ZIRCONIUM AND HAFNIUM

By Joseph Gambogi

Zirconium and hafnium are relatively abundant in the Earth's crust; however, zircon is the primary naturally occurring mineral of commercial significance. Baddeleyite, a natural form of zirconia (ZrO₂), has some minor 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 ilmenite and rutile. 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 decreased 4% in 1996. U.S. production and consumption of zircon concentrates were withheld to avoid disclosing company proprietary data. Domestic production of milled zircon decreased slightly in 1996. According to U.S. Customs trade statistics, the United States was a net importer of zirconium ore and concentrates. However, during 1996 the United Sates was less import reliant than in 1995. Imports of zirconium ore and concentrates increased slightly while exports increased 13%.

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 33 operations surveyed, 23 responded, representing 70% 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 was nearly unchanged compared with that of 1995, while zirconium oxide production increased 6%. (See table 1.)

Zircon is normally produced as a byproduct of the mining and processing of heavy-mineral sands for the titanium minerals rutile and ilmenite. U.S. mine producers of zircon in 1996 were RGC (USA) Mineral Sands, Inc. and E.I. du Pont de Nemours and Co. (DuPont). Both producers mined heavy-mineral sand deposits in Florida. U.S. producers of zirconium and hafnium metal were Wah Chang, Albany, OR, and Western Zirconium, Ogden, UT. Primary zirconium chemicals were produced by Wah Chang and Magnesium Elektron 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.

In 1996, RGC began construction of production facilities at the Old Hickory deposit south of Richmond, VA. Initial production was expected to commence in 1997 with a mine life of approximately 17 years. When the mine is fully operational, RGC expects to produce up to 30,000 metric tons per year of zircon (Mineral Sands Report, 1997b).

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.

Zircon, used for facings on foundry molds, increases resistance to metal penetration and gives 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. Glass tank furnaces use fused cast and bonded alumina-zirconia-silica-base refractories. 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

In 1996, a tight supply of zirconium-base concentrates caused prices to increase significantly compared with those of 1995. Domestic prices of standard-grade zircon increased 31% compared with those of 1995. Prices for imported grades of zircon experienced similar increases. Published prices for zirconium, hafnium, and zirconium oxide products were unchanged. (See table 2.)

Foreign Trade

According to U.S. Customs trade statistics, the United States was a net importer of zirconium ore and concentrates in 1996. U.S. imports of zirconium ore and concentrates were 92,500 tons, nearly unchanged compared with those in 1995. Australia and South Africa supplied about 99% of the imports of ores and concentrates.

The United States was a net exporter of zirconium and hafnium metal in 1996. Imports of unwrought zirconium and waste and scrap metal were 619 tons, a 16% decrease compared with those of 1995. The leading import sources of zirconium were Canada and France. U.S. exports of zirconium metal and waste and scrap were 136 tons, a 17% decrease compared with those of 1995. U.S. imports of unwrought hafnium and waste and scrap were 8 tons, a 60% increase compared with those of 1995. (See tables 3 and 4.)

World Review

Excluding U.S. production, world production of zirconium mineral concentrates in 1996 is estimated to be 857,000 tons, a 4% decrease compared with that of 1995. Australia and South Africa supplied about 84% of all non-U.S. production. World reserves of zircon are estimated to be 32 million tons ZrO₂, while identified world resources of zircon exceed 60 million tons ZrO₂. During 1996, the zirconium industry was active in the exploration and development of mineral deposits on a global basis, particularly in Australia, Kenya, Mozambique, and South Africa. (See table 5.)

Australia.—Australia is the largest producer of zircon concentrates in the world. In 1996, major producers of zircon concentrates were RGC (USA) Mineral Sands Ltd., Westralian Sands Ltd., Tiwest Joint Venture, Cable Sands Ltd., and Consolidated Rutile Ltd. (CRL). Although industry estimates of production were nearly unchanged compared with those of 1995, official sources reported production of zircon concentrates decreased significantly in 1996 (Mineral Sands Report, 1997a).

At the end of 1996, BHP Titanium Minerals Pty. Ltd.'s Beenup project in Western Australia was close to being commissioned. At full capacity, the operation was expected to produce 20,000 tons per year of zircon as a byproduct of its ilmenite production. Shipments of heavy-mineral concentrates were scheduled to begin in 1997 (Broken Hill Proprietary Company, 1996.)

CRL relocated the dredge and floating concentrator from its exhausted Bayside deposit to its Ibis-Alpha heavy- mineral deposit on North Stradbroke Island. During the transition, the plant was upgraded to process up to 3,000 tons of sand per hour. According to the company, the operation has an expected life span of 9 years (Mining Journal, 1996). In 1996, RGC acquired controlling interest in Cudgen RZ Ltd. Through the acquisition, RGC now holds controlling interest in CRL (Industrial Minerals, 1996b).

India.— Cookson Group plc. announced that its joint

venture with Johnson Matthey, Cookson Matthey Ceramics (CMC), was constructing a zircon-base opacifier facility near Bangalore. The new facility adds to the list of international CMC operations in Germany, Italy, Spain, the United Kingdom, and the United States, CMC plans to construct a similar facility in Malaysia. No details regarding capacity were released (Cookson Group plc., 1996).

