François Cardarelli

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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.

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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.

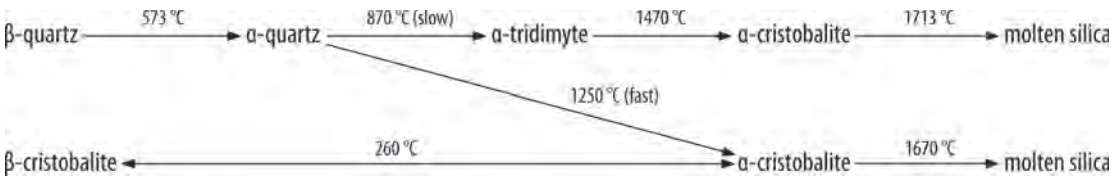

Figure 10.1. Polymorphs of silica (SiO_2)

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

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., 0.6×10^{-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.

Cardarelli, F. (2008) Materials Handbook. A Concise Desktop Reference, 2nd Edition. Springer London.

Table 10.2. Digestion conditions for various bauxitic ore

Bauxitic ore	Digestion reaction	Conditions
Gibbsitic	$2AlO(OH).H_2O + 2NaOH \text{ —> } 2NaAlO_2 + 4H_2O$	Atmospheric pressure $135°C < T < 150°C$
Boehmitic	$2AlO(OH) + 2NaOH \text{ —> } 2NaAlO_2 + 2H_2O$	Atmospheric pressure $205°C < T < 245°C$)
Diasporic	$2AlO(OH) + 2NaOH \text{ —> } 2NaAlO_2 + 2H_2O$	High pressure (3.5–4 MPa) $T > 250°C$

Comminution. First, bauxite run-of-mine ore is crushed using a jaw crusher to produce coarse particles below 30 mm in diameter. It is then washed with water in order to remove clay minerals and silica in an operation called desliming. The washed and crushed ore is then mixed with the recycled caustic liquor downstream from the Bayer process, then ground more finely providing a suspension or slurry of bauxite with 90% of particles with a size less than 300 μm (48 mesh Tyler). This grinding step is required to increase the specific surface area of the bauxite in order to improve the digestion efficiency. The recycled liquor comes from the filtration stage of the hydrate after it has been precipitated. This liquor is enriched in caustic soda (i.e., sodium hydroxide, NaOH) and slacked lime [calcium hydroxide, $Ca(OH)_2$] before grinding to meet the digestion conditions and to be more aggressive toward the bauxite. The permanent recycling of the liquor and, more generally, of the water is at the origin of the synonym for the Bayer process, also called the Bayer cycle. The red bauxite-liquor slurry is preheated before being sent to the digesters for several hours.

Digestion of bauxite. The conditions of digestion are strongly related to the mineralogical composition of the bauxitic ore, that is, whether gibbsite, boehmite, or diaspore is the dominant ore. For instance, a gibbsitic bauxite can be digested under atmospheric pressure, whereas high pressures in excess of 1 MPa and temperatures above 250°C are required to digest the alumina contained in refractory diasporic bauxite. The various digestion conditions are summarized in Table 10.2.

Usually, the slurry is heated in an autoclave at 235 to 250°C under a pressure of 3.5 to 4.0 MPa. During the digestion stage, the hydrated alumina is dissolved by a hot and concentrated caustic liquor in the form of ***sodium aluminate*** ($NaAlO_2$). During the dissolution reaction, the sodium hydroxide reacts with both alumina and silica but not with the other impurities such as calcium, iron, and titanium oxides, which remain as insoluble residues. These insoluble residues sink gradually to the bottom of the tank and the resulting red sludge, called ***red mud***, concentrates at the bottom of the digester. The slurry is diluted after digestion to make settling easier. Slowly heating the solution causes the $Na_2Si(OH)_6$ to precipitate out, removing silica. The bottom solution is then pumped out and filtered and washed while the supernatant liquor is filtered to leave only the aluminum-containing $NaAl(OH)_4$. The clear sodium tetrahydroxyaluminate solution is pumped into a huge tank called a precipitator. There are two objectives in washing the red mud that has been extracted from the settler: to recuperate the spent sodium aluminate, which will be reused in the Bayer cycle, and to remove sodium hydroxide from the red mud for safe disposal as an inert mining residue.

Precipitation. The clear sodium aluminate liquor is cooled down, diluted with the water from the red-mud wash, and acidified by bubbling carbon dioxide (CO_2) gas through the solution. Carbon dioxide forms a weak acid solution of carbonic acid, which neutralizes the sodium hydroxide from the first treatment. This neutralization selectively precipitates the aluminum hydroxide [$Al(OH)_3$] but leaves the remaining traces of silica in solution; the precipitation or the crystallization of the hydrate is also called decomposition. The liquor is

then sent into huge thickening tanks owing to the extremely slow precipitation kinetics. The alumina hydrate slowly precipitates from tank to tank as the temperature goes down. The floating suspension is recuperated in the last thickening tank. Fine particles of aluminum hydrate are usually added to seed the precipitation process of pure alumina particles as the liquor cools. In fact, 90% of the wet aluminum trihydrate recovered after filtration is recycled and used as a crystallization seed. The liquor is then filtered so as to separate the wet hydrate from the liquor. This liquid is then sent to the bauxite digestion tank, where it will be enriched in soda and in lime. The particles of aluminum hydroxide crystals sink to the bottom of the tank, are removed, and are then vacuum dewatered. The ***alumina trihydrate* (ATH)** or ***gibbsite*** [$Al(OH)_3$] obtained can be commercialized as is or it can be calcined into various grades of alumina (Al_2O_3).

Calcination. To produce ***calcined alumina*** (CA), the alumina trihydrate must be calcined into a rotary kiln or a fluidized-bed calciner operating at 1100 to 1300°C to drive off the chemically combined water. Usually, fluidized-bed calciners are restricted to transition aluminas used in the manufacture of metallurgical-grade alumina, while rotary kilns are used for non-metallurgical-grade alumina. All of the characteristics of calcined alumina are extremely variable and depend on the conditions of calcination. Sodium is the major impurity of the alumina produced in the Bayer process; this can be a hindrance for certain technical applications. Several methods for the removal of sodium exist to produce aluminas with a very low sodium content, such as water leaching or the use of silica to form a soluble sodium silicate phase. These reactions compete with the combination of sodium and alumina to form beta-aluminas. The transformation of gibbsite into alpha-alumina successively gives rise to the following phenomena while the temperature is rising: release of water vapor between 250 and 400°C that fluidizes the alumina and, at around 1000 to 1250°C, the exothermic transformation into alpha-alumina occurs. The appearance of alpha-alumina crystallites modifies the morphology of the grains, which become rough and friable. Completion of the transformation of gibbsite into alpha-alumina requires a residence time of at least 1 h. Some halogenated compounds called mineralizers are used to catalyze the transformation of the alpha-alumina crystallites. The mineralizers also form volatile sodium chloride. Calcined alumina consists of alpha-alumina crystallite clusters with a particle size ranging from 0.5 to 10 μm. The higher the calcinations, the larger the crystallites (Figure 10.2).

10.2.3.2 Alumina Hydrates

Aluminum hydroxides and oxihydroxides, formerly called ***aluminas hydrates***, are all produced during the Bayer process described in the preceding paragraphs. All the aluminum hydroxides exhibit the same molecular unit, which consists of an octahedron made of one hexacoordinated aluminum cation surrounded by six oxygen anions [AlO_6^{9-}]. The great stability of this structure is due to the strong Al-O chemical bonds owing to the high polarization of aluminum cations.

Three crystalline polymorphs of alumina trihydrates (ATH) or aluminum trihydroxide [$Al(OH)_3 = Al_2O_3.3H_2O$] exist: ***gibbsite*** or ***hydrargillite*** [γ-$Al(OH)_3$], ***bayerite*** [α-$Al(OH)_3$], and ***nordstrandite*** [β-$Al(OH)_3$]. The octahedrons form a plane framework of hexagonal crowns of $Al(OH)_3$ forming two planes of oxygen atoms in a compact hexagonal network wrapped around a plane of aluminum atoms two thirds of which is occupied. The three minerals differ by the sequence of these sheets. The sequence is (AB BA AB BA…) for gibbsite, (AB AB AB AB…) for bayerite, which is more compact and hence more stable and dense), and (AB BA BA AB…) for the intermediate case of nordstrandite. The sheets are linked together by hydrogen bonds.

Two crystalline polymorphs of monohydrated alumina or aluminum oxihydroxide [$AlO(OH) = Al_2O_3.H_2O$], where the [AlO_6^{9-}] octahedrons share one edge: ***boehmite*** [γ-AlO(OH)];

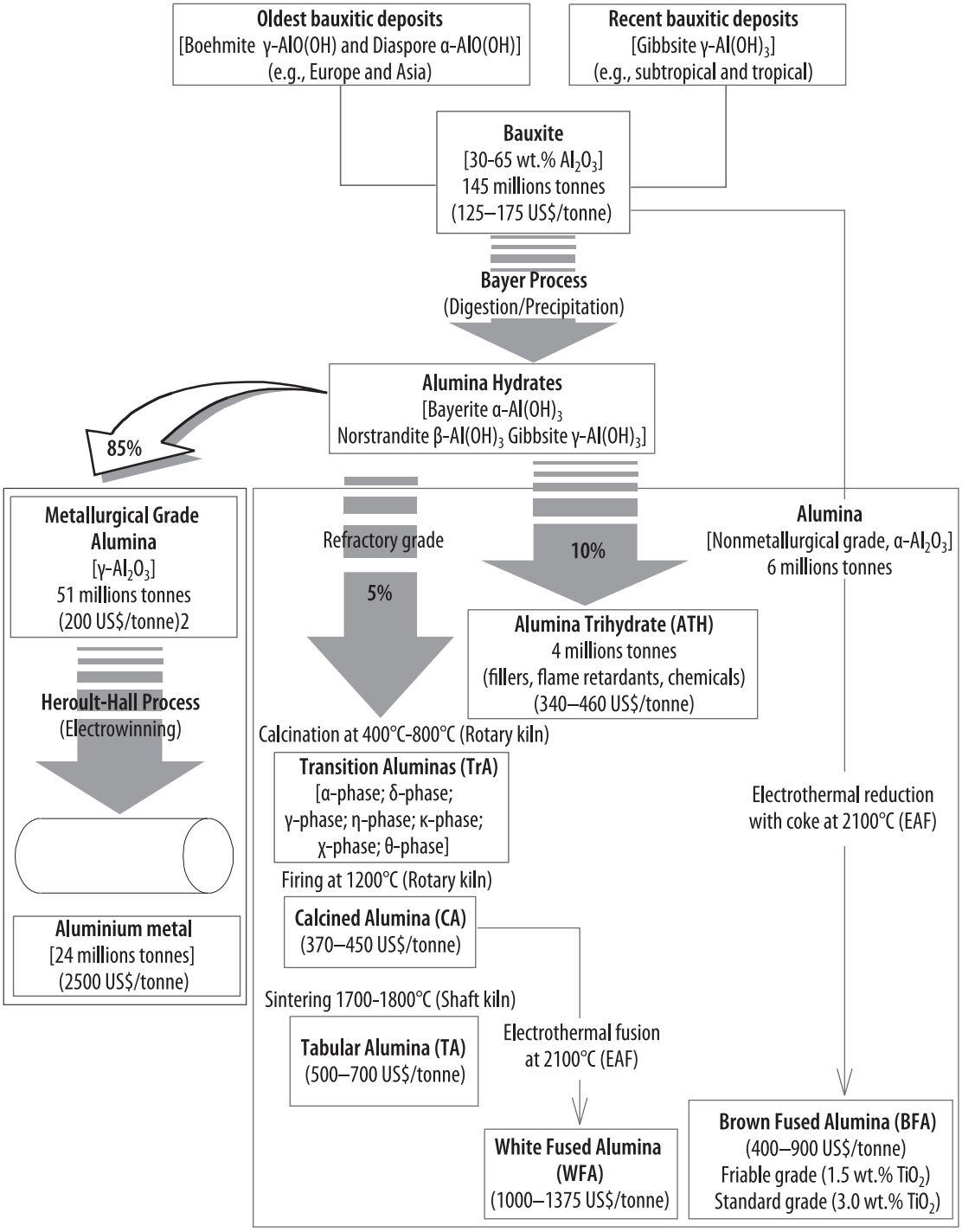

Figure 10.2. Aluminas production flowsheet

and ***diaspore*** [α-AlO(OH)]. The main characteristics of aluminum hydroxides are listed in Table 10.3.

Among all the alumina hydrates, **gibbsite** or gamma-aluminum trihydroxide (ATH) is, after bauxite, by far the most common aluminum commodity. Actually, 85% of the total gibbsite produced by the Bayer process is used to produce ***metallurgical-grade alumina*** for the electrowinning of aluminum metal by the Hall–Heroult process, while 8–10 percent are used for preparing ***non-metallurgical-grade alumina*** required for the manufacture of high

Table 10.3. Alumina hydrates (aluminum trihydroxides and oxihydroxides)

Phase	Chemical formula	Crystal system	Therm. stability range	Density ($kg.m^{-3}$)	Mohs hardness	Tenacity	Average refractive index (n_D)
Gibbsite (hydrargillite)	α-$Al(OH)_3$	Monoclinic	<100	2420	2.5–3.5	Tenacious	1.57–1.59
Bayerite	β-$Al(OH)_3$	Monoclinic	<100	2530	n.d.	Tenacious	1.58–
Nordstrandite	γ-$Al(OH)_3$	Triclinic		2450	3		1.590
Boehmite	γ-AlO(OH)	Orthorhombic	100-350	3010	3.5–4	Highly tenacious	1.65–1.67
Diaspore	α-AlO(OH)	Orthorhombic	100–350	3440	6.5–7	Brittle	1.70–1.75

alumina refractories, abrasives, proppants, and ceramics; the remaining 5 to 7% is used as specialty chemicals such as aluminum chemicals, flocculants, fillers, and flame retardants. High-purity aluminum trihydrate (ATH), with 99.7 wt.% $Al(OH)_3$, is a white solid with a low apparent density of 1200 $kg.m^{-3}$. Due to its low Mohs hardness, ranging between 2.5 and 3.5, it exhibits a low abrasiveness. It is easily flowable and hence can be fluidized. ATH is nonflammable and nonhazardous. It is insoluble in water but becomes soluble in strong mineral acids and bases to form $Al(H_2O)_6^{3+}$ or AlO_2^-, respectively. Its dehydratation reaction is highly endothermic with a specific enthalpy of 1155 $kJ.kg^{-1}$. Gibbsite loses 34.6 wt.% of its mass between 200 and 1200°C. The greatest weight loss occurs between 250 and 400°C, and the fastest dehydration rate occurs at around 350°C. Finally, ATH exhibits good absorption capabilities for aqueous solutions and organic liquids such as oil. ATH absorbs near-ultraviolet radiation with wavelengths below 400 nm. Commercially, ATH is available wet or dry, with wet ATH containing 11 wt.% free moisture. The ten major producers of ATH worldwide are listed in Table 10.4.

The thermal decomposition of alumina hydrates upon firing leads, depending on the intensity of firing, to the formation of four types of aluminas: **transition aluminas**, **calcined aluminas**, **tabular aluminas**, and **fused aluminas**. These four main families of alumina are described below.

Table 10.4. Ten major producers of aluminum trihydroxide (2002)[1]

Company	Country	Annual production capacity (tonnes)
Alcoa	United States	1,200,000
Alcan	Canada	390,000
Ajka Alumina Co.	Hungary	331,000
Sherwin Alumina	United States	300,000
Kaiser Aluminum	United States	300,000
Dadco Alumina & Chemicals	Germany	246,000
VAW Aluminium	Germany	164,000
Indian Aluminium Co. (Indal)	India	140,000
Aluminium Pechiney	France	100,000
National Aluminium Co. (Nalco)	India	27,000

[1] Crossley, P. (2002) ATH flexing its strength. *Ind. Min.*, February 2002, pp. 24–43.

Table 10.5. Transition aluminas and precursors

Precursor	Phase-transformation reactions
Gibbsite	Gibbsite —280°C—> χ-phase —800°C—> κ-phase—1000°C—> α-Al_2O_3
Bayerite	Bayerite —280°C—> η-phase —830°C—> θ-phase—1000°C—> α-Al_2O_3
Boehmite	Boehmite—450°C—> γ-phase —800°C—> δ-phase—920°C—>θ-phase—1050°C—> α-Al_2O_3
Diaspore	Diaspore—500°C—> α-Al_2O_3

10.2.3.3 Transition Aluminas (TrA)

During the thermal decomposition of alumina hydrates, the progressive loss of hydratation water leads to the formation of the so-called ***transition aluminas***, denoted by the common acronym TrA. These are metastable aluminas with an intermediate crystallographic structure ranging between that of alumina hydrates and that of alpha-alumina. The family of transition aluminas includes all aluminas that are obtained by the thermal decomposition of aluminum hydroxides or oxihydroxides, with the exception of alpha-alumina. The different transition aluminas generally coexist, and their proportions depend on the type of precursor hydrate and on the decomposition conditions (i.e., temperature, heating rate, relative humidity). As a general rule, each intermediate alumina hydrate exhibits at least two phase transformations when the temperature rises before reaching the final structure of the alpha alumina: a very disordered low-temperature structure produced by the loss of hydratation water and a high-temperature, well-ordered structure (Table 10.5). The most important properties of all transition aluminas are their intrinsic microporosity and their high specific surface area that can reach up to 400 $m^2.g^{-1}$. Because of their high specific surface areas, combined with their adsorptive capabilities, transition aluminas are able to adsorb huge quantities of polar, acidic, or basic compounds, but the adsorption is not selective. Moreover, transition aluminas are also very reactive chemically. Actually, the adsorption of acid in an aqueous medium always leads to the dissolution of part of the alumina and then the adsorption of the salt that has formed. Finally, when they undergo thermal decomposition above a temperature of 1100°C, all the transition aluminas are transformed irreversibly into calcined aluminas.

Four main processes are used for preparing industrial transition aluminas:

(i) The dehydration of gibbsite performed in a rotary kiln at 400°C. The thermal decomposition of gibbsite at 250°C produces a transition alumina having a large specific surface area. If the process is performed under pressure, a hydrothermal transformation occurs, yielding boehmite. Further dehydration of the boehmite produces a gamma transition alumina with a low specific surface area.

(ii) The activation of gibbsite by flash-firing that consists in firing the ATH in a few seconds at around 400°C. The activated alumina thus obtained is amorphous and very reactive.

(iii) The activation of oxihydroxide gels that are first transformed into grains by various processes and are then activated at between 500 and 600°C in a fluidized bed.

(iv) The activation of bayerite, which consists in agglomerating bayerite into a shaped material by means of an appropriate binder.

10.2.3.4 Calcined Alumina

Aluminum sesquioxide, or α-alumina (α-Al_2O_3), also called ***calcined alumina*** (CA) or ***burned alumina*** in the ceramic and refractory industries, is the final product resulting from the thermal decomposition of all aluminum hydroxides. Actually, in the temperature range 1000–1250°C, the exothermic transformation of transition aluminas into α-Al_2O_3 occurs

irreversibly. The rate of transformation into α-Al_2O_3 depends on the residence time of the aluminum hydroxide at these temperatures. The transformation is usually complete after a few hours at more than 1250°C. Calcined aluminas are prepared by calcination of aluminum hydroxide performed in rotary kilns, fluidized-bed kilns, or tunnel kilns. The α-Al_2O_3 crystallites give a polycrystalline product that becomes friable. Calcined aluminas are offered in a wide variety of technical grades from those containing 100 wt.% α-Al_2O_3 to grades containing some sodium such as soda-alumina, also called ***beta alumina*** [$NaAl_{11}O_{17} = Na_2O{\cdot}11Al_2O_3$], the remaining component being unreacted transition alumina. Some halogenated compounds (e.g., BF_3, BCl_3) called mineralizers are used to catalyze the nucleation of the α-Al_2O_3 crystallites. The mineralizers also form volatile sodium chloride (NaCl), which removes the sodium. Calcined alumina consists of α-Al_2O_3 crystallite clusters with a particle size ranging from 0.5 to 10 μm, and it is hence a polycrystalline material with grains made of several crystallites. The higher the calcination temperature is, the larger the crystallites are. The morphology of crystallites is strongly influenced by the chemical nature of the mineralizer: fluorine produces tabular crystallites with a hexagonal shape, boron gives rounded crystallites, while boron chloride produces round and dense crystals. By contrast with transition aluminas, crystals in calcined alumina are free from micropores, and hence calcined alumina's specific surface area equals the surface area of its crystallites, and the larger they are, the lower the surface area will be. Technical calcined aluminas are classified according to the particle size of their crystallites, the morphology of the crystallites (i.e., angular, rounded, tabular), their sodium content, and, to a lesser extent, the content of other impurities that result mainly from the Bayer process and bauxite. Commercially, four grades of calcined aluminas are distinguished based on their soda content:

(i) ***Standard calcined aluminas*** with a sodium content of between 3000 and 7000 ppm wt. Na_2O.

