BERYLLIUM COMPOUNDS

1. Beryllium Compounds

1.1. Beryllium Carbide.

Beryllium carbide [506-66-1], Be_2C, may be prepared by heating a mixture of beryllium oxide and carbon to 1950–2000°C, or heating a blend of beryllium and carbon powders to 900°C under mechanical pressure of 3.5–6.9 MPa (500–1000 psi). The metal–carbon reaction is easier to carry out and is accompanied by a substantial exotherm. The reaction mass is quite friable and readily converted to a powder for consolidation by hot pressing at temperatures on the order of 1800°C.

Beryllium carbide slowly hydrolyzes to beryllium oxide and methane in the presence of atmospheric moisture although months may be required to complete the reaction. Any carbon contained in beryllium metal is present as the carbide because the solubility of carbon in beryllium is extremely low.

The crystal structure of beryllium carbide is cubic, density = 2.44 g/mL. The melting point is 2250–2400°C and the compound dissociates under vacuum at 2100°C (1). This compound is not used industrially, but Be_2C is a potential first-wall material for fusion reactors, one on the very limited list of possible candidates (see FUSION ENERGY).

1.2. Beryllium Carbonates. Beryllium carbonate tetrahydrate [60883-64-9], $BeCO_3 \cdot 4H_2O$, has been prepared by passing carbon dioxide through an aqueous suspension of beryllium hydroxide. It is unstable and is obtained only when the solution is under carbon dioxide pressure. Beryllium oxide carbonate [66104-25-4] is precipitated when sodium carbonate is added to a beryllium salt solution. Carbon dioxide is evolved. The precipitate appears to be a mixture of beryllium hydroxide and the normal carbonate, $BeCO_3$, and usually contains two to five molecules of $Be(OH)_2$ for each $BeCO_3$.

Soluble beryllium carbonate complexes are produced by dissolving beryllium oxide carbonate or hydroxide in ammonium carbonate. Iron and aluminum hydroxides are insoluble in this solution; hence, the reaction can be used to separate these two elements from beryllium. The resulting solution appears to approach the stoichiometry of a solution of tetraammonium beryllium tricarbonate [65997-36-6], $(NH_4)_4Be(CO_3)_3$. After removal of insoluble impurities, hydrolysis of $(NH_4)_4Be(CO_3)_3$ just below the boiling point gives a granular precipitate of di(beryllium carbonate) beryllium hydroxide [66104-24-3], $2BeCO_3 \cdot Be(OH)_2$, which can be dried to constant weight at 100°C. Decomposition to BeO is nearly complete after 5 days at 200°C. The continued addition of $2BeCO_3 \cdot Be(OH)_2$ and $(NH_4)_2CO_3$ to a warmed solution of $(NH_4)Be(CO_3)_3$ has produced solutions containing up to 42 g/L of Be in which the empirical composition is $(NH_4)_2Be(CO_3)_2$. The solid beryllium oxide carbonate intermediates are obtained by a laboratory procedure for preparing pure beryllium salt solutions by reaction with aqueous mineral or organic acids.

1.3. Beryllium Carboxylates. The beryllium salts of organic acids can be divided into normal carboxylates,$Be(RCOO)_2$, and beryllium oxide carboxylates,$Be_4O(RCOO)_6$. The latter are prepared by dissolving beryllium oxide, hydroxide, or the oxide carbonate in an organic acid, followed by evaporation to give either a solid or an oily liquid. The oxide carboxylate is extracted using chloroform or petroleum ether and recrystallized from the solvent. These compounds are nonelectrolytes, soluble in organic solvents, insoluble in cold water, possess sharp melting points, and can usually be sublimed or distilled without decomposition. The oxide acetate is used as a high purity intermediate for the preparation of commercial beryllium reference solution. The oxide formate requires special preparation by heating the normal formate to 250–260°C or by boiling it with a water suspension containing the calculated amount of beryllium oxide carbonate. The normal beryllium carboxylates must be prepared under strictly anhydrous conditions. The normal acetate is made by treating the oxide acetate with glacialacetic acid andacetyl chloride.

1.4. Beryllium Halides. The properties of the fluoride differ sharply from those of the chloride, bromide, and iodide. Beryllium fluoride is essentially an ionic compound, whereas the other three halides are largely covalent. The fluoroberyllate anion is very stable.

