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材料手册 5

陶瓷 耐火材料 玻璃 聚合物 弹性体

François Cardarelli

Materials Handbook

A Concise Desktop Reference

Second Edition

哈爾濱工業大學出版社
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黑版贸审字08-2014-029号

Reprint from English language edition:
Materials Handbook A Concise Desktop Reference
by François Cardarelli
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图书在版编目（CIP）数据

材料手册. 5，陶瓷、耐火材料、玻璃、聚合物、弹性体：英文/（美）卡达雷利主编. —哈尔滨：哈尔滨工业大学出版社，2014. 4
（Springer手册精选原版系列）
ISBN 978-7-5603-4451-5

Ⅰ.①材… Ⅱ.①卡… Ⅲ.①材料科学-技术手册-英文 Ⅳ.①TB3-62

中国版本图书馆CIP数据核字（2013）第304258号

材料科学与工程
图书工作室

责任编辑 许雅莹 张秀华 杨 桦
出版发行 哈尔滨工业大学出版社
社 址 哈尔滨市南岗区复华四道街10号 邮编 150006
传 真 0451-86414749
网 址 http://hitpress.hit.edu.cn
印 刷 哈尔滨市石桥印务有限公司
开 本 660mm × 980mm 1/16 印张 15
版 次 2014年4月第1版 2014年4月第1次印刷
书 号 ISBN 978-7-5603-4451-5
定 价 76.00元

哈尔滨理工大学 藏書 图書馆

（如因印刷质量问题影响阅读，我社负责调换）

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10 Ceramics, Refractories, and Glasses

10.1 Introduction and Definitions

The word "ceramics" is derived from the Greek *keramos*, meaning solid materials obtained from the firing of clays. According to a broader modern definition, ceramics are either crystalline or amorphous solid materials involving only ionic, covalent, or iono-covalent chemical bonds between metallic and nonmetallic elements. Well-known examples are silica and silicates, alumina, magnesia, calcia, titania, and zirconia. Despite the fact that, historically, oxides and silicates have been of prominent importance among ceramic materials, modern ceramics also include borides, carbides, silicides, nitrides, phosphides, and sulfides.

Several processes, namely calcining and firing, are extensively used in the manufacture of raw and ceramic materials, and they must be clearly defined. Calcining consists in the heat treatment of a raw material prior to being used in the final ceramic material. The purpose of calcination is to remove volatile chemically combined constituents and to produce volume changes. Firing or burning is the final heat treatment performed in a kiln to which a green ceramic material is subjected for the purpose of developing a strong chemical bond and producing other required physical and chemical properties.

As a general rule ceramic materials can be grouped into three main groups: traditional ceramics, refractories and castables, and advanced or engineered ceramics.

Before describing each class, a description of the most common raw materials used in the manufacture of traditional and advanced ceramics, refractories, and glasses is presented below.

10.2 Raw Materials for Ceramics, Refractories and Glasses

10.2.1 Silica

Silica, with the chemical formula SiO_2 and relative molar mass of 60.084, exhibits a complex polymorphism characterized by a large number of reversible and irreversible phase transformations (Figure 10.1) usually associated with important relative volume changes ($\Delta V/V$). At low temperature and pressure *beta-quartz* (**β-quartz**) [14808-60-7] predominates, but above 573°C, it transforms reversibly into the high-temperature *alpha-quartz* (**α-quartz**) [14808-60-7] with a small volume change (0.8 to 1.3 vol.%):

β-quartz <—> α-quartz (573°C)

Quartz exhibits a very low coefficient of thermal expansion (0.5 μm/m.K) and an elevated Mohs hardness of seven. Large and pure single crystals of quartz of gem quality called ***lascas*** are used due to their high purity in the preparation of elemental silicon for semiconductors (see Section 5.8.1).