(ii) ***Intermediate calcined alumina*** with a sodium content of between 1000 and 3000 ppm wt. Na_2O. The sodium content of this grade has been lowered by modifying the conditions of the precipitation of gibbsite or of the calcination.

(iii) ***Low-sodium calcined aluminas*** with a sodium content of between 300 and 1000 ppm wt. Na_2O. These aluminas are usually obtained by washing the precursor or by the extraction of sodium as a volatile compound with the mineralizer during calcination.

(iv) ***High-purity aluminas*** with an extra-low sodium content below 100 ppm wt. Na_2O. These aluminas obtained from an aluminum hydroxide produced by a process other than the Bayer process. The main applications for calcined aluminas are as feedstocks for refractories, glass and enamel, tiles and porcelain, and advanced ceramics. The diversity of applications for calcined aluminas can be explained by the wide range of properties: refractoriness, sinterability, chemical inertness in both oxidizing and reducing atmosphere and in both acid and alkaline media, hardness, wear and abrasion resistance, dimensional stability, high thermal conductivity, electrical resistivity, low dielectric loss and high permittivity, and high ionic conductivity in the case of beta-alumina.

10.2.3.5 Tabular Alumina

Tabular alumina (TA), also called ***sintered alumina***, is produced by the sintering of calcined alumina, which occurs above 1600°C. Sintering is usually performed industrially in a tall shaft kiln equipped with gas burners in the median zone. First, 20-mm balls are made by pelletizing a mixture of ground calcined alumina, reactive micronized alumina, and an appropriate organic binder to ensure the highest green density. Usually boron trichloride is added for the proper removal of sodium as NaCl upon heating. Prior to being fed into the shaft kiln the balls are always dried. The sintering is performed continuously at a high

operating temperature of between 1900°C and 1950°C to obtain the highest mass density of 3550 $kg.m^{-3}$ and a low porosity of 5 vol.% but always below the melting point of α-Al_2O_3 (2050°C). It takes about 15 h for the balls to exit from the bottom of the furnace. After sintering, the balls, which have shrunk by 20 vol.%, are crushed and ground, and iron-rich material is removed by magnetic separation and then sized in several grades. The high purity of tabular alumina (99.8 wt.% Al_2O_3) is due to its low soda content ($Na_2O < 1000$ ppm wt.) and to the absence of nonvolatile mineral additions in the preparation of green balls. The resulting polycrystalline material exhibits large tabular crystals with a hexagonal shape and with a particle size of between 200 and 300 μm. Moreover, the commercial material contains a finer grain size and additives that lower the melting point in the range of 1700°C to 1850°C. The major properties of tabular alumina are a high density, a low open porosity, refractoriness, hardness, chemical inertness, thermal conductivity and dielectric rigidity at high temperatures, dimensional stability, creep and abrasion resistance, and exceptional resistance to thermal shock. These properties explain its development as a refractory raw material and its use in steelmaking and in electric furnaces, especially in Japan, as well as in ceramics, filters for molten metal, fillers for epoxy resins and polyester, inert catalyst supports, and heat conductors.

10.2.3.6 White Fused Alumina

Above 2050°C, pure alumina (Al_2O_3) melts forming a covalent and nonconducting liquid that upon cooling yields a solidified mass of corundum. Corundum is also called in the ceramics and refractory industries ***white fused alumina***. White fused alumina exhibits a fine-grained microstructure with euhedral crystals. Although the operation can be performed commercially on a small industrial scale by the Verneuil technique to produce kilogram-size single crystals (see Gemstones, Section 12.5), most of the large tonnage production uses a tilting electric-arc furnace with three electrodes operating in an AC mode. Once molten and homogeneous, the alumina melt is poured into molds and allowed to cool slowly until demolding. Beta-alumina represents the major impurity observed in white fused alumina due to the concentration of sodium occurring in certain regions. However, the volatilization of the sodium occurs at 2100°C and creates pores that are beneficial. To improve is mechanical strength, usually 2 wt.% of chromia (Cr_2O_3) is added to the melt. Actually, trivalent chromium substitutes isomorphically for the Al^{3+} increasing the toughness of white fused alumina.

10.2.3.7 Brown Fused Alumina

The electrothermal fusion of bauxite at 2100°C yields an impure and brown electrofused alumina product called ***brown fused alumina***, sometimes simply ***brown corundum***. Brown fused alumina exhibits coarse grains, and the major impurity in brown fused alumina is titania or titanium dioxide (TiO_2) coming from the bauxite ore. Therefore, commercially, two grades of brown fused aluminas can be distinguished according to their titania content: the **friable grade**, with 1.5 wt.% TiO_2, and the **standard grade**, with 3 wt.% TiO_2, which exhibits a greater toughness than the friable grade. The toughness of brown fused alumina is higher than that of white fused alumina, and this is due to the titania content, which reduces the size of the crystallites. Brown electrofused alumina is obtained industrially by the simultaneous electrothermal fusion and reduction by coke in a tilting and triphased electric-arc furnace of a blend of bauxite and spent products of white and brown aluminas. During the process, the reduction of iron oxide, silica, and, to a lesser extent, titania produces a titanium-bearing ferrosilicon alloy (FeSi), which is an important byproduct. The dense droplets of ferrosilicon sink by gravity, settling at the bottom of the crucible, and coalesce to form a pool of liquid FeSi. After several castings of the electrofused brown alumina thus produced, the ferrosilicon that has accumulated at the bottom must be tapped by overturning the crucible; this represents an important byproduct. During electrofusion, the raw materials

float over the molten alumina, decreasing the thermal losses by radiation (ca. 900 $kW.m^{-2}$ at 2000°C). Because of the high temperature combined with the corrosiveness of the melt, no container can withstand such melts and skull melting is the only means to contain the molten materials. Actually, a frozen layer forms upon cooling on the inner wall and at the bottom of the crucible that are externally cooled by running water, forming a protective and self-lining skull. In practice, two distinct skulls are formed, on the inner side wall of the furnace the thick skull is made of solidified alumina, while at the bottom a thick skull forms containing titanium carbide (TiC). During the process, the gases resulting from the reduction of various metal oxides with the carbon are mainly CO and SiO. This aspect is of crucial importance both for reasons linked to the process and for safety reasons. Once molten alumina is poured into molds and allowed to cool slowly until demolding, it is crushed and ground while droplets of FeSi are removed by magnetic separation performed with a rotary drum equipped with rare-earth magnets. To ensure that the ferrosilicon is ferromagnetic and hence easily separated from corundum, its silicon content must be less than 21 wt.% Si, but in order to be easily crushed, its silicon content must be at least 13 wt.% Si. Proper operation of the process consists in maintaining a silicon content ranging between these two limits. Moreover, the titanium content is another important parameter to control. If the titanium content is too high, it forms a bed of TiC, reducing the useful depth of the crucible. On the other hand, if the titanium content is too low, the skull at the bottom of the crucible will be too thin. Apart from refractories, brown fused alumina is used in deburring, plunge cut grinding, and sandblasting.

10.2.3.8 Electrofused Alumina-Zirconia

Electrofused alumina-zirconia (EFAZ) is obtained by a process similar to that used for preparing brown fused alumina by electrothermal fusion and reduction by metallurgical coke at 2100°C of a mixture of bauxite ore, zircon sand, and scrap iron in a tilting and triphased electric-arc furnace. After quenching the molten mass, the resulting product obtained is about five times stronger than brown fused alumina.

10.2.3.9 High-Purity Alumina

High-purity alumina contains at least 99.99 wt.% Al_2O_3, with crystallites small in size and morphology. Nearly half the high-purity alumina produced annually is used to manufacture sapphires and, to a lesser extent, as polishing medium for metallographical and optical processes. Four manufacturing processes of ultrapure aluminas are used, using either Bayer gibbsite or aluminum metal.

(i) ***Alum process.*** Gibbsite from the Bayer process is dissolved in an excess of sulfuric acid (H_2SO_4). The resulting liquor is then neutralized by aqueous ammonia and cooled to yield crystals of the double ammonium aluminum sulfate, formerly called ammonium alum [$NH_4Al(SO_4)_2.12H_2O$]. After settling and drying, the dried crystals of alum are calcined above 1000°C, giving a white powder of pure Al_2O_3.

(ii) ***Gel process.*** High-purity aluminum metal is dissolved in an alcoholic solution of KOH into isopropanol. Once dissolved, the aluminum propanolate produced is purified by distillation and hydrolyzed to yield a gel that is later calcined.

(iii) ***Chloride process.*** This process consists in dissolving pure alumina into concentrated hydrochloric acid and precipitating hexahydrated aluminum chloride ($AlCl_3.6H_2O$). After calcination at 1000°C the residue consists of highly pure Al_2O_3.

(iv) ***Alkaline process.*** This process consists in dissolving pure alumina into concentrated sodium hydroxide and precipitating the gibbsite either by Bayer precipitation or by neutralization. Sodium is removed from gibbsite by hydrothermal treatment. All these processes use a tunnel kiln for the final calcination.

10.2.4 Limestone and Lime

Description and general properties. ***Lime*** or ***calcia*** are common names for ***calcium oxide*** [1305-78-8], whose chemical formula is CaO. Lime exhibits a medium density of 3340 $kg.m^{-3}$ and a high melting point of 2899°C. More specifically, ***quicklime*** is calcined calcium oxide (CaO). It reacts vigorously with water according to the following reaction:

$$CaO(s) + H_2O(l) \text{—>} Ca(OH)_2(s).$$

The hydratation of quicklime is highly exothermic and it releases circa 1.19 MJ per kilogram of lime. If not enough water is added, the heat released can increase the temperature of the water until it reaches its boiling point. Once the reaction is complete, the product obtained is ***calcium hydroxide***, $Ca(OH)_2$ [1305-62-0], also called ***hydrated lime*** or ***slaked lime***. The solution saturated with calcium hydroxide is called ***milk of lime*** and has a pH of 12.25. Hydraulic lime is an impure form of lime that will harden under water. Lime has been used for thousands of years for construction. Archeological discoveries in Turkey indicate lime was used as a mortar as far back as 7000 years ago. Ancient Egyptian civilization used lime to make plaster and mortar.

Industrial preparation. Most lime worldwide is obtained from quarries of carbonated rocks such as limestone, marble, chalk, and dolomite, or even from oyster shells. The suitable raw materials are usually selected because of their low silica and iron contents. After the rock is blasted away, the material is then crushed and sized before being calcined into vertical shaft furnaces (Europe) or rotary kilns (USA) at 1010 to 1345°C. During calcination, the carbon dioxide is driven off and leaves calcium oxide or quicklime according to the following reaction:

$$CaCO_3(s) \text{—>} CaO(s) + CO_2(g).$$

Theoretically, 100 kg of pure calcium carbonate yields 56 kg of quicklime.

Industrial applications and uses. Today, nearly 90% of lime is used for chemical and industrial purposes. The largest use of lime is in steel manufacturing, where it is used as a flux to remove impurities such as phosphorus and sulfur. Lime is used in power-plant smokestacks to remove sulfur from emissions. Lime is also used in mining to neutralize acid-mine drainage, paper and paper-pulp production, water treatment and purification, and wastewater treatment. It is used in road construction and traditional building construction. ***Limestone*** is a sedimentary carbonated rock essentially made of calcite [$CaCO_3$, rhombohedral] and hence can be used in place of lime for some industrial applications such as agriculture, as a flux in steelmaking, and in sulfur removal. Limestone is much less expensive than lime (60–100 US$/tonne); however, it is not as reactive as lime, so it may not be the best substitute in all cases. Magnesium hydroxide can be used for pH control. Lime resources are plentiful worldwide. Major producers of lime are the United States (Texas, Alabama, Kentucky, Missouri, Ohio, and Pennsylvania), Canada and Mexico, Belgium, Brazil, China, France, Germany, Italy, Japan, Poland, Romania, and the United Kingdom.

10.2.5 Dolomite and Doloma

10.2.5.1 Dolomite

Description and general properties. Dolomite is a massive calcareous sedimentary rock made of the mineral ***dolomite*** [$CaMg(CO_3)_2$, rhombohedral], first identified by the French geologist D. Dolomieu in 1791 and named by H. Saussure after its discoverer. Dolomite occurs as huge geological formations such as in the northeastern Italian Alps called the Dolomiti. Usually dolomite as a rock contains, apart from dolomite, other carbonates (e.g., calcite,

magnesite, and siderite), along with some silica and alumina, mostly as clays. For commercial purposes, the mass fraction of combined impurities must be below 7 wt.%, above which it becomes unsuitable for industrial use and is then used only for road ballasts and building stones. When the percentage of calcium carbonate ($CaCO_3$) is above 10 wt.% or more over the theoretical composition, the rock is termed calcitic dolomite, while with a departure from theoretical magnesite content the rock is called dolomitic limestone. With variations in $MgCO_3$ between 5 and 10 wt.%, it is called magnesian limestone, and when it contains up to 5 wt.% $MgCO_3$ or less it is considered limestone for all purposes.

Industrial applications and uses. Pure dolomite, without calcining, is chiefly used as refractory, ramming, and felting material in steel-melting shops and as fluxing material in blast-furnace operations in secondary steel and in the production of ferromanganese. Dolomite for use as flux in iron- and steelmaking should be hard, compact, and fine-grained so that it can withstand the burden of batches in blast furnaces as well as the basic steel converter. Dolomite bricks are kept in backup lining because it exhibits a lower thermal conductivity than magnesite. Chemical impurities must be as low as possible, especially phosphorus and sulfur, while silica and alumina are not deleterious for blast furnaces. Moreover, the magnesia in dolomite acts as desulfurizating agent in molten iron metal. Generally, two grades of dolomite are used, one is called blast furnace grade and the other steel melting shop grade. Dolomite is also used to a lesser extent in the glass industry, especially in sheet-glass manufacture. For that application, dolomite should contain no more than 0.1 wt.% Fe_2O_3. It also finds use in the manufacture of mineral wool. Dolomite is also a useful source for the production of magnesite by reacting calcined dolomite with seawater (Section 10.2.6).

10.2.5.2 Calcined and Dead Burned Dolomite (Doloma)

Description and general properties. Like other carbonates, upon heating above 900°C dolomite decomposes completely into a mixture of calcium and magnesium oxides, and carbon dioxide:

$$CaMg(CO_3)_2(s) \longrightarrow CaO(s) + MgO(s) + 2CO_2(g).$$

The product resulting from this relatively low-temperature calcination is highly porous and reactive and is known as ***calcined dolomite*** or simply ***doloma*** or ***dolime*** (i.e., CaO + MgO). Like lime, most dolime is produced either in vertical shaft kilns (Europe and UK) or rotary kilns (USA). Dolime is used in the extractive metallurgy of magnesium metal by the silicothermic process.

Although pure magnesite decomposes at 700°C and calcite at 900°C, dolime is too porous for most refractory uses. Therefore, prior to use it is calcined at a higher temperature of ca. 1700°C. This harsh treatment allows the material to shrink thoroughly and render it less reactive than calcined dolomite. The product obtained is called ***dead burned dolomite*** and is generally used for the refractory made by firing dolomite, with or without additives, at high temperatures to produce dense, well-shrunk particles.

Industrial preparation. Dead burned refractory dolomite is produced in vertical shaft or rotary kilns. Generally high-purity dolomite, with total impurities of less than 3 wt.%, is selected. As it is difficult to densify high-purity dolomite in a rotary kiln, it is customary to use some mineralizers to facilitate sintering. Iron sesquioxide is a common additive. The manufacturing process varies with the grade of dead burned dolomite needed. Most plants use rotary kilns lined in the hot zone with basic bricks and fired with powdered coal. The temperature reached in the hot zone is ca. 1760°C or above when iron oxide is added. After dead burning, dead burned dolomite is cooled in either rotary or reciprocating recuperative coolers. The air used for cooling gets heated and is again used as secondary air for combustion in the kilns.

There is another product known as ***stabilized refractory dolomite***. It is manufactured by a process similar to that of Portland clinker. Dolomite and serpentine, with small amounts of

suitable stabilizing agents, are ground to a slurry in a ball mill. The slurry is fired into a dense mature clinker in a rotary kiln having a temperature on the order of 1760°C.

Industrial applications and uses. Dead burned dolomite exhibits high refractoriness and can withstand temperatures up to 2300°C. It is widely used as a refractory material wherever steel is refined using basic slag. It is used for original hearth installations in open hearth furnaces as well as for hearth maintenance. These hearths are installed using tar-dolomite ramming mixes and rammed dolomite. Dolomite refractories are also used in electrical furnaces and in the cement industry during clinker manufacture.

10.2.6 Magnesite and Magnesia

10.2.6.1 Magnesite

Description and general properties. ***Magnesite*** ($MgCO_3$) is like alumina, that is, it is considered either as an ore for magnesium metal production or as an industrial mineral. When pure, magnesite contains 47.8 wt.% magnesium oxide (MgO) and 52.2 wt.% carbon dioxide. Natural magnesite almost always contains some calcite ($CaCO_3$) and siderite ($FeCO_3$). Magnesium also occurs in dolomite [$FeMg(CO_3)_2$], a sedimentary rock in which $MgCO_3$ constitutes 45.65 wt.% (i.e., 21.7 wt.% MgO) and 54.35 wt.% $CaCO_3$. Magnesite color varies from white, when pure, to yellowish or gray white and brown. Its Mohs hardness ranges from 3.5 to 4.5 and its density varies from 3000 to 3200 $kg.m^{-3}$. A vitreous luster and very slow reaction with cold acids distinguishes magnesite from other carbonates. Magnesite, dolomite, seawater, and lake brines are used as major sources of magnesium metal with the most common source being lake brines and seawater.

Occurrence. Magnesite occurs in two physical forms: as cryptocrystalline or amorphous magnesite and as macrocrystalline magnesite. It occurs in five different ways: as a replacement mineral in carbonate rocks; as an alteration product in ultramafic rocks (e.g., serpentinite, dunite); as a vein-filling material; as a sedimentary rock; and as nodules formed in a lacustrine environment. Replacement-type magnesite deposits involve magnesium-rich hydrothermal fluids entering limestone via openings to produce both magnesite and dolomite. The alteration-type deposits are formed by the action of carbon-dioxide-rich waters on magnesium-rich serpentinite. Sedimentary deposits usually occur as thin layers of variable magnesite quality. Lacustrine magnesite deposits consist of nodules of cryptocrystalline magnesite formed in a lake environment. Both vein filling and sedimentary magnesite occurrences are rarely mined on a large scale.

Mining. All magnesite deposits are mined by open-cut methods. During mining the strip ratio, that is, the quantity of magnesite ore to waste material, may be high. The processing of magnesite ore begins with crushing, screening, and washing. The estimated world economic reserves of magnesite are about 8.60 billion tonnes expressed as $MgCO_3$. China is ranked first, followed by Russia and North Korea.

Industrial applications. Raw magnesite is used for surface coatings, landscaping, ceramics, and as a fire retardant.

