

GERMANIUM

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Germanium is a grayish-white, metallic element with electrical characteristics between those of a metal and an insulator, making it a semiconductor. It is commercially available as a tetrachloride, a high-purity oxide, and in the form of zone-refined metal ingots, single-crystal bars, castings, doped semiconductors, optical materials, optical blanks, and other specialty products. Germanium is used principally in fiber optics, in infrared optics, and in polymerization catalysts. Its excellent mechanical, optical, and electrical properties, as well as its moderate cost and availability in large sizes make it attractive in many aerospace applications.

The domestic germanium industry consisted of two zinc mining operations in Alaska and Tennessee, which supplied byproduct germanium concentrates to the export market, and three refineries, in New York, Oklahoma, and Pennsylvania. The refineries processed manufacturer's scrap, imported semirefined materials, and a small amount of old (postconsumer) scrap. Domestic refinery production, which amounted to slightly less than one-third of the world refinery production in 1997, was estimated to be valued at about \$30 million. Domestic refinery production and consumption for germanium are estimated by the U.S. Geological Survey (USGS) on the basis of discussions with domestic producers. Both domestic refinery production of germanium and U.S. consumption were estimated to have increased moderately in 1997.

The USGS estimated domestic germanium reserves at 450,000 kilograms (kg), equivalent to 16 years of domestic consumption at the 1997 rate; figures for worldwide reserves were not available. Worldwide, germanium resources are associated with zinc and lead-zinc-copper sulfide ores.

As a strategic and critical material, germanium was included in the National Defense Stockpile (NDS) in 1984, with an initial goal of 30,000 kg of germanium metal. In 1987, a new NDS goal of 146,000 kg was established; this was adjusted downward in 1991

to 68,198 kg. In 1995, the Defense Logistics Agency (DLA), which maintains the NDS, made plans to sell germanium at a rate of 4,000 kg per year through 2005. The annual quantity was increased to 6,000 kg in 1997. All of the material offered is zone refined polycrystalline germanium metal (U.S. Department of Defense, 1997). The proposed amount for annual sales is a significant portion of the domestic and world market. After selling 6,553 kg in 1997, the yearend inventory was 61,654 kg of germanium metal.

Production

The USGS estimated domestic refinery production from primary and semirefined materials in 1997 to be 20,000 kg, 11% more than in 1996 and twice as much as in 1993, 1994, or 1995. In 1997, Eagle-Picher Industries Inc.'s Quapaw, OK, Electro-Optic Materials Department remained the largest producer in the

United States, but it was no longer recovering germanium from zinc smelter residues, which typically contain very small amounts of germanium (less than 1%). Eagle-Picher produced germanium from reprocessed scrap, fly ash, germanium concentrates (typically containing 5% germanium or more) and semirefined germanium materials.

Cabot Corp., Revere, PA, and Atomergic Chemetals Corp., Plainview, NY, produced germanium from reprocessed scrap and semirefined foreign material. The zinc refinery at Clarksville, TN, which Savage Resources Ltd. acquired in 1994, continued to produce germanium-rich residues as a byproduct of processing zinc ores from its associated Elmwood-Gordonsville Mine. The new operating company, Savage Zinc, Inc., continued the established practice of shipping these residues to Union Minière's Germanium Business Unit in Belgium for germanium recovery and refining.

Consumption

The USGS estimated domestic consumption of germanium in 1997 at approximately 28,000 kg, a moderate increase from the 1996 level. The domestic use pattern was similar to the world use pattern, which was estimated to be fiber optics 40%, polymerization catalysts 20%, electrical/solar applications 15% to 20%, infrared optics 10%, and other uses (as phosphors, in metallurgy, and in chemotherapy) 10% to 15%.

Fiber optics continued to be the principal industrial end use for germanium in the United States. In the fiber optics sector, germanium was employed as a dopant within the core of many optical fibers used by the telecommunications industry. Germanium lenses and windows are transparent to infrared radiation. Therefore, they can be used in infrared optical systems in the same ways ordinary glass lenses and windows are used in visible light optical systems. These optics are employed principally for military guidance and weapon-sighting applications. Germanium glass was also used for nonmilitary surveillance and monitoring systems in fields such as satellite systems and fire alarms. An increase in consumption for nonmilitary systems has not matched the decline in military consumption, accounting for the decrease noted for the infrared optical sector.

