BISMUTH AND BISMUTH ALLOYS

1. Introduction and History

Bismuth [7440-69-9] (Bi) is a very brittle, silvery metal having a high metallic luster. The element is found in the periodic table of the elements under Group 15 (Va). The atomic number is 83 and the atomic weight is 208.98. Bismuth is next to lead on the periodic table and exhibits many characteristics of lead except that bismuth is considered nontoxic despite its heavy-metal status.

Bismuth was first mentioned in the literature by a German monk named Basil Valentine in the fifteenth century. During the sixteenth century, another German, a scientist, Georgius Agricola, detailed the smelting of bismuth from ore (1). Compounds of bismuth were first used in that century for the relief of stomach disorders. Bismuth compounds are still widely used today for the same purpose, in particular bismuth subsalicylate.

Before the 1800s bismuth was usually referred to as one of the elements with which it was associated, such as antimony, lead, tin, or silver. During the 1800s the metal was refined and proven to be an element. Since that time, many varied uses have been found for the element bismuth from metallurgical applications to fusible alloys to chemical applications.

The Bismuth Institute, located in Belgium, is a nonprofit organization whose sole purpose is to provide information on bismuth and its uses. The Institute publishes papers and abstracts that report advances in the uses of bismuth in *The Bulletin of the Bismuth Institute*. The Bismuth Institute has a Web site: http://www.bismuth.be.

2. Occurrence

Bismuth is a minor metal, that is, it is a mining by-product and is therefore not mined for its own intrinsic value. Usually, bismuth is a by-product of lead or copper ores. However, tungsten ore in China contains bismuth. Until the 1980s some bismuth was mined for its own value from the Tasna mine, which is owned by Comibol, the state-owned mining company of Bolivia. Unfortunately, the fluctuation of world bismuth prices over the years has made it economically impossible to keep that mine open.

Since the late 1990s, however, Corriente Resources of Canada has leased the Tasna mine and has initiated studies into the feasibility of reopening it. This will probably not happen before 1999 and only if bismuth prices rise and remain over the $4.00 level during 1998.

The concentration of bismuth in the earth's crust has not been clearly determined. Estimates range from 0.008 to 0.1 ppm. Oceanic manganese nodules contain bismuth in a range of 0.5–24 ppm. (see OCEAN RAW MATERIALS). Silicic rock contains the next highest concentration of bismuth, at 0.02–0.9 ppm (2).

3. Properties

Bismuth has unique properties that make it a valuable metal for certain industrial applications. These properties are characterized by a low melting point, a high density, and expansion on solidification. Bismuth is one of only two metals that expand on solidification. The solid metal floats on molten metal just as ice floats on water. Gallium is the other metal that does the same. Bismuth is a poor electrical conductor and is the most diamagnetic of the metals. The thermal conductivity of bismuth is lower than that of most other metals. Tables 1 and 2 list many of the properties of bismuth.

4. Production

Bismuth is a mining by-product, primarily from the mining of ores such as copper and lead. Tungsten, tin, and molybdenum ores also may contain bismuth. Significant quantities of bismuth are mined in Australia, Bolivia, Canada, China, Japan, Mexico, Peru, and the United States. Mining & Chemical Products, Ltd., in the United Kingdom and Sidech in Belgium are major refiners of bismuth in the West operating with concentrates. World production is summarized in Table 3 (3).

In Australia, bismuth is mined as a by-product of copper ores and exported for refining. As mentioned earlier, the Tasna mine in Bolivia is the only location in the world where the concentration of bismuth is high enough to make mining for bismuth even remotely worthwhile. That mine was closed during most of the 1980s because the price of bismuth was so low that it was not economical to keep the mine open. Only during the late 1990s was there been renewed interest in opening the Tasna mine.

Table 1. **Physical Properties of Bismuth**

Property	Value
boiling point °C	1,560
Bi–Bi bond length at 25°C, nm	0.309
crystal ionic radius, nm	
Bi^+	0.098
Bi^{3+}	0.096
Bi^{5+}	0.074
crystal structure	Rhombohedral
density, kg/m^3	
20°C	9800
271°C[a]	9740
271°C[b]	10,070
600°C	9660
electrical resistivity, $\Omega\cdot cm$	
0°C	106×10^{-6}
20°C	120×10^{-6}
expansion on freezing, % by volume	3.3
hardness, Mohs scale	2.5
magnetic susceptibility	
solid	-280×10^{-13}
liquid	-10.5×10^{-13}
melting point, °C	271.3
vapor pressure, kPa[c]	
400°C	1.013×10^{-4}
600°C	1.013×10^{-1}
880°C	1.013×10^{2}
1420°C	1.013×10^{5}
viscosity, $mPa\cdot s$	
285°C	1.610
304°C	1.662
365°C	1.460
451°C	1.280
600°C	0.998

[a] Solid.
[b] Liquid.
[c] To convert kPa to psi, divide by 6.895×10^{3}.

Mined bismuth in China is a by-product of tungsten mining operations. Most of the bismuth produced in China is refined from concentrates.