Beryllium fluoride [7787-49-7],BeF_2, is produced commercially by the thermal decomposition of diammonium tetrafluoroberyllate [14874-86-3], $(NH_4)_2BeF_4$. The fluoride and the fluoroberyllates show a strong similarity to silica and the silicates. Like silica, beryllium fluoride readily forms a glass, which on heating >230°C crystallizes spontaneously to give the quartz modification. This quartz modification exists in two forms: The low temperature α-form is converted to the high temperature β-form at 227°C. The melting point of the quartz form of beryllium fluoride appears to be 552°C (2).

Beryllium fluoride is hygroscopic and highly soluble in water, although its dissolution rate is slow. Fluoroberyllates can be readily prepared by crystallization or precipitation from aqueous solution. Compounds containing theBeF^{2-} ion are the most readily obtained, though compounds containing other fluoroberyllate ions can also be obtained, eg, NH_4BeF_3, depending on conditions.

Beryllium chloride [7787-47-5], $BeCl_2$, is prepared by heating a mixture of beryllium oxide and carbon in chloride at 600–800°C. At pressures of 2.7–6.7 Pa (0.02–0.05 mm Hg) beryllium chloride sublimes at 350–380°C. It is easily hydrolyzed by water vapor or in aqueous solutions. Beryllium chloride hydrate [14871-75-1] has been obtained by concentrating a saturated aqueous solution of the chloride in a stream of hydrogen chloride. Chloroberyllate compounds have not been isolated from aqueous solutions, but they have been isolated from anhydrous fused salt mixtures.

Beryllium bromide [7787-46-4], $BeBr_2$, and beryllium iodide [7787-53-3], BeI_2, are prepared by the reaction of bromine or iodine vapors, respectively, with metallic beryllium at 500–700°C. They cannot be prepared by wet methods. Neither compound is of commercial importance and special uses are unknown.

1.5. Beryllium Hydride.

Beryllium hydride [7787-52-2], BeH_2, is best prepared by the controlled pyrolysis of di-*tert*-butyl beryllium [20841-21-7], $C_8H_{18}Be$, at 200°C. Pressure densification of the amorphous pyrolysis product yields 96% pure crystalline BeH_2 having a density near 0.6 g/mL. Di-*tert*-butyl beryllium is prepared by the reaction, in ether, of $BeCl_2$ and *tert*-butyl Grignard reagent, $t\text{-}(C_4H_9)\text{-}MgCl$ (see GRIGNARD REACTION). Metallic beryllium does not react with hydrogen directly to give the hydride (3). Thermally stable to 240°C, crystalline beryllium hydride is resistant to attack by water and common organic solvents. Interest in beryllium hydride has centered on its potential use as a solid propellant rocket fuel. Theoretically, BeH_2 has the highest specific impulse of any fuel material except solid hydrogen.

1.6. Beryllium Hydroxide.

Beryllium hydroxide [13327-32-7], $Be(OH)_2$, exists in three forms. On addition of alkali to a beryllium salt solution to obtain a slightly basic pH, a slimy, gelatinous beryllium hydroxide is produced. Aging this amorphous product results in a metastable tetragonal crystalline form, which after months of standing transforms into a stable orthorhombic crystalline form. The orthorhombic modification is also precipitated from a sodium beryllate solution containing >5 g/L db Be by hydrolysis near the boil. This granular beryllium hydroxide is the readily filtered product from the sulfate extraction processing of beryl to obtain metallic beryllium. When heated, beryllium hydroxide loses water. Most of the water comes off in the 600–700°C region, but temperatures on the order of 950°C are required for complete dehydration to the oxide. There is evidence that beryllium hydroxide exists in the vapor phase above 1200°C (4). Water vapor reacts with BeO to form beryllium hydroxide vapor, which has a partial pressure of 73 Pa (0.55 mm Hg) at 1500°C.

