

BERYLLIUM, BERYLLIUM ALLOYS AND COMPOSITES

1. Beryllium

Beryllium [7440-41-7], Be, specific gravity = 1.848 g/mL, and mp = 1287°C, is the only light metal having a high melting point. The majority of the beryllium commercially produced is used in alloys, principally copper–beryllium alloys (see CAST COPPER ALLOYS). The usage of unalloyed beryllium is based on its nuclear and thermal properties, and its uniquely high specific stiffness, ie, elastic modulus/density values. Beryllium oxide ceramics (qv) are important because of the very high thermal conductivity of the oxide while also serving as an electrical insulator. The only commercial extraction plant operating in the Western world is that of Brush Wellman at Delta, Utah using both beryl and bertrandite ores as input.

1.1. Occurrence. The beryllium content of the earth's surface rocks has been estimated at 4–6 ppm (1). Although 45 beryllium-containing minerals have

been identified, only beryl [1302-52-9] and bertrandite [12161-82-9] are of commercial significance.

Gemstone beryl (emerald, aquamarine, and beryl) approaches a pure beryllium–aluminum–silicate composition, $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. Beryl is widely distributed in fine-grained, unzoned pegmatite dikes and in pockets in zoned pegmatite dikes. Beryl is usually obtained as a by-product from mining zoned pegmatite deposits to recover feldspar [68476-25-5], spodumene [1302-37-0], or mica [12001-26-2]. The crushed ore is hand sorted to yield the characteristically hexagonal-shaped beryl crystals that are frequently green or blue in color. Beryl is primarily obtained from Brazil but commercial deposits also occur in China, Argentina, Africa, India, and Russia. A BeO content of 10% is considered necessary for the economic extraction of beryllium from beryl ore.

Bertrandite, $4\text{BeO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$, became of commercial importance in 1969 when the deposits of Spor Mountain in the Topaz district of Utah were opened. These deposits are believed to have been derived from fluorine-rich hydrothermal solutions at shallow depths (2). Whereas economical beneficiation of these ores averaging <1% BeO has not been achieved, these deposits are commercially viable because of the large reserves present, open-pit mining, and the fact that the beryllium may be extracted by leaching with sulfuric acid. Although some beryl is processed, the majority of beryllium is now obtained from bertrandite.

1.2. Properties. A summary of physical and chemical constants for beryllium is compiled in Table 1 (3–7). One of the more important characteristics of beryllium is its pronounced anisotropy resulting from the close-packed hexagonal crystal structure. This factor must be considered for any property that is known or suspected to be structure sensitive. As an example, the thermal expansion coefficient at 273 K of single-crystal beryllium was measured (8) as 10.6×10^{-6} parallel to the a -axis and 7.7×10^{-6} parallel to the c -axis. The actual expansion of polycrystalline metal then becomes a function of the degree of preferred orientation present and the direction of measurement in wrought beryllium.

Beryllium has high X-ray permeability approximately seventeen times greater than that of aluminum. Natural beryllium contains 100% of the ^9Be isotope. The principal isotopes and respective half-life are ^6Be , 0.4 s; ^7Be , 53 d; ^8Be , 10^{-16} s; ^9Be , stable; ^{10}Be , 2.5×10^6 y. Beryllium can serve as a neutron source through either the (α, n) or $(n, 2n)$ reactions. Beryllium has a low ($9 \times 10^{-30} \text{m}^2$) absorption cross-section and a high ($6 \times 10^{-28} \text{m}^2$) scatter cross-section for thermal neutrons making it useful as a moderator and reflector in nuclear reactors (qv). Such application has been limited, however, because of gas-producing reactions and the reactivity of beryllium toward high temperature water.

At ambient temperatures beryllium is quite resistant to oxidation; highly polished surfaces retain the brilliance for years. At 700°C, oxidation becomes noticeable in the form of interference films, but is slow enough to permit the working of bare beryllium in air at 780°C. Above 850°C, oxidation is rapid to a loosely adherent white oxide. The oxidation rate at 700°C is parabolic but may become linear at this temperature after 24–48 h of exposure. In the presence of moisture this breakaway oxidation occurs more rapidly and more extensively. Beryllium oxide [1304-56-9], BeO, forms rather than beryllium nitride [1304-54-7], Be_3N_2 , but in the absence of oxygen, nitrogen attacks beryllium >900°C.

Table 1. Physical and Chemical Properties of Beryllium

Parameter	Value
at no.	4
at wt.	9.0122
electronic structure	$1s^2 2s^2$
at radius, pm	112.50
at vol at 298 K, mL/mol	4.877
crystal lattice constants, pm	$a = 228.56,$
α -Be, hexagonal close-packed (hcp)	$c = 358.32,$
	$c/a = 1.5677$
β -Be, body-centered cubic (bcc) at 1523 K	$a = 255.0$
transformation pt, hcp to bcc, K	1527
mp, °C	1287
bp, °C	2472
density, g/mL	
at 298 K	1.8477
at 1773 K	1.42
heat of fusion, $\Delta H_{\text{fus}}, \text{J/g}^a$	1357
heat of sublimation, $\Delta H_{\text{sub}}, \text{kJ/g}^a$	35.5–36.6
heat of vaporization, $\Delta H_{\text{v}}, \text{kJ/g}^a$	25.5–34.4
heat of transformation, J/g^a	837
standard entropy, $S^\circ, \text{J/(g}\cdot\text{K)}^a$	1.054
standard enthalpy, $H^\circ, \text{J/g}^a$	216
contraction on solidification, %	3
vapor pressure, MPa ^b	
at 500 K	5.7×10^{-29}
at 1000 K	4.73×10^{-12}
at 1560 K	4.84×10^{-6}
specific heat, $\text{J/(g}\cdot\text{K)}^a$	
at 298 K	1.830
at 700 K	2.740
thermal conductivity at 298 K, $\text{W/(m}\cdot\text{K)}$	220
linear coefficient of thermal expansion, 278–333 K ^c	11.4×10^{-6}
electrical resistivity at 298 K, $\Omega\cdot\text{m}$	4.31×10^{-8}
reflectivity, %	
white light	50–55
infrared (10.6 μm)	98
sound velocity, m/s	12,600

^a To convert J to cal, divide by 4.184.^b To convert MPa to psi, multiply by 145.^c Value is for unworked, isostatically pressed powder metallurgy metal.

Beryllium is susceptible to corrosion under aqueous conditions especially when exposed to solutions containing the chloride ion. It is rapidly attacked by seawater. High purity water, containing small amounts of HNO_3 to passivate stainless steel in the system, was quite inert to beryllium over a period of years in a primary U.S. nuclear test reactor. At high temperatures beryllium reduces water, releasing hydrogen and forming BeO . Due to its position in the emf series, beryllium undergoes galvanic corrosion when coupled in a corrosive environment to the common structural metals; manganese, zinc, and magnesium are the only such metals anodic to beryllium. Protective systems used for beryllium include chromic acid passivation, chromate conversion coatings, chromic acid anodizing, electroless plating (qv), and paints.