Japan.—Tosoh Corp. increased its zirconia powder capacity from 270 to 370 tons per year. Zirconia powder is produced by Tosoh from zircon sand through a batch process of hydrolysis followed by calcining, milling, and spray drying. Increased demand for zirconia powder by the electronics industry was cited as the driving force for the expansion (Industrial Minerals, 1997).

Kenya.—In 1996, Tiomin Resources Inc. identified several mineral sands deposits and acquired an 80% interest in the licensed mineral rights for prospecting areas along the Kenyan coast. Pangea Goldfields Inc. retained 20% interest in the properties. According to Tiomin, a resource of 2 billion tons grading 3% heavy minerals has been defined by preliminary drilling and sampling. In 1996, Tiomin commenced a drilling program on the Mamburi, Sokoke, Kwale, Mombasa, and Sabaki deposit areas (Tiomin Resources Inc., 1996).

Mozambique.—Gencor Ltd. and Edlow Resources' joint venture TiGen completed a prefeasiblity study of a heavy-mineral deposit near Moebase. Exploration results indicated a resource in excess of 1,000 million tons containing 4% heavy minerals. The prefeasibility study concluded ilmenite from the deposit could be used to produce titanium slag suitable for use by chloride-route pigment operations (Gencor Ltd., 1996).

South Africa.—South Africa is the second largest source of zirconium minerals production in the world. Zirconium minerals are produced from three sources. Heavy-mineral mining operations of Richards Bay Minerals and Namakwa Sands Ltd. yield zircon concentrates while baddeleyite is produced at Palabora as a byproduct of open pit copper and phosphate mining.

The Palabora Mining Co. reported production of baddelyite concentrates in 1996 was 11,400 tons, a decrease of 14% compared with that of 1995. Palabora decided to proceed with plans to produce zirconium-based sulfate from zircon. Production is expected to commence in August 1997, with full production of 7,900 tons per year containing 38% ZrO₂ targeted for 1999 (Palabora Mining Company Ltd., 1996).

Iscor Ltd. was proceeding with plans to develop its heavy-mineral production at the Hilendale deposit near KwaZulu-Natal. When completed, capacity at the operation is expected to include 35,000 tons per year of zircon (Iscor Heavy Minerals, 1996)

Vietnam.—Bimal Minerals Co. completed construction and commenced production of heavy-minerals concentrate at its wet separation plant at Cat Khahn in Binh Dinh Province. Bimal is a joint venture between Binh Dinh Minerals Co., Malaysia Mining Co., and Pendorong Co. Bimal plans to truck the concentrate from the wet separation plant to its existing dry separation plant in Degi. Although titanium mineral production

began in 1996, the zircon-bearing fraction from the separation plant was stockpiled for future upgrading (Industrial Minerals, 1996a).

Outlook

Global demand for zirconium materials is expected to increase by 3% annually over the next few years. A relatively tight supply of zircon resulted in increased prices of zirconium products in 1996. 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 Mozambique, South Africa, and the United States, while further exploration and development efforts are likely in India, Kenya, Ukraine, and Vietnam.

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¹Prior to January 1996, published by the U.S. Bureau of Mines.

TABLE 1 SALIENT U.S. ZIRCONIUM STATISTICS 1/

(Metric tons)

	1992	1993	1994	1995	1996
Zircon:					
Production:	_				
Concentrates	108,000	W	W	W	W
Milled zircon	45,100	46,700	53,300	56,000	55,300
Exports	27,900	35,900	32,000	40,300	35,000
Imports for consumption 2/	37,400	70,000	82,000	93,600	92,500
Consumption, apparent 2/	121,000	W	W	W	W
Stocks, Dec. 31: Dealers and consumers 3/	21,600	26,000	30,100	33,400 r/	33,700
Zirconium oxide:					
Production 4/	8,690	10,000	12,100	14,200	15,000
Exports 5/	NA	1,280	1,220	1,680	1,480
Imports for consumption 5/	NA	1,990	2,400	4,370	5,240
Consumption, apparent	NA	W	W	W	W
Stocks, Dec. 31: Producer 4/	719	W	W	W	W

- r/ Revised. 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.

 ${\it TABLE~2} \\ {\it PUBLISHED~YEAREND~PRICES~OF~ZIRCONIUM~AND~HAFNIUM~MATERIALS} \\$

Specification of material		1996
Zircon:	1995	
Domestic, standard-grade, f.o.b. Starke, FL, bulk, per short ton 1/		\$419.00
Domestic, 75% minimum quantity zircon and aluminum silicates, Starke, FL, bulk, per short ton 1/	291.00	381.00
Domestic, premium-grade zircon, Starke, FL, bulk, per short ton 1/	354.00	489.00
Imported sand, ceramic application, f.o.b., bulk, per metric ton 2/	\$290.00 - 360.00	\$410.00 - 440.00
Imported sand, refractory application, f.o.b., bulk, per metric ton 2/	300.00 - 360.00	390.00 - 425.00
Imported sand, foundry sand application, f.o.b., bulk, per metric ton 2/	290.00 - 360.00	380.00 - 420.00
Baddeleyite, imported concentrate: 3/		
98% to 99% ZrO2, minus 100-mesh, c.i.f. Atlantic ports, per pound	.9195	.91
Over 99% ZrO2, minus 100-mesh, c.i.f. Atlantic ports, per pound	1.32 - 1.36	1.13
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