5. Manufacture and Processing

Four basic forms of bismuth are readily available commercially: ingot, needle, pellet, and powder. Bismuth ingots range from 4.5 to 20 kg each depending on the producer. Ingots are used mostly in metallurgical applications and in making fusible alloys. Bismuth needle is typically 0.16 cm (0.0625 in.) in diameter by nominally 2.54 cm (1 in.) in length. Needle is primarily used in the production of bismuth compounds for pharmaceutical and catalyst applications. The high surface area of the needle makes it easy to dissolve in various acids. Bismuth powder is produced in varying mesh sizes for the electronics industry.

Table 2. **Thermochemical and Thermodynamic Properties of Bismuth**

Parameter	Value		
entropy at 298 K, ΔS°, J/(mol·K)[a]	56.9		
entropy of transition, ΔS, J/(mol·K)[a] solid	20.2		
liquid	90.4		
heat capacity, ΔC_p, J/(kg·K)[a] −173.15°C	108		
25°C	122		
25–271°C	$4.49–5.40\times10^{-3}$ T[b]		
271–1027°C[c]	235[d]		
heat of fusion, ΔH_{fus}, kJ/kg[a]	51.816		
heat of transition, ΔH, J/mol[a] solid	11.0		
liquid	172		
heat of vaporization, ΔH_{vap}, kJ/kg[a]	858.29		
	Temperature		
	0°C	25°C	100°C
thermal conductivity, W/(m·K)			
parallel to triagonal axis	5.54	5.30	4.81
perpendicular to triagonal axis	9.53	9.19	8.44
polycrystalline	8.22	7.92	7.22
thermal expansion coefficient, 20–100°C	(1.34×10^{-6})/K		

[a] To convert from J to cal, divide by 4.184.

[b] Temperature in degrees kelvin.

[c] Liquid.

[d] Units are J/(mol·K). To convert from J to cal, divide by 4.184.

Bismuth pellets range in size from 4.5 to 50 g and are used for metallurgical additives. Their convenient size and specific weights make them particularly useful as feedstock when a given quantity of bismuth must be added regularly to a melt. They are used primarily in cast iron additions, but this use is declining.

5.1. Fabrication. The principal portion of the *bismuth* in *copper ores* follows the copper into the matte. During the conversion of the matte to blister copper, most of the bismuth fumes off. The fumes are caught in the baghouse or Cottrell system along with other elements such as lead, arsenic, and antimony. The dusts are transferred to the lead-smelting operation. The portion of the bismuth remaining with the blister copper is separated during the electrolytic refining in the slimes. The procedure for handling the slimes results in collection of the bismuth in the lead bullion (4).

Table 3. **Annual Bismuth Production in tons**[a]

	Year				
World Production[b]	1992	1993	1994	1995	1996
mines	2870	3220	3060	3490	3440[c]
refineries	3710	4360	4080	4260	4230[c]

[a] Reference 3.

[b] Excluding the United States.

[c] Estimated.

The bismuth that is found in the lead ore accompanies the lead through the smelting operation right up to the last refining steps. The removal of bismuth then requires special techniques; the most common are the Betterton–Kroll and the Betts processes (5).

5.2. Betterton–Kroll Process. Metallic calcium and magnesium are added to the lead bullion in a melt and form ternary compounds that melt higher than lead and are lower in density. On cooling of the lead bath to a temperature close to the melting point of lead, the intermetallic compounds high in bismuth content solidify and float to the top, where they are removed by skimming.

The bismuth–calcium–magnesium dross also contains lead that must be removed. The dross is heated in a kettle to free any entrapped lead that melts and forms a pool under the dross. This lead is cast and returned to the bismuth separation cycle. The dross is then melted and treated with chlorine and/or lead chloride to remove the calcium and magnesium. The resulting molten metal is an alloy of bismuth and lead, high in bismuth, which is then treated to produce refined bismuth metal.

5.3. Betts Electrolytic Process. The Betts process starts with lead bullion, which may carry tin, silver, gold, bismuth, copper, antimony, arsenic, selenium, tellurium, and other impurities, but should contain at least 90% lead (6,7). If more than 0.01% tin is present, it is usually removed from the bullion first by means of a tin-drossing operation (see TIN AND TIN ALLOYS DETERMINING). The lead bullion is cast as plates or anodes, and numerous anodes are set in parallel in each electrolytic cell. Between the anodes, thin sheets of pure lead are hung from conductor bars to form the cathodes. Several cells are connected in series.

The electrolyte is a solution of lead fluosilicate [25808-74-6] ($PbSiF_6$), and fluosilicic acid [16961-83-4] (H_2SiF_6), containing a small amount of glue or other suitable agent. Direct current is passed through the cells to dissolve the lead from the anodes and deposit it on the cathodes. The impurities in the lead anodes are insoluble under the conditions of normal cell operation and remain on the face of the anodes as a porous slime blanket. The finished cathodes are withdrawn from the cells, washed, and melted to refined lead. The scrap anodes are withdrawn, and the slime is washed free of soluble matter, either while still on the anode or after it has been removed by cleaning. The cleaned anode scrap is returned to the anode-casting kettle for recasting.