Beryllium reacts readily with sulfuric, hydrochloric, and hydrofluoric acids. Dilute nitric acid attacks the metal slowly, whereas concentrated nitric acid has little effect. Hot concentrated alkalis give hydrogen and the amphoteric beryllium hydroxide [13327-32-7], $\text{Be}(\text{OH})_2$. Unlike the aluminates, the beryllates are hydrolyzed at the boil.

Beryllium reacts with fused alkali halides releasing the alkali metal until equilibrium is established. It does not react with fused halides of the alkaline earth metals to release the alkaline earth metal. Water-insoluble fluoroberyllates, however, are formed in a fused-salt system whenever barium or calcium fluoride is present. Beryllium reduces halides of aluminum and heavier elements. Alkaline earth metals can be used effectively to reduce beryllium from its halides, but the use of alkaline earth's other than magnesium [7439-95-4] is economically unattractive because of the formation of water-insoluble fluoroberyllates. Formation of these fluorides precludes efficient recovery of the unreduced beryllium from the reaction products in subsequent processing operations.

Chemically, beryllium is closely related to aluminum [7429-90-5] from which complete separation is difficult.

1.3. Ore Processing. *Sulfate Extraction of Beryl.* The Kjellgren-Sawyer sulfate process (9) is used commercially for the extraction of beryl. The ore is melted at 1650°C and quenched by pouring into water. The resulting noncrystalline glass is heat-treated at $900\text{--}950^\circ\text{C}$ to further increase the reactivity of the beryllium component. After grinding to $<74\text{ }\mu\text{m}$ (200 mesh), a slurry of the powder in concentrated sulfuric acid [7664-93-9] is heated to $250\text{--}300^\circ\text{C}$ converting the beryllium and aluminum to soluble sulfates. The silica fraction remains in the dehydrated, water-insoluble form. The nearly dry mass is leached with water using a countercurrent decantation washing procedure and the resulting solution is fed to the same type of solvent extraction process as that used for bertrandite extraction.

Extraction of Bertrandite. Bertrandite-containing tuff from the Spor Mountain deposits is wet milled to provide a thixotropic, pumpable slurry of below $840\text{ }\mu\text{m}$ (-20 mesh) particles. This slurry is leached with sulfuric acid at temperatures near the boiling point. The resulting beryllium sulfate [13510-49-1] solution is separated from unreacted solids by countercurrent decantation thickener operations. The solution contains $0.4\text{--}0.7\text{ g/L Be}$, 4.7 g/L Al , $3\text{--}5\text{ g/L Mg}$, and 1.5 g/L Fe , plus minor impurities including uranium [7440-61-1], rare earths, zirconium [7440-67-7], titanium [7440-32-6], and zinc [7440-66-6]. Water conservation practices are essential in semiarid Utah, so the wash water introduced in the countercurrent decantation separation of beryllium solutions from solids is utilized in the wet milling operation.

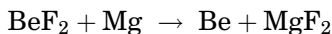
A beryllium concentrate is produced from the leach solution by the countercurrent solvent extraction process (10). Kerosene [8008-20-6] containing di(2-ethylhexyl) phosphate [298-07-7] is the water immiscible beryllium extractant. Warming accelerates the slow extraction of beryllium at room temperature. The raffinate from the solvent extraction contains most of the aluminum and all of the magnesium contained in the leach solution.

The loaded organic phase is stripped of beryllium using an aqueous ammonium carbonate [506-87-6] solution, apparently as a highly soluble ammonium

beryllium carbonate [65997-36-6] complex, $(\text{NH}_4)_4\text{Be}(\text{CO}_3)_3$. All of the iron [7439-89-6] contained in the leach solution is coextracted with the beryllium. Heating the strip solution to $\sim 70^\circ\text{C}$ separates the iron and a small amount of coextracted aluminum as hydroxide or basic carbonate precipitates, which are removed by filtration. The stripped organic phase is treated with sulfuric acid to recover the di(2-ethylhexyl)phosphate.

Heating the ammonium beryllium carbonate solution to 95°C causes nearly quantitative precipitation of beryllium basic carbonate [66104-24-3], $\text{Be}(\text{OH})_2 \cdot 2\text{BeCO}_3$. Evolved carbon dioxide and ammonia are recovered for recycle as the strip solution. Continued heating of the beryllium basic carbonate slurry to 165°C liberates the remaining carbon dioxide and the resulting beryllium hydroxide [13327-32-7] intermediate is recovered by filtration. The hydroxide is the basic raw material for processing into beryllium metal, copper–beryllium and other alloys, and beryllia [1304-56-9] for ceramic products. This process recovers $\sim 90\%$ of the beryllium content of bertrandite.

1.4. Production of Beryllium Metal. *Reduction of Beryllium Fluoride with Magnesium.* The Schwenzfeier process (11) is used to prepare a purified, anhydrous beryllium fluoride [7787-49-7], BeF_2 , for reduction to the metal. Beryllium hydroxide is dissolved in ammonium bifluoride solution to give a concentration of 20 g/L Be at pH 5.5. The solution is made basic by the addition of solid calcium carbonate and heating to 80°C precipitating residual aluminum. Lead dioxide is added to the solution to convert manganese [7439-96-5] to insoluble MnO_2 and to precipitate chromium [7440-47-3] as insoluble lead chromate. After filtration, ammonium sulfide is added to the filtrate to remove heavy-metal impurities and any solubilized lead from the lead dioxide treatment. After filtration and balancing to the proper stoichiometry, ammonium fluoroberyllate [14874-86-3], $(\text{NH}_4)_2\text{BeF}_4$, is crystallized by concurrent evaporation under vacuum. The salt is continuously removed by centrifugation and washed lightly, the mother liquor and washings being returned to the evaporator. The $(\text{NH}_4)_2\text{BeF}_4$ is charged into inductively heated, graphite-lined furnaces where it is thermally decomposed to beryllium fluoride and ammonium fluoride. The ammonium fluoride is vaporized into fume collectors for recycle to the dissolving process. The molten beryllium fluoride flows continuously from the bottom of the furnace and is solidified as a glassy product on a water-cooled casting wheel (12).



The reduction of beryllium fluoride using magnesium has not been forced above an 85% yield. Complications include: volatilization of unreacted magnesium resulting from the exotherm of the reaction; oxidation of the beryllium because, unlike most metals, beryllium floats on the reaction slag and is not protected from oxygen; and the viscous nature of the magnesium fluoride slag at the melting point of beryllium making complete metal collection difficult.

In commercial practice (13), $\sim 70\%$ of the stoichiometric magnesium is used, which gives an excess of beryllium fluoride principally to provide a fluid slag under reduction conditions enabling metal collection. Magnesium metal and beryllium fluoride in the solid form are charged into a graphite crucible at a temperature of $\sim 900^\circ\text{C}$. When the exothermic reaction is completed, the reaction products are heated to $\sim 1300^\circ\text{C}$ to allow molten beryllium to separate and

float on top of the slag. The molten metal and slag are then poured into a graphite-receiving pot where both solidify. The mixed reaction product is then crushed and water-leached in a ball mill. The excess beryllium fluoride quickly dissolves causing disintegration of the reaction mass and liberation of the beryllium as generally spherical pebbles. The leach liquor in this step is continuously passed through the ball mill removing the fine, insoluble magnesium fluoride particles and leaving the beryllium pebble in the mill body. The magnesium fluoride is filtered from the leach water and discarded. The leach water containing the excess beryllium fluoride is recycled to the aqueous portion of the fluoride preparation process. The beryllium pebble contains ~97% beryllium along with entrapped reduction slag and unreacted magnesium metal.