10.2.6.2 Caustic Seawater and Calcined Magnesia

Industrial preparation. Raw magnesite coming from the run-of-mine is calcined between 700 and 1000°C in a vertical shaft kiln and decomposes yielding magnesium oxide or magnesia (MgO) and giving off carbon dioxide gas:

$$MgCO_3(s) \text{ —> } MgO(s) + CO_2(g).$$

The product obtained is called ***caustic-calcined magnesia*** (CCM), also called ***natural magnesia***. The purity of CCM ranges usually between 75 and 96 wt.% MgO, with most of the impurities (e.g., Fe_2O_3, Al_2O_3, SiO_2, etc.) coming from the raw material used.

When a higher-purity magnesia is required, another more energy demanding route consists in preparing directly magnesium oxide from seawater or magnesium-rich brines. Prior to being processed, seawater is pumped and its impurities, mostly carbonates along with dissolved carbon dioxide, are removed. Usually, a hydrotreater removes CO_2 as calcium carbonate by the addition of milk of lime, $Ca(OH)_2$. Afterwards, the addition of hydrochloric acid removes the dissolved CO_2 as gaseous carbon dioxide with an efficiency of 95%. On the other hand, either ***quicklime*** (CaO) obtained from the calcination of pure limestone[2] or, better, ***dolime*** (i.e., CaO and MgO) obtained from the calcination of dolomitic limestone is prepared in a vertical shaft kiln. Once cooled, quicklime or dolime is then slacked with water to yield ***milk lime***, $Ca(OH)_2$. The operation is performed in a rotary slacker from which any traces of calcium carbonate are removed by centrifugation. The milk of lime is added to the decarbonated seawater for precipitating magnesium as brucite [$Mg(OH)_2$]. The milky slurry is filtrated to recover the magnesium hydroxide. The filtration cake is then sintered into a rotary kiln to obtain the so-called ***seawater magnesia clinker***, also called ***synthetic magnesia***, with a purity of at least 97 wt.% MgO.

Both grades of caustic magnesia readily react with water to give ***magnesium hydroxide*** or ***brucite*** [$Mg(OH)_2$], also called slacked or ***spent magnesia***:

$$MgO(s) + H_2O(l) \longrightarrow Mg(OH)_2(s).$$

Due to its alkaline properties and its poor solubility, when an excess of caustic magnesia is mixed with water, it gives a slurry called milk of magnesia with a pH of 10.25, and hence most heavy metals (e.g., Ni) are precipitated as metal hydroxides and then can be either removed by decantation, centrifugation, or filtration or stabilized in situ after drying of the slurry.

Industrial applications and uses. Magnesium hydroxide or brucite is used in sugar refining, as a flame and smoke retardant, in wastewater treatment, and finally in pharmaceuticals. Caustic magnesia is extensively used in acid mine drainage and wastewater treatment to precipitate deleterious metals. On the other hand, caustic-calcined magnesite is used in agriculture as a food supplement in fertilizers, in environmental applications, and in the chemical industry for making magnesium oxychloride and oxysulfate cements that are resilient, fireproof, spark proof, and vermin proof; it is also used as filler in paints, paper, and plastic.

The building industry consumes large quantities of caustic-calcined magnesite for use as a flooring material, in wall boards, and in acoustic tiles. Worldwide annual production is 1,000,000 tonnes of synthetic magnesia.

Prices (2006). Prices are roughly 200 US$/tonne for natural magnesia and up to 400 US$/tonne for synthetic magnesia.

10.2.6.3 Dead Burned Magnesia

When caustic magnesia is further heated at temperatures of between 1530 and 2300°C, the grains of magnesia become sintered and the product obtained is nonhygroscopic and exhibits exceptional stability and strength at high temperatures. This fine-grained product, with a density of 3400 $kg.m^{-3}$, an average periclase grain size above 120 μm that contains at least 97 wt.% MgO, is known as ***dead burned magnesia*** or ***sintered magnesia***. Worldwide circa 7.5 million tonnes of dead burned magnesia are produced annually. Dead burned magnesia and fused magnesia, due to their refractoriness, are used in the manufacture of basic refractories for iron- and steelmaking, nonferrous metallurgy, and finally in cement kilns. Eighty-five percent of the world production is used as ***refractory grade*** dead burned magnesia essentially as a refractory material because of its inertness and high melting point, while the remaining 15% is used in the cement industry, glassmaking, and the metallurgy of nonferrous metals.

[2] In the early days of the Dow Chemical process for producing magnesium metal, tonnes of Oyster shells were used as a source of pure calcium carbonate for the preparation of magnesia from seawater.

10.2.6.4 Electrofused Magnesia

Electrofused magnesia is obtained when dead burned magnesia is melted in an electric-arc furnace at temperatures above the melting point of MgO (2800°C) and pouring the melt into a mold. After cooling and demolding and then crushing, so-called ***electrofused magnesia***, or simply ***fused alumina***, is obtained. It has a higher mechanical strength, high resistance to abrasion, and a higher chemical stability than dead burned magnesia. It is used in the manufacture of premium-grade refractory bricks used in the high wear hot spots of basic oxygen furnaces and electric-arc or similar furnaces where temperatures can approach 950°C.

10.2.6.5 Seawater Magnesia Clinker

Magnesia is also produced from the processing of seawater and magnesium-rich brines. This is a much more complex and energy-demanding process than the processing of natural magnesite.

10.2.7 Titania

Titanium dioxide [13463-67-7], chemical formula TiO_2 and relative molecular molar mass of 79.8788, occurs in nature in three polymorphic crystal forms: ***anatase***, ***rutile***, and ***brookite***. Moreover, under high pressure, the structure of all three polymorphs of titanium dioxide may be converted into that of α-PbO_2. The main properties of the three polymorphs are summarized in Table 10.6.

10.2.7.1 Rutile

Rutile [131-80-2], among other polymorphs of titanium dioxide, is the most thermodynamically stable structure, and thus rutile is the major naturally occurring mineral of pure titanium dioxide and is much more common than either anatase or brookite. It is usually colored red or brownish red by transmitted light owing to trace impurities such as Fe, Nb, Ta, and, to a lesser extent, Sn, Cr, and V. The preparation of single crystals of rutile at the laboratory scale can be performed using Verneuil's flame fusion method,[3] while its large-scale industrial preparation is based on the sulfate and chloride processes (see Titanium). The crystallographic structure of rutile is a flat tetragonal prism where each tetravalent titanium cation is hexacoordinated to six almost equidistant oxygen anions, and each oxygen anion to three titanium anions. The TiO_6^{8-} octahedra are arranged in chains parallel to the *c*-axis. The oxygen atoms are arranged in the form of a somewhat distorted octahedron with each octahedron sharing one edge with adjacent members of the chain. The O-Ti-O bond angles are 90° by symmetry, 80.8°, and 99.2°, respectively. Highly pure rutile is an excellent electrical insulator at room temperature. However, its electrical conductivity, which is highly anisotropic, rises rapidly with temperature owing to the reversible lost of oxygen atoms that leads to a departure from ideal stoichiometry. Hence, upon heating rutile gives an *n*-type semiconductor[4] and its conductivity can increase up to 100 $S.cm^{-1}$ for the composition $TiO_{1.75}$.[5] Expression for the intrinsic conductivity expressed in $S.cm^{-1}$ of single crystals of rutile as a function of temperature have been given by Cronmeyer,[6,7] where the two subscript symbols // and + refer to the *c*-axis.

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[3] Verneuil, A. (1902) *Compt. Rend. Acad. Sci.*, 135, 791.
[4] Grant, F.A. (1959) *Rev. Mod. Phys.*, 31, 646.
[5] Verwey, E.J.W. (1947) *Philips Tech. Rev.* 9, 46.
[6] Cronmeyer, D.C. (1952) *Phys. Rev.*, 87, 876.
[7] Cronmeyer, D.C. (1959) *Phys. Rev.*, 113, 1222.

Table 10.6. Properties of titanium-dioxide polymorphic phases

Phase [CAS RN]	Crystal system, space group, and space lattice parameters	Refractive indices (for λ_D = 589.3 nm)	Miscellaneous properties (density[8], etc.)
Anatase[9] [1317-70-0]	Tetragonal ($I4_1/amd$, Z = 4) a = 379.3 pm c = 951.2 pm Ti-O: 191 pm (2) – 195 pm (4) Packing fraction = 70%	Uniaxial (–) n_ε = 2.4880 n_ω = 2.5612	Black to red $\rho_{calc.}$ = 3877 kg.m^{-3} *trans. temp.* 700°C ε_r = 48 HM = 5.5 – 6.0
Rutile[10] [131-80-2]	Tetragonal ($P4_2/mnm$, Z = 2) a = 459.37 pm c = 296.18 pm Ti-O: 194.4 pm (4) – 198.8 pm (2) Packing fraction = 77%	Uniaxial (+) n_ε = 2.6124 n_ω = 2.8993	Reddish brown $\rho_{calc.}$ = 4245 kg.m^{-3} *m.p.* = 1847°C $\sigma_e = 10^{-14}$ S.cm^{-1} $\chi_m = +74 \times 10^{-9}$ emu[11] ε_r = 110 – 117 HM = 6.0 – 6.5
Brookite[12] [12188-41-9]	Orthorhombic (*Pbca*, Z = 8) a = 545.6 pm b = 918.2 pm c = 514.3 pm Ti-O: 184 pm – 203 pm	Biaxial () n_α = 2.5831 n_β = 2.5843 n_γ = 2.7004	$\rho_{calc.}$ = 4130 kg.m^{-3} *m.p.* = 1900°C ε_r = 78 HM = 5.5 – 6.0
TiO_2 II high-pressure phase (40 kbar, 450°C)[13]	Orthorhombic (*Pbcn*, oP12, Z = 4) a = 551.5 pm b = 549.7 pm c = 493.9 pm Ti-O: 191 pm (4) – 205 pm (2)	n.a.	n.a.
TiO_2 III high-pressure phase	Hexagonal hP48		

$$\ln \sigma_+ = 7.92 - 17{,}600/T \quad (623.15\ \text{K} - 1123.15\ \text{K})$$
$$= 11.10 - 21{,}200/T \quad (1123.15\ \text{K} - 1673.15\ \text{K})$$

$$\ln \sigma_{//} = 8.43 - 17{,}600/T \quad (773.15\ \text{K} - 1223.15\ \text{K})$$
$$= 11.30 - 21{,}200/T \quad (1223.15\ \text{K} - 1673.15\ \text{K})$$

On the other hand, the electrical conductivity of single crystals of highly pure rutile is strongly affected by the doping of the crystal lattice with traces (i.e., less than 0.1 ppm wt.) of transition-metal cations (e.g., Cr^{3+}, V^{4+}, Nb^{4+}, Nb^{5+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Ni^{3+}, and Cu^{2+}).

From an optical point of view, rutile, which is uniaxial (-), exhibits a high refractive index even higher than that of diamond and is transparent from visible to near-infrared radiation with wavelengths ranging from 408 nm to 5000 nm. However, at the blue end of the visible spectrum the strong absorption band of rutile at 385 nm renders the rutile pigment slightly brighter than anatase, which explains its typical yellow undertone. For that reason it can be used efficiently as sunscreen. When heated in air to ca. 900°C the powdered material

[8] Theoretical density calculated from crystal lattice parameters.
[9] Pascal, P. (1963) Nouveau Traité de Chimie Minérale, Tome IX. Masson & Cie, Paris.
[10] Meagher, E.P.; Lager, G.A. (1979) Polyhedral thermal expansion in the TiO_2 polymorphs: refinement of the crystal structures of rutile and brookite at high temperature. *Can. Mineral.*, **17**, 77–85.
[11] Wide range also reported in the litterature from –300 to $+370 \times 10^{-9}$ emu owing to slight departure from stoichiometry and doping with paramgnetic impurities leads to positive susceptibilities.
[12] Weyl, R. (1959) *Z. Krist*. **111**, 401.
[13] Simons, P.Y.; Dachille, F. (1967) *Acta Cryst*., **23**, 334.

becomes lemon-yellow and exhibits a maximum absorption edge at 476 nm, but coloring disappears on cooling. In addition, doped rutile is phototropic, that is, it exhibits a reversible darkening when exposed to light.[14] On the other hand, rutile exhibits strong photocatalytic properties. As for electrical properties, metallic trace impurities strongly affect the whiteness of rutile. Even minute concentrations on the order of a few parts per million by weight may be sufficient to impart color. Thus in the industrial production of the whitest rutile, it is essential that other chromophoric transition elements not be present in the feedstock or be removed during the processing. Of these, chromium (Cr), vanadium (V), iron (Fe), and, to a lesser extent, niobium (Nb) are particularly deleterious in discoloring rutile. Generally, the colors are too intense to arise from crystal-field effects only but may arise from the excitation of the *d*-electrons of the impurity metal cation into the conduction band of the crystal lattice. From a chemical point of view, titanium dioxide is relatively inert chemically and resists attack from most chemical reagents. This property is further enhanced after titanium dioxide has been calcined at high temperatures.

10.2.7.2 Anatase

The lattice structure of ***anatase*** [1317-70-0] is also tetragonal, but the lower packing fraction of the crystal lattice explains why anatase crystal exhibits both a lower hardness and refractive indices than rutile. Nevertheless, because the crystal lattice energies of the two phases are quite similar, anatase remains metastable over long periods of time despite being less thermodynamically stable. However, above 700°C, the irreversible and rapid monotropic conversion of anatase to rutile occurs. From an optical point of view, anatase exhibits a greater transparency in the near-UV than rutile. The absorption edge being at 385 nm, this explains why anatase absorbs less light at the blue end of the visible spectrum and has a blue tone. Although anatase was the first pigment to be produced commercially and represented a step-change in optical performance over the pigments that preceded it, rutile remains the preferred pigment because of its higher refractive index and lower photocatalytic activity. Actually, rutile ensures greater stability and durability of the paint made from it (less chalking). However, anatase is required in certain applications, especially where low abrasivity may be an issue. Thus anatase pigments were originally the preferred choice for paper filling and coating and also for delustring of synthetic fibers, where the color of the application may degrade by abrasion of metal during frequent rubbing contact with machinery during processing.

10.2.7.3 Brookite

Brookite [12188-41-9], which exhibits an orthorhombic crystal lattice, is more difficult to produce than rutile and anatase, and for that reason it has never been used industrially, especially in the white pigment industry.

Apart from the well-known titanium-dioxide phases mentioned above, other titanium oxides exists such as titanium hemioxide (Ti_2O), titanium monoxide (TiO), titanium sesquioxide (Ti_2O_3), and *anosovite* (Ti_3O_5).

See Table 10.6, page 615.

10.2.7.4 Anosovite

Anosovite [12065-65-5], chemical formula Ti_3O_5, was identified by Ehrlich[15] in the Ti-O binary phase diagram, in the region between 62.3 and 64.3 at.% oxygen. It can be prepared in the following ways:

[14] Weyl, W.A.; Forland, T. (1950) *Ind. Eng. Chem.*, 42, 257.
[15] Ehrlich, P.Z. (1939) *Elektrochem.*, 45, 362.

(i) By the hydrogen reduction of solid TiO_2 at temperature around 1300°C[16] according to the following reaction scheme:

$$3TiO_2(s) + H_2(g) \longrightarrow T_3O_5(s) + H_2O(g) \qquad (1300°C)$$

(ii) By mixing intimately stoichiometric quantities of titanium metal and titanium dioxide in an electric-arc furnace under an argon atmosphere according to the following reaction scheme:

$$5TiO_2(s) + Ti(s) \longrightarrow 2T_3O_5(s) \qquad (1150°C)$$

followed by annealing in a vacuum of the crushed material for 2 weeks at 1150°C in a sealed silica tube. This oxide is dimorphic with a rapid phase transition from semiconductor to metal occurring at roughly 120°C.

$$\alpha\text{-}Ti_3O_5 \longrightarrow \beta\text{-}Ti_3O_5 \qquad (120°C)$$

The low-temperature form (α-Ti_3O_5), also called ***anosovite type I***, crystallizes with a monoclinic unit cell with the Ti-O bond distances ranging from 178 to 221 pm. The structure can be described in terms of TiO_6^{8-} octahedra joined by sharing the edge and corners to form an infinite three-dimensional network. Anosovite I is obtained by the hydrogen reduction of pure rutile at 1300°C. The high-temperature form (β-Ti_3O_5), also called ***anosovite type II***, is a slightly deformed pseudobrookite structure (AB_2O_5) with the Ti-O bond distances ranging from 191 to 210 pm. The type II is obtained by hydrogen reduction at 1500°C with magnesia as a catalyst. The anasovite type II is similar to that identified in titanium slags.[17] It can be stabilized at room temperature with a small amount of iron.

10.2.7.5 Titanium Sesquioxide

Titanium sesquioxide [1344-54-3], chemical formula Ti_2O_3, exists within a rather narrow range of homogeneity, from 59.4 to 60.8 at.% oxygen ($TiO_{1.49}$–$TiO_{1.51}$). It has a corundum structure and is isomorphous with hematite and ilmenite. It may be prepared by reduction of titania by hydrogen gas at 1000°C or as powder by reacting titanium metal with a stoichiometric amount of TiO_2 at 1600°C as follows:

$$Ti(s) + 3TiO_2(s) \longrightarrow 2\ Ti_2O_3(s) \qquad (1600°C).$$

10.2.7.6 Titanium Monoxide or Hongquiite

Titanium monoxide or ***hongquiite*** [12137-20-1], chemical formula TiO, exhibits a very wide range of composition, extending approximately from 42 to 54 at. % oxygen ($TiO_{0.64}$ to $TiO_{1.26}$). It may be prepared by direct reduction by mixing stoichiometric amounts of titanium metal and titanium dioxide into a molybdenum crucible at 1600°C or reduction of the titanium dioxide with hydrogen under pressure at 130 atm and 2000°C.

$$Ti\ (s) + TiO_2(s) \longrightarrow 2\ TiO(s) \qquad (1600°C)$$

On heating the monoxide in air, the compound reverts to other titanium oxides as a function of temperature increase[18]:

$$TiO(s) \longrightarrow Ti_2O_3(s) \qquad (200°C),$$

$$TiO(s) \longrightarrow Ti_3O_5(s) \qquad (250–350°C),$$

$$TiO(s) \longrightarrow TiO_2(s) \qquad (350°C).$$

[16] Ehrlich, P. (1941) *Z. Anorg. Allgem. Chem.*, 247, 53.
[17] Reznichenko, V.A.; Khalimov, F.B. (1959) Reduction of titanium dioxide with hydrogen. *Titan i Ego Splavy,* 2, 11–15.
[18] Wyss, R. (1948) *Ann. Chim.* 3, 215.

Its crystal structure has varying proportions of both titanium and oxygen vacancies. Density and y-ray lattice parameter measurements have shown that a third of the oxygen sites are vacant in $TiO_{0.7}$, a quarter of the titanium sites are vacant in $TiO_{1.25}$, and even in stoichiometric TiO about 15% of both sites are vacant. Above 990°C, the vacancies are arranged randomly, giving rise to diffraction patterns typical of the cubic NaCl-type structure.

10.2.7.7 Titanium Hemioxide

Oxygen is soluble in alpha-titanium until the composition $TiO_{0.5}$ (alpha-case) is formed, with the oxygen atoms supposedly being randomly distributed in the octahedral interstices of the hexagonally close-packed titanium lattice.[19]

10.2.7.8 Andersson–Magnéli Phases

In addition, a major series is represented by Andersson–Magnéli's phases[20] that consist of a continuous series of substoichiometric titanium oxides, characterized by the general formula Ti_nO_{2n-1}, where *n* is an integer greater than 4 (i.e., Ti_4O_7, Ti_5O_9, Ti_6O_{11}, Ti_7O_{13}, etc.).

See Table 10.7, page 619.

10.2.8 Zircon and Zirconia

10.2.8.1 Zircon

Zircon [10101-52-7], chemical formula $ZrSiO_4$, is an accessory nesosilicate mineral found in granites and, due to its high Mohs hardness of 7.5 and chemical inertness, it concentrates in the weathering products of mother igneous rocks such as in alluvial placer deposits and beach sands. Because of its chemical inertness and high melting point, zircon is wetted less easily by molten metal, producing smoother surfaces on iron, high alloy steel, aluminum, and bronze casting. The largest use of zircon is as foundry sand, where zircon is used as the basic mold material, as facing material on mold cores, and in ram mixes. Zircon-sand molds have greater thermal shock resistance and better dimensional stability than quartz-sand molds. Zircon grains are usually bonded with sodium silicate. Major producers of zircon sand are Richards Bay Minerals (Rio Tinto plc-BHP Billiton) located on the coastline of the KwaZulu-Natal region of the Republic of South Africa, followed by the Australian mining company Iluka. Both produce zircon sand as coproduct during mineral dressing of weathered ilmenite and rutile from beach mineral sands.