The washed slime is dried and melted to produce slag and metal. The slag is usually purified by selective reduction and smelted to produce antimonial lead. The metal is treated in the molten state by selective oxidation for the removal of arsenic, antimony, and some of the lead. It is then transferred to a cupel furnace, where the oxidation is continued until only the silver–gold alloy (doré) remains. The bismuth-rich cupel slags are crushed, mixed with a small amount of sulfur, and reduced with carbon to a copper matte and impure bismuth metal; the latter is transferred to the bismuth refining plant.

The gases from the several furnaces treating the slimes carry bismuth, silver, gold, and other values as particulates, which are recovered via Cottrell precipitation, baghouses, or scrubbers.

5.4. Recovery of Bismuth from Tin Concentrates. Bismuth is leached from roasted tin concentrates and other bismuth-bearing materials by means of hydrochloric acid. The acid leach liquor is clarified by settling or filtration, and the bismuth is precipitated as bismuth oxychloride [7787-59-9] (BiOCl), when the liquors are diluted using large volumes of water. The impure bismuth oxychloride is usually redissolved in hydrochloric acid and re-precipitated by diluting several times. It is then dried, mixed with soda ash and carbon, and reduced to metal. The wet bismuth oxychloride may also be reduced to metal by means of iron or zinc in the presence of hydrochloric acid. The metallic bismuth produced by the oxychloride method requires additional refining.

The Sperry process for making white lead in an electrolytic cell recovers bismuth as a by-product in the anode slimes.

The crystallization process for concentrating bismuth in lead by squeezing the eutectic (high in bismuth) liquid out of the solidified high-lead portion at a temperature within the melting range of the alloy is seldom used.

5.5. Refining.

The alloy of bismuth and lead from the separation procedures is treated with molten caustic soda to remove traces of such acidic elements as arsenic and tellurium (4). It is then subjected to the Parkes desilverization process to remove the silver and gold present. This process is also used to remove these elements from lead.

The desilverized alloy now contains bismuth as well as lead and zinc. Removed of the lead and zinc is facilitated by the fact that the formation of zinc and lead chlorides precedes the formation of bismuth chloride [7787-60-2] ($BiCl_3$), when the alloy is treated at 500°C with chlorine gas. Zinc chloride [7646-85-7] ($ZnCl_2$), forms first, and after its removal lead chloride [7758-95-4] ($PbCl_2$), forms preferentially. This process is continued until the desired level of lead removal has been reached. The bismuth is given a final oxidation with air and caustic soda; the refined product typically has a purity of 99.997%.

6. Economic Aspects

In order to adequately discuss the economics of bismuth, it must first be reiterated that bismuth is a minor metal. The supply of bismuth is not easily changed because it is dependent on the supply of the associated metals with which it is mined. Operation of the normal principles of supply and demand with minor metals differs from that with major metals. When the need for copper or zinc increases, it is possible to mine more copper or zinc. This is not the case with a minor metal. To increase the supply of bismuth, it would be necessary to mine more copper or lead to get more bismuth from the ore. It does not make economic sense for copper and lead mines to increase production in order to produce more of what is in effect a contaminant in the ore. It would also cause the prices of those metals to fall as excess material would become available on the market.

The amount of bismuth in the world is finite, of course, as are all nonrenewable resources. Bismuth reserves can be divided into categories described as “currently economic,” “marginally economic,” and “subeconomic” resources on the basis of bismuth concentration, current mining techniques, and current refining capabilities. With the crustal abundance of bismuth ranging from 0.008 to 24 ppm, there are clearly reserves where it is not possible to recover the bismuth present. Table 4 lists the world currently economic bismuth reserves as determined by a joint U.S. Bureau of Mines Geological Survey in 1992.

Table 4. **Bismuth Reserves, Currently Economic**[a]

Continent	Country	Tons	Subtotal[b]
Asia	China	20,000	—
	Japan	9,000	—
	Republic of Korea	4,000	33,000
Australia	Australia	18,000	18,000
Europe		16,000	16,000
North America	Canada	5,000	—
	Mexico	10,000	—
	USA	9,000	24,000
South America	Bolivia	5,000	—
	Peru	11,000	16,000

[a] *Source*: Reference 8

[b] World Total Reserves 107,000 tonnes.

With the growing interest in the uses of bismuth, especially as a replacement option for lead in many applications, a new assessment of the world bismuth reserves would be warranted. However, the figures from the 1992 survey (Table 4) are the most recent available In addition to the currently economic reserves of 107,000 tonnes, it is estimated that there is a reserve base including economic, marginally economic, and subeconomic reserves totaling in excess of 200,000 tons. The Tasna mine, if reopened, could in conjunction with Adex Mining/Mount Pleasant, New Brunswick, Canada, add in excess of 50,000 tons to this figure (9).

The world production of refined bismuth for 1996 was approximately 5500 tons. Belgium, China, Mexico and Peru were the largest producers, with Japan not far behind (see Fig. 1).