Electrolytic Processes. The electrolytic procedures for both electrowinning and electrorefining beryllium have primarily involved electrolysis of the beryllium chloride [7787-47-5], BeCl_2 , in a variety of fused-salt baths. The chloride readily hydrolyzes making the use of dry methods mandatory for its preparation (see BBERYLLIUM COMPOUNDS). For both ecological and economic reasons there is no electrolytically derived beryllium available in the market place.

Commercial electrorefining of beryllium has been carried out to obtain a purer metal than the magnesium-reduced beryllium. The most notable purification obtained with respect to iron was specified as 300 ppm maximum, and typically between 100 and 200 ppm Fe as contrasted with the 500–1000 ppm, found in the Mg-reduced beryllium metal. There are no metallurgical advantages to having a metal of improved purity. However, high purity foil is used in some instrumentation X-ray windows.

Vacuum Melting and Casting. A vacuum melting operation is required for beryllium regardless of its origin. The magnesium-reduced pebble contains trapped slag and unreacted magnesium. The electrolytically derived materials contain entrapped electrolyte not removed by aqueous leaching. Vacuum melting is carried out in induction-heated vacuum furnaces using MgO crucibles and graphite ingot molds. The free magnesium and excess beryllium fluoride or electrolyte vaporize during the melting cycle. Nonvolatiles, such as beryllium oxide, magnesium fluoride, and beryllium carbide [506-66-1], separate from the molten metal as a dross that sinks to and adheres to the bottom of the crucible. The purified metal is poured into ingots weighing ~180 kg. This operation also serves as the recycle point for valuable beryllium scrap such as machining chip and trimmings.

Because beryllium is primarily used as a powder metallurgy product or as an alloying agent, casting technology in the conventional metallurgical sense is not commonly utilized with the pure metal.

1.5. Fabrication. Beryllium has a close-packed hexagonal crystal structure. At room temperature there are no slip systems operating in a direction outside the basal plane, which sharply restricts ductility. Extensive attempts to increase ductility by purification have not been successful, apparently because of a degree of covalent bonding along the c axis, although bonding along the a axis is metallic at temperatures above 200°C beryllium exhibits substantial ductility. Alloying has not as yet been found advantageous and the metal is used alone.

Most beryllium hardware is produced by powder metallurgy techniques achieving fine-grained microstructure having a nearly random crystallographic

orientation thus providing a strong material with substantial ductility at room temperature. For some specialized applications, sheet and foil have been rolled from cast beryllium ingot. Such material exhibits an average grain size of 50–100 μm as compared to the typical 12 μm or less of the powder metallurgy products.

Beryllium powder is manufactured from vacuum-cast ingot using impact grinding or jet milling. The casting is first reduced to chip by a machining operation such as lathe turning. The chip is then pneumatically directed against a beryllium target using high pressure, dry air producing a powder of $<44\ \mu\text{m}$ (-325 mesh) after appropriate screening. Finer powders, eg, less than 20 μm , are prepared by ball milling with tungsten carbide or steel balls followed by air classification.

Beryllium powder is consolidated by a variety of powder metallurgy processes to near-full density bodies (99+% of theoretical density) (see METALLURGY, POWDER). Vacuum hot-pressing of right circular cylinders at 1000–1200°C at 7 MPa (1000 psi) using graphite tooling has been the most commonly used procedure, particularly where large shapes are desired. The pressing sizes that can be produced range from 18 to 183 cm in diameter and 15 to 168 cm in length. The largest pressing made to date weighed ~ 3000 kg.

Hot-isostatic-pressing (HIP) is replacing the vacuum hot-pressing procedure for all but the largest shapes. This process, in the case of beryllium involves loading the beryllium powder into a mild steel can of the desired configuration, outgassing the powder under vacuum, subsequently sealing the can, and applying argon gas pressure to the can in an isostatic manner in a cold-wall pressure vessel having an internal furnace heated to the appropriate temperature. The usual processing conditions for beryllium are 103 MPa (15,000 psi) at 1000°C. The advantages of the HIP process include the economics of consolidating the powder to near the final desired shape as contrasted to the right circular cylinder limitation of the vacuum hot-pressing procedure, a shorter floor-to-floor time for a given shape, essentially full density (at 100% of theoretical), and higher strengths than the hot-pressed material because there is little or no grain growth during the HIP procedure.

Cold-isostatic-pressing followed by vacuum sintering or HIP is also used to manufacture smaller intricate shapes. In this instance, beryllium powder is loaded into shaped rubber bags and pressed isostatically in a pressure chamber up to 410 MPa (60,000 psi). After the pressing operation the rubber bag is stripped from the part which is then vacuum sintered to $\sim 99\%$ of theoretical density at about 1200°C. If full theoretical density is required, the sintered part may be simply given a HIP cycle because there is no open porosity after vacuum sintering. In a similar manner, conventional axial cold-pressing followed by vacuum sintering is commercially used for small (under 1 kg) parts where appropriate.

Beryllium sheet is produced by rolling powder metallurgy billets clad in steel cans at 750–790°C. Beryllium foil down to 12.5 μm (0.0005 in.) in gauge is commercially available. Extrusion is also carried out in this temperature region, again using steel cans to contain the powder metallurgy billet. Working of beryllium results in the establishment of a high degree of preferred crystallographic orientation, generally enhancing the properties in the direction of working, but impairing properties normal to the working direction. This is

Table 2. Commercial Grades of Vacuum Hot-Pressed Beryllium, Composition by weight

	S-65	S-200F	I-70A	I-220B
Be, min %	99.0	98.5	99.0	98.0
BeO, max %	1.0	1.5	0.7	2.2
Al, max ppm	600	1000	700	1000
C, max ppm	1000	1500	700	1500
Fe, max ppm	800	1300	1000	1500
Mg, max ppm	600	800	700	800
Si, max ppm	600	600	700	800
other, each max ppm	400	400	400	400

particularly true for tensile elongation. Cross-rolling schedules are followed in rolling that ensure good tensile elongation in the plane of the sheet (10% minimum by specification; 20% is not unusual), but the strain capacity in the thickness direction is limited. The preferred orientation problem has limited the use of wrought beryllium; many shapes other than common structurals are usually machined from billets where standard metallurgical practice with other metals would involve rolled, extruded, or forged components.

The chemical composition and guaranteed tensile properties of the available commercial grades of beryllium in the vacuum hot-pressed form are summarized in Tables 2 and 3. Other consolidation procedures have similar specification property levels. The S-65 grade is of particular interest in that a room temperature minimum tensile elongation of 3% is guaranteed when tested in any direction. This strain capacity is achieved through control of the beryllium oxide content to <1%, control and balancing of impurities such as iron and aluminum, and consolidation by techniques which maximize randomization of the crystallographic texture.

