CHAPTER 12.5

Beryllium

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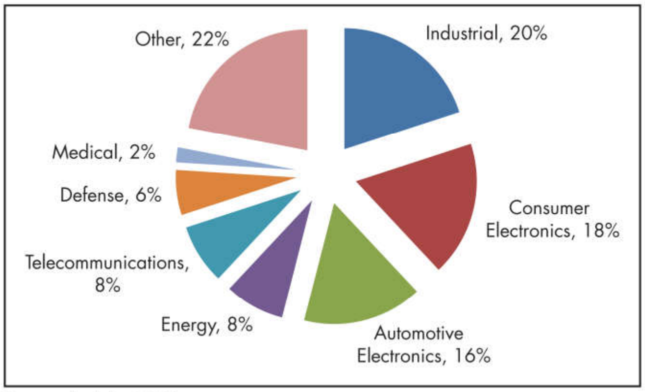
Beryllium is one of 12 "strategic and critical materials" as defined by section 12(1) of the Stock Piling Act of the National Defense Stockpile program that is recommended to be stocked in 2015 at all times. A strategic and critical material is defined as: "(i) would be needed to supply the military, industrial, and essential civilian needs of the United States during a national emergency and (ii) are not found or produced in the United States in sufficient quantities to meet such need" (Under Secretary of Defense for Acquisition, Technology and Logistics 2015).

Beryllium metal and alloys are used in many military and aerospace applications. Beryllium metal has the highest specific stiffness of any structural metal and incredibly high thermal conductivity and heat capacity. The United States continues to be the largest extractor, producer, fabricator, and consumer of beryllium in the world. There is only one producer in the United States that is fully integrated. Materion Corporation has the largest reserves of beryllium ore in the form bertrandite, controlling roughly 65% of the reserves and covering 85% of the world's needs. A yearly extraction of 200–300 t (metric tons) of beryllium ore has been enough to cover the world's demand after the end of the Cold War (Jaskula 2016). Other producers in China, Russia, and Kazakhstan contribute to the world production of beryllium, mostly supplying the Asian markets.

Beryllium metal and its composites are mostly used in defense, space, and scientific applications. Beryllium alloys in the form of strip and bulk products (such as copper-beryllium [Cu-Be]) and beryllium oxide ceramics, however, are typically used in industrial and commercial applications. Figure 1 shows the distribution of beryllium use based on market application.

Beryllium compounds and alloys have been known to have detrimental health effects on some people. For example, beryllium metal, beryllium oxide, and beryllium-copper in the form of very small dust particles may sensitize an individual if inhaled and may lead to a condition known as chronic beryllium disease. Other compounds, such as solutions containing beryllium fluoride if in contact with the skin, may produce a condition known as acute beryllium disease. It is highly recommended that safety data sheets for beryllium-containing materials be reviewed carefully when handling.



Source: Jaskula 2016

Figure 1 Beryllium metal, alloys, and composites distribution based on sales revenues

BERYLLIUM MINERALS AND ORES

The common sources for beryllium are bertrandite and beryl minerals. Beryl is a beryllium-aluminum-silicate containing roughly 67 wt % silica, 19 wt % alumina, and 14 wt % beryllium oxide. Examples of beryllium-rich beryl include emeralds and aquamarine. Economically minable grades of beryl ore typically contain 6–12 wt %. BeO. Beryl ore mining is not a primary operation in most cases, and rather, it is a secondary operation from the extraction of mica and lithium minerals. The concentration of beryl ores is typically done by hand sorting, as the amounts involved are not significant enough to justify large investment of capital equipment. Sources of beryl ores include Brazil, South Africa, and Mozambique (Jaskula 2016).

The other source of beryllium of high importance is bertrandite, which is a beryllium-silicate-hydroxide mineral with composition $Be_4Si_2O_7(OH)_2$. In the United States, the development of the large Spor Mountain bertrandite reserve in Utah decreased the amount of beryl required from international sources. The tuffs of rhyolitic nature in the Utah source

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contain 0.1–1.0 wt % of BeO. Depending on the market value of beryllium, the economically minable amounts can vary, beginning at 0.20–0.70 wt %. BeO. Despite the bertrandite ore grade being lower than that of beryl ore, the recovery of beryllium from these ores is less energy intensive (Montoya et al. 1962).