At a temperature of 870°C, α-quartz transforms irreversibly into *alpha-tridymite* (**α-tridymite**, orthorhombic) [15468-32-3] with an important volume change of 14.4 vol.% as follows:

α-quartz —> α-tridymite (870°C)

But in practice, the kinetic of the above reaction is too slow, and tridymite never forms below 1250°C, and hence at 1250°C or 1050°C in the presence of impurities, α-quartz transforms irreversibly into *alpha-cristoballite* (**α-cristoballite**, tetragonal) [14464-46-1] with an important volume change (17.4 vol.%) as follows:

α-quartz —> α-cristoballite (1250°C)

However, if the temperature is raised to 1470°C, α-tridymite transforms also irreversibly into *alpha-cristoballite* (**α-cristoballite**) without any change in volume as follows:

α-tridymite —> α-cristoballite (1470°C)

On cooling α-cristoballite transforms reversibly into *beta-cristoballite* (**β-cristoballite**, cubic) at 260°C with a volume change 0 2.0 to 2.8 vol.%:

α-cristoballite <—> β-cristoballite (260°C)

Finally, α-cristoballite melts at 1713°C while α-tridymite melts at 1670°C. Upon cooling silica melt yields amorphous ***fused silica*** [60676-86-0].

There also exist two high-pressure polymorphs of silica called ***coesite*** and ***stishovite*** (see Section 12.7) that occur in strongly mechanically deformed metamorphic rocks (e.g., impactites), but these two phases are usually not encountered in ceramics, refractories, and glasses.

Industrially, silica products are classified into two main groups: ***natural silica*** products —quartzite, silica sand, and diatomite—and ***specialty silicas*** including fumed silica, silica gel, microsilica, precipitated silica, fused silica, and vitreous silica.

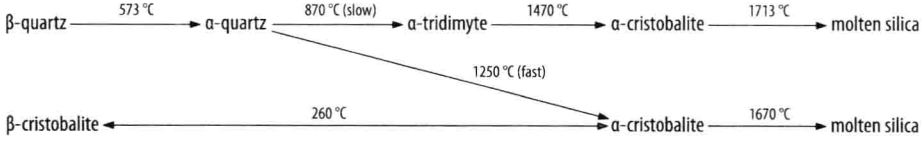

Figure 10.1. Polymorphs of silica (SiO_2)

10.2.1.1 Quartz, Quartzite, and Silica Sand

Quartz is extensively found in nature either as a major mineral in most igneous (e.g., granite), sedimentary (e.g., sand and sandstone), and metamorphic rocks (e.g., quartzite and gneiss). In the case of ceramics, refractories, and glasses, raw quartz is essentially mined as ***round silica sand*** from glacial deposits, beach sands, crushed sandstones, or high-quality quartzite with a silica content of more than 97 wt.% SiO_2. ***Quartzite*** can be either of sedimentary origin with detrital grains of quartz cemented by secondary silica or of metamorphic origin from the contact metamorphism of sandstones or tectonically deformed sandstones. For the most demanding applications, the run-of-mine is even washed with hydrochloric acid to remove traces of iron and aluminum sesquioxides and magnesium and calcium carbonates. Because quartzite consists mainly of beta-quartz, during firing, quartzite is subject to a behavior related to the polymorphism of silica. However, sedimentary quartzite transforms more rapidly than metamorphic equivalent.

Price (2006). Silica sand is priced 15–40 US$/tonne.

10.2.1.2 Diatomite

Diatomaceous earth, or simply ***diatomite***, formerly called ***Kieselguhr***, is a sedimentary rock of biological origin formed by the accumulation at the bottom of the ocean of siliceous skeletons of diatoms, or unicellular algae. Once-calcined diatomite is a white and lightweight material with a mass density ranging from 190 to 275 $kg.m^{-3}$. Diatomite is a highly porous material that exhibits high absorption capabilities and has a good chemical inertness. Major applications are filtering aids, metal polishing, thermal insulation, and Portland cement.

Price (2006). Diatomite is priced 700–800 US$/tonne.