1.6. Economic Aspects. The largest consumption of beryllium is in the form of alloys, principally the copper–beryllium series. The consumption of the pure metal has been quite cyclic in nature depending on specific governmental programs in armaments, nuclear energy, and space. The amount of beryllium extracted from bertrandite has ranged between 150 and 270 metric tons per year since 1986 (14). Small quantities of beryl were also processed during this period.

Table 3. Tensile Properties of Beryllium Commercial Grades at Ambient Temperatures^a

	S-65B	S-200F	I-70A	I-220B
Tensile strength, min MPa ^b				
Ultimate	290	324	241	379
Yield strength ^c	207	241	172	276
Elongation, min %	3	2	2	2
Microyield, min MPa ^b		27	12	34

^a Young's Modulus is 303 GPa (4.4×10^7 psi) and the Poisson's ratio = 0.07.

^b To convert MPa to psi, multiply by 145.

^c 0.2% offset.

The price of beryllium oxide powder was \$154/kg in 2001. The beryllium content of copper–beryllium master alloy was \$352/kg. Pure beryllium powder was priced at \$615/kg whereas simple shapes in vacuum hot-pressed material were priced at about \$685/kg in 2001.

1.7. Analysis. Instrumental methods such as atomic absorption and emission spectrometry, and gamma activation are employed in most beryllium determinations; however, gravimetric and tritrimetric methods remain useful when high accuracy is required.

Beryllium in reference standards is determined by precipitation of beryllium hydroxide using ammonia. The precipitate is ignited to beryllium oxide and weighed. Interfering elements that precipitate must be removed or masked. Excess ammonia minimizes coprecipitation of manganese, cobalt, copper, nickel, and zinc. Ethylenedinitrilo tetraacetate (EDTA) minimizes precipitation of aluminum, chromium, and iron and further reduces coprecipitation of manganese, cobalt, copper, nickel, and zinc. Alternatively, aluminum, iron, titanium, zirconium, cobalt, nickel, copper, cadmium, and zinc can be removed by precipitation with 8-hydroxyquinoline prior to addition of ammonia. Fluoride, citrate, and tartrate prevent complete precipitation of beryllium and must be absent. Fluoride can be removed by strong fuming in sulfuric acid; phosphate can be removed by precipitation with ammonium molybdate; and silica contamination of the ignited beryllium oxide can be eliminated by adding sulfuric and hydrofluoric acids to the crucible, fuming to dryness, and re-igniting to constant weight (15,16).

Assay of beryllium metal and beryllium compounds is usually accomplished by titration. The sample is dissolved in sulfuric acid. Solution pH is adjusted to 8.5 using sodium hydroxide. The beryllium hydroxide precipitate is redissolved by addition of excess sodium fluoride. Liberated hydroxide is titrated with sulfuric acid. The beryllium content of the sample is calculated from the titration volume. Standards containing known beryllium concentrations must be analyzed along with the samples, as complexation of beryllium by fluoride is not quantitative. Titration rate and hold times are critical; therefore use of an automatic titrator is recommended. Other fluoride-complexing elements such as aluminum, silicon, zirconium, hafnium, uranium, thorium, and rare earth elements must be absent, or must be corrected for if present in small amounts. Copper–beryllium and nickel–beryllium alloys can be analyzed by titration if the beryllium is first separated from copper, nickel, and cobalt by ammonium hydroxide precipitation (15,16).

Optical emission or atomic absorption spectrophotometry usually analyzes beryllium alloys. Low voltage spark emission spectrometry is used for the analysis of most copper–beryllium alloys. Spectral interferences, other interelement effects, metallurgical effects, and sample inhomogeneity can degrade accuracy and precision and must be considered when constructing a method (17).

Inductively coupled argon plasma (ICP) and direct current argon plasma (DCP) atomic emission spectrometry are solution techniques that have been applied to copper–beryllium, nickel–beryllium, and aluminum–beryllium alloys, beryllium compounds, and process solutions. The internal reference method, essential in spark source emission spectrometry, is also useful in minimizing drift in plasma emission spectrometry (17). Electrothermal (graphite

furnace) atomic absorption spectrophotometry is employed if the beryllium concentration is very low (17–19).

The commercial ores, beryl and bertrandite, are usually decomposed by fusion using sodium carbonate. The melt is dissolved in a mixture of sulfuric and hydrofluoric acids and the solution is evaporated to strong fumes to drive off silicon tetrafluoride, diluted, then analyzed by atomic absorption or plasma emission spectrometry. If sodium or silicon are also to be determined, the ore may be fused with a mixture of lithium metaborate and lithium tetraborate, and the melt dissolved in nitric and hydrofluoric acids (17).

Metallic impurities in beryllium metal were formerly determined by dc arc emission spectrography, following dissolution of the sample in sulfuric acid and calcination to the oxide (16). This technique is still used to determine less common trace elements in nuclear-grade beryllium. However, the common metallic impurities are more conveniently and accurately determined by dc plasma emission spectrometry, following dissolution of the sample in a hydrochloric–nitric–hydrofluoric acid mixture. Thermal neutron activation analysis has been used to complement dc plasma and dc arc emission spectrometry in the analysis of nuclear-grade beryllium.

The methods of choice for beryllium oxide in beryllium metal are inert gas fusion and fast neutron activation. In the inert gas fusion technique, the sample is fused with nickel metal in a graphite crucible under a stream of helium or argon. Beryllium oxide is reduced, and the evolved carbon monoxide is measured by infrared absorption spectrometry. Beryllium nitride decomposes under the same fusion conditions and may be determined by measurement of the evolved nitrogen. Oxygen may also be determined by activation with 14-MeV neutrons (20). The only significant interferents in the neutron activation technique are fluorine and boron, which are seldom encountered in beryllium metal samples.

Total carbon in beryllium is determined by combustion of the sample, along with an accelerator mixture of tin, iron, and copper, in a stream of oxygen (15,16). The evolved carbon dioxide is usually measured by infrared absorption spectrometry. Beryllium carbide can be determined without interference from graphitic carbon by dissolution of the sample in a strong base. Beryllium carbide is converted to methane, which can be determined directly by gas chromatography. Alternatively, the evolved methane can be oxidized to carbon dioxide, which is determined gravimetrically (16).

Chlorine and fluorine in beryllium metal are isolated by pyrohydrolysis or by distillation (21). Fluoride and chloride in the condensate are determined by ion-selective electrode or colorimetrically.

The gamma activation (photoneutron) method is virtually interference-free and applicable to all types of samples. The sample is irradiated with gamma rays from an ^{124}Sb source and detectors arrayed around the samples count emitted neutrons. The neutron flux is proportional to the beryllium content of the sample. A nearly linear response from 0.01 to 100% beryllium is obtained using 25 g of sample and counting times of 200 s. The method is nondestructive, rapid, and requires minimal sample preparation. Minor interferences result from very high concentrations of neutron- or gamma-absorbing elements. Solid and liquid samples can both be analyzed directly; however, sample geometry is critical. Heavy lead shielding is needed to protect the operator. The source, which requires a

license in the United States, must be replaced several times per year to maintain a satisfactory counting rate (22,23).