China's production has remained relatively stable over the last several years. During that time, however, world demand for bismuth has increased, so China's market share has been reduced, in effect from 30 to 20%. The Chinese influence on bismuth market prices is disproportionate to their market share,

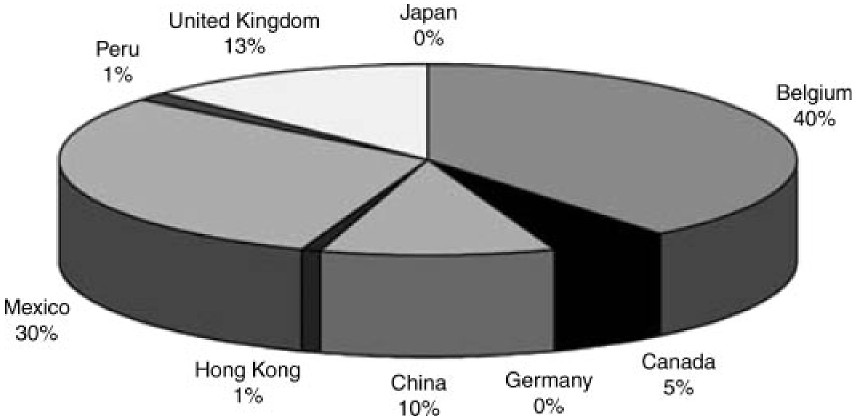

Fig. 1. 1996 bismuth imports by country (in tons).

Table 5. **World Bismuth Mine and Refinery Production**[a]

	Mine									
Country	1992	1993	1994	1995	1996	1992	1993	1994	1995	1996
Belgium[b]	—	—	—	—	—	800	950	900	800	800
Bolivia	—	—	—	121	125	30	7	36	19	20
Bulgaria[b]	40	40	40	40	40	40	40	40	40	40
Canada	224	144	129	187	185	—	—	—	—	—
China[b]	820	740	610	740	700	1060	1050	850	800	800
Italy	—	—	—	—	—	20	—	5[b]	5[b]	5
Japan	159[b]	149[b]	152[b]	177[b]	169	530	497	505	591	563
Kazakstan[b]	160	160	160	155	155	170	170	170	166	160
Korea, Republic of	9[b]	5[b]	—	—	—	9	5	—	—	—
Mexico	807	908	900[b]	995	1000	550[b]	650[b]	650[b]	924	925
Peru	550[b]	1000[b]	1000[b]	1000[b]	1000	419	937	871	870[b]	870
Romania[b]	50	40	40	40	40	50	35	35	35	35
Russia[b]	5	4	4	4	4	10	9	9	10	10
Serbia and Montenegro	10	5	5[b]	5[b]	5	20	10	<0.5	<0.5	<0.5
Tajikistan[b]	20	16	12	11	5	—	—	—	—	—
Uzbekistan[b]	15	10	10	10	11	—	—	—	—	—
Total	*3870*	*3220*	*3060*	*3490*	*3440*	*3710*	*4360*	*4070*	*4260*	*4230*

[a] *Source*: Reference 10. *Note*: World totals and estimated data are rounded and may not add to totals shown. United States values have been withheld to avoid disclosing company proprietary information.

[b] Estimated.

however. By multichannelling material through Hong Kong traders, the availability of material is exaggerated. Some Chinese suppliers renege on delivery when they see bismuth prices rising, thus causing short-term shortage of metal (9).

In Japan, production was down in 1996 from 1995. In Peru, Centromin produced their highest output ever at 939 tons. This was a substantial increase over 1995 production. At Penoles of Mexico, higher bismuth concentrations caused increased yields in production over the previous year. Table 5 shows world production for the late 1990s.

The United States is and has always been highly dependent on bismuth imports because domestic usage has greatly exceeded domestic production. That situation worsened during 1997. Asarco, the only U.S. producer of bismuth, closed its Omaha, Nebraska refinery and smelter. In 1996, the United States imported 1490 tonnes of bismuth (3). Of this amount, approximately 40% came from Belgium; 30%, from Mexico; and 13%, from the United Kingdom. Through November 1997, the United States had imported 2040 tonnes of bismuth, representing a 36% increase over the previous year. Part of this was due to the need to replace the Asarco production.

Also in the United States, the federal government has been considered a producer of sorts since the late 1990s. The U.S. Defense Logistics Agency (DLA) built up a stockpile of about 994 tonnes of bismuth over the years. Beginning in the early 1990s the government began to sell off its stockpile, selling over

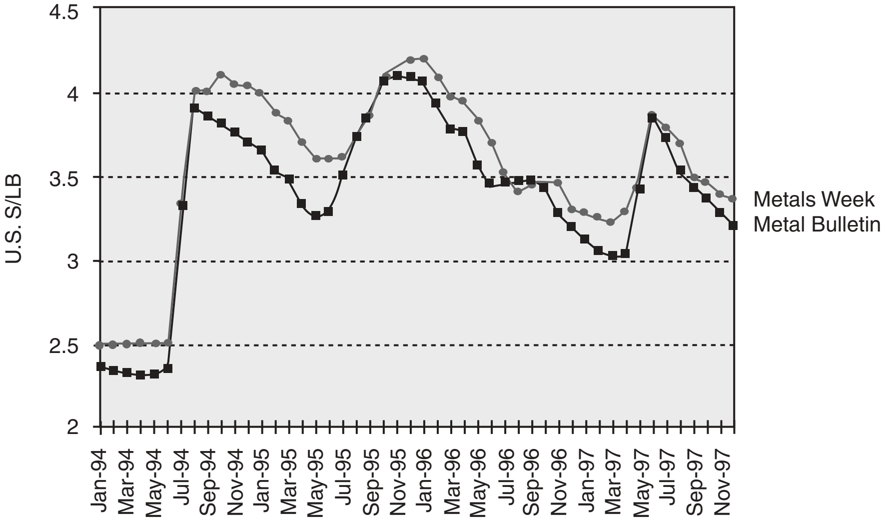

Fig. 2. Bismuth prices 1994–1997.

