rods because of its high thermal neutron absorption cross section. However, the largest end use for hafnium metal is as an alloy addition in superalloys.

#### Prices

Increased demand, primarily from the ceramic industry, caused prices of zircon-base concentrates to increase by about 38% from the 1994 level. Published prices for zirconium, hafnium, and zirconium oxide products were unchanged. (See table 2.)

#### **Foreign Trade**

In 1995, the United States was a net importer of zirconium ore and concentrates. Australia and the South Africa supplied about 98% of the imports of ores and concentrates. Overall imports of ore and concentrates increased about 14% from those of the previous year.

In contrast to 1994, the United States was a net importer of zirconium and hafnium metal in 1995. Imports of unwrought and waste and scrap zirconium metal increased 317% compared with those of the previous year. U.S. imports of zirconium from

France, Germany, Japan, and the United Kingdom increased significantly. U.S. imports of unwrought and waste and scrap hafnium were nearly unchanged. *(See tables 3 and 4.)* 

#### **World Review**

World production of zirconium mineral concentrates was estimated to have increased 3% compared with that of 1994. Australia and South Africa supplied an estimated 85% of the total world production. (*See table 5.*)

*Australia.*—Broken Hill Proprietary Co. made plans to proceed with the development of the Beenup deposit in Western Australia. The operation, scheduled to be commissioned in 1996, was expected to produce 600,000 metric tons per year of ilmenite and 20,000 tons per year of zircon.<sup>2</sup>

RZM Pty. announced the closure of its Tomango milling operations. RZM was awaiting mining leases for mining operations at Clybucca, which would supply the milling plant. According to the company, the operation would be closed for an indefinite period of time.<sup>3</sup>

*China.*—Owing to increased consumption in the ceramic industry, China's imports of zircon sand, flour, and zirconium silicates increased dramatically in 1995. According to industry reports, Chinese demand for zircon was estimated to be 158,000 tons in 1995.<sup>4</sup>

*Germany.*—At yearend, Du Pont agreed to acquire the organometallic titanates and zirconates businesses of Hüls AG. Under the terms of the agreement, Hüls would manufacture organometallics at its Rheinfelden, Germany, facility, and Du Pont would continue to produce the product at its Deepwater, NJ, facility.<sup>5</sup>

**United Kingdom.**—Alcan Aluminum PLC was in the process of divesting itself of 12 downstream businesses, including MEL Chemicals Inc. In 1995, MEL was a major producer of zirconia and zirconia chemicals with operations in Swinton, Manchester, and Flemington, NJ (Magnesium Electron). The new owners were institutional investors led by Mercury Development Capital, Morgan Grenfell Development Capital, and CVC Capital Partners.<sup>6</sup>

#### Outlook

Zircon's major end use recently has moved from refractories to opacification. The trend of higher growth in opacification is likely to continue with increased demand most evident in Asia and Europe. The tight supply of zircon resulted in increased prices of zirconium products in 1995. However, over the next few years, the supply and demand of zircon is expected to be in closer balance. Expansions in supply are expected in Australia, Africa, and the United States, while exploration and development efforts are likely in Brazil, Canada, Russia, and Vietnam. Global demand for zirconium materials is expected to increase 3% annually over the next few years.

<sup>1</sup>Mining Journal. Mineral Sands Reviewed. V. 327, No. 8402, Nov. 1, 1996, pp. 358-359.

<sup>2</sup>Industrial Minerals. BHP's Beenup Minsand Project to Go Ahead. No. 329, Feb. 1995, p. 8.

<sup>3</sup>———. Licensing Hold Up Leads RZM to Force Majeure. No. 338, Nov. 1995, p. 15.

<sup>4</sup>Roskill's Letter from Japan. Zircon: China Leads Growth in Demand. No. 237, Jan. 1996, p. 12.

<sup>5</sup>Chemical Marketing Reporter. Du Pont Buys Titanates. Jan. 1, 1996, p. 9.

<sup>6</sup>Alcan Aluminum Ltd. Company Press Release. Alcan Aluminum Limited Completes Sale of British Alcan Downstream Businesses. Feb. 12, 1996, 3 pp.

#### **OTHER SOURCES OF INFORMATION**

#### **U.S. Geological Survey Publications**

Zirconium and Hafnium. Ch. in Mineral Commodity Summaries, annual.

- Klemic, H., S. P. Marsh, and M. Cooper. Zirconium and Hafnium Ch. in United States Mineral Resources, USGS Professional Paper 820, ed. by D. A. Brobst and W. P. Pratt, 1973, pp. 713-722.
- Towner, R. R., International Strategic Minerals Inventory Summary Report-Zirconium. USGS Circular 930-L, 1992, 47 pp.