Environmental and biological samples are usually analyzed for beryllium by atomic absorption, using a nitrous oxide—acetylene flame for high concentrations and the graphite furnace for low concentrations. Organic matter in biological samples and air samples collected on filter paper is removed by wet ashing with an oxidizing acid mixture. If refractory beryllium oxide is present, hydrofluoric acid is added to complete its dissolution. Plasma emission spectrometry offers beryllium detection limits that are nearly as good as graphite furnace atomic absorption, as well as reduced interferences and multielement capability. Beryllium in environmental samples has also been converted to volatile complexes for determination by gas chromatography, but this technique has not achieved widespread use (17,24,25).

Spectrophotometric and fluorometric reagents, once used extensively for determination of beryllium (26,27), are seldom employed. Reviews of beryllium analysis are available (15–17,24–30).

1.8. Safe Handling. Beryllium, beryllium-containing alloys and composites, and beryllium oxide ceramic in solid or massive form present no special health risk (31). However, like many industrial materials, beryllium, beryllium-containing alloys and composites, and beryllium oxide ceramic may present a health risk if handled improperly. Care must be taken in the fabrication and processing of beryllium products to avoid inhalation of airborne beryllium-containing particulate such as dust, mist, or fume in excess of the prescribed occupational exposure limits. Inhalation of fine airborne beryllium may cause chronic beryllium disease, a serious lung disorder, in certain sensitive individuals. The biomedical and environmental aspects of beryllium have been summarized (32).

1.9. Occupational Exposure Limits. The U.S. Occupational Safety and Health Administration (OSHA) has set mandatory limits for occupational respiratory exposures. The OSHA Permissible Exposure Limits (PELs) for beryllium are (1) the time-weighted average (TWA) exposure over an 8-h day is not to exceed beryllium concentrations of $2 \mu\text{g}/\text{m}^3$ of air; (2) the Ceiling exposure should not exceed beryllium concentrations of $5 \mu\text{g}/\text{m}^3$ of air for a 30-min period; and, (3) the Peak exposure should never exceed $25 \mu\text{g}/\text{m}^3$ (33). It remains the best practice to maintain levels of all forms of airborne beryllium as low as reasonably achievable. To protect the general public from environmental exposure to airborne beryllium, the U.S. Environmental Protection Agency has established a beryllium standard of 10 g/day as a permissible emission into the air surrounding a plant (34).

Control Measures. Operations capable of generating airborne beryllium-containing particulate, such as melting, machining, welding, grinding, etc, can be effectively controlled using a combination of engineering controls such as local exhaust ventilation and other work practice controls such as wet methods, personal protective equipment (PPE), and housekeeping. The type and capacity of local exhaust ventilation required will depend upon the amount and speed of particle generation. Protective overgarments or work clothing must be worn by persons who may come in contact with dust, mist or fume. Used disposable clothing should be containerized and disposed of in a manner that prevents airborne exposure during subsequent handling activities. Contaminated work clothing

and overgarments must be managed in a manner that prevents secondary airborne exposure to family or laundry personnel handling soiled work clothing. When controls are inadequate, or are being developed and potential exposures are above the occupational exposure limits, approved respirators must be used as specified by an Industrial Hygienist or other qualified professional. To determine the effectiveness of engineering and work practice controls and measure the extent of potential exposure, workplace air monitoring should be periodically conducted by prescribed air sampling and analytical methods. Detailed environmental, health and safety guidance is provided by the manufacturer in the Material Safety Data Sheet (MSDS).

Recycling. Beryllium, beryllium-containing alloys, and beryllium oxide ceramic can be recycled. Because of the high cost of producing beryllium, producers repurchase clean scrap from customers for recycling and reuse.

1.10. Uses. The applications for beryllium center around its nuclear and thermal properties, uniquely high specific modulus or stiffness considered on a weight basis, and excellent dimensional stability along with good machinability. These properties are all combined with a relatively high melting point for a light metal. Beryllium is used extensively as a radiation window, both in source and detector applications, because of its ability to transmit radiation, particularly low energy X-rays.

Beryllium is used in the space shuttle orbiter as window frames, umbilical doors, and the navigation base assembly. An important application for beryllium is inertial guidance components for missiles and aircraft. Here the lightweight, high elastic modulus, dimensional stability, and the capability of being machined to extremely close tolerances are all important.

Beryllium is important as a sensor support material in advanced fire-control and navigation systems for military helicopters and fighter aircraft utilizing the low weight and high stiffness of the material to isolate instrumentation from vibration. It is also used for scanning mirrors in tank fire-control systems.

Beryllium is used in satellite structures in the form of both sheet and extruded tubing and is a very important material for all types of space optics. Beryllium oxide ceramic applications take advantage of high room temperature thermal conductivity, very low electrical conductivity, and high transparency to microwaves in microelectronic substrate applications.

2. Beryllium Composites

Beryllium's reactivity limits its uses in the formulation of composite materials. There are only two composite formulations available. These are beryllium–aluminum and beryllium–beryllium oxides. The composition and important physical and mechanical properties for these composites are given in Tables 4, 5, and 6.

Beryllium-Aluminum (Be–Al) was reintroduced into the marketplace in 1990. Invented in the 1960s, a 62 wt% beryllium balance aluminum formulation was patented and trademarked as Lockalloy. Production of Lockalloy ceased in the 1970s. In 1990, BeAl was reintroduced into the market as AlBeMet. It's initial application replaced an aluminum alloy in an actuator arm (the device

Table 4. **Composition of Beryllium Composites**

Composite	Trade name	Beryllium	Aluminum	Beryl oxide
beryllium aluminum	AlBeMet			
	AlBeMet 162	62 wt %	38 wt %	
	AlBeMet 140	40 wt %	60 wt %	
beryllium– beryllium oxide	E-Material			
	E-60	40 vol %		60 vol %
	E-40	60 vol %		40 vol %
	E-20	80 vol %		20 vol %

that holds the read–write heads) for a computer hard disk drive assembly. Significant applications for beryllium aluminum currently include aircraft structures, avionics, satellite structures, electronics and automobile racecars. Beryllium–aluminum is available in wrought, cast and semisolid product (35) forms. The beryllium content of these materials varies from a low of 20 wt% to a high of 65%. The attractive properties of this composite are: low density, high stiffness, high thermal conductivity, high heat capacity and a moderate coefficient of thermal expansion. For parts where stiffness is important to their design, aluminum beryllium will save one-half the weight over an equivalent aluminum part.

A beryllium–beryllium oxide (Be–BeO) composite (36,37) was introduced in 1990. This composite is available in 60, 40, and 20 vol% beryllium oxide. The attributes of Be and BeO are a low density, high stiffness, high thermal conductivity, high heat capacity and a low-coefficient of thermal expansion (CTE). The CTE can be tailored to match the CTE of other electronic materials such as gallium arsenide and silicon by varying the volume percent beryllium oxide in the composite. This composite is used primarily in weight sensitive space and aircraft electronics. The Be–BeO stiffness/density ratio translates into thermal management components that are one-half to one-tenth the weight of the same component in competing materials.