BENEFICIATION OF BERYLLIUM-CONTAINING ORES

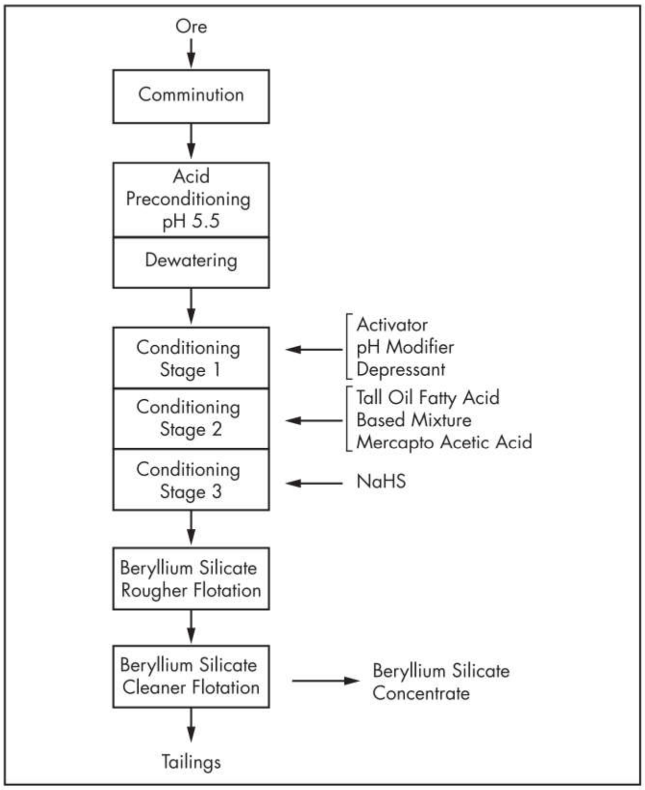
Hand picking is currently the method of choice for concentrating beryl and bertrandite ores. The investment of capital equipment cannot be justified to concentrate these ores because of the relatively low demand for beryllium. Portable *beryl pickers* or *berylometers* have been made to aid in the location and selection of high beryllium-containing ores. The suspected beryllium-containing ore body is irradiated with a gamma source. The beryllium contained in the minerals has the natural isotope Be^9, which emits a neutron and forms the Be^8 isotope under gamma radiation. Within the same berylometer, there is a Geiger counter that quantifies the amount of neutrons emitted and correlates it with a precalibrated concentration of beryllium (Darwin and Buddery 1960).

The relatively low density of beryl and bertrandite makes them difficult to concentrate using density means versus quartz and other gangue minerals. The magnetic properties are also nondistinguishable from gangue minerals. The most promising beneficiation process is flotation. In the 1960s, the following process was defined (Havens 1963):

1. Phenacite, bertrandite, and beryl are separated from associated minerals, such as quartz, calcite, manganocalcite, fluorite, sericite, apatite, and micas, using fatty acid flotation.
2. Fluoride ions and polyphosphate ions depressants are added to prevent the entry of undesired minerals into the froth. Crushed ore in the form of an aqueous pulp is treated with a water-soluble fluoride, such as sodium fluoride, and a water-soluble polyphosphate, such as sodium hexametaphosphate with and without tetrasodium pyrophosphate.
3. A flocculating agent, such as alum or aluminum sulfate, is useful in flocculating the concentrate or froth for fast removal from the flotation cell.
4. After the conditioning time, a collector oil, such as oleic acid, tall oil fatty acid, or fish oil fatty acids, is added to the pulp. After an additional conditioning period, air is passed into the pulp, and the froth concentrate is recovered.
5. The residual pulp is reconditioned with sodium hexametaphosphate and fatty acid collector and froth floated again, recovering a second concentrate that may be treated separately.
6. The process is carried out at room temperature and atmospheric pressure conditions.

More recently, Bulatovic (1988) patented a process for the beneficiation of bertrandite ores. Figure 2 shows a general schematic of the following process:

1. The ore is ground to a P_{80} of –400 mesh (37 µm).
2. Sulfuric acid is added as a preconditioner, adjusting the pH between 5 and 5.5. After the pretreatment, the slurry is thickened to 65 wt % solids.