#### **Other Sources**

- American Metal Market, daily newspaper.
- Chemical Engineering, biweekly.
- Chemical Week, weekly.
- Engineering and Mining Journal, monthly.

Industrial Minerals (London), monthly.

Metal Bulletin (London), semiweekly.

Mining Engineering, monthly.

Mining Magazine and Mining Journal (London), monthly and weekly.

Platt's Metals Week, weekly.

Roskill Information Services Ltd. (London). The Economics of Zirconium, 7th edition, 1992.

## TABLE 1 SALIENT U.S. ZIRCONIUM STATISTICS 1/

#### (Metric tons)

	1991	1992	1993	1994	1995
Zircon:					
Production:					
Concentrates	103,000	108,000	W	W	W
Milled zircon	44,400	45,100	46,700	53,300	56,000
Exports	31,300	27,900	35,900	32,000	40,300
Imports for consumption 2/	35,700	37,400	70,000	82,000	93,600
Consumption, apparent 2/	111,000	121,000	W	W	W
Stocks, Dec. 31: Dealers and consumers 3/	24,400	21,600	26,000	30,100	33,100
Zirconium oxide:					
Production 4/	9,750	8,690	10,000	12,100	14,200
Exports 5/	NA	NA	1,280	1,220	1,680
Imports for consumption 5/	NA	NA	1,990	2,400	4,370
Consumption, apparent	NA	NA	W	W	W
Stocks, Dec. 31: Producer 4/	872	719	W	W	W

NA Not available. W Withheld to avoid disclosing company proprietary data.

1/ Data are rounded to three significant digits.

2/ Includes insignificant amounts of baddeleyite.

3/ Excludes foundries.

4/ Excludes intermediate oxides associated with metal production.

5/ Includes germanium oxides and zirconium dioxides.

TABLE 2
PUBLISHED YEAREND PRICES OF ZIRCONIUM AND HAFNIUM MATERIALS

Specification of material	1994	1995
Zircon:	_	
Domestic, standard-grade, f.o.b. Starke, FL, bulk, per short ton 1/	\$278.00	\$319.00
Domestic, 75% minimum quantity zircon and aluminum silicates, Starke, FL, bulk, per short ton 1/	254.00	291.00
Domestic, premium-grade zircon, Starke, FL, bulk, per short ton 1/	309.00	354.00
Imported sand, ceramic application, f.o.b., bulk, per metric ton 2/	\$230.00 - 240.00	\$290.00 - 360.00
Imported sand, refractory application, f.o.b., bulk, per metric ton 2/	230.00 - 240.00	300.00 - 360.00
Imported sand, foundry sand application, f.o.b., bulk, per metric ton 2/	210.00 - 230.00	290.00 - 360.00
Baddeleyite, imported concentrate: 3/	_	
98% to 99% ZrO2, minus 100-mesh, c.i.f. Atlantic ports, per pound	.82 .88	.91 .95
99%+ ZrO2, minus 325-mesh, c.i.f. Atlantic ports, per pound	1.13	
Over 99% ZrO2, minus 100-mesh, c.i.f. Atlantic ports, per pound		1.32 - 1.36
Zirconium oxide: 4/	_	
Powder, commercial grade, drums, 2,000-pound minimum, per pound	3.00 - 6.60	3.00 - 6.60
Electronic, same basis, per pound	3.50 - 8.00	3.50 - 8.00
Insulating, stabilized, 325° F, same basis, per pound	3.35 - 4.00	3.35 - 4.00
Insulating, unstabilized, 325° F, same basis, per pound	3.35 - 4.00	3.35 - 4.00
Dense, stabilized, 300° F, same basis, per pound	3.60	3.60
Zirconium: 5/		
Powder, per pound	75.00 - 150.00	75.00 - 150.00
Sponge, per pound	9.00 - 12.00	9.00 - 12.00
Sheets, strip, bars, per pound	20.00 - 50.00	20.00 - 50.00
Hafnium: Sponge, per pound 5/	75.00 - 95.00	75.00 - 95.00

1/ E. I. du Pont de Nemours & Co. Inc. price list, July 1, 1994, and July 1, 1995, respectively.

2/ Industrial Minerals (London). No. 327, Dec. 1994, p. 63 and No. 339, Dec. 1995, p. 65.

3/ American Vermiculite Corp. baddeleyite price lists.

4/ Chemical Marketing Reporter. V. 247, No. 1, Jan. 2, 1995; and v. 248, No. 26, Dec. 25, 1995, p. 33.

5/ American Metal Market. V. 102, No. 232, Dec. 2, 1994, p. 6 and v. 103, No. 250, Dec. 29, 1995, p. 6.