2.1. Fabrication. The primary method of manufacturing composites of beryllium is powder processes. The beryllium–beryllium oxide composite (36) is produced by blending S200F beryllium powder with a relatively coarse crystalline beryllium oxide powder (38). The coarse beryllium oxide crystals are necessary to obtain the high thermal performance of this composite. The beryllium/beryllium oxide powders are blended, loaded into a steel can, the can's gas is evacuated, and the can is sealed. This sealed, evacuated can is consolidated to a 99+% dense block using hot isostatic pressing. Beryllium–beryllium oxide parts are fabricated from this block using conventional sawing and machining practices.

Most of the metal–metal beryllium–aluminum composite is manufactured from a gas atomized beryllium–aluminum powder. This powder is produced by melting beryllium and aluminum in the proper proportion. This molten metal is poured through a round orifice to produce a thin stream of liquid metal. High pressure gas is used to break this stream up into small droplets and cool these droplets to a fine spherical solid powder.

Table 5. Important Physical and Mechanical Properties of Beryllium–Aluminum

Product	Product form	Tensile ultimate strength (MPa)	Tensile yield strength (0.2% offset) MPa	Elong. %	Density g/cm ³	Stiffness modulus GPa	Young's modulus GPa	CTE pPM K	Thermal conductivity W/M/ K
<i>Composite—beryllium aluminum</i>									
AlBeMet 162	extruded ^a	427	317	11	2.10	200		13.9	220
AlBeMet 162	hot isotatic pressed block	289	220	5	2.10	200		13.9	220
AlBeMet 140	rolled sheet	270	185	14	2.26	170		16.4	210

^a Longitudinal direction.

Table 6. Important Physical and Mechanical Properties of Beryllium–Beryllium Oxide

Product	Product form	Density g/cm ³	Stiffness Young' modulus GPa	CTE PPM/K	Thermal conductivity w/m/k
<i>Composite—beryllium–beryllium oxide</i>					
E-60	hot isostatic pressed block	2.52	330	6.1	230
E-40	hot isostatic pressed block	2.30	317	7.5	220
E-20	hot isostatic pressed block	2.06	303	8.7	210

The most popular consolidation method for beryllium–aluminum powder is hot isostatic pressing. Beryllium–aluminum powder is loaded into a steel container. The gas in this container is removed using a vacuum pump while the powder-filled can is heated. The sealed, degassed steel can is consolidated using hot isostatic pressure.

An alternative to consolidation by hot isostatic pressure is to extrude the powder filled can through a die using an extrusion press. Here, the sealed, degassed cans are right cylindrically shaped to accommodate the extrusion press. These cans are heated and placed into the extrusion press and pressed or forced through a die significantly smaller than the powder-filled can.

Either the hot isostatic pressing or extruding produces essentially 100% dense metal. Extrusion would be the preferred method of producing right regular shapes such as a rod or tube. Irregular shapes or parts too large for extrusion (extrusion equipment limits one to a 10-in. diameter cylindrical rod) are produced by conventional machining practices from the hot isostatically pressed block. Blocks as large as 150 cm in diameter and 250 cm long can be produced.

There is a small amount of beryllium–aluminum produced by an investment casting (39,40), process. It is very difficult to produce good castings of beryllium aluminum because of the 618°C difference in the melting points of the two metals. In casting, the beryllium solidifies first producing a rigid but porous network of solid surrounded by molten aluminum. As the cast cools, this aluminum solidifies shrinking in volume. This volume reduction leaves behind pores or voids as the aluminum has difficulty feeding this solidifying contracting aluminum pocket through the rigid beryllium network. These pores compromise the mechanical and physical properties of the beryllium aluminum composite such that casting can only currently produce a few parts.

3. Alloys Containing Beryllium

A small beryllium addition produces strong effects in several base metals. In copper and nickel this alloying element promotes strengthening through

precipitation hardening. In aluminum alloys a small addition improves oxidation resistance, castability, and workability. Other advantages are produced in magnesium, gold, and zinc. Many other alloying compositions have been researched (41), but no alloy with commercial importance approaching these dilute alloys has emerged.

3.1. Copper Beryllium Alloys. Wrought copper–beryllium alloys rank high among copper alloys in attainable strength and, at this high strength, useful levels of electrical and thermal conductivity are retained (see COPPER ALLOYS). Applications include uses in electronic components where their strength-formability-elastic modulus combination leads to use as electronic connector contacts (42); electrical equipment where fatigue strength, conductivity, and thermal relaxation resistance leads to use as switch and relay blades; control bearings where antigalling features are important; housings for magnetic sensing devices where low magnetic susceptibility is critical; and resistance welding systems where hot-hardness and conductivity are important in structural components.

Hardness, thermal conductivity, and castability are important in most casting alloy applications. For example, casting alloys are used in molds for plastic component production where fine cast-in detail such as wood or leather texture is desired. These alloys are also used for thermal management in welding equipment, waveguides, and mold components such as core pins. High strength alloys are used in sporting equipment such as investment cast golf club heads. Cast master alloys of beryllium in copper, nickel, and aluminum are used in preparing casting alloys or otherwise treating alloy melts.

Because these alloys are precipitation hardenable, they can be customized for specific requirements across a wide range of property combinations. Advances in composition control, processing, and recycling technology have broadened the capabilities and expanded the range of application. Data sheets published by the manufacturers and others (43) give compositions, properties, and typical applications.

Composition and Properties. Commercial wrought copper–beryllium alloys contain 0.2–2.0 wt % beryllium, and 0.2–2.7 wt % cobalt [7440-48-4] or up to 2.2 wt % nickel [7440-02-0], in copper [7440-50-8]. Casting alloys are somewhat richer, having up to 2.85 wt % beryllium. Within this composition window, two distinct classes, which are referred to as the “high strength” alloys, and the “high conductivity” alloys, are available. Beryllium in the high strength alloys imparts a gold luster whereas the high conductivity alloys appear reddish, like copper, in color. Compositions and physical properties of these alloys are given in Table 7.

Alloy C17200 is foremost among the wrought high strength alloys in industrial importance. A free-machining version, containing a small lead addition to C17200 and available only as rod and wire, is designated C17300. The wrought high conductivity alloys have traditionally contained 0.2–0.7 wt % Be and up to 2.5 wt % Co or Ni. Alloy developments have focused on leaner wrought high conductivity compositions such as C17410, having up to 0.4 wt % Be and 0.6 wt % Co and, most recently, C17460 with similar Be content and up to 1.4 wt % Ni. The high strength casting alloys contain 1.6–2.85 wt % Be, nominally 0.5 wt % Co, and a small silicon addition. A minor titanium addition or increased cobalt

Table 7. **Physical Properties of Cast and Wrought Copper–Beryllium Alloys^a**

Product form	Alloy	Major constituents(a)					Density (g/cm ³)	Elastic modulus (GPa)	Thermal expansion coefficient (ppm/C) 20–200 C	Thermal conductivity (w/m c)	Melting range (C)
		Be	Co	Ni	Si	Pb					
wrought	C17200	1.80–2.00	0.25				8.36	131	17	105	870–980
	C17300	1.80–2.00	0.25			0.3	8.41	131	17	105	890–1000
wrought	C17510	0.2–0.6		1.7			8.83	138	18	240	1000–1070
	C17410	0.15–0.50	0.5				8.80	138	18	230	1020–1070
	C17460	0.15–0.50		1.25			8.80	138	18	222	1030–1080
cast	C82500	1.90–2.25	0.4		0.25		8.30	130	18	97	870–970
	C82800	2.50–2.85	0.4		0.25		8.14	130	18	90	850–930
cast	C82200	0.35–0.80		1.7			8.83	140	18	195–250	1040–1080

^a Weight percent (wt %). Balance copper + residual elements. Nominal unless range is shown

content is used for grain refinement. The high conductivity casting alloys contain up to 0.8 wt % Be. In all cases, the third element addition, either cobalt or nickel, is needed to restrict grain growth during annealing by establishing a dispersion of beryllide particles in the matrix. In the high strength alloys this third element addition also retards softening from overaging during precipitation hardening.