100 tonnes each year. Although this amount does not include the DLA in the list of top producers, it is a significant quantity of material to be sold each year. At the end of 1997, the DLA sold the last of its stockpile.

6.1. Pricing.

There are two 6.1. published prices for bismuth. In Europe, the Metal Bulletin publishes prices twice each week listing both a high and a low for bismuth. In the United States, Platt's Metals Week magazine publishes a weekly price that also lists both highs and lows. The American price is usually about \$0.10–\$0.20/lb higher than the London price. Since the 1970s bismuth prices have ranged from an all time low of less than \$1.50/lb (\$3.30/kg) in summer 1982 to an all-time high of over \$20.00/lb (\$44.09/kg) in May 1974.

In 1994–1997, bismuth prices were more stable than during the 1970s and 1980s. During that 4-year period, the price averaged \$3.56/lb (\$7.848/kg) for Metals Week and \$3.40/lb (\$7.496/kg) for the London Metal Bulletin price. The lowest price for this period was the January 1994 average for Metals Week at \$2.48/lb (\$5.467/kg) and the April 1994 price for LMB at \$2.325/lb (\$5.126/kg). The highest prices were in January 1996 at \$4.20/lb (\$9.259/kg) for Metals Week and November 1995 for the London Metal Bulletin at \$4.097/lb (\$9.032/kg). Figure 2 shows the bismuth price averages of those four years.

7. Grades and Specifications

The purity of bismuth ranges from 99.99 to 99.999% depending on the use. Ingot for metallurgical and fusible alloy applications is commercially available at 99.99% pure. Needle for catalyst and other chemical applications is usually supplied as 99.99% pure. Pharmaceuticals require bismuth to be minimum 99.997% pure. This is typically supplied as needle. Needle of 99.999% purity is useful for the manufacture of high-purity bismuth compounds for medical, electronic and ceramic applications.

8. Analytical Methods

Many of the methods available for determination of bismuth are not very selective; thus it is necessary to separate the bismuth from interfering substances. Titration of bismuth with EDTA (ethylenediamine tetraacetic acid) has been found to be one of the best general methods for determining both macroscale and semimicroscale quantities of bismuth (11). The method is fast, accurate, and convenient. Few foreign ions in moderate amounts interfere. The titration is best carried out at a pH between 1.5 and 2.0. When the endpoint is detected by photometric methods, the titration of bismuth as dilute as 10^{-6} molar is feasible.

For the determination of trace amounts of bismuth, atomic absorption spectrometry is probably the most sensitive method. A procedure involving the generation of bismuthine by the use of sodium borohydride followed by flameless atomic absorption spectrometry has been described (12). The sensitivity of this method is given as 10 ppb/0.0044 A, where A is an absorbance unit; the precision is 6.7% for 25 pg of bismuth. The low neutron cross section of bismuth virtually rules out any determination of bismuth based on neutron absorption or neutron activation.

9. Environmental Concerns

Bismuth is considered both nontoxic and noncarcinogenic despite the fact that it is a heavy metal. It exhibits many of the characteristics of lead, which is next to it on the periodic table of the elements, yet it is not poisonous as lead. The Bismuth Institute published a report written by Yves Palmieri entitled *Bismuth: An Amazingly Green Environmentally-Minded Element* (13). In this report, Mr. Palmieri lists many of the characteristics as well as the many uses of bismuth, describes instances where bismuth has replaced lead because of the toxicity of lead, and explains why bismuth is more than just nonhazardous. It actually has a beneficial influence on human health (13).

9.1. Recycling and Disposal.

Bismuth has been involved in recycling since long before recycling became mandated by the Environmental Protection Agency. Because bismuth alloys melt at relatively low temperatures, it is relatively easy to reclaim and reprocess them. In a simplified application, the bismuth alloy to be reclaimed is simply melted and slowly cooled to allow some of the contaminants to float out and the dross skimmed. The resulting alloy can then be analyzed for metal ratios and used to make other bismuth alloys. Bismuth-containing materials should not be disposed of because of the ease in refining and the inherent value of the bismuth contained in the material.

9.2. Health and Safety Factors.

No industrial poisoning from bismuth has been reported (14). The use of bismuth compounds in the medical field for several hundred years indicates the safety of the material. However, precautions

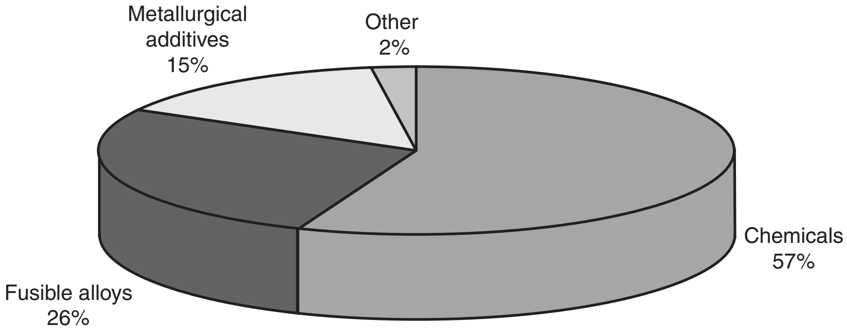

Fig. 3. Bismuth usage in 1996.

should be taken against the careless handling of bismuth and its compounds; ingestion and inhalation of dusts and fumes should be avoided.