10.2.1.3 Fumed Silica

Fumed silicas are submicrometric particles of amorphous silica produced industrially by burning ***silicon tetrachloride*** or ***tetrachlorosilane*** ($SiCl_4$) using an oxygen-hydrogen burner. The continuous process requires high-purity silicon tetrachloride, which is a byproduct of the carbochlorination of zircon sand for the production of zirconium tetrachloride by companies like Western Zirconium and Wah Chang in the United States or CEZUS in France (see Section 4.3.3, Zirconium and Zirconium Alloys) Fumed silicas usually receives an after-treatment that consists in coating the surface of particles with silanes or silicones in order to enhance hydrophobicity or improve dispersion in aqueous solution. In 2004, the annual production of fumed silica worldwide reached ca. 100,000 tonnes. The German company Degussa-Hüls, with its brand name ***Aerosil®***, is the world leader with half of the world production, followed by Cabot Corp. in the USA.

10.2.1.4 Silica Gels and Sol–Gel Silica

Silica gels are dispersions of colloidal silica obtained by a sol–gel process. The process consists in precipitating colloidal silica from an aqueous solution of sodium silicate by adding hydrochloric or sulfuric acid. The colloidal precipitate or gel consists mainly of hydrated silica ($SiO_2.nH_2O$). After filtration the precipitated silica is washed in order to remove residual salts and stabilized by adding ammonia or sodium hydroxide. The stabilized gel is then dried and later calcined to obtain an activated material, usually in the form of small beads. Major producers are E.I. DuPont de Nemours, Akzo, and Nalco Chemicals Co.

10.2.1.5 Precipitated Silica

Precipitated silica is obtained like silica gel by acidifying an aqueous solution of sodium silicate. Precipitated silica is used as filler in rubber for automobile tires and reinforcement particulate in elastomers, and as a flatting agent in paints and coatings for improving the

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flatness of coatings. About 850,000 tonnes are produced annually worldwide. Major producers of precipitated silica are PPG Industries and Rhodia.

10.2.1.6 Microsilica

Microsilica, also called ***silica-fume***, is a submicronic amorphous silica with 90 to 98 wt.% SiO_2 and a low bulk density ranging from 200 to 450 $kg.m^{-3}$. It forms most of the dust and other particulates in the off-gases produced during the electrothermal production of ferrosilicon (Fe-Si) or silicon (Si). The dust is collected in baghouses and bagged without further treatment. Due to its high surface area, microsilica reacts readily with hydrated calcium silicates forming strong bonds, and for that reason it is sometimes called reactive silica. Therefore the addition of microsilica to hydraulic cements improves their mechanical strength, reduces their permeability, and enhances their workability, cohesiveness, and flowing properties and hence is extensively used as an additive to cements and monolithic refractories. Annually, ca. 300,000 tonnes of microsilicas are produced worldwide. Major producers are obviously silicon or ferrosilicon producers such as Elkem in Canada and Norway and Fesil in Norway.

10.2.1.7 Vitreous or Amorphous Silica

High-purity amorphous or ***fused silica***, also called ***vitreous silica***, when optically translucent is a high-performance ceramic obtained by electrothermal fusion of high-grade silica sand with a silica content above 99.5 wt.% SiO_2 into an AC electric-arc furnace (EAF) at a temperature of around 1800 to 2100°C. The melt is then rapidly quenched to prevent crystallization.

Fused silica has a mass density of 2200 $kg.m^{-3}$ while ***vitreous silica*** is slightly denser with a density of 2210 $kg.m^{-3}$. Mechanically, fused silica is a relatively strong but brittle material with a tensile strength of 28 MPa, a compressive strength of 1450 MPa, and a Mohs hardness of 5. Both grades exhibit an extremely low coefficient of thermal expansion (e.g., $0.6 \times 10^{-6}\ K^{-1}$ from 20 to 1000°C) and a remarkable thermal shock resistance together with a low thermal conductivity. Fused silica, with a dielectric field strength of 16 $MV.m^{-1}$, exhibits also excellent electrical insulation capabilities up to 1000°C. When heated above 1150°C, fused silica converts irreversibly into α-cristoballite as follows:

fused silica —> α-cristoballite (1150°C)

Fused silica begins to soften at 1670°C and melt at 1755°C. From a chemical point of view, fused silica possesses an excellent corrosion resistance to most chemicals, especially strong mineral acids, molten metals, and molten glasses.