Thermal Treatments. The copper–beryllium alloys are classic precipitation strengthening systems. Hardening occurs because the solubility of beryllium is much less at low temperatures than at higher temperatures. In practice, the hardening process is conducted in two steps: solution treatment, commonly called solution annealing or simply annealing, followed by precipitation hardening, also known as age hardening. Some users of the alloys prefer to do the age hardening themselves after part forming.

Solution annealing consists of heating below the solidus temperature to dissolve beryllium in the copper matrix, then rapidly quenching to room temperature to retain beryllium in supersaturated solid solution. The high strength alloys are typically annealed in the range 760–800°C and the high conductivity alloys in the range of 900–955°C. It is not necessary to hold the metal at the annealing temperature for more than a few minutes to affect solution treatment. As a guide, thin strip or wire are annealed in less than two minutes, heavy section products, once they reach the annealing temperature, are usually held at temperature for 30 min or less. In this state the alloy is soft and highly workable and therefore may be readily rolled or drawn into strip or wire.

Precipitation hardening involves reheating solution annealed, or solution annealed and cold-worked, material for a time sufficient to nucleate and grow the submicroscopic beryllium-rich precipitates responsible for hardening. For the high strength alloys, age hardening is typically performed in the range of 260–400°C for 0.1–4 h. The high conductivity alloys are age hardened in the range of 425–565°C for 0.5–8 h. Cold-work between solution annealing and hardening increases both the magnitude and rate of strengthening response for wrought products. Up to 37% cold work imparted by cold rolling or drawing, can be provided in commercial products.

During the precipitation process, strength increases, passes through a peak, and then decreases more gradually, ultimately reaching a steady-state level. Electrical conductivity is lowest in the solution-annealed condition because of the beryllium dissolved in the copper matrix. During age hardening, electrical conductivity increases steadily as dissolved beryllium precipitates. Characteristic curves describing this behavior at various hardening temperatures are useful in process control.

The mechanical and electrical properties of selected high strength alloys in cast and wrought forms are provided in Table 8. A similar compilation for the high conductivity alloys is given in Table 8. The mechanical properties shown in the tables correspond to standard hardening times and temperatures and therefore are close to peak conditions. Considerable latitude exists for achieving a wide variety of special mechanical and electrical property combinations.

Melting, Casting, and Hot Working. The first step in the manufacture of copper–beryllium is production of a nominally 4 wt % Be master alloy by carbothermic reduction of beryllium oxide under molten copper in an electric arc furnace. This master alloy is remelted in coreless induction furnaces and diluted

Table 8. **Mechanical Properties and Electrical Conductivity of Selected Cast and Wrought High Conductivity Copper–Beryllium Alloys**

Product form	Alloy	Temper	Precipitation heat treatment	Yield strength 0.2% offset (MPa)	Ultimate tensile strength (MPa)	Elongation (% in 50.8 mm)	Rockwell hardness	Electrical conductivity (%IACS)
wrought	C17510	annealed/age hardened	2–3 h at 480C or Mill	550–890	680–900	10–25	B20–45	45–60
		cold rolled/age hardened		650–830	750–940	8–20	B78–88	48–60
			Mill					
	C17410	cold rolled/age hardened ^a	Mill	550–825	655–895	7–20	B89–102	45–55
	C17460	cold rolled/age hardened ^a	Mill	655–860	795–860	10 min		50 min
cast	C82200	as-cast	3 h at 340C Annealed + 3 h at 340C	150–240	310–410	15–25	B50–65	
		cast/aged		170–380	380–520	10–20	B65–90	45–50
		annealed/aged		480–550	620–760	3–15	B92–100	45–50

^a Combined property range for two ascending cold rolled/age hardened (mill hardened) tempers of each of these alloys.

with additional copper, cobalt or nickel, and recycled scrap to adjust the final composition. Melts are directly chill-cast into rectangular or round billets for hot-working to wrought product forms or are poured as ingots for remelting into cast products. The semicontinuously cast rectangular billets are hot-rolled to plate or to coils of hot band for conversion to strip. Round billets are hot-extruded to bar, seamless tube, or rod coil. Hot-working temperatures typically coincide with solution annealing temperatures; about 705–815°C for the high strength alloys and ~815–925°C for the high conductivity alloys. Hot-worked products are softened as needed by solution annealing before further processing.

Finishing. Subsequent processing of wrought copper–beryllium alloys typically includes one or more cycles of cold-working and intermediate solution annealing. Chemical cleaning is performed after each anneal. Processing after the final anneal may include cold-rolling, heat treatment to specified strength levels (mill hardening, with subsequent chemical cleaning), and, for strip, slitting to specified width. Wrought products are also treated with corrosion inhibiting films to extend shelf life. During manufacture, mill products are monitored for stringent control of as-cast composition, nonmetallic inclusion content, intermediate and finish annealed grain size, dimensional consistency, as-shipped mechanical properties, age hardening response, and surface condition. Mill hardened products are solderable and platable as-shipped. User-age hardened products typically require chemical cleaning prior to soldering or plating.

Cast Products. The copper–beryllium alloys can be melted in resistance, gas, induction, and electric arc furnaces. Induction furnaces, in particular, allow close control of melt temperature and agitation to minimize gas absorption, beryllium loss, and dross formation. Drossing is minimized by melting under inert gas or in air melting by use of a graphite cover. Furnace refractories suitable for melting copper–beryllium casting alloys include clay graphite, silicon carbide, alumina, magnesia, and zirconia. High silica refractories may react with copper–beryllium melts. Most common casting methods for copper-base alloys are applicable to copper–beryllium. These include pressure casting, investment casting, centrifugal casting, the Shaw process, die casting, and casting in permanent, ceramic, and various types of sand molds. Shrinkage is similar to tin bronze and less than that of aluminum, silicon, or manganese bronze. Metal or graphite chills may be placed in sand molds to promote directional solidification and reduce shrinkage porosity.

Impurities above maximum levels indicated in published specifications (44) can affect the properties of the finished casting. Silicon, eg, is normally added to many of the copper–beryllium casting alloys to promote fluidity, but excess silicon reduces ductility. Excessive zinc, tin, phosphorus, lead, and chromium behave similarly. Aluminum and iron reduce age hardening response, and degrade electrical and thermal properties.

Copper–beryllium alloy castings can be precipitation hardened in the as-cast condition, however, maximum precipitation hardened strength is achieved by solution annealing the castings, followed by age hardening.