10.2.8.2 Zirconia

Description and general properties. Pure zirconium dioxide (ZrO_2), also called ***zirconia***, is a dense material (5850 $kg.m^{-3}$) that exhibits a high temperature of fusion (2710°C) and a good thermal conductivity (1.8 $Wm^{-1}K^{-1}$). Electrically speaking, zirconia is a dielectric at room temperature but becomes a good ionic conductor at high temperatures. Actually, cubic zirconia is a solid ionic electrolyte that allows oxygen anions to migrate through the crystal structure under an electric field at temperatures above 800°C. Optically, zirconia has a high index of refraction, which allows it to be used for increasing the refractive index of some optical glasses. Chemically, zirconia exhibits an excellent chemical inertness and corrosion resistance to many strong mineral acids, liquid metals, and molten salts up to high temperatures well above the melting point of alumina. Zirconia is not wetted by many metals and is therefore an excellent crucible material when corrosive melts (e.g., molten alumina and titanium slag)

[19] McQuillan, A.D.; McQuillan, M.D. (1956) *Titanium*. Butterworths, London.
[20] Andersson, S.; Collen, B.; Kuylenstierna, U.; Magneli, A. (1957) *Acta Chem. Scand.*, 11, 1641.

Table 10.7. Properties of other titanium oxides

Titanium oxide	Formula	Rel.molar mass (M_r)	wt.% Ti	Color, crystal lattice structure, space group (SG), Pearson symbol, lattice parameters, physical properties
Andersson–Magnéli phases	$Ti_{10}O_{19}$	780.6886	61.1	Triclinic
	Ti_9O_{17}	701.0198	61.2	Triclinic; S.G. P1; aP52
	Ti_8O_{15}	621.3510	61.4	Triclinic, S.G. A1; aC92
	Ti_7O_{13}	541.6822	61.6	Triclinic; S.G. P1; aP40
	Ti_6O_{11}	462.0134	61.9	Triclinic; S.G. A1; aC68
	Ti_5O_9	382.3446	62.3	Triclinic; S.G. P1; aP28
	Ti_4O_7	302.6758	63.0	Triclinic; S.G. P1; aP44
Anosovite [12065-65-5]	Ti_3O_5	223.0070	64.1	Dark blue; dimorphic (120°C) Low T: Anasovite-type I Monoclinic, C2/m, $Z = 4$ $a = 975.2$ pm; $b = 380.2$ pm; $c = 944.2$ pm; $\beta = 91.55°$ High T: Pseudobrookite (orthorhombic) $\rho_{calc.} = 4900$ kg.m^{-3} *m.p.* = 1777°C
Titanium sesquioxide [1344-54-3]	Ti_2O_3	143.3382	66.5	Dark violet to purple violet Corundum type $a = 515.5$ pm; $c = 1361$ pm $\rho_{calc.} = 4486$ kg.m^{-3} *m.p.* = 1839°C $c_p = 679$ J.kg^{-1}.K^{-1} $\chi_m = +63 \times 10^{-6}$ emu
Titanium monoxide or hongquiite [12137-20-1]	TiO	63.6694	74.9	Gold-bronze Halite-type (cubic) $a = 417$ pm $\rho_{calc.} = 4888$ kg.m^{-3} *m.p.* = 1750°C $c_p = 628$ J.kg^{-1}.K^{-1} $\alpha = 9.19$ μ/m.K $\chi_m = +88 \times 10^{-6}$ emu
Titanium hemioxide	Ti_2O	111.3394	85.6	Metallic gray

are absent. It can be used continuously or intermittently at temperatures up to 2200°C in neutral or oxidizing atmospheres. However, above 1600°C, zirconia reacts with alumina, and above 1650°C, in contact with carbon, zirconia forms zirconium carbide (ZrC). It has been used successfully for melting alloy steels and the noble metals. Nevertheless, zirconia in its chemically pure state exhibits poor mechanical and thermal properties that are inappropriate for use in structural and advanced ceramics. Actually, the polymorphism of pure zirconia exhibits deleterious phase transitions between room temperature and its melting point (Figure 10.3). These phase changes, accompanied by important relative volume changes, create a dense population of microcracks for the sake of toughness and thermal shock resistance.

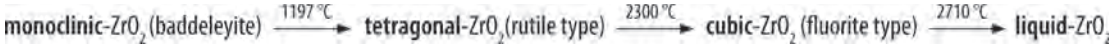

Figure 10.3. Polymorphs of zirconia (ZrO_2)

At room temperature, pure zirconia is essentially made of monoclinic ***baddeleyite*** with a density of 5850 $kg.m^{-3}$ and a coefficient of linear thermal expansion of $6.5 \times 10^{-6}\ K^{-1}$, which is stable up to the transition temperature of 1197°C, at which it transforms into tetragonal zirconia (i.e., rutile type) with a density of 6045 $kg.m^{-3}$. This inversion in crystalline structure causes an important volume change upon heating (V/V = +7.0 vol.%). Due to the inversion, pure zirconia is highly sensitive to thermal shocks:

$$ZrO_2\ (\text{monoclinic}) \text{ —> } ZrO_2\ (\text{tetragonal}) \qquad T_t = 1197°C.$$

Afterwards, above 2300°C, tetragonal zirconia transforms into high-temperature cubic zirconia (i.e., fluorite type) with a mass density of 5500 $kg.m^{-3}$ and a coefficient of linear thermal expansion of $10.5 \times 10^{-6}\ K^{-1}$:

$$ZrO_2\ (\text{tetragonal}) \text{ —> } ZrO_2\ (\text{cubic}) \qquad T_t = 2300°C.$$

Finally, at 2710°C zirconia melts, giving molten zirconia:

$$ZrO_2(\text{cubic}) \text{ —> } ZrO_2(l) \qquad T_f = 2710°C.$$

However, to prevent the first disastrous phase transition, it is possible to stabilize high-temperature cubic zirconia introducing foreign bivalent, trivalent, and/or tetravalent cations into its structure. Once stabilized, zirconia is stable from room temperature up to its melting point without any phase changes, and its thermal expansion varies linearly with temperature. The doped material demonstrates superior mechanical, thermal, and electrical properties owing to the modification of its crystal structure. Major lattice stabilizers are, for instance, calcia (CaO), magnesia (MgO), ceria (CeO_2), yttria (Y_2O_3), and lanthania (La_2O_3), which are introduced into the material prior to firing. The stabilized zirconia is then extremely resistant to thermal shock. Actually, white hot parts can be quenched in cold water or liquid nitrogen without break. Usually, calcia is the most widely used addition commercially, not only because it is a cheap raw material but also because the cubic form remains stable at all temperatures, whereas the magnesia-stabilized form may revert to the monoclinic structure at low temperature.

Commercial zirconia grades. Usually ***unstabilized zirconia*** (i.e., fully monoclinic), ***partially stabilized zirconia***, and ***stabilized zirconia*** (i.e., completely cubic) grades exist commercially and are available among advanced ceramic producers worldwide (e.g., Zircoa, Vesuvius, and Degussa), and they are briefly described below.

(i) **Unstabilized zirconia.** As indicated previously, pure zirconia is monoclinic at room temperature and changes to the denser tetragonal form at 1100°C, which involves a large volume change and creates microcracks within its structure. However, pure zirconia is an important constituent of ceramic colors and an important component of lead-zirconia-titanate electronic ceramics. Pure zirconia can be used as an additive to enhance the properties of other oxide refractories. It is particularly advantageous when added to high-fired magnesia and alumina bodies. It promotes sinterability and, with alumina, contributes to abrasive characteristics.

(ii) **Partially stabilized zirconia.** Partially stabilized zirconia (PSZ) is a mixture of various zirconia polymorphs, because insufficient cubic-phase-forming oxide has been added and a cubic plus metastable tetragonal ZrO_2 mixture is obtained. A smaller addition of stabilizer to pure zirconia will bring its structure into a tetragonal phase at a temperature higher than 1100°C, and a mixture of cubic phase and monoclinic or tetragonal phase at a lower temperature. Therefore, partially stabilized zirconia is also called ***tetragonal zirconia polycrystal*** **(TZP)**, which is usually a zirconia doped with 2 to 3 mol.% of yttria and which has a fine-grained microstructure (i.e., 0.5 to 0.8 μm) that exhibits most impressive mechanical properties at room temperature. Usually such PSZ consists of more than 8 mol.% MgO (2.77 wt.%), 8 mol% CaO (3.81 wt.%), or 3 to

4 mol.% Y_2O_3 (5.4 to 7.1 wt.%). PSZ is a transformation-toughened material. Microcracks and induced stress may be two explanations for the toughening in partially stabilized zirconia. Microcracks arise due to the difference in the thermal expansion between the cubic-phase particle and monoclinic or tetragonal-phase particles in the PSZ. This difference creates microcracks that dissipate the energy of propagating cracks. The induced-stress explanation depends upon the tetragonal-to-monoclinic transformation, once the application temperature passes the transformation temperature at about 1000° C. The pure zirconia particles in PSZ can metastably retain the high-temperature tetragonal phase. The cubic matrix provides a compressive force that maintains the tetragonal phase. Stress energies from propagating cracks cause the transition from the metastable tetragonal to the stable monoclinic zirconia. The energy used by this transformation is sufficient to slow or stop propagation of the cracks. PSZ has been used where extremely high temperatures are required. PSZ is also used experimentally as heat engine components, such as cylinder liners, piston caps, and valve seats.

(3) **Fully stabilized zirconia (CSZ).** Fully stabilized zirconia, also called cubic stabilized zirconia (CSZ), is essentially a single-phase cubic material with large grain sizes of 10 to 150 μm that result when the stabilizer content and sintering temperature place it entirely in the cubic-phase region. Generally, the addition of more than 16 mol.% CaO (7.9 wt.%), 16 mol.% MgO (5.86 wt.%), or 8 mol.% Y_2O_3 (13.75 wt.%) to a zirconia structure is needed to form a fully stabilized zirconia. Its structure becomes cubic solid solution, which has no phase transformation from room temperature up to 2710°C. Fully yttria-stabilized zirconia (YSZ) is an excellent oxygen anion conductor that has been used extensively either as oxygen sensor or anion exchange membrane in solid oxide fuel cells (SOFCs). Other applications include grinding media and advanced ceramics due to its hardness and high thermal shock resistance.

Preparation of unstabilized zirconia. Zirconia is usually produced from zircon flour. Although the carbochlorination of zircon produces zirconium tetrachloride that can be oxidized to yield zirconia, such a method is only restricted to the production of zirconium metal (see Zirconium and Zirconium alloys). Therefore, to produce zirconia from zircon, the first step is to convert zircon to zirconyl chloride dihydrate. The process starts with the preparation of disodium metazirconate (Na_2ZrO_3) by digesting zircon into molten sodium hydroxide as follows:

$$ZrSiO_4(s) + NaOH(l) \text{ —> } Na_2ZrO_3(s).$$

Then the sodium zirconate is dissovled in concentrated hydrochloric acid:

$$Na_2ZrO_3(s) + 2HCl(l) \text{ —> } ZrOCl_2 \cdot 8H_2O(s).$$

There are two methods used to make zirconia from zirconyl chloride dihydrate ($ZrOCl_2.8H_2O$): thermal decomposition and precipitation.

In the thermal decomposition method, upon heating above 200°C, zirconyl chloride dihydrate loses its hydratation water as follows:

$$ZrOCl_2 \cdot 8H_2O(s) \text{ —> } ZrOCl_2(s) + 8H_2O(g).$$

Afterwards, at a higher temperature anhydrous $ZrOCl_2$ decomposes during calcination into chlorine gas and yields zirconia:

$$ZrOCl_2(s) + 1/2O2(g) \text{ —> } ZrO_2(s) + Cl_2(g).$$

The zirconia lumps obtained from the calcination then undergo a size-reduction process, such as ball milling, into the particle size range needed, usually up to –325 mesh. Thermal decomposition is hence an energy-demanding process from which it is not easy to produce zirconia powders with a high purity and fine particle size.

In the precipitation method, zircornyl chloride dihydrate is dissolved into water, and after addition of aqueous ammonia a precipitate of zirconium hydroxide is obtained:

$$ZrOCl_2 + 4NH_4^+ + 4OH^- \text{ —> } Zr(OH)_4(s) + NH_4^+ + Cl^-.$$

The precipitate of zirconium hydroxide ($Zr(OH)_4$) is washed in order to obtain a chlorine-free product. The solid is recovered by filtration to yield a wet powder that after calcination and quenching into liquid nitrogen yield a high-quality zirconia powder:

$$Zr(OH)_4(s) \text{ —> } ZrO_2(s) + 2H_2O(g).$$

By this method, the grain size, particle shape, agglomerate size, and specific surface area can be modified within a certain degree by controlling the precipitation and calcination conditions. Furthermore, its purity is also more easily controlled. For the applications of zirconiain the slip casting, tape casting, mold injection, particle size, specific surface, etc. are important characteristics. Well-controlled precipitated zirconia powder can be fairly uniform and fine.

Preparation of stabilized zirconia. In order to achieve the requirement of the presence of cubic and tetragonal phases in the microstructure of zirconia, stabilizers, i.e., magnesia, calcia, or yttria must be introduced into pure zirconia powders prior to sintering. Stabilized zirconia can be formed during a process called *in situ* stabilizing. Before the forming processes, such as molding, pressing, or casting, a blend of fine particles of stabilizer and monoclinic zirconia is prepared. Then the mixture is used for forming of green body. The phase conversion is accomplished by sintering the doped zirconia at 1700°C. During the firing (sintering), the phase conversion takes place. On the other hand, high-quality stabilized zirconia powder is made by a coprecipitation process. Stabilizers are then introduced before precipitation of zirconium hydroxide.

Preparation of fused zirconia. Production of electrofused or simply fused zirconia consists in removing silica from zircon by melting zircon sand with coke into an electric arc furnace at temperatures of around 2800 to 3000°C. During the electrothermal process, silica is reduced to volatile silicon monoxide (SiO), which escapes the furnace and leaves molten zirconia. On rapid cooling, a granular material is produced that is screened and crushed. Usually, the monoclinic zirconia produced contains less than 0.2 wt.% silica.

Preparation of zirconia by alkaline leaching. Zircon is roasted with sodium hydroxide and calcia at 600 to 1000°C. During the process silica reacts with calcium and sodium to yield calcium and sodium metasilicates. After acid leaching, the product is dyed and calcined to yield pure zirconia with less than 0.10 wt.% residual silica.

The major producers of zirconia are listed in Table 10.8.

Table 10.8. Major producers of zirconia

Country	Company name	Plant location	Annual nameplate capacity (tonnes)
United States	Washington Mills Electro Minerals Corp.	Niagara Falls, NY	1500
	Ferro Electronic Materials Systems	Niagara Falls, NY	4000
	Universal America	Greeneville, TN	6000
	Saint-Gobain Ceramic Materials	Huntsville, AL	6000
United Kingdom	Unitec Ceramics	Stattford	200
France	SEPZirPro	Le Pontet	8000
Australia	Australia Fused Materials	Rockingham, WA	4000
South Africa	Foskor	Phalaborwa	4000

Table 10.8. *(continued)*

Country	Company name	Plant location	Annual nameplate capacity (tonnes)
Japan	JACO Co.	Osaka	
	Showa Denco Ceramics	Shiojiri	1000
	Fukushima Steel Works	Fukushima	
	JFE Material Co.	Imizu	1000
	IDU Co.	Kochi	1500
China	Shanghai Zirconium Products	Shanghai	
	Yingkou Astron Chemical Co.	Bayuquan	9000
	Zhenzou Fused Zirconia Co.	Zhengzou	5500

10.2.9 Carbon and Graphite

10.2.9.1 Description and General Properties

Graphite [7440-44-0] is one of the two allotropic forms of the chemical element carbon, the other two being diamond (see Section 12.5). Graphite crystallizes in the hexagonal system. It has a black to steel gray color and usually leaves a black streak on the hand when touched because of its extreme softness and greasiness. It is opaque, even in the finest flakes. Graphite exhibits a high thermal conductivity close to that of copper alloys (Table 10.9). An important limitation of this material is its low tensile strength, and all components manufactured from carbon or graphite are highly susceptible to brittle fracture by mechanical shock or vibrations. Graphite is almost completely inert to all but the most severe oxidizing conditions, especially acids. Actually, graphite is recommended for use in 60 wt.% HF, 20 wt.% HNO_3, 96 wt.% H_2SO_4, bromine, fluorine, or iodine. The excellent heat-transfer property of impervious graphite has made it very popular in heat exchangers handling corrosive media, but also for a number of other devices used in the chemical-process industries such as piping, pumps, valves, brick lining for process or storage vessels, anode materials in electrochemical processes, and ring packing for columns. Impervious graphite is also used for liquid metal-handling devices. It has high refractoriness; actually, graphite is highly refractory up to temperatures approaching 3000°C in an inert atmosphere or in a vacuum. However, if oxygen is present, it burns between 620 and 720°C. Graphite has an extraordinarily low coefficient of friction under practically all working conditions. This property is invaluable in lubricants. It diminishes friction and tends to keep the moving surface cool. Dry graphite, as well as graphite mixed with grease and oil, is used as a lubricant for heavy and light bearings. Graphite grease is used as a heavy-duty lubricant where high temperatures may tend to remove the grease. All grades of graphite, especially high-grade amorphous and crystalline graphite, can behave as colloids; for example, in suspension in an oil base, they are used as lubricants. Properties of selected commercial grades of graphite are listed in Table 10.10.

10.2.9.2 Natural Occurrence and Mining

Graphite is usually found in metamorphic rocks as veins, lenses, and pockets and as thin laminae disseminated in gneisses, schists, and phyllites. Depending upon the mode of occurrence and origin, it is graded into three forms: ***flake graphite*** found in metamorphosed rocks as vein deposits, ***crystalline graphite*** found as fissure-filled veins, and ***cryptocrystalline graphite***

Table 10.9. Selected properties of different carbon products[21]

Carbon derivate	Density (ρ/kg.m^{-3})	Young's modulus (E/GPa)	Compressive strength (MPa)	Flexural strength (MPa)	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})	Coeff. linear thermal expansion (α /10^{-6}K^{-1})	Electrical resistivity (ρ/μΩ.cm)	Vickers hardness (HV)
Graphite (industrial)	1400–2266	3–12	14–42	5–21	85–350	709	1.3–3.8	1385	HM 1
Pyrolitic carbon (impervious graphite)	1400–2210	16–30	72	32	480–1950	707	4.5	1500	145
Diamond	3514	900	7000	n.a.	900–2300	506	2.16	10^{16}	8000
Vitreous carbon (treated at 1000°C)	1500–1550	28	300	100	4	710	3.2	5500	225
Vitreous carbon (treated at 2500°C)	1500–1550	22	150–200	60–80	8	710	3.2	4500	150–175

Table 10.10. Properties of industrial graphite grades from SGL Carbon

Graphite or carbon grade	Bulk density (ρ/kg.m^{-3})	Open porosity (vol.%)	Average grain size (μm)	Medium pore size (μm)	Dry air permeability at 20°C (cm^2.s^{-1})	Rockwell hardness (HR)	Shore hardness	Flexural strength (MPa)	Compressive strength (MPa)	Young's modulus (E/GPa)	Specific electrical resistivity (ρ/μΩ.cm)	Thermal conductivity (k/W·m^{-1}·K^{-1})	Thermal expansion coefficient (20–200°C) (μm/m.K)	Ash content (ppm wt.)
HLM	1700–1780	17–23	1.65	n.a.	n.a.	n.a.	n.a.	15–18	37–44	7.4–10.2	940–1240	105–180	1.4–3.6	1000–3000
MNC	1800	14	200	n.a.	n.a.	n.a.	n.a.	40	55–60	16	1000	130	1.5	1500
MNT	1750	16	400	n.a.	n.a.	n.a.	n.a.	20	28–30	15	1000	130	1	4000
R4340	1720	15	15	2	0.15	80	50	45	90	10.5	1200	90	2.9	200
R4500	1770	13	10	1.5	0.1	70	65	50	120	10.5	1400	80	3.9	200
R4550	1830	10	10	1.5	0.04	95	75	60	125	11.5	1300	100	4	20
R4820	1820	10	20	2.5	0.1	100	65	45	105	11	1150	125	4.2	50
R6300	1730	15	20	2	0.1	80	50	40	90	10	1700	65	3.8	n.a.
R6340	1720	15	15	2	0.15	80	50	45	90	10.5	1200	90	4	
R6500	1770	13	10	1.5	0.1	70	65	50	120	10.5	1400	80	5	
R6510	1830	10	10	1.5	0.04	95	75	60	125	11.5	1300	90	5.1	
R6650	1840	10	7	0.8	0.03	95	75	65	150	12.5	1400	90	5	
R6710	1880	10	3	0.6	0.01	110	80	85	170	13.5	1300	100	5.8	
R6810	1800	11	20	2.5	0.3	95	75	45	100	10	1000	130	5.2	
R6830	1820	9.5	20	2.5	0.1	95	75	50	100	10	1000	130	5	
R8710	1880	10	3	0.6	0.01	110	80	85	170	13.5	1300	100	4.7	200

[21] Technical data from various producers such as Le Carbone Lorraine, Sigradur, SGL, and Tokkai.

formed in metamorphosed coal beds. Natural graphite occurs in many parts of the world in fair abundance and it has been used in various applications. In nature, graphite is found usually in association with feldspars, mica, quartz, pyroxene, rutile, pyrites, and apatite. These impurities are associated with vein graphite. The impurities with amorphous graphite are shale, slate, sandstone, quartz, and limestone. Graphite is found in almost every country, but Ceylon, Madagascar, Mexico, western Germany, and Korea all possess particularly plentiful reserves. Major industrial producers of graphite are South Korea, the largest producer in the world, followed by Austria.