10. Uses and Market Demand

The uses of bismuth can be broken down into three primary categories: chemical, metallurgical additive, and fusible alloy (see Fig. 3). The individual categories can be subdivided into numerous lesser categories as listed in Table 6 and described in the following paragraphs.

The chemical category is broken down into pharmaceuticals, cosmetics, catalysts, industrial pigments, and electronics. As stated earlier, bismuth salts have been used for medicinal purposes for hundreds of years. About 90% of bismuth usage was for pharmaceuticals prior to the 1930s (10,15–17). From that point until the 1970s, research produced new applications that greatly expanded the uses of the metal. At that point the pharmaceutical use accounted for about 50% of total bismuth consumption. By 1991, the fusible alloy category along with the other subdivisions each accounted for about 10% of the bismuth usage. Pharmaceutical usage was down to 20% by the 1990s.

Table 6. **U.S. Consumption by Category in tons**

	Year				
Use	1993[a]	1994[a]	1995[b]	1996[b]	1997[c]
chemicals[d]	750	841	1320	855	841
fusible alloys	256	276	544	401	490
metallurgical additives	232	325	257	231	258
other	59	26	27	35	25
Total	*1300*	*1470*	*2150*	*1520*	*1610*

[a] Reference 16.
[b] Reference 10.
[c] Reference 17.
[d] Includes pharmaceuticals, cosmatics, catalysts, and electronics.

The use of bismuth in metallurgical applications increased greatly in the 1990s. With the many environmental concerns about the use of lead, bismuth has been found to be a suitable replacement for lead in many areas. Bismuth is used to replace the lead in some brass water fittings. In conjunction with tin, bismuth is used in replacing lead in bronze bearings (18). It is also used in place of lead in heat-treating applications and in galvanizing operations. Because of recent developments, bismuth, alloyed with a small amount of tin, is being used to make shotgun ammunition.

As a metallurgical additive, bismuth is used in the manufacturing of free-machining steel and free-machining aluminum. The amount of bismuth added can range from 0.003 to 0.10% depending on the type of steel or aluminum. The tiny droplets of bismuth dispersed within the alloy melt when they come in contact with the cutting edge lubricating it. The bismuth addition enhances the action of lead in the steel by producing less frictional resistance at the cutting edge of the tool. This produces thinner and smaller chips, higher productivity, and better surface finish.

11. Bismuth Alloys

Because bismuth expands on solidification and because it alloys with certain other metals to give low-melting alloys, bismuth is particularly well suited for a number of uses. Alloys of bismuth can be made that expand, shrink, or remain dimensionally stable on solidification. So, bismuth alloys have lent themselves to a wide range of industrial applications. Composition and uses are summarized in Table 7.

11.1. Uses of Alloys.

Anchoring. Bismuth alloys that expand on solidification are particularly useful for aligning and setting punches in a die plate. It is much easier to melt and pour an alloy around a punch than to machine the entire die plate and punch at the same time. This method also makes it easier to relocate parts or change dies. The low temperatures involved do not cause distortion.

Radiation Shielding. Bismuth, like lead, absorbs radiation. Therefore, bismuth alloys are widely used in the medical industry during radiation therapy.

The alloy is cast into a block in the shape of various organs that are to be shielded. Then the alloy block is mounted on a glass plate located between the patient and the radiation source. The bismuth alloy absorbs the radiation

Table 7. **Alloy Compositions and Uses**

Melting Point, °C	Bismuth	Lead	Tin	Cadmium	Indium	Uses[a]
47	44.7	22.6	8.3	5.3	19.1	FSD, LB
70	50	26.7	13.3	10	0	FSD, LB, RS, T, W
95	52.5	32	15.5	0	0	FSD, RS
138	58	0	42	0	0	FC, FSD, SMF, W
138/170	40	0	60	0	0	FSD, IC

[a] *Abbreviations*: FC = fusible core; FSD = fusible safety devices; IC = investment casting; LB = lens blocking; RS = radiation shielding; SMF = sheetmetal forming; T = tube bending; W = work holding.

aimed at the organs it is intended to protect, thus shielding vital organs from unnecessary radiation exposure. The same block is stored and reused for the same patient repeatedly until treatment is complete. Since these alloys melt at low temperatures, usually 158 or 203°F, they are easily melted and recast for use on other patients.

Electromagnetic and Radiofrequency Shielding. Because bismuth is highly diamagnetic, its alloys are quite useful in applications where electronic equipment must be protected from outside interference or where equipment can cause outside interference. This is an important application in the design and construction of medical testing equipment that uses high-powered electromagnetics. These alloys can be easily cast into or sprayed onto the surface of the area needed for maximum shielding.