1.7. Beryllium Intermetallic Compounds.

Beryllium forms intermetallic compounds, referred to as beryllides, with most metals. They are usually

Table 1. **High Temperature Oxidation Resistant Beryllides**

Beryllide system	Compound formula	CAS Registry Number	Melting point, °C	X-ray density, g/mL	Be, wt %
hafnium	$HfBe_{13}$		1595	3.93	39.7
	Hf_2Be_{17}		<1750	4.78	30.0
molybdenum	$MoBe_{12}$		~ 1705	3.03	53.2
niobium	$NbBe_{12}$	[12010-12-7]	1690	2.92	53.8
	Nb_2Be_{17}	[12010-34-3]	1705	3.28	45.2
titanium	$TiBe_{12}$	[12232-67-6]	1595	2.26	69.3
	Ti_2Be_{17}		1630	2.46	61.5
tantalum	$TaBe_{12}$	[12010-13-8]	1850	4.18	37.4
	Ta_2Be_{17}		1990	5.05	29.8
zirconium	$ZrBe_{13}$	[12010-33-2]	1925	2.72	56.2
	Zr_2Be_{17}		1980	3.08	45.7

prepared by a solid-state reaction of the blended powder constituents at ~1260°C. Fabrication of the reacted powders into specific shapes is carried out by standard powder metallurgical techniques such as vacuum hot pressing or hot isostatic pressing (see METALLURGY, POWDER). The properties exhibited by some beryllides include excellent oxidation resistance, high strength at elevated temperature, good thermal conductivity, and low densities as compared with refractory metals and ceramic materials (see CERAMICS; REFRACTORIES). Table 1 lists melting points and densities of some of the more promising oxidation-resistant beryllides (5).

The beryllides, being intermetallic compounds, are hard, strong materials which exhibit little ductility at room temperature. Strength properties increase gradually as a function of temperature up to ~870°C, above which a sharp increase in strength occurs, peaking in the region of 1260°C; the modulus of rupture values exceed 280 MPa (40,000 psi) at this latter temperature.

Similar to some other intermetallic compounds, most notably molybdeum disilicide [12136-78-6], $MoSi_2$, certain beryllides show anomalous oxidation behavior exhibiting excellent oxidation resistance at high temperature, eg, 1260°C, but little or no oxidation resistance in some lower temperature range. Such behavior was observed in the 700–870°C range for Nb_2Be_{17}, $NbBe_{12}$, Zr_2Be_{17}, and $ZrBe_{13}$, but not for other compounds listed in Table 1 (6). Complete disintegration of the vulnerable beryllides into powder occurred within 24 h. The addition of small amounts of aluminum [7429-90-5] metal, or the nickel–aluminum (1:1) [12003-78-0] compound NiAl solved this problem.

The beryllides continue to be of interest for high temperature aerospace applications because of their oxidation resistance, low density, and high strength at elevated temperature (7). The limited strain capacity of the materials, particularly at low temperatures, has thus far prevented actual use.

1.8. Beryllium Nitrate. Beryllium nitrate tetrahydrate [13516-48-0], $Be(NO_3)_2 \cdot 4H_2O$, is prepared by crystallization from a solution of beryllium hydroxide or beryllium oxide carbonate in a slight excess of dilute nitric acid. After dissolution is complete, the solution is poured into plastic bags and cooled to room temperature. The crystallization is started by seeding. Crystallization from more concentrated acids yields crystals with less water of hydration. On heating >100°C, beryllium nitrate decomposes with simultaneous loss of water and oxides of nitrogen. Decomposition is complete >250°C.

1.9. Beryllium Nitride. Beryllium nitride [1304-54-7], Be_3N_2, is prepared by the reaction of metallic beryllium and ammonia gas at 1100°C. It is a white crystalline material melting at 2200°C with decomposition. The sublimation rate becomes appreciable in a vacuum at 2000°C. Beryllium nitrate is rapidly oxidized by air at 600°C and like the carbide is hydrolyzed by moisture. The oxide forms on beryllium metal in air at elevated temperatures, but in the absence of oxygen, beryllium reacts with nitrogen to form the nitride. When hot pressing mixtures of beryllium nitride and silicon nitride, Si_3N_4, at 1700°C, beryllium silicon nitride [12265-44-0], $BeSiN_2$, is obtained. $BeSiN_2$ may have application as a ceramic material.

1.10. Beryllium Oxalate. Beryllium oxalate trihydrate [15771-43-4], $BeC_2O_4{\cdot}3H_2O$, is obtained by evaporating a solution of beryllium hydroxide or oxide carbonate in a slight excess of oxalic acid. The compound is very soluble in water. Beryllium oxalate is important for the preparation of ultrapure beryllium hydroxide by thermal decomposition >320°C. The latter is frequently used as a standard for spectrographic analysis of beryllium compounds.