Graphite is usually obtained by underground mining and, to a lesser extent, by hydraulic mining such as in Madagascar. Afterwards, beneficiation of the run-of-mine consists in using the intrinsic floatation ability of natural graphite without having to use a collector. However, the recovery of flake graphite from disseminated deposits is difficult, and several proprietary processes have been developed by many companies. This difficulty arises because fine grinding is not efficient and reduces the size and also lowers the price and value of the graphite.

10.2.9.3 Industrial Preparation and Processing

Impervious graphite is manufactured by processing graphite at temperatures above 2000°C using Acheson furnaces (Section 10.2.10), evacuating the pores, and impregnating with a phenolic resin. The impregnation seals the porosity.

10.2.9.4 Industrial Applications and Uses

Flake graphite containing 80 to 85 wt.% C is used for crucible manufacture; 93 wt.% C and above is preferred for the manufacture of lubricants, and graphite with 40 to 70 wt.% C is used for foundry facings. Natural graphite, refined or otherwise pure, having a carbon content of not less than 95%, is used in the manufacture of carbon rods for dry battery cells. Graphite crucibles are manufactured by pressing a mixture of graphite, clay, and silica sand (formerly called ***plumbago***) and heating the pressed article at a high temperature in an inert atmosphere. Flake graphite is the best material, although crystalline graphite is also used. Crucibles made of graphite are used for melting nonferrous metals, especially brass and aluminum. Coarse-grained flake graphite from Malagasy is regarded as standard for crucible manufacture.

The utility of graphite is dependent largely upon its type, i.e., flake, lumpy, or amorphous. The flake-type graphite is found to possess extremely low resistivity to electrical conductance. The electrical resistivity decreases with an increase in flaky particles. In addition, the bulk density decreases progressively as the particles become more and more flaky. Because of this property in flake graphite, it enjoys widespread use in the manufacture of carbon electrodes, plates, and brushes required in the electrical industry and dry-cell batteries. In the manufacture of plates and brushes, however, flake graphite has been substituted to some extent by synthetic, amorphous, crystalline graphite, and acetylene black. Graphite electrodes serve to give conductivity to the mass of manganese dioxide used in dry batteries.

10.2.10 Silicon Carbide

10.2.10.1 Description and General Properties

Silicon carbide [409-21-2], chemical formula SiC and relative molar mass 40.097, is an important advanced ceramic with a high melting point (2830°C), a high thermal conductivity (135 $Wm^{-1}K^{-1}$), and extremely high Mohs hardness of 9. Silicon carbide is also has a wide band gap for a semiconductor (2.3 eV). The preparation of silicon carbide involves the reaction of silica sand (SiO_2) and carbon (C) at a high temperature (between 1600 and 2500°C).

$$SiO_2(s) + C(s) \longrightarrow SiC(s) + CO(g)$$

The first observation of silicon carbide was made in 1824 by Jöns Jacob Berzelius.[22] It was first prepared industrially in 1893 by the American chemist Edward Goodrich Acheson, who patented both the batch process and the electric furnace for making synthetic silicon-carbide powder.[23] In 1894 he established the Carborundum Company in Monongahela City, PA, to manufacture bulk synthetic silicon carbide commercialized under the trade name ***Carborundum***™. Silicon carbide was initially used to produce grinding wheels, whetstones, knife sharpeners, and powdered abrasives. Despite being extremely rare in nature, when it occurs as a mineral it is called ***moissanite*** after the French chemist Henri Moissan who discovered it in a meteorite[24] in 1905.

Polymorphism and polytypism. Silicon carbide has two polymorphs. At temperatures above 2000°C alpha silicon carbide (α-SiC), with a hexagonal crystal structure, is the more stable polymorph with iridescent and twinned crystals with a metallic luster. At temperatures lower than 2000°C, beta silicon carbide (β-SiC) exhibits a face-centered cubic (fcc) crystal structure.

Moreover, α-SiC exists as different hexagonal polytypes with a carbon atom situated above the center of a triangle of Si atoms and underneath a Si atom belonging to the next layer. The difference between polytypes is the stacking sequence between succeeding double layers of carbon and silicon atoms. If the first double layer is called the A position, the next layer that can be placed according to a close-packed structure will be placed on the B position or the C position. The different polytypes will be constructed by permutations of these three positions. For instance, the 2H-SiC polytype will have a stacking sequence ABAB… The number thus denotes the periodicity and the letter the resulting structure, which in this case is hexagonal. The 3C-SiC polytype is the only cubic polytype and it has a stacking sequence ABCABC… or ACBACB… The cell lattice parameter a, between neighboring silicon or carbon atoms, is ca. 308 pm for all polytypes. The carbon atom is positioned at the center of mass of the tetragonal structure outlined by the four neighboring Si atoms so that the distance between the C atom and each of the Si atoms is the same. Geometrical considerations require that the C-Si distance be exactly $a(3/8)^{1/2}$ (189 pm). The distance between two silicon planes is thus $a(2/3)^{1/2}$ (252 pm). The height of a unit cell, c, varies between the different polytypes. The ratio (c/a) thus differs from polytype to polytype but is always close to the ideal for a close-packed structure. The actual ratio for the 2H-, 4H- and 6H-SiC polytypes is closed to ideal ratios for these polytypes, that is, $(8/3)^{1/2}$, $2(8/3)^{1/2}$, and $3(8/3)^{1/2}$, respectively.

The different polytypes exhibit different electronic and optical properties. The bandgaps at 4.2 K of the different polytypes range between 2.39 eV for 3C-SiC and 3.33 eV for the 2H-SiC polytype. The important polytypes 6H-SiC and 4H-SiC have bandgaps of 3.02 eV and 3.27 eV, respectively. All polytypes are extremely hard, chemically inert, and have a high thermal conductivity. Properties such as the breakdown voltage, the saturated drift velocity, and the impurity ionization energies are all specific for the different polytypes.

Silicon carbide has long been recognized as an ideal ceramic material for applications where high hardness and stiffness, mechanical strength at elevated temperatures, high thermal conductivity, low coefficient of thermal expansion, and resistance to wear and abrasion are of primary importance. Moreover, because of its low density it offers greater advantages compared to other ceramics.

10.2.10.2 Industrial Preparation

The Acheson process. This process, invented by Edward Goodrich Acheson in 1893, was extensively used for making silicon carbide and was the only industrial process available for

[22] Berzelius, J.J. (1824) *Ann. Phys.*, Leipzig, **1**, 169.

[23] Acheson, E.G. (1893) Production of crystalline artificial carbonaceous materials. US Patent 492,767, February 28, 1893.

[24] Moissan, H. (1905) *C.R. Acad. Sci. Paris*, **140**, 405.

making bulk abrasive materials until the mid-1950s. The simplicity of the process makes it useful for production of huge quantities of silicon carbide suitable for grinding and cutting purposes. Some of the material produced by the Acheson process may, however, have adequate quality for electronic device production. A mixture of 50 wt.% silica, 40 wt. coke, 7 wt.% sawdust, and 3 wt.% rocksalt is heated in an electric resisting furnace. The heating is accomplished by a core made of graphite and coke called a resistor placed centrally in the furnace. The mixture of reactants is placed around this core. The mixture is then heated to reach a maximum temperature of ca. 2700°C, after which the temperature is gradually lowered. After the furnace has been fired, the outermost volume, which did not reach such high temperatures, consists of an unreacted mixture. Inside this is a volume where the temperature has not reached 1800°C. In this volume the mixture has reacted to form amorphous SiC. Close to the resistor, where the highest temperatures are obtained, SiC will be produced at first. As the temperature increases in the furnace, this will decompose again into graphite and silicon. The graphite will remain at the core; however, silicon reacts again with carbon to form SiC in colder parts of the furnace. The outer layer of graphite contains SiC in the form of threads of crystallites radiating from the core. The size of the crystallites decreases with increasing distance from the core. The purpose of the sawdust is to make the mixture porous in such a way that the huge amounts of carbon monoxide produced in the reaction may escape. High pressures of gas may locally be built up to form voids and channels to more porous parts of the mixture to eventually find its way out. The common salt serves as a purifier of the mixture. The chlorine reacts with metal impurities to form volatile metal chlorides (e.g., $FeCl_3$, $MgCl_2$), which escape. As a consequence of the furnace geometry, the material formed in the Acheson furnace varies in purity, according to its distance from the graphite resistor that is the heat source. The color changes to blue and black at a greater distance from the resistor, and these darker crystals are less pure and usually doped with aluminum, which increases electrical conductivity. A higher grade of silicon carbide for electronic application can be obtained from a more expensive process described below.

Lely process. A major improvement to the Acheson process is the process developed by J.A. Lely,[25] a scientist at Philips Research Laboratories in Eindhoven, in 1955. The process is similar to that observed in the voids and channels of the Acheson process. Lumps of SiC are packed between two concentric graphite tubes. The inner tube is thereafter withdrawn, leaving a cylinder of SiC lumps inside the outer graphite tube called the crucible. The crucible is closed with a graphite or SiC lid and placed inside a furnace. The crucible is heated to ca. 2500°C in an inert atmosphere of argon at atmospheric pressure. At this temperature SiC sublimes appreciably, leaving a graphite layer at the outermost part of the cylinder, and small platelets start to evolve from the innermost parts of the SiC cylinder. These platelets successively grow to larger sizes during a prolonged heating at this temperature. Each platelet is attached on one edge to an original lump of SiC. On the top and bottom of the cylinder a thick dense layer of SiC is formed. The quality of these crystals can be very high; however, the yield of the process is low, the sizes are irregular, the shape of the crystals is normally hexagonal, and there exists no polytype control. The purity of the crystals is largely governed by the starting material, which may be obtained in a high-purity form. The use of high-quality Lely grown material as substrate for a succeeding epitaxial growth is highly advantageous with regard to the high crystalline quality obtained from these substrates.

The modified Lely process. Despite the high crystalline quality that may be obtained with the Lely method, it has never been considered an important technique for future commercial exploitation on account of the low yield and irregular sizes. In the modified Lely process, which is a seeded sublimation growth process, these problems are overcome, though at the price of a considerably lower crystalline quality. In the modified Lely technique, SiC powder or lumps of SiC are placed inside a cylindrical graphite crucible. The crucible is closed with

[25] Lely, J.A. (1955) Berichte der Deutschen Keramischen Gesellschaft, **32**, 229.

a graphite lid onto which a seed crystal is attached. The crucible is heated to ca. 2200°C normally in an inert argon atmosphere at a reduced pressure. A temperature gradient is applied over the length of the crucible in such a way that the SiC powder at the bottom of the crucible is at a higher temperature than the seed crystal. The temperature gradient is typically kept in a range on the order of 20 to 40°C/cm. The SiC powder sublimes at the high temperature and the volume inside the crucible is filled with a vapor of progressive composition (e.g., Si_2C, SiC_2, Si_2, and Si). Since the temperature gradient is chosen such that the coldest part of the crucible is the position of the seed, the vapor will condense on this and the crystal will grow. The growth rate is largely governed by the temperature, the pressure, and the temperature gradient; however, experiments have shown that also the source-to-seed distance may have some influence. It has also been experimentally confirmed that different growth temperatures and the orientation of the seed crystal give rise to different polytypes.

10.2.10.3 Grades of Silicon Carbide

Several commercial grades of SiC are available on the market:

(i) ***Electrically conductive sintered alpha silicon carbide.*** This is a dense type of SiC and has superior resistance to oxidation, corrosion, wear, and chemical attacks. The single-phase SiC also has high strength and good thermal conductivity.

(ii) ***Black silicon carbide*** (98.5 wt.% SiC) is composed of premium-grade, medium-high-density, high-intensity magnetically treated SiC in which most impurities have been removed from the carbide.

(iii) ***CVD silicon carbide*** (99.9995 wt.% SiC) is a unique type of silicon carbide due to its purity, homogeneity, and chemical and oxidation resistance. It is thermally stable, is very cleanable and polishable, and is dimensionally stable.

(iv) ***Green silicon carbide*** (99.5 wt.% SiC) is an extremely hard synthetic material that possesses very high thermal conductivity. It is also able to maintain its strength at elevated temperatures. General applications of green SiC are in aerospace, blasting, coatings, composites, refractories, compounds, and kiln furniture, and it is used as an abrasive as honing stones, lapping, polishing, sawing silicon and quartz, and in grinding wheels.

Prices (2006). Silicon carbide is priced from 1150 to 1700 US$/tonne.

10.2.11 Properties of Raw Materials Used in Ceramics, Refractories, and Glasses

Table 10.11. Selected properties and prices of raw materials used in ceramics and refractories

Raw material	Apparent density ($kg.m^{-3}$)	Bulk density ($kg.m^{-3}$)	Bond's work index[26] ($kWh/tonne^{-1}$)	Abrasion index[27]	Average price (2006) (US$/tonne)
Alumina (fused)	3480	961	58.18	0.6447	1250–1700
Bauxite (chunk)	2380	1200–1360	9.45	0.1200	125–200
Chrome ore	4060		9.60	0.1200	150–250

[26] The Bond's index is the energy per unit mass of material required to grind it from until 80 wt.% pass 325 mesh, here it is expressed in KWh per short ton (2000 lb.).

[27] The abrasion index is defined as the mass fraction lost by a steel padle beating during 1 hour a charge of 1.6 kg of the material having pellets dimension 3/4 in x 1/2 in with 80 wt.% of the final final product passing 13.25 mm.

Table 10.11. *(continued)*

Raw material	Apparent density ($kg.m^{-3}$)	Bulk density ($kg.m^{-3}$)	Bond's work index ($kWh.tonne^{-1}$)	Abrasion index	Average price (2006) (US$/tonne)
Coke	1510	400–720	20.70	0.3095	
Dolomite (lump)	2820	1440–1600	11.31	0.016	
Feldspar (ground)	2590	1050–1121	11.67	n.a.	60–100
Graphite	1750	450–640	45.03		420–1000
Hematite	5260	3600	12.68		30–50
Ilmenite	4270	2240	13.11		80–100
Kaolin	2600	2600	7.10		
Lime	3340	960–1080			
Limestone	2690	1340–1440	11.61	0.0256	30–40
Magnesite	2980		16.80	0.075	130–180
Silicon carbide	2730		26.17		1200–1700
Quartzite (chunk)	2650		12.77	0.6905	n.a.
Zircon (flour)	4600				700–800

10.3 Traditional Ceramics

Traditional ceramics are those obtained only from the firing of clay-based materials. The common initial composition before firing consists usually of a ***clay mineral*** (i.e., phyllosilicate minerals such as ***kaolinite***, ***montmorillonite***, or ***illite***), ***fluxing agents*** or ***fluxes*** [e.g., feldspars: K-feldspars (orthoclases) and Ca-Na-feldspars (plagioclases)], and ***filler materials*** (e.g., silica, alumina, magnesia). The traditional ceramics can be prepared using two main groups of clays: kaolin or china clays made from the phyllosilicate kaolinite and, to a lesser extent, micas, but free of quartz; and ball clays containing a mixture of kaolinite, montmorillonite, illite, and micas.

Table 10.12. Examples of traditional ceramics

Type	Properties	Applications
Fired bricks	Porosity: 15–30% Firing temperature: 950–1050°C Enameled or not	Bricks, pipes, ducts, walls, ground floors
China	Porosity: 10–15% Firing temperature: 950–1200°C Enamel, opacity	Sanitation, tile
Stoneware	Porosity: 0.5–3% Firing temperature: 1100–1300°C Glassy surface	Crucible, labware, pipe
Porcelain	Porosity: 0–2% Firing temperature: 1100–1400°C Glassy, translucent	Insulators, labware, cookware

The classical procedure for preparing traditional ceramics consists of the following operation sequence: raw material selection and preparation (i.e., grinding, mixing), forming (e.g., molding, extrusion, slip casting, and die pressing), drying, prefiring operations (i.e., glazing), firing, and postfiring operation (e.g., enameling, cleaning, and machining). The common classes of traditional ceramics are ***whitewares*** (e.g., stoneware, china, and porcelain), ***glazes***, ***porcelain enamels***, high-temperature refractories, mortars, cements, and concretes (see Chapter 15).

10.4 Refractories

Refractories perform four basic functions:

(i) they act as a thermal barrier between a hot medium (e.g., flue gases, liquid metal, molten slags, and molten salts) and the wall of the containing vessel;
(ii) they insure a strong physical protection, preventing the erosion of walls by the circulating hot medium;
(iii) they represent a chemical protective barrier against corrosion;
(iv) they act as thermal insulation, insuring heat retention.

As a rule of thumb, an insulating material is considered a refractory material if its melting or solidus temperature is well above the melting point of pure iron (1539°C), i.e., if it exhibits a ***Seger's pyrometric cone*** equivalent of No. 26 or more (Table 10.19). Moreover, the maximum operating temperature of a refractory material is usually 150°C lower than its pyrometric cone equivalent.

10.4.1 Classification of Refractories

The ***classification of refractories*** can be approached in a number of different ways: chemical composition, type of applications, or operating temperature range.