Tube Bending. The search for high-strength, low-weight structural materials produced the use of hollow tubes of many metals and alloys as structural components. These materials must often be bent and shaped to fit. Bending an empty tube causes distortion of the shape of the tube by flattening or wrinkling. These tubes can be filled with a low-melting bismuth alloy that allows the tube to be bent as if it were solid, thus eliminating distortion. Then the alloy can be easily melted out of the tube and reused.

Fusible Safety Devices. Low-melting bismuth alloys, especially those that are eutectic, have found numerous uses in safety devices. These alloys can be cast into any shape necessary in order to be used in a plug or switch that must function at a given temperature. Sprinkler heads, high-pressure valve fittings, and meat timers are among the devices that contain low-melting bismuth alloys.

Lens Blocking. Bismuth alloys have become particularly useful in the optical industry for securing lenses for grinding processes. The low melting point provides that the lenses may be secured without preheating. The alloys have high strength so that good control is maintained during the grinding process. The density of the alloy provides for a dampening of the vibrations caused by the grinding. After processing, the lenses are immersed in hot-water bath to remove the alloy, which is reused.

Fusible Core Technology. This is currently the fastest growing area of bismuth alloy use today. Low melting bismuth alloys make it possible to produce items having complex internal cavities that cannot be produced using conventional core molds. These alloys are dimensionally stable so that when they are cast they result in a core piece that has the most exact detail and surface finish required. These alloys are being used in the electroforming industry as well as the plastics industry, where cost and weight reduction have become critical. Once molding or electroforming is complete, the part is immersed in a heat bath that melts out the alloy for reuse. This process is especially useful in the automotive industry for the manufacture of lightweight plastic air-intake manifolds.

Steel Quenching. Bismuth and bismuth–lead alloys are used in the processing of some steel products. The thermal conductivity of bismuth makes it ideal for use in tempering steel. The use of bismuth or bismuth–lead alloy in place of pure lead has the advantage of lowering the operating temperature of the bath as well as reducing adherence of alloy to the steel.

Proof Casting of Dies and Molds. Low-melting alloys make the process of diemaking faster and easier. The low-temperature alloys can be cast into a mold pattern at virtually any point in the manufacturing process without long delays in production and without the possibility of heat distortion. These alloys produce a casting that is exact in detail, requiring no curing time. The casting can then be inspected and measured to gauge the accuracy of the dies. After the alloy has been measured and tested, it can be melted and is completely reusable.

Work Holding and Work Supporting. Low-melting bismuth alloys have been used to solve two problems in machining operations: (1) these alloys are used to hold parts that need machining but have no regular side that can be clamped, and (2) bismuth alloys provide a method of support for parts such as turbine blade vanes that are not stiff enough to stand alone for machining.

Sheetmetal Forming Dies. Engineers have found that the low melting alloys, because they are tough and durable, are suitable for making castings that produce hundreds of pressings in sheetmetal of normal materials from aluminum to titanium. Once a given short run of pressings is complete, the tooling can be melted easily and used for another tooling job.

Lead-Free Waterfowl Shot. Waterfowl poisoning from lead shot has been a conservationists concern for years. Research has indicated that a large percentage of waterfowl have been poisoned by ingestion of lead shot. This prompted the search for an alternative to lead shot.

The first alternative was steel shot. This posed two problems to hunters. The first is that since lead shot is much denser than steel shot, the velocity

Table 8. **Properties of Low Melting Bismuth Alloys**

	Alloy			
Property	47°C	70°C	138°C	138/170°C
melting point or range, °C (°F)	47.5 (117)	70 (158)	138.5 (281)	138.5–170 (281–338)
density, lb/in.^{3} (g/cm^3)	0.34 (9.36)	0.35 (9.67)	0.31 (8.58)	0.30 (8.21)
specific heat, cal/g·C[a]				
solid	0.039	0.035	0.040	0.043
liquid	0.047	0.044	0.048	0.051
heat of fusion, cal/g	8.8	9.5	10.7	10.6
coefficient of thermal expansion, 1×10^{-6} °C	25	22	15	15
thermal conductivity	0.035	0.043	0.044	0.071
electric conductivity (% of pure copper)	3.09	3.54	2.88	5.00
resistivity, μΩ·cm	55.0	48.0	59.0	34.0
Brinell hardness (2-mm ball, 4-kg load)	14.5/16.5	13/14.5	23/23	23.5/24
tensile strength, lb/in.^{2} (Pa)[b]	4868–5337	2668–3775	8701–9013	8459–9041
maximum sustained load, lb/in.^{2} (Pa)[b]				
30 s	NA[c]	10,000	15,000	15,000
300 s	NA[c]	4,000	9,000	9,500

[a] To convert calories to joules, multiply by 4.184.

[b] To convert pounds force per square inch to pascals, multiply by 6.895×10^3.

[c] Not available.