Source: Bulatovic 1988

Figure 2 Flotation process for the concentration of phenacite and bertrandite ores

3. The pretreated slurry is treated with sodium carbonate to adjust the pH to 9.5. Sodium fluoride is typically used as an activator, but sodium silico-hexafluoride can also be used.
4. Sodium hexametaphosphate and carboxymethyl cellulose are used as depressants for albite, mica, carbonates, fluorite, and siliceous gangues. The conditioning stage is followed by the addition of the collector mixture.
5. The collector mixture consists of cresylic acid, an aliphatic alcohol, and kerosene.
6. The conditioning is followed by a conventional rougher and cleaner flotation stages.

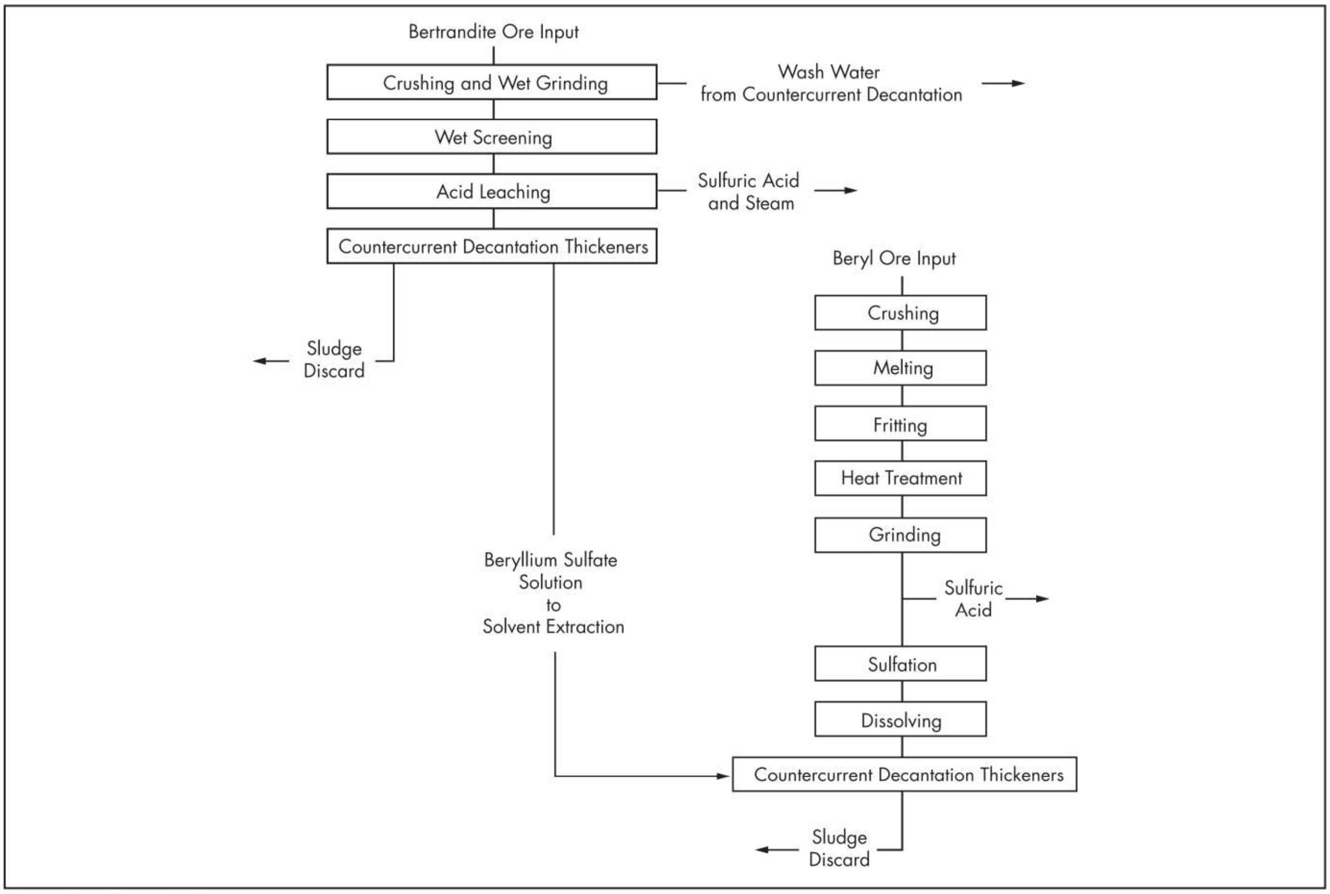
There has been a renewed interest in developing processes for the beneficiation of bertrandite, particularly in China. Some conditions are very similar, with variations in the chemicals used (Wei et al. 2009).