Table 10.13. Classification of refractory by end user

Rank	Refractory industry users	End user
1	Cement and lime production	Building industry
2	Iron and steelmaking	
3	Glass industry	Automotive industry
4	Nonferrous metals production	
5	Oil and gas industries	
6	Waste incineration	Other
7	Basic industries	

Table 10.14. Classification of primary refractories by chemistry

Category (definition)	**Description**
Basic refractories (i.e., essentially made of calcined magnesite or magnesia, MgO)	Dolomite Dead burned magnesia (min. 95 wt.% MgO) Dead burned magnesia with chromite Fused magnesia Magnesia-carbon bricks
High alumina (i.e., with an alumina content greater than 47.5 wt.% Al_2O_3)	50%, 60%, 70%, 80% Al_2O_3 (±2.5), 85%, 90% Al_2O_3 (±2.0), 99% Al_2O_3 (>97%), Mullite ($3Al_2O_3.2SiO_2$) Chemically bonded bricks (75–85 wt.% Al_2O_3) Alumina-chrome bricks Alumina-carbon bricks
Fireclay (i.e., made of fired aluminum phyllosilicates or clays)	Super-duty (40–44 wt.% Al_2O_3) High-duty Medium-duty Low-duty Semisilica (18–25 wt.% Al_2O_3, 72–80 wt.% SiO_2)
Silica	Silica bricks
Advanced	Graphite and carbon ceramics Silicon carbide Zircon ($ZrSiO_4$) and fused zirconia (ZrO_2) Fused silica Fused alumina (brown and white) Fused and cast refractories

10.4.2 Properties of Refractories

Table 10.15. Selected physical properties of refractories

Refractory materials	Density (ρ/kg.m^{-3})	Melting point (°C)	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})
Alumina brick (64–65 wt.% Al_2O_3)	1842	1650–2030	4.67	
Brick, fireclay	2000		1.0042	753
Brick, hard-fired silica (94–95 wt.% silica)	1800		1.6736	753.10
Brick, high alumina (53 wt.% alumina) (20% porosity)	2330		1.3807	753
Brick, high alumina (83 wt.% alumina) (28% porosity)	2570		1.5062	753
Brick, high alumina (87 wt.% alumina) (22% porosity)	2850		2.9288	753
Brick, kaolin insulating (heavy)	430		0.2510	774
Brick, kaolin insulating (light)	300		0.0837	774
Brick, magnesite (86 wt.% MgO) (17.8% porosity)	2920		3.6819	837
Brick, magnesite (87 wt.% MgO)	2530		3.8493	837

Cardarelli, F. (2008) Materials Handbook. A Concise Desktop Reference, 2nd Edition. Springer London.

Table 10.15. *(continued)*

Refractory materials	Density (ρ/kg.m^{-3})	Melting point (°C)	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})
Brick, magnesite (89 wt.% MgO)	2670		3.4727	837
Brick, magnesite (90 wt.% MgO) (14.5% porosity)	3080		4.9371	837
Brick, magnesite (93 wt.% MgO) (22.6% porosity)	2760		4.8116	837
Brick, normal fireclay (22% porosity)	1980		1.2970	732
Brick, siliceous (25% porosity)	1930		0.9372	753
Brick, siliceous fireclay (23% porosity)	2000		1.0878	753
Brick, sillimanite (22% porosity)	2310		1.4644	711
Brick, stabilized dolomite (22% porosity)	2700		1.6736	837
Brick, vermiculite	485		0.1674	837
Calcium oxide (pressed)	3030		13.8070	753
Calcium oxide(packed powder)	1700		0.3180	753
Carbon brick (99 wt.% graphite)	1682	3500	3.6	
Carbon brick (fired)	1470		3.5982	707
Chrome brick (100 wt.% Cr_2O_3)	2900–3100	1900	2.3	
Chrome brick (32 wt.% Cr_2O_3)	3200		1.1715	627.60
Chrome-magnesite brick	3000		2.0920	753.10
Chrome-magnesite brick (52 wt.% MgO, 23 wt.% Cr_2O_3)	3100	3045	3.5	
Diabasic glass (artificial)	2400		1.1715	753
Diatomaceous earth brick	440		0.0877	795.00
Diatomaceous earth brick (850°C)	440		0.0921	795.00
Diatomaceous earth brick (fused at 1100°C)	600		0.2218	795.00
Diatomaceous earth brick (high burn)	590		0.2259	795.00
Diatomaceous earth brick (molded)	610		0.2427	795.00
Dolomite (fired) (55 wt.% CaO, 37 wt.% MgO)	2700	2000		
Dolomite brick, stabilized (22 wt.% silica)	2700		1.6736	837
Egyptian fire (64–71 wt.% silica)	950		0.3138	732.20
Egyptian firebrick (64–71 wt.% silica)	950		0.3138	732
Fireclay brick (54 wt.% SiO_2, 40 wt.% Al_2O_3)	2146–2243	1740	0.3–1.6	
Fireclay brick, Missouri	2645		1.0042	960
Fireclay brick, normal (22 wt.% water)	1980		1.2970	732
Fireclay brick, siliceous (23 wt.% water)	2000		1.0878	753
Forsterite brick (58 wt.%MgO, 38 wt.%SiO_2) (20% porosity)	2760		1.0042	795.00
Fused-alumina brick (96 wt.% alumina) (22% porosity)	2900		3.0962	753.10
Fused-alumina brick (96 wt.% alumina) (22% porosity)	2900		3.0962	753.10
High-alumina brick (90–99 wt.% Al_2O_3)	2810–2970	1760–2030	3.12	
Kaolin brick, insulating (dense)	430		0.2511	774

Table 10.15. *(continued)*

Refractory materials	Density (ρ/kg.m^{-3})	Melting point (°C)	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})
Kaolin brick, insulating (light)	300		0.0837	774
Magnesite brick (95.5 wt.% MgO)	2531–2900	2150	3.7–4.4	
Mullite brick (71 wt.% Al_2O_3)	2450	1810	7.1	
Silica brick (95–99 wt.% SiO_2)	1842	1765	1.5	
Silicon carbide brick (80–90 wt.% SiC)	,595	2305	20.5	
Vermiculite brick	485		0.1674	837
Vermiculite insulating powder	270		0.1213	837
Vermiculite, expanded (heavy)	300		0.0690	753
Vermiculite, expanded (light)	220		0.0711	753
Zircon brick (99 wt.% $ZrSiO_4$)	3204	1700	2.6	
Zirconia (stabilized) brick	3925	2650	2.0	

Silica brick. The earliest silica bricks were composed of crushed minerals of 90 wt.% silica, with as much as 3.5 wt.% flux materials (i.e., usually CaO), and fired at about 1010°C. These bricks found use primarily in steel mills and coke-byproduct operations, from the second quarter of this century in chemical service, primarily in strong phosphoric acid exposures where shale and fireclay brick do not long survive. They can serve in higher-temperature service to about 1093°C and are more resistant to thermal shock due to their greater porosity, as high as 16%. When used in chemical service, those of the highest silica content (not below 98 wt.% SiO_2) should be used. The purity of the silica and its percentage of alkali, along with the manufacturing techniques, determine the uniformity or the wideness of ranges of the physical properties. Ranges of chemical composition of silica brick are 98.6 to 99.6 wt.% SiO_2, 0.2 to 0.5 wt.% Al_2O_3, 0.02 to 0.3 wt.% Fe_2O_3, 0.02 to 0.1 wt.% MgO, 0.02 to 0.03 wt.%CaO, and 0.01 to 0.2 wt.% (Na_2O, K_2O, Li_2O). Silica brick serves well and for long periods in acid service, except for hydrofluoric, without noticeable damage, showing greater resistance, especially to strong hot mineral acids, and particularly phosphoric rather than acid brick, and in halogen exposures, except fluorine, solvents, and organic chemical exposures. Silica bricks are not recommended for service in strong alkali environments. They also exhibit better shock resistance than shale or fireclay acid brick, but they have lower strength and abrasion resistance.

Porcelain brick. Porcelain bricks are made from high-fired clays, the temperature of firing depending on the amount of alumina in the clay, 15% to 38% usually at ca. 1200 to 1300°C, 85% at 1500 to 1550°C, and 95 to 98% at 1600 to 1700°C. The bodies of these bricks are extremely dense and nonporous, with zero absorption, and a Mohs hardness ranging from 6 to 9 for 99 wt.% alumina. As alumina content increases, Mohs hardness, the maximum service temperature, and chemical resistance increase. Major uses of porcelain include: the lining of ball mills, where they will outlast almost all other abrasion-resistant linings, and employment (glazed) as pole line hardware for the power industry where, exposed to abrasion, weathering, and cycling temperature changes, they outlast all other materials in similar service. All chemists and laboratory personnel are familiar with glass and porcelain equipment, and so are aware of the fact that they give excellent service in hot chemicals except

hydrofluoric acid and acid fluorides and strong sodium or potassium hydroxides, especially in the molten state. Due to the high cost of porcelain brick, they are used sparingly in the process industries, chiefly in dye manufacture, due to their density for the prevention of interbatch contamination and ease of cleaning. The use of porcelain brick is primarily limited by its cost.

10.4.3 Major Refractory Manufacturers

Table 10.16. Major manufacturers of refractories worldwide

Company (Brands)	Location and Address	Refractory applications
Minerals Technologies (MinteQ)	Chrysler Building, 405 Lexington Ave., New York, NY 10174-1901, USA Telephone: +1 (732) 257-1227 E-mail: Minteq.ProductInfo@minteq.com URL: http://www.minteq.com/	Monolithic refractories and castables
Resco Products (Resco and National)	2 Penn Center, West Suite 430, Pittsburgh, PA 15276, USA Telephone: (412) 494-4491 Fax: (412) 494-4571 URL: http://www.rescoproducts.com/	Iron- and steelmaking Nonferrous smelting (Cu, Al) Fireclays and bricks Glassmaking processes Waste incinerators Hydrocarbon processing Power generation
RHI AG (Didier, Radex, and Veitscher)	Wienerbergstrasse 11 A-1100 Vienna, Austria Telephone: +43 (0) 50 213-0 Fax: +43 (0) 50 213-6213 E-mail: rhi@rhi-ag.com URL: http://www.rhi.at/	Iron- and steelmaking Cement and lime kilns Glassmaking processes Nonferrous smelting (Cu, Al, Ni, Sn, Zn) Petrochemical and hydrocarbon processes Oil refineries
SANAC Spa	Viale Certosa, 249, I-20151 Milano, Italy Telephone: (+39) 02307 00335 Fax: (+39) 02380 11158 URL: http://www.sanac.com/	Iron and steelmaking Glassmaking processes Castables Resin-bonded alumina
Shinagawa Refractories	1-7,Kudan-kita 4-chome,Chiyodaku, Tokyo 102-0073 Japan Telephone: +81 3-5215-9700 Fax: +81 3-5215-9720 URL: http://www.shinagawa.co.jp/	Iron- and steelmaking Nonferrous metals (Cu, Zn, Pb,and Al) Cement and lime kilns Refractories for gas, petroleum, and chemical plants Refractories for cement and lime kilns Glassmaking processes and ceramic firing kilns Petrochemical and hydrocarbon processes Oil refineries Waste incinerators
Vesuvius USA Corp.	P.O. Box 4014, Newton Drive 1404 Champaign, IL 61822 USA Telephone: +1 (217) 351-5000 Fax: +1 (217) 351-5031 URL: http://www.vesuvius.com/	Iron and steelmaking Foundry Aluminum smelters Glassmaking processes

10.5 Advanced Ceramics

Advanced ceramics or ***engineered ceramics***, also formerly called ***industrial ceramics***, are various inorganic chemical compounds, not necessarily oxides and silicates, that exhibit improved physical and chemical properties and can be grouped according to their field of application: electrical (e.g., semiconductors, insulators, dielectrics, piezo- and pyroelectrics, and superconductors), optical (e.g., phosphors, lasing crystals, mirrors, and reflectors), magnetics (e.g., permanent magnets), and structural ceramics. The properties of these ceramic materials are extensively described in the section in the book relative to their properties (e.g., insulators in dielectrics materials and superconducting ceramics in the superconductor section). Hereafter, dedicated sections on selected advanced ceramic materials are presented, providing a brief description, the general physical and chemical properties, along with method of preparation, industrial applications, and major producers.

10.5.1 Silicon Nitride

10.5.1.1 Description and General Properties

Silicon nitride [12033-89-5], chemical formula Si_3N_4 and relative molecular mass of 140.284, is a medium-density ceramic material (3290 $kg.m^{-3}$). The high flexural strength (830 MPa), high fracture toughness (6.1 $MPa.m^{-1/2}$), and creep resistance, even at elevated temperatures, ensure a high temperature strength to silicon nitride. Moreover, its low thermal expansion coefficient (3.3 μm/m.K), combined with a Young's modulus of 310 GPa, confers upon silicon nitride a superior thermal shock resistance compared with most ceramic materials. This set of extreme properties, together with a good oxidation resistance, were the major reasons of its first development in the late 1960s for replacing superalloys in advanced turbine and reciprocating engines to give higher operating temperatures and efficiencies. Although the ultimate goal of ceramic engines has never been achieved, silicon nitride has been used extensively in a number of other industrial applications, such as engine components, bearings, and cutting tools. In general, silicon nitride exhibits higher temperature capabilities than most metals, combining high mechanical strength and creep resistance with oxidation resistance. From a chemical point of view, silicon nitride exhibits an excellent corrosion resistance to numerous molten nonferrous metals such as Al, Pb, Zn, Cd, Bi, Rb, and Sn and molten salts like NaCl-KCl, NaF, and silicate glasses. However, it is corroded by molten Mg, Ti, V, Cr, Fe, and Co, and salts like cryolite, KOH, and Na_2O.

10.5.1.2 Industrial Preparation and Grades

Pure silicon nitride is difficult to produce as a fully dense material because it does not readily sinter and cannot be heated above 1850°C because it decomposes into silicon and nitrogen. Dense silicon nitride can only be made using sintering aids or by the direct nitriding of silicon. Therefore, the final material properties strongly depend on the fabrication method, and hence commercial silicon nitride cannot be considered a single material. Three grades of silicon nitride are available commercially:

(i) ***Reaction bonded silicon nitride*** (RBSN) is a high-purity grade of silicon nitride prepared by direct nitriding of compacted silicon powder. The incomplete nitriding reaction leads to densities of only 70 to 80% of the theoretical density and usually ranges from 2300 to 2700 $kg.m^{-3}$. It exhibits excellent thermal shock resistance and an outstanding corrosion resistance to molten nonferrous metals, especially aluminum metal. Reaction-bonded silicon nitride represents a cheaper alternative to the fully dense silicon nitride and can be machined to close tolerance (near-net shape) without the need for expensive diamond grinding.

(ii) ***Hot-pressed silicon nitride*** (HPSN) is obtained by applying both heat and pressure through a graphite die using sintering aids. However, most hot-pressed silicon nitride grades can be formulated with a minimum amount of densification aids. These compositions offer the highest mechanical strength of other silicon nitride grades. The major drawbacks are that only simple shaped billets can be produced by this process and the preparation of finished components requires expensive machining by utilizing diamond grinding.

(iii) ***Sintered silicon nitride*** (SSN) consists of a family of fully dense materials having a range of compositions that can be produced in cost-effective, complex net shape. The green compacts, made of powders with a high surface area, are fired under a nitrogen atmosphere, without applying pressure. This grade of silicon nitride has the best combination of properties, making it the leading technical ceramic for a number of structural applications including automotive engine parts, bearings, and ceramic armor.

(iv) ***Hot isostatically pressed silicon nitride*** (HIPSN) is obtained by glass-encapsulated parts that are placed in a high-pressure vessel or autoclave, with heat and pressure applied. The result is a slight decrease in strength but a substantial improvement in reliability. The material is used currently in niche market applications, for example, in reciprocating engine components and turbochargers, bearings, metal cutting and shaping tools, and hot metal handling.

10.5.2 Silicon Aluminum Oxynitride (SiAlON)

Description and general properties. ***Sialon*** is the commercial acronym for ***silicon aluminum oxynitride*** (SiAlON), that is, an alloy of silicon nitride (Si_3N_4) and aluminum oxide (Al_2O_3). Sialon is in fact a fine-grained nonporous advanced ceramic material with less than 1 vol.% open porosities. Sialon is made of a silicon nitride ceramic with a small percentage of aluminum oxide. Its generally adopted chemical formula is $Si_{6-x}Al_xO_xN_{8-x}$. This superior refractory material has the combined properties of silicon nitride, i.e., high-temperature strength, hardness, fracture toughness, and low thermal expansion, and that of aluminum oxide, i.e., corrosion resistance, chemical inertness, high temperature capabilities, and oxidation resistance. Sialon exhibits a medium density of 3400 $kg.m^{-3}$, a low Young's modulus of 288 MPa, a bulk modulus of 220 GPa, and a shear modulus of 120 GPa with a Poisson ratio of 0.25. Moreover, it has a flexural strength of 760 MPa, an elevated Vickers hardness (1430 to 1850 HV), and a good fracture toughness (6.0 to 7.5 $MPa.m^{-1/2}$). In addition, like pure silicon nitride, the combination of a low Young's modulus of 288 GPa with a low coefficient of linear thermal expansion (3 μm/m.K) ensures an excellent thermal shock resistance together with a low thermal conductivity of 15 to 20 $W.m^{-1}K^{-1}$. Most refractory products are capable of surviving one or two specific environments that typically involve high temperature, mechanical abuse, corrosion, wear, or electrical resistance. Sialon is perfect for molten-metal applications and high wear or high impact environments up to 1250°C. Moreover, sialon exhibits a good oxidation resistance in air up to 1500°C imparted by its alumina content, and it has an outstanding corrosion resistance to molten nonferrous metals. Moreover, it is neither wetted nor corroded by molten aluminum, brass, bronze, and other common industrial metals.

Industrial applications. Typical uses are as protection sheath for immersion thermocouples used in nonferrous metal melting, immersion heater and burner tubes, degassing and injector tubes in nonferrous metallurgy, metal feed tubes in aluminum die casting, welding, and brazing fixtures and pins.

10.5.3 Boron Carbide

10.5.3.1 Description and General Properties

Boron carbide [12069-32-8], with its chemical formula B_4C and its rhombohedral crystal lattice, is a low-density black solid (2512 $kg.m^{-3}$) with a metallic luster. Its high refractoriness due to its high melting point (2450°C) allows it to be used for high-temperature applications. On the other hand, it is the hardest manmade solid (HK 3200) after synthetic diamond. Actually under high temperatures above 1300°C, its hardness exceeds that of diamond and cubic boron nitride. A Poisson ratio of 0.21 indicates its high anisotropy. It has a high compressive strength that may vary according to its density and percentage purity. It has a very low thermal conductivity (27 W/m.K). With such a strength-to-density ratio and low thermal conductivity, boron carbide looks promising and ideal for a wide variety of applications. Because of its high hardness, boron carbide succeeded in replacing diamond as a lapping material. Boron carbide is a material with excellent properties. It has a list of important properties such as ultimate strength-to-weight (density) ratio, exceptionally high hardness, and high melting and oxidation temperatures (500°C). In addition, it has a very low thermal expansion coefficient (5.73 μm/mK). However, owing to its high Young's modulus, it possesses less thermal shock resistance. Boron carbide is stable toward dilute and concentrated acids and alkalis and inert to most organic compounds. It is slowly attacked by mixtures of hydrofluoric-sulfuric acids or hydrofluoric-nitric acids. It resists attack by water vapor at 200 to 300°C. However, it is attacked rapidly when put in contact with molten alkali and acidic salts to form borates. In addition, B_4C is characterized by a very high oxidation temperature.

10.5.3.2 Industrial Preparation

Boron carbide is either prepared from boron ores or from pure boron. The process involves the reduction of a boron compound. Usually, boron carbide is obtained by reacting boric acid or boron oxide and carbon at ca. 2500°C in an electric-arc furnace.

$$2B_2O_3(s) + 7C(s) \longrightarrow B_4C(s) + 6CO(g)$$

Its composition is variable over a relatively wide range. The boron/carbon ratio ranges from 3.8 to 10.4. Technical-grade boron carbide values are typically between 3.9 and 4.3. Later, the powder obtained is transformed into dense parts by hot pressing or cold forming and sintering. The cold formed and sintered material is less expensive, but sintering aids or other added bonding agents seriously degrade the material properties.

10.5.3.3 Industrial Applications and Uses

The applications of boron carbide are as wear-resistant components. Armor tiles in military applications such as in light hard bulletproof armor for helicopters and tanks or as thermal shield for the space shuttles. It is used in abrasives as lapping and polishing powders and in raw materials in preparing other boron compounds, notably titanium diboride. It is also us as an insert for spray nozzles and bearing liners and wire drawing guides. Finally, because of its boron content and elevated resistance to high temperatures, boron carbide is used as a shield for neutrons in nuclear reactors.