Common industrial uses for fused silica are steelmaking, coke making, metallurgy, glass production, nonferrous foundries, precision foundries, ceramics, the chemical industry, the nuclear industry, and finally aeronautics.

10.2.2 Aluminosilicates

From a geological point of view, clays are soft, fine-grained, and residual sedimentary rocks resulting from the weathering of feldspars (e.g., orthoclases and plagioclases) and ferromagnesian silicates (e.g., micas, amphiboles) contained in igneous and metamorphic rocks. Hence clays are always made of various hydrated aluminosilicates, mainly kaolinite but also illite and montmorillonite, all exhibiting the typical structure of sheet silicates (i.e., phyllosilicates). When a clay is fired, it loses its absorbed water between 100 and 200°C. Secondly, its major phyllosilicate mineral, ***kaolinite*** $[Al_4(Si_4O_{10})(OH)_8 = 2Al_2O_3{\cdot}4SiO_2{\cdot}4H_2O]$, dehydrates between 500 and 600°C, giving off its water to form ***metakaolin*** $[Al_2Si_2O_7 = 2Al_2O_3{\cdot}2SiO_2]$:

$$Al_4[Si_4O_{10}(OH)_8] \text{ —> } 2Al_2Si_2O_7 + 4H_2O \ (500°C < T < 600°C).$$

Above 800°C an important chemical change takes place with the formation of one of the three aluminosilicate polymorphs (Al_2SiO_5), i.e., ***andalusite***, ***kyanite***, or ***sillimanite***, and free silica according to the overall chemical reaction:

$$2Al_2Si_2O_7 \text{ —> } 2Al_2SiO_5 + 2SiO_2 \text{ (at } T > 800°C).$$

If firing is carried out above 1595°C, the highly refractory mineral ***mullite*** then forms (see mullite) with an additional liberation of free silica that melts according to the following chemical reaction:

$$3Al_2SiO_5 \text{ —> } Al_6Si_2O_{13} + SiO_2 \text{ (at } T > 1600°C).$$

Refractory fireclays embrace all types of clays commercially available. Because of the abundant supply of fireclay and its comparative cheapness, refractory bricks made out of it are the most common and extensively used in all places of heat generation. In fact, several technical designations are used in the ceramic industry for classifying refractory clays; these are fire clay, China clay, ball clay, flint clay, and chamotte.

10.2.2.1 Fireclay

Description and general properties. Fireclay denotes a silica-rich natural clay that can withstand a high firing temperature above the ***pyrometric cone equivalent*** (PCE; Table 10.19) of 19 without melting, cracking, deforming, disintegrating, or softening. Typically, a good fireclay should have 24 to 26 vol.% plasticity, and shrinkage after firing should be within 6 to 8 vol.% maximum. Fireclays are mostly made of kaolinite, but some Fe_2O_3 and minor amounts of Na_2O, K_2O, CaO, MgO, and TiO_2 are invariably present depending on the mineralogy and geology of the deposit, making it gray in color. Upon firing, fireclay yields a strong ceramic product with a composition close to the theoretical composition of ***metakaolin*** (i.e., 54.1 wt.% SiO_2 and 45.9 wt.% Al_2O_3), but in practice it contains between 50 and 60 wt.% SiO_2, 24 and 32 wt.% Al_2O_3, no more than 25 wt.% Fe_2O_3 and a loss on ignition of 9 to 12 wt.%. Fireclay is classified under acid refractories, that is, refractories that are not attacked by acid slags. In practice, refractoriness and plasticity are the two main properties required for the manufacture of refractory bricks; hence fireclays are grouped according to the maximum service temperature of the final product before melting in: ***low-duty fireclay*** (max. 870°C, PCE 18 to 28), ***medium-duty fireclay*** (max. 1315°C, PCE 30), ***high-duty fireclay*** (max. 1480°C, PCE 32), and ***super-duty fireclay*** (max. 1480°C–1619°C, PCE 35). In practice, it has been observed that the higher the alumina content in the fireclay, the higher the melting point. All fireclays are not necessarily plastic clays. In such cases, some plastic clay, like ball clay, is added to increase plasticity to a suitable degree. A good fireclay should have 24 to 26% plasticity, and shrinkage after firing should be within 6 to 8% maximum. It should also not contain more than 25% Fe_2O_3.