EXTRACTION OF BERYLLIUM

Many processes have been suggested for the extraction of elemental beryllium from ore concentrates (Walsh 2009). In this chapter, only the process currently in production and most economically viable is reviewed. Other important extraction methods include the electrolysis of beryllium-containing molten salts.

BERYLLIUM HYDROXIDE PRODUCTION

The current preferred method of extraction is the sulfate process for decomposing the ore and recovering the beryllium



Source: Stonehouse 1986

Figure 3 Beryllium sulfate solution production from bertrandite and beryl concentrates

oxide component (Sawyer and Kjellgren 1935; Kjellgren 1946). In the sulfate process for beryllia production, water-soluble beryllium and aluminum sulfates are formed by reacting beryl or bertrandite with sulfuric acid at 400°C. The process starts by activating the beryl ore by melting and rapid quenching into a frit material using cold water. The energy consumption imposes an economic trade-off, forcing the use of high-grade beryl ore containing 6–10 wt % beryllium oxide. Bertrandite, conversely, does not require this frit-forming step because it reacts readily with the sulfuric acid solution. Silica is precipitated out as an insoluble compound. The sulfate reactions can be described as follows:

$$3BeO\cdot Al_2O_3\cdot 6SiO_2 + 6H_2SO_4 = 3BeSO_4 + Al_2(SO_4)_3 + 6SiO_2 + 6H_2O \quad \textbf{(EQ 1)}$$

$$Be_4Si_2O_7(OH)_2 + 4H_2SO_4 = 4BeSO_4 + 2SiO_2 + 5H_2O \quad \textbf{(EQ 2)}$$

Figure 3 shows a flowchart of the process that uses both beryl and bertrandite ore concentrates down to the beryllium sulfate solution (Stonehouse 1986).

The slurry is passed through a series of countercurrent decantation vats for washing and recovering the soluble beryllium sulfate from the siliceous solids. The typical overflow leach solution contains roughly 12 g/L beryllium in approximately 0.5 M free sulfuric acid. The leach solution typically contains more than 90% of the beryllium content of the input concentrate (Stonehouse 1986).

The next steps consist of a series of purification processes to reject the impurities before beryllium hydroxide recovery. Several methods have been suggested for separating iron, aluminum, and other heavy metals from the beryllium sulfate solution, but the reaction with ammonium or potassium sulfate to form an alum is the process used nowadays.