10.5.4 Boron Nitride

10.5.4.1 Description and General Properties

Boron nitride [10043-11-5], chemical formula BN, exists as three different poly-morphs: ***alpha-boron nitride*** (α-BN), a soft and ductile polymorph ($\rho = 2280$ $kg.m^{-3}$ and *m.p.* = 2700°C)

with a hexagonal crystal lattice similar to that of graphite, also called ***hexagonal boron nitride*** (HBN) or ***white graphite***; ***beta-boron nitride*** (β-BN), the hardest manmade material and densest polymorph (ρ = 3480 kg.m^{-3}, *m.p.* = 3027°C), with a cubic crystal lattice similar to that of diamond, also called cubic boron nitride (CBN) or ***borazon***; and (iii) ***pyrolitic boron nitride*** (PBN). From a chemical point of view, boron nitride oxidizes readily in air at temperatures above 1100°C, forming a thing protective layer of boric acid (H_3BO_3) on its surface that prevents further oxidation as long as it coats the material. Boron nitride is stable in reducing atmospheres up to 1500°C.

10.5.4.2 Industrial Preparation

Cubic BN, or borazon, is produced by subjecting hexagonal BN to extreme pressure and heat in a process similar to that used to produce synthetic diamonds. Melting of either phase is possible only with a high nitrogen overpressure. The alpha-phase decomposes above 2700°C at atmospheric pressure and at ca. 1980°C in a vacuum.

Hexagonal BN is manufactured using hot pressing or pyrolytic deposition techniques. These processes cause orientation of the hexagonal crystals, resulting in varying degrees of anisotropy. There is one pyrolytic technique that forms a random crystal orientation and an isotropic body; however, the density reaches only 50 to 60% of the theoretical density. Both manufacturing processes yield high purity, usually greater than 99 wt.% BN. The major impurity in the hot-pressed materials is boric oxide, which tends to hydrolyze in the presence of water, degrading the dielectric and thermal-shock properties of the material. The addition of calcia reduces the water absorption. Hexagonal hot-pressed BN is available in a variety of sizes and shapes, while the pyrolytic hexagonal material is currently available in thin layers only.

10.5.4.3 Industrial Applications and Uses

The major industrial applications of hexagonal boron nitride rely on its high thermal conductivity, excellent dielectric properties, self-lubrication, chemical inertness, nontoxicity, and ease of machining. These are, for instance, mold wash for releasing molds, high-temperature lubricants, insulating filler material in composite materials, as an additive in silicone oils and synthetic resins, as filler for tubular heaters, and in neutron absorbers. On the other hand, the industrial applications of cubic boron nitride rely on its high hardness and are mainly as abrasives.

10.5.5 Titanium Diboride

10.5.5.1 Description and General Properties

Titanium diboride [12045-63-5], chemical formula TiB_2, is a dense (4520 kg.m^{-3}) and high-melting-point (2980°C) advanced ceramic material. Due to its high elastic modulus of 510 to 575 GPa, titanium diboride exhibits an excellent stiffness-to-density ratio. It is also a hard material with a Vickers hardness (3370) superior to that of tungsten carbide, and its fracture toughness (5 to 7 MPa.m$^{1/2}$) is even greater than that of silicon nitride. The high flexural strength (350 to 575 MPa), combined with a high compressive strength (670 MPa), allows it to be used in military and ballistic applications. As expected from its hexagonal crystal lattice, it is highly anisotropic with a Poisson ratio of 0.18 to 0.20. It retains its mechanical strength up to very high temperatures. By contrast with most ceramics, it is a good electrical conductor, with an electrical resistivity of only 15 μΩ.cm, and has a good thermal conductivity (65 W m^{-1}K^{-1}); its linear coefficient of thermal expansion is 6.4 μm/m K. From a chemical point of view, TiB_2 is not attacked either by concentrated strong mineral acids such as hydrochloric acid or hydroflouric acids. Titanium diboride also has a very good oxidation

resistance up to 1400°C. TiB_2 has excellent wettability and stability in liquid metals such as aluminum and zinc and has many applications as a corrosion-resistant material such as crucibles and cutting tools in addition to some military applications.

10.5.5.2 Industrial Preparation and Processing

The most common process for producing large quantities of titanium diboride is by reacting titania (TiO_2) with carbon and boron carbide (B_4C) or boron sesquioxide (B_2O_3) as follows:

$$2TiO_2(s) + C(s) + B_4C(s) \longrightarrow 2TiB_2(s) + 2CO_2(g),$$

$$2TiO_2(s) + 5C(s) + 5B_2O_3(s) \longrightarrow 2TiB_2(s) + 5CO_2(g).$$

The final purity of the powder depends on the purity of the raw materials. Generally, several different grades of TiO_2, carbon, B_4C, and B_2O_3 can be used for the production of a wide panel of TiB_2 products, depending on the required grain size, purity, and price. Vacuum-arc melting is used to produce a fully dense, single-phase titanium diboride. Graphite hearths are commonly used; the molten titanium diboride wets the graphite and exhibits excellent fluidity, and shapes are produced both by gravity and tilt-pour-casting methods. Sintered parts of titanium diboride are usually produced by either hot pressing or pressureless sintering, although hot isostatic pressing HIP has also been used. Quite a number of different sintering methods and sintering aids are used to produce fully dense parts of titanium diboride. Hot pressing of titanium diboride is performed at temperatures above 1800°C in a vacuum or 1900°C in an inert argon atmosphere. However, hot pressing is expensive and the net-shape fabrication is not possible, hence the required shape must still be machined from the hot-pressed billet. Some usual sintering aids used for hot-pressed parts include iron, nickel, cobalt, carbon, tungsten, and tungsten carbide. Pressureless sintering of titanium diboride is a cheaper method for the production of net-shaped parts. Due to the high melting point of titanium diboride, sintering temperatures in excess of 2000°C are often required to promote sintering. Another method, called high-temperature synthesis (HTS), uses a powdered reducing metal such as magnesium or aluminum, and powders of titanium oxide and boron oxide. The materials are mixed and placed in a high-temperature crucible. This mixture is then ignited, and the self-sustaining reaction produces titanium diboride particles dispersed within a matrix of alumina or magnesia. After leaching the reaction mass, it remains as micrometric titanium diboride particles.

The major producers of titanium diboride are Advanced Refractory Technologies, Advanced Ceramics Corp., and Cerac in the United States, H.C. Starck and Electroschmeltzwerk Kempten in Germany, Denka in Japan, and Borides Ceramics and Composites in the UK.

10.5.5.3 Industrial Applications and Uses

Titanium diboride was originally developed to make lightweight armor for US and Soviet army tanks. It also has many commercial applications such as nozzles, seals, cutting tools, dies, wear parts due to its corrosion resistance, and also molten-metal crucibles and electrodes. It is used in crucibles due to its high melting point and chemical inertness.

10.5.6 Tungsten Carbides and Hardmetal

10.5.6.1 Description and General Properties

Tungsten carbide, or ***hardmetal***, was developed in the 1920s for wear-resistant dies to draw incandescent-lamp filament wire. Earlier efforts to manufacture the WC-W_2C eutectic alloy was unsuccessful because of its inherent brittleness; therefore researchers diverted their attention to powder metallurgy techniques. At present, these powder metallurgy techniques are

Table 10.17. Properties of selected hardmetals

Hardmetal (wt.%)	Density (ρ/kg.m^{-3})	Young's modulus (E/GPa)	Transverse rupture strength (MPa)	Compressive strength (MPa)	Vickers hardness (HV/kgf.mm^{-2})	Thermal conductivity (k/Wm^{-1}K^{-1})	Coefficient of linear thermal expansion (10^{-6} K^{-1})	Electrical resistivity ($\mu\Omega$.cm)
100WC	15,700	707	296–490	2937	1800–2000		5.7–7.2	53
97WC–3Co	15,150	655	979–1175	5778	1600–1700	87.9		
95.5WC–4.5Co	15,050	627	1172–1372	5681	1550–1650	83.7	3.4	
94.5WC–5.5Co	14,800	607	1565–1765	4895	1500–1600	79.5	3.6	20
91WC–9Co	14,600	579	1469–1862	4702	1400–1500	75.3		
89WC–11Co	14,150	565	1565–1958	4502	1300–1400	66.9	3.8	18
87WC–13Co	14,080	545	1662–2,55	4406	1250–1350	58.6		
85WC–15Co	13,800	538	1765–2151	3820	1150–1250		6.0	
80WC–20Co	13,300	490	1958–2544	3330	1050–1150		4.7	
75WC–25Co	13,000	459	1765–2648	3130	900–1000		5.0	
70WC–30Co	12,500				850–950			

being further developed and refined to reduce manufacturing costs and improve performance. Tungsten carbide is in fact a composite material called ***cermet*** or hardmetal made of tungsten carbides in a metal matrix of cobalt. Tungsten carbide is harder than most steels, has greater mechanical strength, transfers heat quickly, and resists wear and abrasion better than other metals. Among the materials that resist severe wear, corrosion, impact, and abrasion, tungsten carbide is superior. Tungsten carbide is a dense (15,630 kg.m^{-3}) and very hard ceramic material (1700–2400 HK). It exhibits outstanding mechanical properties with a Young's modulus of 668 GPa, a tensile strength of 344 MPa, and a compressive strength of 2683–2958 MPa. It has a high melting point of 2777°C and a thermal conductivity at 100°C of 86 W/mK.

10.5.6.2 Industrial Preparation

Most cemented carbides are manufactured by powder metallurgy, which consists in the preparation of the tungsten-carbide powder, powder consolidation, sintering, and postsintering forming. Tungsten-carbide powder is usually obtained by a carburization process and mixed with a relatively ductile matrix material such as cobalt, nickel, or iron and paraffin wax in either an attrition or ball mill to produce a composite powder. Spray drying yields uniform, spheroidized particles that are 100 to 200 mm in diameter. The powder is then consolidated into net and near-net-shape green compacts and billets by pressing and extrusion. Pressed billets can also be machined to shape before sintering. The density of the green compacts is around 45 to 65% of the theoretical. The green parts are then dewaxed at a temperature between 200 and 400°C and are then presintered between 600 and 900°C to impart adequate strength for handling. An alternative technology is a combination sinter-HIP process that combines dewaxing, presintering, vacuum sintering, and low-pressure HIP to speed up the overall cycle time.

10.5.6.3 Industrial Applications and Uses

Tungsten carbide can be used for a wide variety of applications. It has many applications that utilize its corrosion-resistant property such as wear plates, drawing dies, and wear parts for wire wearing machines. There are other applications that make use of its high hardness

such as punches, bushings, dies, cylinders, discs, rings, and intricate shapes as well as performs and blanks. There are other minor applications such as in rusticator blades, sander nozzles, air jets, and sander guns. Tungsten carbide is also used primarily and extensively for making drill-tip tunneling, rock crushing, mining, and quarrying purposes, i.e., for most geological activities. Tungsten carbide is also made into tiles for wear and abrasion resistance. It is also very useful in rebuilding worn parts. The application of tungsten carbide on industrial wearing surfaces has been proven to greatly enhance the performance factors for a whole spectrum of industrial applications. The service life of many kinds of machinery can be greatly prolonged by surface coating of wear-prone materials with tungsten carbide.

10.5.7 Practical Data for Ceramists and Refractory Engineers

10.5.7.1 Temperature of Color

In practice, the temperature of an incandescent body can be estimated roughly from the color of radiation emitted according to a practical scale described in Table 10.18.

Table 10.18. Practical color scale for temperature of incandescent body

Color	Temperature range (°C)
Lowest visible red	475
Lowest visible red to dark red	475–650
Dark red to cherry red	650–750
Cherry red to bright cherry red	750–815
Bright cherry red to orange	815–900
Orange to yellow	900–1090
Yellow to light yellow	1090–1315
Light yellow to white	1315–1540
White to dazzling white	1540 and higher

10.5.7.2 Pyrometric Cone Equivalents

The ***pyrometric cone equivalent*** (PCE), a special ceramic material, was introduced by Segers and standardized by Edward Orton, Jr. It is determined by testing the refractory against a series of standardized test pieces, cone shaped and having a ceramic composition with different softening points, one withstanding a slightly higher temperature than the other.

The test pieces are generally made to form triangular pyramids having a height four times the base. The softening point is reached depending upon the temperature and the rate of heat increase. Cones are numbered from 022, 021, 020, 02, 01, 1, and 2 to 42. Where the softening range in cones is too close, for example, in 21, 22, 24, and 25, they are omitted from the series, and where the temperature range is widely spaced, extra cones like 31.5, 32.5, etc. are added. At a temperature increase rate of 20°C per hour, the cones numbering 022 to 01 have softening points between 585 and 1110°C, and those numbered 1 to 35 have softening points between 1125 and 1775°C. Thus, the predetermined pyrometric cone equivalents of standard test pieces are placed along with cones made of the samples being tested in the furnace, and the PCE of the samples are determined by visual comparison. The softening point is noticed when the tip of the cone starts bending with the rise in temperature.

Table 10.19. Temperature equivalents (°C) of pyrometric cones and pyrometric cone equivalents

Cone No.	Heating rate for large cones		Heating rate for small cones	Pyrometric cone equivalent (PCE)
	60°C/h	150°C/h	300°C/h	150°C/h
022	585	600		
021	602	614	643	
020	625	635	666	
019	668	683	723	
018	696	717	752	
017	727	747	784	
016	767	792	825	
015	790	804	843	
014	834	838		
013	869	852		
012	866	884		
011	886	894		
010	887	894	919	
09	915	923	955	
08	945	955	983	
07	973	984	1008	
06	991	999	1023	
05	1031	1046	1062	
04	1050	1060	1098	
03	1086	1101	1131	
02	1101	1120	1148	
01	1117	1137	1178	
1	1136	1152	1179	
2	1142	1162	1179	
3	1152	1168	1196	
4	1168	1186	1209	
5	1177	1196	1221	
6	1201	1222	1255	
7	1215	1240	1264	
8	1236	1260	1300	
9	1260	1280	1317	
10	1285	1305	1330	
11	1294	1315	1366	
12	1306	1326	1355	1337
13	1321	1346		1349
14	1388	1366		1398
15	1424	1431		1430
16	1455	1473		1491

Table 10.19. *(continued)*

Cone No.	Heating rate for large cones		Heating rate for small cones	Pyrometric cone equivalent (PCE)
	60°C/h	150°C/h	300°C/h	150°C/h
17	1477	1485		1512
18	1500	1506		1522
19	1520	1528		1541
20	1542	1549		1564
23	1586	1590		1605
26	**1589**	**1605**		**1621**
27	1614	1627		1640
28	1614	1633		1646
29	1624	1645		1659
30	1636	1654		1665
31	1661	1679		1683
31 $^{1}/_{2}$	1706			1699
32		1717		1717
32 $^{1}/_{2}$	1718	1730		1724
33	1732	1741		1743
34	1757	1759		1763
35	1784	1784		1785
36	1798	1796		1804
37				1820
38				1835
39				1865
40				1885
41				1970
42				2015

Reference: Standard Pyrometric Cones. Edward Orton, Jr.Ceramic Foundation, Columbus, OH

10.6 Standards for Testing Refractories

Table 10.20. ASTM standards for testing refractories

ASTM standard	Description
ASTM C-16	Load-testing refractory brick at high temperatures
ASTM C-20	Apparent porosity, water absorption, apparent specific gravity, and bulk density of burned refractory brick and shapes by boiling water
ASTM C-24	Pyrometric cone equivalent of fireclay and high-alumina refractory materials
ASTM C-67	Brick and structural clay-tile testing
ASTM C-92	Sieve analysis and water content of refractory materials
ASTM C-93	Cold crushing strength and modulus of rupture of insulating firebrick

Table 10.20. *(continued)*

ASTM standard	Description
ASTM C-113	Reheat change of refractory brick
ASTM C-133	Cold crushing strength and modulus of rupture of refractories
ASTM C-134	Size and bulk density of refractory brick and insulating firebrick
ASTM C-135	True specific gravity of refractory materials by water immersion
ASTM C-167	Thickness and density of blanket or batt thermal insulations
ASTM C-179	Drying and linear change in refractory plastic and ramming mix specimens
ASTM C-181	Workability index of fireclay and high-alumina plastic refractories
ASTM C-182	Thermal conductivity of insulating firebrick
ASTM C-198	Cold bonding strength of refractory mortar
ASTM C-199	Pier test of refractory mortars
ASTM C-201	Thermal conductivity of refractories
ASTM C-202	Thermal conductivity of refractory brick
ASTM C-210	Reheat change in insulating firebrick
ASTM D-257	DC resistance or conductance of insulating materials
ASTM C-279	Chemical-resistant masonry units
ASTM C-288	Disintegration of refractories in an atmosphere of carbon monoxide
ASTM C-336	Annealing point and strain point of glass by fiber elongation
ASTM C-338	Softening point of glass by fiber elongation
ASTM C-356	Linear shrinkage of preformed high-temperature thermal insulation subjected to soaking heat
ASTM C-357	Bulk density of granular refractory materials
ASTM C-373	Water absorption, bulk density, apparent porosity, and apparent specific gravity of fired whiteware products
ASTM C-417	Thermal conductivity of unfired monolithic refractories
ASTM C-454	Disintegration of carbon refractories by alkali
ASTM C-491	Modulus of rupture of air-setting plastic refractories
ASTM C-559	Bulk density by physical measurements of manufactured carbon and graphite articles
ASTM C-561	Ash in a graphite sample
ASTM C-577	Permeability of refractories
ASTM C-583	Modulus of rupture of refractory materials at elevated temperatures
ASTM C-598	Annealing point and strain point of glass by beam bending
ASTM C-605	Reheat change of fireclay nozzles and sleeves
ASTM C-611	Electrical resistivity of manufactured carbon and graphite articles at room temperature
ASTM C-651	Flexural strength of manufactured carbon and graphite articles using four-point loading at room temperature
ASTM C-695	Compressive strength of carbon and graphite
ASTM C-704	Abrasion resistance of refractory materials at room temperature
ASTM C-747	Modulus of elasticity and fundamental frequencies of carbon and graphite materials by sonic resonance
ASTM C-767	Thermal conductivity of carbon refractories

Table 10.20. *(continued)*

ASTM standard	Description
ASTM C-769	Sonic velocity in manufactured carbon and graphite materials for use in obtaining an approximate Young's modulus
ASTM C-830	Apparent porosity, liquid absorption, apparent specific gravity, and bulk density of refractory shapes by vacuum pressure
ASTM C-831	Residual carbon, apparent residual carbon, and apparent carbon yield in coked-carbon-containing bricks and shapes
ASTM C-832	Measuring the thermal expansion and creep of refractories under load
ASTM C-838	Bulk density of as-manufactured carbon and graphite shapes
ASTM C-860	Determining and measuring consistency of refractory concrete
ASTM C-862	Preparing refractory concrete specimens by casting
ASTM C-863	Evaluating oxidation resistance of silicon carbide refractories at elevated temperatures
ASTM C-865	Firing refractory concrete specimens
ASTM C-885	Young's modulus of refractory shapes by sonic resonance
ASTM C-892	Unfiberized shot content of inorganic fibrous blankets
ASTM C-914	Bulk density and volume of solid refractories by wax immersion
ASTM C-973	Preparing test specimens from basic refractory gunning products by pressing
ASTM C-974	Preparing test specimens from basic refractory castable products by casting
ASTM C-975	Preparing test specimens from basic refractory ramming products by pressing
ASTM C-1025	Modulus of rupture in bending of electrode graphite
ASTM C-1039	Apparent porosity, apparent specific gravity, and bulk density of graphite electrodes
ASTM C-1054	Pressing and drying refractory plastic and ramming mix specimens
ASTM C-1099	Modulus of rupture of carbon-containing refractory materials at elevated temperatures
ASTM C-1100	Ribbon thermal shock testing of refractory materials
ASTM C-1113	Thermal conductivity of refractories by hot wire
ASTM C-1161	Flexural strength of advanced ceramics at ambient temperature
ASTM C-1171	Quantitatively measuring the effect of thermal cycling on refractories
ASTM C-1259	Dynamic Young's modulus, shear modulus, and Poisson ratio for advanced ceramics by impulse excitation of vibration