Prices

In 1995, domestic producer prices for germanium metal and dioxide increased for the first time over the long-standing price levels established in late 1981 (\$1,060 and \$660 per kilogram, respectively). Throughout this 15-year period, significant discounting by producers occurred because of competition from imported materials. In 1995 and 1996, producer prices for zone refined metal reportedly reached \$1,375 and \$2,000/kg, respectively, and germanium dioxide producer prices rose to \$880

and \$1,300/kg, respectively. In 1997, the prices fell back to \$1,475/kg for the metal and \$950/kg for the dioxide.

Free market prices for germanium dioxide, published by *Metal Bulletin*, started 1997 at \$1,200 to \$1,280/kg and ended the year in the \$675 to \$750/kg range. The price for Belgian-produced germanium dioxide, published by *Metal Bulletin*, remained at \$935/kg throughout 1997, the same level as in most of 1996. The dramatic fall in prices for 1997 was caused by a weakening of demand in the second half of the year and stockpile sales from Russia, the United States, and the Ukraine.

Adequate supply for consumers and potential sales from national stockpiles kept prices from going up although the U.S. DLA refused to sell metal below \$1,350/kg in mid-summer (Mining Journal, 1997).

Foreign Trade

In 1997, the estimated germanium content of imports was approximately 24,000 kg, about 14% less than in 1996. Russia, Belgium, China, the Ukraine, and the United Kingdom, in descending order of shipments, accounted for approximately 91% of U.S. germanium imports for 1997. (See table 1.) Imports directly attributable to China and countries of the former Soviet Union amounted to about 60% of the total. Trade reliance on large shipments from these countries is a fairly new pattern, beginning in 1993.

World Review

World refinery production of primary germanium was estimated at 63,000 kg in 1997, an increase of about 19% from 1996 production levels; and 18,000 kg of germanium was recycled worldwide. Sales from the Russian and Ukrainian stockpiles totaled almost 20,000 kg. The world total market supply was slightly more than 105 metric tons (t) in 1997. Consumption lagged behind this total, allowing 10 t of metal to increase producer stocks. World consumption was nearly 10% higher than was reported for 1996 (Roskill's Letter from Japan, 1997). Most of the growth is due to the strength of the fiber optics sector.

Japan.—Although the Japanese market for polyethylene terephthalate (PET) containers has shown steady growth in almost every year of this decade, the market for germanium dioxide for catalysts used in the production of PET softened in 1997 due to weakness in the Yen and the Japanese economy and more effective recycling programs for PET. Catalysts for PET constitute 71% of the germanium market in Japan. Recycled PET consumption quadrupled in Japan in 1997 and rose from 3% to 11% of the market (Roskill's Letter from Japan, 1997).

Ukraine.—Ukraine's Zaporozhye titanium/magnesium plant sold more than 4 t of germanium from government reserves to raise money for modernization. The metal was sold to two European companies. The value of the sale was estimated at more than \$6 million (Metal Bulletin, 1997a).

Current Research and Technology

The task of accurately aligning and affixing fibers or lenses to the photonic devices such as fiber optic cables or laser diodes, commonly known as "pigtailling," remains one of the most difficult and expensive steps in the manufacturing process. Automation is finding wider acceptance as a means for lowering costs and providing improved quality and performance in high-volume applications. Operators only load and unload the parts and interface with sophisticated control software. In a recent demonstration of the next level of automation at Lawrence Livermore National laboratory, an automated fiber-pigtailling machine loaded, aligned, and epoxy-bonded conveyor-loaded trays of multichannel waveguides without operator assistance (Heyler, 1997).

Germanium is used in gallium arsenide/germanium solar cells that reduce weight and increase power available to NASA's Earth Observing System spacecraft. The new cells produce twice as much power and are 20% to 30% smaller and 20% to 25% lighter than conventional silicon solar cells. This is a big enough difference to allow launch by means of a less expensive rocket (McHale, 1997).