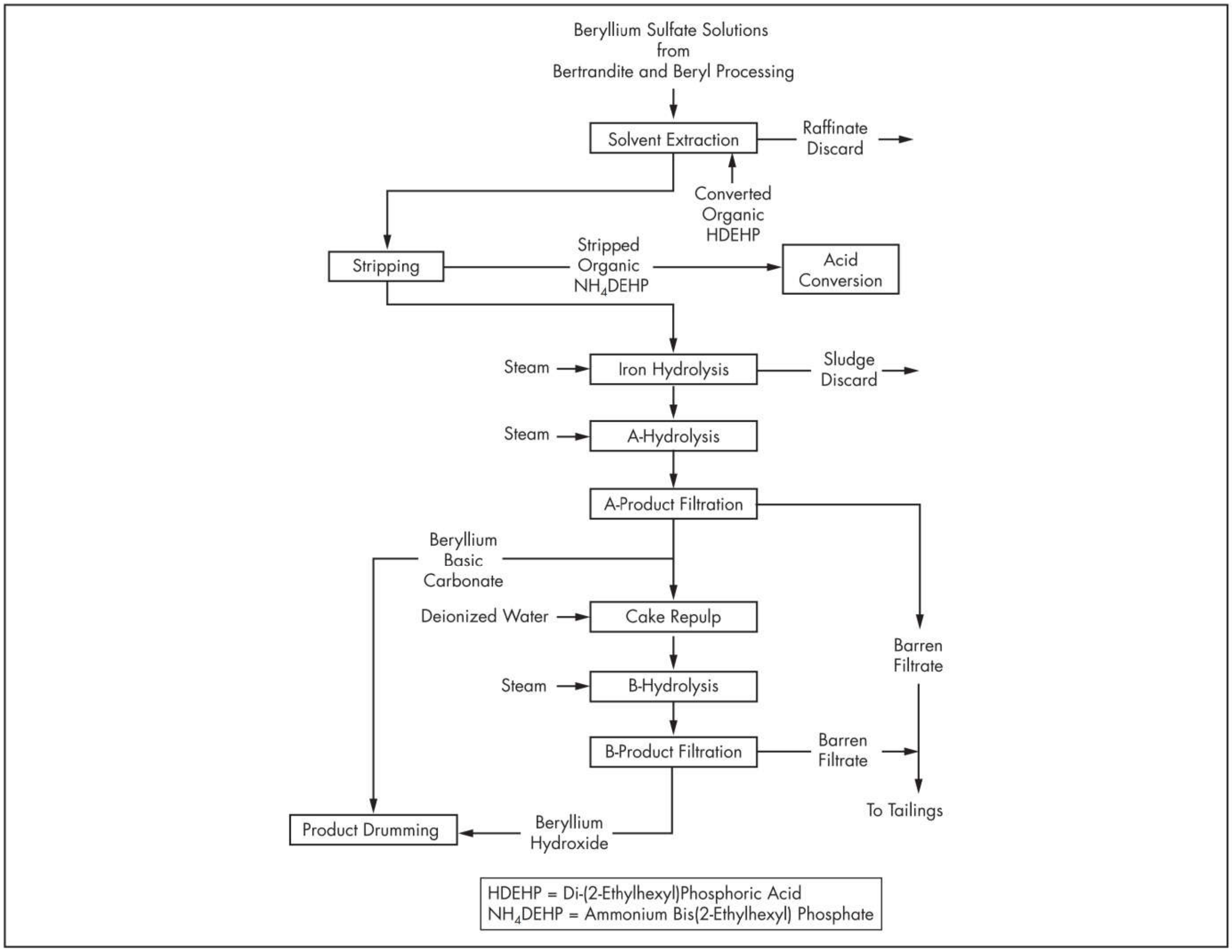
The free sulfuric acid leach liquor is neutralized with aqueous ammonia to pH = 1, creating enough ammonium sulfate to form ammonium alum. By cooling below 15°C, the crystallization of ammonium alum, $Al_2(SO_4)_3\cdot(NH_4)_2SO_4\cdot 24H_2O$ is promoted. The crystals produced are removed by centrifugation. Organic chelating agents, such as the sodium salts of ethylenediaminetetraacetic acid (EDTA) and triethanolamine, are added to the centrifugate. The sequential additions of sodium hydroxide then yield the intermediate reactions:

$$BeSO_4 + 2NaOH = Na_2SO_4 + \alpha - Be(OH)_2 \quad \textbf{(EQ 3)}$$

$$\alpha - Be(OH)_2 + 2NaOH = Na_2BeO_2 + 2H_2O \quad \textbf{(EQ 4)}$$

The sodium beryllate solution is passed through a heat exchanger that hydrolyzes it and precipitates it into β-beryllium hydroxide:

$$Na_2BeO_2 + 2H_2O = 2NaOH + \beta - Be(OH)_2 \quad \textbf{(EQ 5)}$$



Source: Stonehouse 1986

Figure 4 Purification and precipitation of beryllium hydroxide from beryllium sulfate

The granular hydroxide produced is separated in continuous centrifuges, where it is washed and dewatered to less than 10 wt % free water.

Figure 4 shows the purification steps and precipitation of the beryllium hydroxide just described (Stonehouse 1986).

The original Sawyer–Kjellgren process just described was subsequently modified using solvent extraction technology with the sulfate leach solution. Foos and Maddox (1966) mention the recovery of beryllium from the organic extraction solvent by separation with aqueous ammonium carbonate. This ammonium beryllium carbonate solution is purified and boiled to precipitate beryllium basic carbonate. The beryllium hydroxide is then formed by a pressure hydrolysis step at 165°C. As before, the granular beryllium hydroxide is recovered by filtration.