1.11. Beryllium Oxide. Beryllium oxide [1304-56-9], BeO, is the most important high purity commercial beryllium chemical. In the primary industrial process, beryllium hydroxide extracted from ore is dissolved in sulfuric acid. The solution is filtered to remove insoluble oxide and sulfate impurities. The resulting clear filtrate is concentrated by evaporation and upon cooling high purity beryllium sulfate, $BeSO_4{\cdot}4H_2O$, crystallizes. This salt is calcined at carefully controlled temperatures between 1150 and 1450°C, selected to give tailored properties of the beryllium oxide powders as required by the individual beryllia ceramic fabricators. Commercial beryllium oxide powder calcined at 1150°C consists of crystallites predominately 0.1–0.2 μm in size. Powder particles are made up of clusters or aggregates of the smaller crystallites.

Ceramic-grade beryllium oxide has also been manufactured by a process wherein organic chelating agents (qv) were added to the filtered beryllium sulfate solution. Beryllium hydroxide is then precipitated using ammonium hydroxide, filtered, and carefully calcined to obtain a high purity beryllium oxide powder.

High purity beryllium oxide powder is fabricated by classical ceramic-forming processes such as dry pressing, isostatic pressing, extrusion, tape casting, and slip casting. Additives consisting of the oxides of magnesium, aluminum, or silicon, or various combinations are frequently included in the ceramic mixes to improve the reproducibility of sintering and resultant properties. The green compact of formed beryllia is commonly sintered at 1500–1600°C in dry air or dry hydrogen. Moisture in the sintering atmosphere affects the surface characteristics such as roughness, texture, and microstructure (8). The sintering operation produces beryllia ceramics at 95–97% of the theoretical density with an average grain size between 6 and 30 μm. Higher density may be achieved by hot pressing high purity beryllia powder.

Beryllia ceramics offer the advantages of a unique combination of high thermal conductivity and heat capacity with high electrical resistivity (9). Thermal conductivity equals that of most metals; at room temperature, beryllia has a

Table 2. **Properties of High Purity Beryllium Oxide Ceramics**

Property	Value
specific heat, J/(g K)[a]	1.050
thermal conductivity, W/(mK)	
at 25°C	290–330
at 100°C	190–220
dielectric constant (loss tangent)	
1 MHz at 25°C	6.55–6.72 (0.00005–0.00016)
1 MHz at 100°C	6.55–6.75 (0.00007–0.00019)
1 GHz at 25°C	6.72–6.75 (0.00006–0.00035)
1 GHz at 100°C	6.72–6.81 (0.00014–0.00051)
9.3 GHz at 25°C	6.77 (0.00007–0.00031)
9.3 GHz at 100°C	6.77 (0.00026–0.00047)
volume resistivity, Ωm	
at 25°C	$2.0 \times 10^{14} - 1.3 \times 10^{15}$
at 100°C	$1.4 \times 10^{11} - 5.0 \times 10^{11}$
coefficient of thermal expansion, K^{-1}	
at 100°C	9.7×10^{-6}
at 500°C	13.3×10^{-6}
tensile strength, MPa[b]	150
compressive strength, MPa[b]	1400
modulus of rupture, MPa[b]	250
modulus of elasticity, GPa[b]	345
Poisson's ratio	0.164–0.380

[a] To convert J to cal, divide by 4.184.
[b] To convert MPa to psi, multiply by 145.

thermal conductivity above that of pure aluminum and 75% that of copper. Properties illustrating the utility of beryllia ceramics are shown in Table 2.

Beryllia ceramic parts are frequently used in electronic and microelectronic applications requiring thermal dissipation (see CERAMICS AS ELECTRICAL MATERIALS). Beryllia substrates are commonly metallized using refractory metallizations such as molybdenum–manganese or using evaporated films of chromium, titanium, and nickel–chromium alloys. Semiconductor devices and integrated circuits (qv) can be bonded by such metallization for removal of heat.

Beryllium oxide is used in automotive ignition systems, lasers, electronic circuits for computers heat sinks, and microwave oven components (10).

1.12. Beryllium Sulfate. Beryllium sulfate tetrahydrate [7787-56-6], $BeSO_4 \cdot 4H_2O$, is produced commercially in a highly purified state by fractional crystallization from a beryllium sulfate solution obtained by the reaction of beryllium hydroxide and sulfuric acid. The salt is used primarily for the production of beryllium oxide powder for ceramics. Beryllium sulfate dihydrate [14215-00-0], is obtained by heating the tetrahydrate at 92°C. Anhydrous beryllium sulfate [13510-49-1] results on heating the dihydrate in air to 400°C. Decomposition to BeO starts at ~650°C, the rate is accelerated by heating up to 1450°C. At 750°C the vapor pressure of SO_3 over $BeSO_4$ is 48.7 kPa (365 mm Hg).