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 ${\bf TABLE~3} \\ {\bf U.S.~EXPORTS~OF~ZIRCONIUM,~BY~CLASS~AND~COUNTRY~1/}$

	19	95	1996	
	Quantity	Value	Quantity	Value
Class and country	(metric tons)	(thousands)	(metric tons)	(thousands)
Ore and concentrates:				
Argentina	554	\$217	234	\$272
Belgium	365	198	672	390
Brazil	1,190	354	1,590	706
Canada	7,850	3,150	7,920	3,780
China	1,080	974	349	474
Colombia	2,510	1,910	1,800	2,050
Dominican Republic	234	236	255	303
Ecuador	153	106	127	147
France	 791	451	1,090	836
Germany	8,790	3,450	8,420	4,320
Hong Kong		758	1,560	1,660
Indonesia	624	592	429	519
Ireland			114	134
Italy	956	298	166	114
Japan	659	267	268	102
Korea, Republic of	158	85	347	251
Malaysia	273	263	136	159
Mexico	8,770	2,800	5,110	2,420
Pakistan	371	313	20	15
Philippines	215	192	78	92
Singapore	78	92	215	272
Spain	201	99	276	269
Sweden			528	259
Taiwan	286	222	195	206
United Kingdom	1,770	1,500	1,330	1,040
Venezuela	1,380	1,260	1,480	1,650
Other	287	226	338	324
Total	40,300	20,000	35,000	22,800
Unwrought zirconium and waste and scrap:				
Japan	58	1,620	32	713
United Kingdom	24	627	41	1,250
Other	81 r/	2,270 r/	64	1,580
Total	164	4,520	136	3,550
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r/ Revised.

Source: Bureau of the Census.

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

 ${\bf TABLE~4} \\ {\bf U.S.~IMPORTS~FOR~CONSUMPTION~OF~ZIRCONIUM~AND~HAFNIUM,~BY~CLASS~AND~COUNTRY~1/}$

	19	95	1996	
	Quantity	Value	Quantity	Value
Class and country	(metric tons)	(thousands)	(metric tons)	(thousands)
Zirconium ore and concentrates:				
Australia	52,900	\$12,000	44,500	\$15,000
South Africa	38,800	10,500	47,100	19,700
Other	1,860	2,960	943	1,530
Total	93,600	25,400	92,500	36,200
Zirconium, unwrought and waste and scrap:				
Canada	185 r/	1,190 r/	117	1,630
France	393 r/	31,200 r/	309	23,100
Germany	82 r/	10,800 r/	46	7,770
Japan	38 r/	725 r/	44	1,690
Netherlands			37	2,480
United Kingdom	15 r/	172 r/	28	161
Other		588 r/	38	922
Total	735 r/	44,600 r/	619	37,800
Hafnium, unwrought and waste and scrap:				
Australia			(2/)	32
France	5	827	7	1,190
Germany	(2/)	186	1	311
Hong Kong	(2/)	113		
United Kingdom			(2/)	46
Total	5	1,130	8	1,580
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r/ Revised.

Source: Bureau of the Census.

 ${\bf TABLE~5}$ ZIRCONIUM MINERAL CONCENTRATES: WORLD PRODUCTION, BY COUNTRY 1/2/

(Metric tons)

Country	1992	1993	1994	1995	1996 e/
Australia	355,000	414,000	502,000	505,000 r/	462,000 3/
Brazil 4/	16,874	13,252	17,064 r/	16,343 r/	16,500
China e/	15,000	15,000	15,000	15,000	15,000
India e/	18,000	17,000	18,000	18,000	19,000
Indonesia e/	2,500	2,500	2,500	2,000	2,000
Malaysia	2,608	2,184	1,656	3,790	3,600
Russia e/ 5/	3,000	2,500	2,500	2,500	2,500
Sierra Leone e/	1,329 3/	1,200 r/	1,300		
South Africa e/ 6/	243,000	243,000	226,000	250,000	260,000
Sri Lanka	13,368	14,401	22,310	20,000 e/	21,000
Thailand	1,723	707	326	r/	
Ukraine e/	75,000	70,000	65,000	60,000	55,000
United States	108,000	W	W	W	W
Total	856,000	796,000 r/	874,000	893,000 r/	857,000

e/ Estimated. r/ Revised. W Withheld to avoid disclosing company proprietary data.

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

^{2/} Less than 1/2 unit.

^{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 June 18, 1997.

^{3/} Reported figure.

^{4/} Includes production of baddeleyite-caldasite.

^{5/} Includes production of baddeleyite.

^{6/} Includes production of zircon and baddeleyite.