Outlook

In 1997, worldwide germanium supplies exceeded demand for this specialty metal and its related products only because material was available from recycling and national stockpiles. Increased production from North America, releases from the national stockpile holdings of Russia, the Ukraine, and the United States, and increased shipments from China continued to meet the demand and allowed up to 10 t of metal to be restocked by producers. However, future germanium supplies could tighten if increased demand from the fiber optics sector continues as has been projected (Talmedge, 1997), and new or expanded sources of supply are not brought on-line in the near future. In fact, if present production levels are not increased, when stockpiles are exhausted, prices of refined germanium may be expected to rise again to elevated levels (Roskill's Letter from Japan, 1997). If prices remain elevated, competition from alternative materials will become an increasingly significant factor in germanium markets, and recycling will grow (Metal Bulletin, 1997b).

References Cited

- Heyler, Randy, 1997, Automation boosts low-cost fiber pigtailling: *Photonics Spectra*, v. 31, no. 1, p. 100-101.
- McHale, John, 1997, TRW uses first flexible blanket gallium arsenide solar array: *Military and Aerospace Electronics*, v. 8, no. 7, p. 4.
- Metal Bulletin, 1997a, Germanium quiet as Ukrainian material is released: *Metal Bulletin*, no. 8160, March 10, p. 9.
- 1997b, Prices continue to drift lower, demand firm: *Metal Bulletin*, no. 8191, June 30, p. 8.
- Mining Journal, 1997, Minor metals in July: *Mining Journal*, v. 239, no. 8441, August 8, p. 125.
- Roskill's Letter from Japan, 1997, Germanium—Growth in demand led by the use of high-purity germanium tetrachloride in optical fibres: *Roskill's Letter from Japan*, no. 256, August, p. 2-6.

Talmedge, D.M., 1997, North American market for singlemode fiberoptic interconnect hardware to reach \$457.6 million by 2001: *Fiberoptic Product News*, v. 12, no. 2, p. 13.

U.S. Department of Defense, 1997, Strategic and critical materials report to the Congress: U.S. Department of Defense, January 15, Washington, DC, 48 p.

SOURCES OF INFORMATION

U.S. Geological Survey Publications

Germanium. Ch. in *Mineral Commodity Summaries*, annual.¹

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

Germanium. Ch. in *Minerals Yearbook*, annual.¹

Gallium, germanium, and indium. Ch. in *United States mineral resources*, U.S. Geological Survey Professional Paper 820, 1973.

Other

Germanium. Ch. in *Mineral facts and problems*, U.S. Bureau of Mines Bulletin 675, 1985.

Platt's Metals Week.

TABLE 1
U.S. IMPORTS OF GERMANIUM, BY CLASS AND COUNTRY 1/

Class and country	1996		1997	
	Gross weight (kilograms)	Value	Gross weight (kilograms)	Value
Unwrought and waste and scrap:				
Australia	--	--	5	\$11,500
Austria	6	\$6,170	--	--
Belgium	3,960	6,700,000	6,680	13,100,000
Canada	1	4,430	57	83,200
China	2,860	4,490,000	3,420	5,240,000
Estonia	169	254,000	37	44,800
Finland	64	70,500	--	--
France	26	36,300	--	--
Germany	493	306,000	272	348,000
Hong Kong	50	45,800	63	152,000
Israel	106	229,000	91	154,000
Japan	96	180,000	--	--
Korea, Republic of	--	--	100	25,000
Latvia	96	95,600	--	--
Netherlands	108	75,400	83	157,000
Romania	39	19,000	--	--
Russia	14,600	13,100,000	8,420	11,800,000
Spain	--	--	500	601,000
Taiwan	--	--	846	67,700
Ukraine	296	447,000	2,000	3,180,000
United Kingdom	4,550	4,720,000	1,090	1,410,000
Total	27,500	30,800,000	23,700	36,500,000

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

Source: Bureau of the Census.