Industrial preparation. Mined clay is stacked in the factory yard and allowed to weather for about 1 year. For daily production of different types of refractories, this weathered clay is taken and mixed in different percentages with ***grog*** (i.e., ***spent fireclay***). The mixture is sent to the grinding mill from where it is transferred to the pug mill. In the pug mill a suitable proportion of water is added so as to give it proper plasticity. The mold is supplied to different machines for making standard bricks or shapes. Intricate shapes are made by hand. The bricks thus made are then dried in hot floor driers and after drying are loaded in kilns for firing. The firing ranges are, of course, different for different grades of refractories. After firing, the kilns are allowed to cool, then the bricks are unloaded. Upon burning fireclay is converted into a stonelike material that is highly resistant to water and acids, while manufacturing high aluminous fire-bricks bauxite is added along with grog in suitable proportions.

Industrial applications and uses. As a general rule fireclays are used in both ***shaped refractories*** (i.e., bricks) and ***monolithic refractories*** (i.e., castables), while super-duty plastic fireclay is used in the preparation of castable recipes. Therefore, the major applications of

fireclays are in power generation, such as in boiler furnaces, in glass-melting furnaces, in chimney linings, in pottery kilns, and finally in blast furnaces where the backup lining is done almost entirely with fireclay bricks. Pouring refractories like sleeves, nozzles, stoppers, and tuyers are also made of fireclay.

10.2.2.2 China Clay

China clay or ***kaolin***, the purest white porcelain discovered and used by the Chinese since ancient times, has always been a much-prized material. Outside of China, a few deposits were found in some parts of Europe and in the United States early in the 18th century. China clay occurs in deposits in the form of china clay rock, a mixture of up to 15 wt.% china clay and up to 10 wt.% mica muscovite, the remainder being free silica as quartz. But the terms china clay and kaolin are not well defined; sometimes they are synonyms for a group of similar clays, and sometimes kaolin refers to those obtained in the United States and china clay to those that are imported. Others use the term china clays for the more plastic of the kaolins. China clays have long been used in the ceramics industry, especially in whitewares and fine porcelains, because they can be easily molded, have a fine texture, and are white when fired. France's clays are made into the famous Sèvres and Limoges potteries. These clays are also used as a filler in making paper. In the United States, deposits are found primarily in Georgia, North Carolina, and Pennsylvania; china clay is also mined in England (Cornwall) and France.

Industrial preparation. The extraction of china clay from its deposits is usually performed in three steps: open-pit mining, mineral processing and beneficiation, and drying. Open-pit operations require the removal of ground overlying the clay (i.e., overburden). The exposed clay is then mined by a hydraulic mining process, that is, a high-pressure water jet from a water cannon called a monitor erodes the faces of the pit. This liberates from the quarry face the china clay, together with sand and mica. The slurry formed flows to the lowest part of the pit or sink, where it is pumped by centrifugal pumps to classifiers, where coarse silica sand is removed. The silica sand is later reused for landscape rehabilitation. The remaining suspension of clay is transported by underground pipeline to the mineral-processing and beneficiation plant, where a series of gravity separation techniques are used to remove particulate materials such as quartz, mica, and feldspars. Sometimes the purified clay slurry undergoes an additional chemical bleaching process that greatly improves its whiteness. The refined clay suspension is then filtrated, and the filtration cake with a moisture content of about 25 wt.% passes through a thermal drier fired by natural gas to yield a final product with 10 wt.% moisture. The end product is normally sold in pelletized form with a pellet size ranging from 6 to 12 mm.