 TABLE 3

 U.S. EXPORTS OF ZIRCONIUM, BY CLASS AND COUNTRY 1/

	19	19	1995	
	Quantity	Value	Quantity	Value
Class and country	(metric tons)	(thousands)	(metric tons)	(thousands)
Ore and concentrates:				
Argentina	272 r.	/ \$155	554	\$217
Belgium	110	50	365	198
Brazil	1,210	290	1,190	354
Canada	3,860	2,190	7,850	3,150
China	- 565	404	1,080	974
Colombia	2,350	1,580	2,510	1,910
Dominican Republic	- 98	72	234	236
Ecuador	153	92	153	106
France	660	291	791	451
Germany	5,940	1,930	8,790	3,450
Hong Kong	- 95	64	779	758
Indonesia	175	114	624	592
Italy	104	49	956	298
Japan	223	239	659	267
Korea, Republic of	- 113	60 r	/ 158	85
Malaysia	175	123	273	263
Mexico	9,300	2,790	8,770	2,800
Netherlands	2,320	580		
Pakistan	176	122	371	313
Philippines	- 59	43	215	192
Singapore	488	314	78	92
Spain	30	13	201	99
Taiwan	576	382	286	222
United Kingdom	630	323	1,770	1,500
Venezuela	1,390	926	1,380	1,260
Other	959	r/ 711	r/ 287	226
Total	32,000	13,900	40,300	20,000
Unwrought zirconium and waste and scrap:				
Japan	119	4,630	58	1,620
Other	- 104	1,940	105	2,900
Total	223	6,570	164	4,520

r/ Revised.

 $1/\operatorname{Data}$  are rounded to three significant digits; may not add to totals shown.

Source: Bureau of the Census.

TABLE 4

#### U.S. IMPORTS FOR CONSUMPTION OF ZIRCONIUM AND HAFNIUM, BY CLASS AND COUNTRY 1/

	1994		1995	
	Quantity	Value	Quantity	Value
Class and country	(metric tons)	(thousands)	(metric tons)	(thousands)
Zirconium ore and concentrates: 2/				
Australia	45,500	\$6,960	52,900	\$12,000
South Africa	35,800	6,850	38,800	10,500
Other	714	1,070	1,860	2,960
Total	82,000	14,900	93,600	25,400
Zirconium, unwrought and waste and scrap:				
Canada	57	58	66	66
France	28	198	161	167
Germany	49	637	379	385
Japan	29	42	105	111
United Kingdom	19	130	66	70
Other	5 r/	46 r/	7	8
Total	188	1,110	785	807
Hafnium, unwrought and waste and scrap:				
France	4	783	5	827
Germany	(3/)	86	(3/)	186
Hong Kong			(3/)	113
United Kingdom	(3/)	2		
Total	5	871	5	1,130

r/ Revised.

1/ Data are rounded to three significant digits; may not add to totals shown.

2/ Australia and South Africa are believed to be point of origin; other countries are point of shipment.

3/ Less than 1/2 unit.

Source: Bureau of the Census.

#### TABLE 5

#### ZIRCONIUM MINERAL CONCENTRATES: WORLD PRODUCTION, BY COUNTRY $1/\,2/$

#### (Metric tons)

Country	1991	1992	1993	1994	1995 e/
Australia	292,000	355,000	414,000	502,000	510,000 3/
Brazil 4/	18,590	16,874	13,252 r/	17,061 r/	15,000
China e/	15,000	15,000	15,000	15,000	15,000
India e/	18,200	18,000	17,000 r/	18,000	18,000
Indonesia e/	2,500	2,500	2,500	2,500	2,000
Malaysia	5,579	2,608	2,184	1,656	3,790 3/
Russia e/ 5/	XX	3,000	2,500	2,500	2,500
Sierra Leone	1,119	1,329		1,300 e/	
South Africa e/ 6/	230,000	243,000 r/	243,000 r/	226,000 r/	250,000
Sri Lanka	26,123	13,368	14,401	22,310 r/	20,000
Thailand	2,573	1,723	707	326 r/	300
Ukraine e/	XX	75,000	70,000	65,000	60,000
U.S.S.R. e/ 7/	80,000	XX	XX	XX	XX
United States	103,000	108,000	W	W	W
Total	795,000	856,000 r/	795,000 r/	874,000 r/	897,000

e/ Estimated. r/ Revised. W Withheld to avoid disclosing company proprietary data. XX Not applicable.

1/World totals, U.S. data, and estimated data are rounded to three significant digits; may not add to totals shown.

2/ Includes data available through July, 19, 1996.

3/ Reported figure.

4/ Includes production of baddeleyite-caldasite.

5/ Includes production of baddeleyite.

6/ Includes production of zircon and baddeleyite.

7/ Dissolved in Dec. 1991.