Nickel–Beryllium Alloys. Dilute alloys of beryllium in nickel, like their copper–beryllium counterparts, are age hardenable (45). Nickel–beryllium alloys are distinguished by very high strength; good bend formability in strip; and high resistance to fatigue, elevated temperature softening, stress relaxation,

and corrosion. Wrought nickel–beryllium is available as strip, rod, and wire and is used in mechanical, electrical, and electronic components that must exhibit good spring properties at elevated temperatures. Examples include thermostats, bellows, pressure sensing diaphragms, other high reliability mechanical springs, plus burn-in connectors and sockets.

A variety of nickel–beryllium casting alloys exhibit strengths nearly as high as the wrought products with castability advantages. Casting alloys are used in molds and cores for glass and plastic molding, and in jewelry and dental applications by virtue of their high replication of detail in the investment casting process. Nickel–beryllium has also been used in golf club heads by reason of its good castability, excellent hardness and ductility combination and corrosion resistance.

Composition and Properties. A single composition, UNS NO3360, is supplied in wrought form. Nickel–beryllium casting alloys include 6 wt % Be master alloy, a series with 2.2–2.6 wt % Be including one with a minor carbon addition for enhanced machinability, and a series of ternary nickel–base alloys with up to 2.75 wt % Be and 12 wt % Cr. Composition and physical properties of several of these alloys are presented in Table 9; mechanical properties are given in Table 10. Although displaying only a fraction of the conductivity of copper–beryllium, nickel–beryllium exceeds the conductivity of stainless steel and most other nickel–base alloys by a factor of 2–3 because of its relatively low total alloy content.

Thermal Treatments. Processing of nickel–beryllium alloys is analogous to processing high strength copper–beryllium. The alloys are solution annealed at a temperature high in the alpha nickel region to dissolve a maximum amount of beryllium, then rapidly quenched to room temperature to create a supersaturated solid solution. Precipitation hardening involves heating to a temperature

Table 9. Properties of Cast and Wrought Nickel–Beryllium Alloys^a

Constituents wt % ^b							
Alloy ^c	Be	Other	Density g/ml	Elastic modulus GPa ^d	Thermal Expansion coefficient ppm/°C ^e	Thermal conductivity W/(mK)	Melting range °C
NO3360 ^f	1.80–2.05	0.5 Ti	8.27	195–210	4.5	28	1195–1325
M220C	2.0	0.5 C	8.08–8.19	179–193	4.8	36.9 ^g	1150
(NO3220)						51.1 ^h	(solidus)
42C	2.75	12.0 Cr	7.8	193		34.6 ⁱ	1165
							(solidus)

^a Tabulated properties apply to age hardened products

^b The remainder is nickel and residual elements. Nominal unless range is shown.

^c Alloy is cast unless otherwise indicated.

^d To convert GPa to psi, multiply by 1.45×10^5

^e From 20 to 550°C

^f Wrought alloy.

^g At 38°C

^h At 538°C

ⁱ At 93°C

Table 10. Mechanical Properties of Cast and Wrought Beryllium Nickel Alloys

Temper	Heat treatment ^a	Yield strength 0.2% offset MPa ^b	Ultimate tensile strength, MPa ^b	Elongation, % in 50.8 mm ^c	Rockwell hardness	Electrical conductivity IACS %c
<i>Wrought Alloy NO3360</i>						
annealed		275–485	655–895	30	A39–57	4
cold-rolled		1035–1310	1065–1310	1	A55–75	4
annealed/age hardened	2.5	1035 ^c	1480 ^c	12	15N78–86	6
cold-rolled/age/ hardened	1.5	1585 ^c	1860 ^c	8	15N83–90	6
mill hardened		690–860	1065–1240	14		5
mill hardened		1515–1690	1790–2000	8		5
<i>Cast Alloy M220C (NO3220)</i>						
annealed		345 ^c	760 ^c	35	B95 ^c	
annealed/age hardened	3	1380 ^c	1620 ^c	4	C54 ^c	
<i>Cast Alloy 42C</i>						
annealed/age hardened	3		1034 ^c	6	C38 ^c	5

^a Time given is at 510°C.^b To convert from MPa to ps, multiply by 145.^c Value given is minimum value.

below the equilibrium solvus to nucleate and grow metastable Be -rich precipitates that harden the matrix. Wrought NO3360 is typically solution annealed at ~1000°C. Cold-work up to ~40% may be imparted between solution annealing and aging to increase the rate and magnitude of the age hardening response. Aging to peak strength is performed at 510°C, up to 2.5 h for annealed and 1.5 h for cold-worked material. Under-, peak-, and overaging behavior are displayed in Table 10. To improve the machinability of N03360 rod the solution annealed and optionally cold worked material may be underaged briefly at 412°C to a hardness of about Rockwell C 25-30, which reduces gumminess and benefits machined surface finish. Final peak age hardening at 510°C is performed after machining to impart full hardness. The cast binary alloys are solution annealed at ~1065°C and aged at 510°C for 3 h. Cast ternary alloys are annealed near 1090°C and given the same aging treatment. Castings are typically used in the solution annealed and aged condition for maximum strength. Unlike copper–beryllium alloy castings, nickel–beryllium castings exhibit little or no age hardening response in the as-cast condition.

Production. Manufacturing of nickel–beryllium products commences with induction melting of a charge consisting of 6% Be–Ni master alloy, additive elements, and recycled scrap. The 6% Be–Ni master is produced by induction melting commercial purity beryllium and nickel rather than by carbothermic

reduction of beryllium oxide as for copper–beryllium master. Rectangular or round billets are semicontinuously cast for hot-working to strip or round products. Hot-rolling and extrusion are performed in the vicinity of the solution annealing temperature, $\sim 980^{\circ}\text{C}$. The hot-worked products are brought to a ready-to-finish size by one or more iterations of solution annealing and cold-working. Mechanical or chemical cleaning is required after each anneal to remove oxide films. A final solution anneal establishes the finished grain size and age hardening response. Cold-working and mill age hardening may follow the final anneal.

Nickel–beryllium casting alloys are readily air melted, in electric or induction furnaces. Melt surface protection is supplied by a blanket of argon gas or an alumina-base slag cover. Furnace linings or crucibles of magnesia are preferred, with zirconium silicate or mullite also adequate. Sand, investment, ceramic, and permanent mold materials are appropriate for these alloys. Beryllium in the composition is an effective deoxidizer and scavenger of sulfur and nitrogen.

Aluminum-Beryllium Alloys. Small additions of beryllium to aluminum systems are known to improve consistency (38). When as little as 0.005–0.05 wt % beryllium is added as a master alloy to an aluminum alloy during melting, a protective surface oxide film is formed. This film reduces drossing, increases cleanliness, and improves fluidity. Preferentially oxidizable alloy additions such as magnesium and sodium are protected from oxidation during melting and casting. Hydrogen absorption is also reduced, as are mold reactions. Castings thus have improved surface finish, consistent strength, and higher ductility. Additional benefits cited include reduced tarnishing, improved buffing and polishing response, and consistency of aging response, particularly in alloys containing magnesium or silicon. Applications include aircraft skin panels and aircraft structural castings in alloy A357.

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