10.2.2.3 Ball Clay

Ball clay, like china clay, is a variety of kaolin. It differs from china clay in having a higher plasticity and less refractoriness. In chemical composition, ball and china clays do not differ greatly except that the former contains a larger proportion of silica. Its name is derived from the practice of removing it in the form of ball-like lumps from clay pits in the UK. The main utility of ball clay is its plasticity, and it is mixed with nonplastic or less plastic clays to make them acquire the requisite plasticity. The high plasticity of ball clay is attributed to the fact that it is fine-grained and contains a small amount of montmorillonite. Over 85% of the particle sizes present in ball clay are of 1 μm or less in diameter. It is light to white in color and on firing may be white buff. The pyrometric cone equivalent to ball clay hardly ever exceeds 33. Usually the following mass fractions of ball clay are commonly used in various types of ceramic compositions: vitreous sanitaryware 10 to 40 wt.%, chinaware 6 to 15 wt.%, floor and wall tiles 12 to 35 wt.%, spark plug porcelain 10 to 35 wt.%, semivitreous whiteware

20 to 45 wt.%, and glass melting-pot bodies 15 to 20 wt.%. The wide use of ball clay is mainly due to its contribution of workability, plasticity, and strength to bodies in drying. Ball clay, on the other hand, also imparts high-drying shrinkage, which is accompanied by a tendency toward warping, cracking, and sometimes even dunting. This undesirable property is compensated by the addition of grog.

Industrial applications. Filler for paper and board, coating clays, ceramics, bone china, hard porcelain, fine earthenware, porous wall tiles, electrical porcelain, semivitreous china, glazes, porcelain, enamels, filler for plastics, rubbers and paints, cosmetics, insecticides, dusting and medicine, textiles, and white cement.

10.2.2.4 Other Refractory Clays

Flint clay or hard clay. This is a hardened and brittle clay material having a conchoidal fracture like flint that resists slacking in water but becomes plastic upon wet grinding.

Chamotte. Chamotte denotes a mixture of calcined clay and spent ground bricks. It is also called fireclay mortar.

Diaspore clay. This is a high-alumina material containing 70 to 80 wt.% Al_2O_3 after firing of a mixture of diasporic bauxite and clay.

10.2.2.5 Andalusite, Kyanite, and Sillimanite

Andalusite, kyanite, and sillimanite are three polymorphs minerals that belong to the nesosilicate minerals. Hence they have the same chemical formula [$Al_2SiO_5 = Al_2O_3 \cdot SiO_2$] and all contain theoretically 62.92 wt.% Al_2O_3 and 37.08 wt.% SiO_2. They are distinguished from one another by their occurrence and physical and optical properties (see Section 12.7, Minerals and Gemstones Properties Table). Kyanite is easily distinguished from sillimanite or andalusite by its tabular, long-bladed, or acicular habit and by its bluish color and slightly lower hardness than sillimanite and andalusite.

Sillimanite, kyanite, and andalusite are all ***mullite-forming minerals***, that is, on firing they decompose into mullite and vitreous silica (see mullite) according to the chemical reaction:

$$3Al_2SiO_5 \text{ —> } Al_6Si_2O_{13} + SiO_2.$$

However, each polymorph exhibits a different decomposition behavior. Actually, the decomposition of kyanite is unpredictable; it first starts to decompose slowly at 1310°C, and the reaction disrupts at about 1350 to 1380°C with an important volume expansion of 17 vol.%. For that reason, kyanite must always be calcined prior to being incorporated into a refractory in order to avoid blistering and spalling. By contrast, andalusite decomposes gradually from 1380 to1400°C with a low volume increase of 5 to 6 vol.%, while sillimanite does not change into mullite until the temperature reaches 1545°C with a volume expansion of 5 to 6 vol.%.

In nature, these three minerals are originally found in metamorphic rocks, but, due to their high Mohs hardness and relative chemical inertness, they resist weathering processes and are also ubiquitous in mineral sands. For instance, sillimanite is extensively mined as a byproduct of beach mineral sand operations in South Africa and Australia. Sillimanite minerals are predominantly used in refractories and technical porcelains. Sillimanite refractories cut into various shapes and sizes or made out of bonded particles are used in industries like cement, ceramics, glass making, metal smelting, refinery and treatment, tar distillation, coal carbonization, chemical manufacture, and iron foundries. Kyanite in the form of mullite is widely used in the manufacture of glass, burner tips, spark plugs, heating elements, and high-voltage electrical insulations and in the ceramic industry. India is the largest producer of kyanite in the world.