Table 9. **Growth and Shrinkage of Low-Melting Alloys**[a]

	Alloy			
Time after Casting	47°C	70°C	138°C	138/170°C
6 min	−0.00025	0.00490	−0.00010	0.00030
20 min	−0.00030	0.00565	.00000	0.00035
1 h	−0.00025	0.00570	0.00015	0.00060
8 h	−0.00020	0.00600	0.00045	0.00095
1 day	−0.00015	0.00615	0.00060	0.00105
1 month	0.00025	0.00635	0.00090	0.00120

[a] Cumulative changes, inches per inch relative to cold mold dimensions. Test bar $\frac{1}{2}\times\frac{1}{2}\times10$ in. (1.27×1.27×25.4 cm).

and accuracy of shot changed drastically from that of lead. The second problem is that since steel shot is much harder than lead shot, hunters were finding that the shot was damaging the gun barrels. The development of a bismuth–tin alloy shot has provided the means to solve all of these problems: (*1*) the bismuth–tin alloy used in the new shot is not poisonous to waterfowl, so the conservationists' problem is solved; (*2*) bismuth–tin shot is close to lead in density, so accuracy and velocity are not drastically changed from those of lead shot; and (*3*) the new alloy is not as hard as steel, so there is no damage to gun barrels.

Table 8 lists some of the properties of low-melting bismuth alloys. It is the various combinations of these properties that make the appropriate for the uses described above.

Bismuth's almost unique property of expansion on solidification makes the alloys of bismuth particularly useful for various applications. For example, in the work-holding applications, it is useful for the alloy to expand on solidification in order to adequately hold the piece in question. In the fusible core application, it would be a problem for the alloy to expand significantly on solidification as this would distort the dimensions of the final product. Therefore an alloy with minimal final expansion would be best suited for this use. Table 9 below lists the growth and shrinkage of some of the alloys.

BIBLIOGRAPHY

"Bismuth and Bismuth Alloys" in *ECT* 1st ed., Vol. 2, pp. 526–533, by W. C. Smith, Cerro de Pasco Copper Co.; in *ECT* 2nd ed., Vol. 3, pp. 527–535, by H. E. Howe, American Smelting and Refining Co.; in *ECT* 3rd ed., Vol. 3, pp. 912–921, by S. C. Carapella, Jr. and H. E. Howe, American Smelting and Refining Co. "Bismuth and Bismuth Alloys" in *ECT* 4th ed., Vol. 4, pp. 237–245, by Mark J. Chagnon, Metalspecialties, Inc.; "Bismuth and Bismuth Alloys" in *ECT* (online), posting date: December 4, 2000, by Mark J. Chagnon, Metalspecialties, Inc.

CITED PUBLICATIONS

1. B. Dibner, *Agricola on Metals*, Burndy Library, Norwalk, Conn., 1958, p. 41.
2. J. W. Hasler, M. H. Miller, and R. M. Chapman, *United States Mineral Resources*, Geological Survey Professional Paper 820, U.S. Department of the Interior, Washington, D.C., 1973, p. 96.

3. *Mineral Industry Surveys, Bismuth Annual Review*, U.S. Bureau of Mines, Washington, D.C., 1990.
4. A. R. Powell, in A. R. Powell, *papers of the Institute of Mining and Metallurgy Symposium*, Institute of Mining and Metallurgy, London, UK, 1950, 245–257.
5. J. O. Betterton and Y. E. Levebeff, *Metallurgy of Lead and Zinc*, American Institute of Mining and Metallurgy Engineers, New York, 1936.
6. P. M. Gruzensky and W. J. Crawford, *U.S. Bur. Mines Inf. Circ.*, 7681 (1954).
7. F. Vogel, *Metall Berlin* **21**(2), 122 (1967).
8. M. D. Fickling, Review of Bismuth in 1993, *Mining Journal* Annual Review, 1994.
9. M. D. Fickling, Review of Bismuth in 1996, *Mining Journal* Annual Review, 1997 .
10. *Mineral Industry Surveys, Bismuth Annual Review*, U.S. Department of the Interior. Bureau of Mines, Washington, D.C., 1996.
11. J. S. Fritz, in I. M. Kolthoff and P. J. Elving, eds., *Treatise on Analytical Chemistry*, Part II **Vol. 8**, J Wiley & Sons, Inc., New York, 1963, pp. 147–175.
12. D. S. Lee, *Anal. Chem.* **54**, 1682 (1982).
13. Y. Palmieri, *An Amazingly "Green" Environmentally-Minded Element*, The Bismuth Institute, 1992.
14. N. I. Sax, *Dangerous Properties of Industrial Materials*, 4th ed., Van Nostrand Reinhold Co., New York, 1975, p. 459.
15. J. F. Carlin, Jr., *Mineral Facts and Problems*, U.S. Bureau of Mines, Washington, D.C., 1985, p. 1.
16. *Mineral Industry Surveys, Bismuth Annual Review*, U.S. Department of the Interior, Bureau of Mines, Washington, D.C. 1994.
17. *Mineral Industry Surveys, Bismuth In The Fourth Quarter*, U.S. Department of the Interior, U.S. Geological Survey, Reston, Va., 1997.
18. P. Koslosky, Jr., in *The Bulletin of the Bismuth Institute* **Vol. 69**, Bismuth Institute, Grimbergen, Belgium, 1996, pp. 1–2.

General References

R. C. Weast, ed., *CRC Handbook of Chemistry and Physics*, 71st ed., CRC Press, Boca Raton, Fla., 1991.

L. G. Stevens and C. E. T. White, *The Metals Handbook*, Vol. **2**, 10th ed., ASM International, 1990, 750–757.

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