Once the beryllium hydroxide has been produced, different processes exist to produce beryllium metal, copper-beryllium alloys, and beryllium oxide ceramics.

BERYLLIUM OXIDE

In a straightforward approach, beryllium oxide is produced from beryllium hydroxide directly by calcining. One drawback, however, is that the BeO powders contain elevated levels of fluorine or other impurities, which are detrimental to some of the high-density beryllium oxide ceramics. One alternative process proposed by Gadeau (1933) describes beryllium hydroxide preparation from beryl ore that is reacted with sodium fluorosilicate. The reaction forms a solution of sodium fluoroberyllate. The sodium fluoroberyllate is dried and mixed with sodium carbonate and calcined above 525°C. This second calcination product is leached in water to solubilize the sodium fluoride. A wet paste of beryllium oxide is obtained after solid–liquid separation and several water washings of the solid. Unfortunately, this wet paste of beryllium oxide retains elevated levels of fluoride and sodium, which are unsuitable for beryllium oxide ceramics.

Another commercial process for producing beryllium oxide involves a two-step process where the conversion of beryllium hydroxide to beryllium sulfate tetrahydrate is followed by the calcination of the hydrated sulfate to the oxide at temperatures higher than 1,100°C. This process produces SO_2, which requires secondary recovery processing to convert the acidic off-gas to a nonhazardous usable form. This process can be modified by using urea, ammonium oxalate, ammonium acetate, or ammonium sulfate. These chemicals are selected because of their ability to be completely removed during calcination. The addition of these substances is described by Schwenzfeier and Pomelee (1965).

The production of beryllium oxide makes possible the conversion of this material into usable ceramic materials, incorporation of beryllium into copper alloys, and preparation of metal matrix composites with beryllium metal.

BERYLLIUM METAL

In the past, the two commercial methods that were practiced for producing beryllium were based on converting the beryllium hydroxide into a chloride or a fluoride. Today, the preferred production process for beryllium metal extraction is the reduction of beryllium fluoride with magnesium (Stonehouse 1986). The production of beryllium fluoride from hydroxide takes place in two steps. First, the beryllium hydroxide is reacted with ammonium bifluoride, producing ammonium fluoroberyllate; then, the fluoroberyllate is thermally decomposed at elevated temperatures (>125°C) to produce beryllium fluoride and volatile ammonium fluoride:

$$Be(OH)_2 + 2NH_4{\cdot}HF_2 = (NH_4)_2BeF_4 + 2H_2O \qquad \textbf{(EQ 6)}$$

$$(NH_4)_2BeF_4 = BeF_2 + 2NH_4F \qquad \textbf{(EQ 7)}$$

The beryllium fluoride produced is then mixed with magnesium metal, which is heated to at least the melting point of beryllium metal (1,286°C). The magnesiothermic reduction kinetics increase considerably above 850°C, after both the magnesium and the beryllium fluoride are molten.

$$BeF_2 + Mg = MgF_2 + Be \qquad \textbf{(EQ 8)}$$

To enhance the yield of beryllium produced, an excess amount of beryllium fluoride helps in fragmenting the slag and releasing the entrapped beryllium globules. Once the temperature goes above the melting point of beryllium, fairly large pieces of beryllium coalesce.

After the beryllium metal has been cleaned and slag removed, it typically goes to a vacuum melting process to produce beryllium billets, which are then turned into chips and subsequently powder, which feeds the powder metallurgy process for making basic shapes or near-net shapes.

COPPER-BERYLLIUM ALLOYS

Copper-beryllium alloys are still one of the principle uses for beryllium, especially in a structural material. Copper-beryllium alloys with 0.008–5 wt % Be have been produced both by vacuum casting plus hot rolling and by vacuum casting and extrusion (London 1979). Copper and nickel alloys benefit from the addition of a few percentage points of beryllium, which significantly improves their mechanical properties.

Early in the 1900s, master alloys of copper-beryllium were produced by electrolysis methods. In 1939, Sawyer and Kjellgren replaced this process by the now more common carbothermic reduction of BeO in the presence of molten copper. An arc furnace is charged with copper and BeO, which reacts with carbon to reduce the BeO to beryllium metal, which then incorporates into the molten copper. The process operates in the temperature range from 1,800° to 2,100°C (Cribb and Ali 1994).

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