10.2.2.6 Mullite

Mullite [$Al_6Si_2O_{13} = 3Al_2O_3{\cdot}2SiO_2$], with 71.8 wt.% Al_2O_3, is an important silicate mineral that occurs in high-silica alumina refractories. Mullite exhibits a high melting point of 1810°C combined with low thermal expansion coefficients (i.e., 4.5×10^{-6} K^{-1} parallel to the *a*-axis and 5.7×10^{-6} K^{-1} parallel to the *c*-axis), a good mechanical strength with a tensile strength of 62 MPa, and resilience at elevated temperatures that make mullite a highly suitable mineral for highly refractory materials. In nature, mullite is an extremely scarce mineral that occurs only in melted argillaceous inclusions entrapped in lavas from the Cenozoic Era on the Island of Mull, Scotland, but no deposit was found to be economically minable.

Synthetic mullite is formed in high-silica alumina refractories during the firing process at high temperature, the major raw materials being kaolin, alumina, and clays and to a lesser extent kyanite, when available. Actually, when a fire clay is fired, its major phyllosilicate mineral, the kaolinite $Al_4(Si_4O_{10})(OH)_8$, first gives off its water, and above 800°C an important chemical change takes place with the formation of one of the three aluminosilicate polymorphs (Al_2SiO_5), i.e., andalusite, kyanite, or sillimanite, and free silica according to the following chemical reaction:

$$Al_4(Si_4O_{10})(OH)_8 \text{ —> } 2Al_2SiO_5 + 2SiO_2 + 4H_2O \text{ (at } T > 800°C).$$

If firing is carried out above 1595°C, the highly refractory mineral mullite then forms with an additional liberation of free silica that melts according to the following chemical reaction:

$$3Al_2SiO_5 \text{ —> } Al_6Si_2O_{13} + SiO_2 \text{ (at } T > 1600°C).$$

For that reason, high-silica alumina refractories containing less than 71.8 wt.% Al_2O_3 are limited in their use to temperatures below 1595°C. Above 71.8 wt.% Al_2O_3, mullite alone or mullite plus corundum (α-Al_2O_3) coexists with a liquidus at 1840°C. Therefore, the use of ***high-alumina refractories*** is suited for iron- and steelmaking for firebrick and ladles and furnace linings. Two grades of synthetic mullite are available for refractories: ***sintered mullite*** is obtained by calcination of bauxitic kaolin or a blend of bauxite, aluminas, and kaolin or, to a lesser extent, kyanite; ***electrofused mullite*** is made by the electrothermal melting at 2200°C of a mixture of silica sand and bauxite or diasporic clay in an electric-arc furnace. Mullites are formulated to produce dense shapes, some in a glass matrix to yield maximum thermal shock resistance and good mechanical strength. Dense electrofused mullite in a glassy matrix formulated to offer a high-quality economical insulating tubing for thermocouple applications is an extremely versatile and economically viable material. Its workability allows for an extensive range and flexibility in fabrication. It is well suited for the casting of special shapes. Its typical applications are insulators in oxidizing conditions for noble-metal thermocouples used in conditions up to 1450°C, spark plugs, protection tubes, target and sight tubes, furnace muffles, diffusion liners, combustion tubes, radiant furnace tubes, and kiln rollers. Major producers of sintered mullite are C-E Minerals, Andersonville, GA in the USA, followed by several Chinese producers, while Washington Mills Electro Minerals Corp. in Niagara Falls, NY leads the production of electrofused mullite.