2. Economic Aspects

Beryllium is principally consumed in the metallic form, either as an alloy constituent or as the pure metal. Consequently, there is no industry associated with beryllium compounds except for beryllium oxide, BeO, which is commercially important as a ceramic material. Beryllium oxide powder was available at \$ 45/kg (\$ 100/lb) in 2001 (11).

3. Health and Safety Factors

Beryllium-containing materials can be potentially harmful if mishandled. Care must be taken in the fabrication and processing of beryllium products to avoid inhalation of airborne beryllium particulate matter such as dusts, mists, or fumes in excess of prescribed work place limits. Inhalation of fine airborne beryllium may cause chronic beryllium disease, a serious lung disorder, in certain sensitive individuals. However, most people, perhaps as many as 99%, do not react to beryllium exposure at any level (see BERYLLIUM AND BERYLLIUM ALLOYS). International Agency for Research on Cancer (IARC) classified beryllium and beryllium compounds as carcinogenic to humans (10,12).

BIBLIOGRAPHY

"Beryllium Compounds" in *ECT* 1st ed., Vol. 2, pp. 505–509, by B. R. F. Kjellgren, The Brush Beryllium Company; "Beryllium and Beryllium Oxides" in Suppl. 2, pp. 86–89, by B. R. F. Kjellgren, The Brush Beryllium Company; "Beryllium Compounds" in *ECT* 2nd ed., Vol. 3, pp. 474–480, by C. W. Schwenzfeier, Jr., The Brush Beryllium Company; "Beryllides" in Suppl. 2, pp. 73–80, by A. J. Stonehouse, The Brush Beryllium Company; "Beryllium Compounds" in *ECT* 3rd ed., Vol. 3, pp. 824–829, by K. Walsh and G. H. Rees, Brush Wellman Inc.; in *ECT* 4th ed., Vol. 4, pp. 147–153, by A. James Stonehouse and Mark N. Emly, Brush Wellman, Inc.

CITED PUBLICATIONS

1. W. W. Beaver, in D. W. White and J. E. Burke, eds., *The Metal Beryllium, American Society for Metals*, Novelty, Ohio, 1955, pp. 570–598.
2. A. R. Taylor and T. E. Gardner, *U.S. Bur. Mines Rep. Invest.* 6664 (1964).
3. R. W. Baker and co-workers, *J. Org. Chem.* **159**, 123 (1978).
4. W. A. Young, *J. Phys. Chem.* **64**, 1003 (1960).
5. A. J. Stonehouse and co-workers, in J. T. Weber and co-workers, *Compounds of Interest in Nuclear Reactor Technology*, AIME, New York, 1964, pp. 445–455.
6. R. M. Paine and co-workers, in Ref. 5, pp. 495–509.
7. R. L. Fleischer and R. J. Zabala, *Metall. Trans. A* **20**(7), 1279 (July 1989).
8. W. W. Beaver and co-workers, *J. Nucl. Mater.* **14**, 326 (1964).
9. A. Goldsmith, H. J. Hirschhorn, and T. E. Waterman, *Thermophysical Properties of Solid Materials*, Vol. 3, *Ceramics*, Armour Research Foundation, WADC-TR-58-476, revised, Nov. 1960, pp. 67, 69–70, 81.
10. M. M. Mroz and co-workers, in E. Bingham, B. Cohrseen, and C. H. Powell, eds., *Patty's Toxicology*, 5th ed., Vol. 2, John Wiley & Sons, Inc., New York, 2001, Chapt. 27.
11. L. D. Cunningham, "Beryllium", *Mineral Commodity Summaries*, U.S. Geological Survey, Jan 2002.

12. International Agency for Research on Cancer (IARC), *Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans; Beryllium, cadmium, mercury, and exposures in the glass manufacturing industry*. Vol. 58, IARC, Lyon, France, 1993, pp. 41–117.

GENERAL REFERENCES

D. A. Everest, *The Chemistry of Beryllium*, Elsevier Publishing Company, Amsterdam/London/New York, 1964.

"Argnoberyllium compounds" in *G. Melins Handbook of Inorganic Chemistry*, Part 1, 8th ed., 1987.

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