10.2.3 Bauxite and Aluminas

10.2.3.1 Bauxite

Bauxite is the major source of ***aluminum sesquioxide*** (***alumina***, Al_2O_3) worldwide. Bauxite is a soft and red clay, rich in alumina, and its name originates from Les Baux de Provence, a small village located in the region of Arles in southeastern France, where it was first discovered in 1821 by P. Berthier. From a geological point of view bauxite is defined as a residual sedimentary rock in the laterite family that results from *in situ* superficial weathering in

Table 10.1. Mineralogy and chemistry of bauxite

Oxide	Chemical composition (wt.%)	Mineralogy
Alumina (Al_2O_3)	35 to 65	Gibbsite, boehmite and diaspore
Silica (SiO_2)	0.5 to 10	Quartz, chalcedony, kaolinite
Ferric oxide (Fe_2O_3)	2 to 30	Goethite, hematite and siderite
Titania (TiO_2)	0.5 to 8	Rutile and anatase
Calcia (CaO)	0 to 5.5	Calcite, magnesite and dolomite

moist tropical climates of clays, clayey limestones, or high-alumina-content silicoaluminous igneous and metamorphic rocks containing feldspars and micas. Around the world there is a restricted number of geographical locations containing bauxite deposits of commercial interest. Their occurrence and origin can be explained by both plate tectonics and climatic conditions. Actually, during weathering water-soluble cations (e.g., Na, K, Ca, and Mg) and part of the silica (SiO_2) are leached by rainwater acidified by the organic decomposition of humus, leaving only insoluble aluminum and iron sesquioxides and a lesser amount of titania (TiO_2). Hence, insoluble cations such as iron (III) and aluminum (III) associated with clays and silica remain in the materials. Bauxite is a sedimentary rock, so it has neither a precise definition nor chemical formula. From a mineralogical point of view, bauxite is mainly composed of hydrated alumina minerals such as ***gibbsite*** [$Al(OH)_3$ or $Al_2O_3.3H_2O$, monoclinic] in recent tropical and equatorial bauxite deposits, while ***boehmite*** [AlO(OH) or $Al_2O_3.H_2O$, orthorhombic] and, to a lesser extent, *diaspore* [AlO(OH) or $Al_2O_3.H_2O$, orthorhombic] are the major minerals in subtropical and temperate bauxite old deposits. The average chemical composition of bauxite is 45 to 60 wt.% Al_2O_3 and 10 to 30 wt.% Fe_2O_3, the remainder consisting of silica, calcia, titanium dioxide, and water. The typical mineralogy and chemical composition of bauxite is presented in Table 10.1. The different types of bauxite are only distinguished according to their mineralogical composition. They are then called gibbsitic, boehmitic, or diasporic bauxite. Gibbsitic bauxite predominates. It is geologically the youngest and situated in tropical or subtropical regions, very close to the ground surface (e.g., laterites). The oldest deposits, which are mainly found in Europe (e.g., Gardanne in France, and Patras in Greece) and in Asia, mainly contain boehmite and diaspore. Most of the time they are underground deposits.

According to the US Geological Survey, the world's bauxite resources are estimated to be 55 to 75 billion tonnes located mainly in South America (33%), Africa (27%), Asia (17%), Oceania (13%), and elsewhere (10%). Today, Australia supplies 35% of the demand worldwide for bauxite, South America 25%, and Africa 15%. The current reserves are estimated at being able to supply worldwide demand for more than two centuries. Note that about 95% of bauxite is of the metallurgical grade and hence used for the production of primary aluminum metal.

Bayer process. Because bauxite exhibits a high alumina content and its worldwide reserves are sufficient to satisfy demand for a few centuries, it is the best feedstock for producing alumina and then aluminum. Actually, today, more than 95% of alumina worldwide is extracted from bauxite using the Bayer process, which was invented in 1887, just one year after the invention of the Hall–Heroult electrolytic process. This Bayer process was implemented for the first time in 1893, in France, at Gardanne. However, the conditions for implementing the process strongly depend on the type of bauxitic ore used. For instance, refractory-type diasporic bauxite must be digested at a higher temperature than gibbsitic bauxite. Therefore, the selection of the type of bauxite to be used is a critical factor affecting the design of the alumina plant. A brief description of the Bayer process is given hereafter.

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