Table 10.21. ISO standards for testing refractories

ISO standard	Description
ISO 10058: 1992	Magnesites and dolomites – chemical analysis
ISO 10059-1: 1992	Dense, shaped refractory products – determination of cold compressive strength. Part 1: Referee test without packing
ISO 10059-2: 2003	Dense, shaped refractory products – determination of cold compressive strength. Part 2: Test with packing
ISO 10060: 1993	Dense, shaped refractory products – test methods for products containing carbon
ISO 10080: 1990	Refractory products – classification of dense, shaped acid-resisting products
ISO 10081-1: 2003	Classification of dense shaped refractory products. Part 1: Alumina-silica

Table 10.21. *(continued)*

ISO standard	Description
ISO 10081-2: 2003	Classification of dense shaped refractory products. Part 2: Basic products containing less than 7% residual carbon
ISO 10081-3: 2003	Classification of dense shaped refractory products. Part 3: Basic products containing from 7 to 50% residual carbon
ISO 10635: 1999	Refractory products – methods of testing for ceramic fiber products
ISO 1146: 1988	Pyrometric reference cones for laboratory use – specification
ISO 12676: 2000	Refractory products – determination of resistance to carbon monoxide
ISO 12677: 2003	Chemical analysis of refractory products by XRF – fused cast bead method
ISO 12678-1: 1996	Refractory products – measurement of dimensions and external defects of refractory bricks. Part 1: Dimensions and conformity to drawings
ISO 12678-2: 1996	Refractory products – measurement of dimensions and external defects of refractory bricks. Part 2: Corner and edge defects and other surface imperfections
ISO 12680-1: 2005	Methods of testing of refractory products. Part 1: Determination of dynamic Young's modulus (MOE) by impulse excitation of vibration
ISO 13765-1: 2004	Refractory mortars. Part 1: Determination of consistency using the penetrating-cone method
ISO 13765-2: 2004	Refractory mortars. Part 2: Determination of consistency using the reciprocating-flow-table method
ISO 13765-3: 2004	Refractory mortars. Part 3: Determination of joint stability
ISO 13765-4: 2004	Refractory mortars. Part 4: Determination of flexural bonding strength
ISO 13765-5: 2004	Refractory mortars. Part 5: Determination of grain-size distribution (sieve analysis)
ISO 13765-6: 2004	Refractory mortars. Part 6: Determination of moisture content of ready-mixed mortars
ISO 1893: 2005	Refractory products – determination of refractoriness under load – differential method with rising temperature
ISO 1927: 1984	Prepared unshaped refractory materials (dense and insulating) – classification
ISO 20182: 2005	Refractory test-piece preparation – gunning refractory panels by pneumatic-nozzle mixing-type guns
ISO 2245: 1990	Shaped insulating refractory products – classification
ISO 2477: 2005	Shaped insulating refractory products – determination of permanent change in dimensions on heating
ISO 2478: 1987	Dense shaped refractory products – determination of permanent change in dimensions on heating
ISO 3187: 1989	Refractory products – determination of creep in compression
ISO 5013: 1985	Refractory products – determination of modulus of rupture at elevated temperatures
ISO 5014: 1997	Dense and insulating shaped refractory products – determination of modulus of rupture at ambient temperature
ISO 5016: 1997	Shaped insulating refractory products – determination of bulk density and true porosity
ISO 5017: 1998	Dense shaped refractory products – determination of bulk density, apparent porosity, and true porosity
ISO 5018: 1983	Refractory materials – determination of true density
ISO 5019-1: 1984	Refractory bricks – dimensions. Part 1: Rectangular bricks
ISO 5019-2: 1984	Refractory bricks – dimensions. Part 2: Arch bricks

Table 10.21. *(continued)*

ISO standard	Description
ISO 5019-3: 1984	Refractory bricks – dimensions. Part 3: Rectangular checker bricks for regenerative furnaces
ISO 5019-4: 1988	Refractory bricks – dimensions. Part 4: Dome bricks for electric-arc furnace roofs
ISO 5019-5: 1984	Refractory bricks – dimensions. Part 5: Skewbacks
ISO 5019-6: 2005	Refractory bricks – dimensions. Part 6: Basic bricks for oxygen steelmaking converters
ISO 5022: 1979	Shaped refractory products – sampling and acceptance testing
ISO 528: 1983	Refractory products – determination of pyrometric cone equivalent (refractoriness)
ISO 5417: 1986	Refractory bricks for use in rotary kilns – dimensions
ISO 836: 2001	Terminology for refractories
ISO 8656-1: 1988	Refractory products – sampling of raw materials and unshaped products. Part 1: Sampling scheme
ISO 8840: 1987	Refractory materials – determination of bulk density of granular materials (grain density)
ISO 8841: 1991	Dense, shaped refractory products – determination of permeability to gases
ISO 8890: 1988	Dense shaped refractory products – determination of resistance to sulfuric acid
ISO 8894-1: 1987	Refractory materials – determination of thermal conductivity. Part 1: Hot-wire method (cross-array)
ISO 8894-2: 1990	Refractory materials – determination of thermal conductivity. Part 2: Hot-wire method (parallel)
ISO 8895: 2004	Shaped insulating refractory products – determination of cold crushing strength
ISO 9205: 1988	Refractory bricks for use in rotary kilns – hot-face identification marking

10.7 Properties of Pure Ceramics (Borides, Carbides, Nitrides, Silicides, and Oxides)

See Table 10.22, pages 648–669.

Table 10.22. Selected physical properties of advanced ceramics (borides, carbides, nitrides, silicides, and oxides)

IUPAC name (synonyms, common trade names)	Theoretical chemical formula, [CAS RN], relative molecular mass ($^{12}C = 12.000$)	Crystal system, lattice parameters, structure type, Strukturbericht, Pearson, space group, structure type (Z)	Density (ρ/kg.m^{-3})	Electrical resistivity (ρ/μΩ.cm)	Dielectric permittivity [1MHz] (ε_r / nil)	Dielectric field strength (E_d/MV.m^{-1})	Dissipation or tangent loss factor ($tan\delta$)	Melting point ($m.p.$/°C)	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})	Coeff. linear thermal expansion (α/10^{-6}K^{-1})	Young's or elastic modulus (E/GPa)	Coulomb's or shear modulus (G/GPa)	Bulk or compression modulus (K/GPa)	Poisson ratio (ν)	Ultimate tensile strength (σ_{UTS}/MPa)	Flexural strength (τ/MPa)	Compressive strength (σ/MPa)	Fracture toughness (K_{1C}/MPa.m$^{1/2}$)	Vickers or Knoop Hardness (HV or HK/GPa) (/HM)	Other physicochemical Properties, oxidation and corrosion resistance[28], and major uses.
Borides																						
Aluminum diboride	AlB_2 [12041-50-8] 48.604	Hexagonal a = 300.50 pm c = 325.30 pm C32, *hP3*, P6/mmm, AlB_2 type (Z = 1)	3190	n.a.	n.a.	n.a.	n.a.	1654		897.87											9.61 HK	Temp. transition to AlB_{12} at 920°C. Soluble in dilute HCl. Nuclear shielding material
Aluminum dodecaboride	AlB_{12} [12041-54-2] 156.714	Tetragonal a = 1016 pm c = 1428 pm	2580	n.a.	n.a.	n.a.	n.a.	2421		954.48											23.55–25.50 HK	Soluble in hot HNO_3, insoluble in other acids and alkalis. Neutron shielding material
Barium hexaboride	BaB_6 [] 202.193	Cubic a = pm $D2_1$, cP7, Pm3m CaB_6 type (Z = 1)	4350	77				2270				385										Black cubic crystals
Beryllium boride	Be_2B [12536-52-6] 46.589		n.a.	n.a.	n.a.	n.a.	n.a.	1160														
Beryllium diboride	BeB_2 [12228-40-9] 30.634	Hexagonal a = 979 pm c = 955 pm	2420	10,000	n.a.	n.a.	n.a.	1970														Better air oxidation resistance than any other beryllium boride (Be_2B, BeB_2) in temperature range 1000–1200°C
Beryllium hemiboride	Be_4B [12536-51-5]	Cubic a = 467.00 pm C1, cF12, Fm3m, CaF_2 type (Z = 4)	1890	1000	n.a.	n.a.	n.a.	1520													8.53	
Beryllium hexaboride	BeB_6 [12429-94-6]	Tetragonal a = 1016 pm c = 1428 pm	2330	10^{13}	n.a.	n.a.	n.a.	2070														
Beryllium boride	BeB [12228-40-9]		n.a.	n.a.	n.a.	n.a.	n.a.	1970														
Boron	β-B [7440-42-8] 10.811	Trigonal (rhombohedral) a = 1017 pm α = 65°12' *hR105*, R3m, β-B type	2460	18,000	n.a.	n.a.	n.a.	2190				320									20.15 (HM 11)	Brown or dark powder, unreactive to oxygen, water, acids, and alkalis. ΔH_{sup} = 480 kJ/mol

Calcium hexaboride	CaB_6 [12007-99-7] 104.944	Cubic a = 413.77 pm $D2_1$, cP7, Pm3m CaB_6 type (Z = 1)	2460	222				2235	39.29		6.48	451												
Cerium hexaboride	CeB_6 [12008-02-5] 204.981	Cubic a = 4 pm $D2_1$, cP7, Pm3m CaB_6 type (Z = 1)	4870					2550																Blue hexagonal crystals
Chromium boride	Cr_3B_3 [12007-38-4] 292.414	Orthorhombic a = 302.6 pm b = 1811.5 pm c = 295.4 pm $D8_1$, $tI32$, I4/mcm, Cr_3B_3 type (Z = 4)	6100	n.a.	n.a.	n.a.	1900	15.8		13.7														
Chromium diboride	CrB_2 [12007-16-8] 73.618	Hexagonal a = 292.9 pm c = 306.6 pm C32, $hP3$, P6/mmm, AlB_2 type (Z = 1)	5160–5220	21	n.a.	n.a.	1850–2200	20–32	712	6.2–7.5	211	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	17.65	Strongly corroded by molten metals such as Mg, Al, Na, Cu, Si, V, Cr, Mn, Fe, and Ni; corrosion resistant to liquid metals Cu, Zn, Sn, Rb, and Bi					
Chromium boride	CrB [12006-79-0] 62.807	Tetragonal a = 294.00 pm c = 1572.00 pm B_f, oC8, Cmcm CrB type (Z = 4)	6200	64.0	n.a.	n.a.	2100	n.a.	20.1		12.3					607	1300							
Cobalt hemiboride	Co2B [12045-01-1] 128.677		8100				1280																	
Cobalt boride	CoB [12006-77-8] 69.744		7250				1460																	
Hafnium diboride	HfB_2 [12007-23-7] 200.112	Hexagonal a = 314.20 pm c = 347.60 pm C32, $hP3$, P6/mmm, AlB_2 type (Z = 1)	11,190	8.8–11	n.a.	n.a.	3249	57.1	247.11	6.3–7.56	500			0.12		350		28.44 and 23.54 HK	Gray crystals. HfB_2 exhibits the greatest oxidation resistance of all refractory group IV and V borides above 1090°C. Attacked by hydrogen fluoride gas (HF) but resists fluorine gas up to 590°C and is less resistant than zirconium diboride					
Hafnium boride	HfB [] 189.301	Cubic NaCl type	12,800				2899												Gray hexagonal crystals					
Iron diboride	FeB_2 [12006-86-9] 122.501	Tetragonal	7300				1389																	
Iron boride	FeB [12006-84-7] 66.656	Orthorhombic	7000																					

Table 10.22. *(continued)*

IUPAC name (synonyms, common trade names)	Theoretical chemical formula, [CAS RN], relative molecular mass ($^{12}C = 12.000$)	Crystal system, lattice parameters, structure type, Strukturbericht, Pearson, space group, structure type (Z)	Density (ρ/kg.m^{-3})	Electrical resistivity (ρ/μΩ.cm)	Dielectric permittivity [1MHz] (ε_r / nil)	Dielectric field strength (E_d/MV.m^{-1})	Dissipation or tangent loss factor ($tan\delta$)	Melting point ($m.p.$/°C)	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})	Coeff. linear thermal expansion (α/10^{-6}K^{-1})	Young's or elastic modulus (E/GPa)	Coulomb's or shear modulus (G/GPa)	Bulk or compression modulus (K/GPa)	Poisson ratio (ν)	Ultimate tensile strength (σ_{UTS}/MPa)	Flexural strength (π/MPa)	Compressive strength (σ/MPa)	Fracture toughness (K_{1C}/MPa.m$^{1/2}$)	Vickers or Knoop Hardness (HV or HK/GPa) (/HM)	Other physicochemical Properties, oxidation and corrosion resistance, and major uses.
Lanthanum hexaboride	LaB_6 [12008-21-8] 203.772	Cubic a = 415.7 pm $D2_1$, cP7, Pm3m CaB_6 type (Z = 1)	4760	17.4	n.a.	n.a.	n.a.	2715	47.7		6.4	479					126					Wear-resistant, semiconducting, thermoionic conductor film
Molybdenum boride	Mo_2B_5 [12007-97-5] 245.935	Trigonal a = 301.2 pm c = 2093.7 pm $D8_l$, *hR7*, R3m Mo_2B_5 type (Z = 1)	7480	25–55	n.a.	n.a.	n.a.	1600	50		8.6	672					345					Corroded by molten metals Al, Mg, V, Cr, Mn, Fe, Ni, Cu, Nb, Mo, and Ta; corrosion resistant to molten Cd, Sn, Bi, and Rb
Molybdenum diboride	MoB_2 117.59	Hexagonal a = 305.00 pm c = 311.30 pm C32, *hP3*, P6/mmm, AlB_2 type (Z = 1)	7780	45	n.a.	n.a.	n.a.	2100		527	7.7									12.55		
Molybdenum hemiboride	Mo_2B [12006-99-4] 202.691	Tetragonal a = 554.3 pm c = 473.5 pm C16, *tI12*, I4/mcm, $CuAl_2$ type (Z = 4)	9260	40	n.a.	n.a.	n.a.	2280		377	5.0									(HM 8–9)	Corrosion-resistant film
Molybdenum boride	MoB 106.77	Tetragonal a = 311.0 c = 169.5 B_f, *tI4*, I4/amd MoB type (Z = 2)	8770	α–MoB 45, β–MoB 25	n.a.	n.a.	n.a.	2180		368										15.40	
Niobium diboride	ε–NbB_2 [12007-29-3] 114.528	Hexagonal a = 308.90 pm c = 330.03 pm C32, *hP3*, P6/mmm, AlB_2 type (Z = 1)	6970	26–65	n.a.	n.a.	n.a.	2900	17–23.5	418	8.0–8.6	637	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	30.70 (HM>8)	Corrosion resistant to molten Ta while corroded by molten rhenium
Niobium boride	δ–NbB [12045-19-1] 103.717	Orthorhombic a = 329.8 pm b = 316.6 pm c = 87.23 pm B_h, oC8, Cmcm, CrB type (Z = 4)	7570	40–64.5	n.a.	n.a.	n.a.	2270–2917	15.6	n.a.	12.9	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.		Wear-resistant and semiconductive films, neutron-absorbing layer on nuclear fuel pellets
Silicon hexaboride	SiB_6 [12008-29-6]	Trigonal (rhombohedral)	2430	200,000	n.a.	n.a.	n.a.	1950														

Silicon tetraboride	SiB_4 [12007-81-7] 71.330		2400	n.a.	n.a.	n.a.	1870 (dec.)																		
Tantalum diboride	TaB_2 [12077-35-1] 202.570	Hexagonal a = 309.80 pm c = 324.10 pm C32, *hP3*, P6/mmm, AlB_2 type (Z = 1)	12,540	33–75	n.a.	n.a.	3037–3200	10.9–16.0	237.55	8.2–8.8	257	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	(HM>8)	n.a.	Gray metallic powder. Severe oxidation in air above 800°C. Corroded by molten metals Nb, Mo, Ta, and Re.
Tantalum boride	TaB [12007-07-7] 191.759	Orthorhombic a = 327.6 pm b = 866.9 pm c = 315.7 pm B_2, oC8, Cmcm CrB type (Z = 4)	14,190	100	n.a.	n.a.	2340–3090		246.85	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	21.57 (HM>8)	n.a.	Severe oxidation above 1100–1400°C in air
Thorium hexaboride	ThB_6 [12229-63-9] 296.904	Cubic a = 411.2 pm $D2_1$, cP7, Pm3m CaB_6 type (Z = 1)	6800	n.a.	n.a.	n.a.	2149	44.8		7.8												
Thorium tetraboride	ThB_4 [12007-83-9] 275.53	Tetragonal a = 725.6 pm c = 411.3 pm $D1_4$, *tP20*, P4/mbm, ThB_4 type (Z = 4)	8450	n.a.	n.a.	n.a.	2500	25	510	7.9	148			137								
Titanium boride	TiB [] 58.678	Cubic	5260				2060															
Titanium diboride	TiB_2 [12045-63-5] 69.489	Hexagonal a = 302.8 pm c = 322.8 pm C32, *hP3*, P6/mmm, AlB_2 type (Z = 1)	4520	16–28.4	n.a.	n.a.	2980–3225	64.4–96	637.22	7.6–8.64	372–551	n.a.	0.11	131	240–400	669	6.2–6.7	33.05 (HM>9) 31.87 HK	Gray crystals, superconducting at 1.26 K. High-temperature electrical conductor, used as crucible material for handling molten metals such as Al, Zn, Cd, Bi, Sn, and Rb; strongly corroded by liquid metals such as Ti, Zr, V, Nb, Ta, Cr, Mn, Fe, Co, Ni, and Cu. Begins to be oxidized in air above 1100–1400°C. Corrosion resistance in hot concentrated brines. Maximum operating temperature 1000°C (reducing) and 800°C (oxidizing).		
Tungsten hemiboride	W_2B [12007-10-2] 378.491	Tetragonal a = 556.4 pm c = 474.0 pm C16, *tI12*, I4/mcm, $CuAl_2$ type (Z = 4)	16,720	n.a.	n.a.	n.a.	2670		168	6.7								23.73 (HM 9)		Black powder
Tungsten boride	WB [12007-09-9] 194.651	Tetragonal a = 311.5 pm c = 1692 pm	15,200–16,000	4.1	n.a.	n.a.	2660			6.9								13.63 (HM 9)		Black powder

Table 10.22. *(continued)*

IUPAC name (synonyms, common trade names)	Theoretical chemical formula, [CAS RN], relative molecular mass ($^{12}C = 12.000$)	Crystal system, lattice parameters, structure type, Strukturbericht, Pearson, space group, structure type (Z)	Density (ρ/kg.m^{-3})	Electrical resistivity (ρ/μΩ.cm)	Dielectric permittivity [1MHz] (ε_r / nil)	Dielectric field strength (E_d/MV.m^{-1})	Dissipation or tangent loss factor ($tan\delta$)	Melting point ($m.p.$/°C)	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})	Coeff. linear thermal expansion (α/10^{-6}K^{-1})	Young's or elastic modulus (E/GPa)	Coulomb's or shear modulus (G/GPa)	Bulk or compression modulus (K/GPa)	Poisson ratio (ν)	Ultimate tensile strength (σ_{UTS}/MPa)	Flexural strength (π/MPa)	Compressive strength (σ/MPa)	Fracture toughness (K_{1C}/MPa.m$^{1/2}$)	Vickers or Knoop Hardness (HV or HK/GPa) (/HM)	Other physicochemical Properties, oxidation and corrosion resistance, and major uses.	
Uranium diboride	UB_2 [12007-36-2] 259.651	Hexagonal a = 313.10 pm c = 398.70 pm C32, *hP3*, P6/mmm, AlB_2 type	12,710	n.a.	n.a.	n.a.	n.a.	2385	51.9		9.0											
Uranium dodecaboride	UB_{12} 367.91	Cubic *a* = 747.3 pm D2$_3$, *cF52*, Fm3m, UB_{12} type (Z = 4)	5820	n.a.	n.a.	n.a.	n.a.	1500			4.6											
Uranium tetraboride	UB_4 [12007-84-0] 281.273	Tetragonal *a* = 707.5 pm *c* = 397.9 pm D1$_4$, *tP20*, P4/mbm, ThB_4 type (Z = 4)	5350	n.a.	n.a.	n.a.	n.a.	2495	4.0		7.0	440					413		24.52			
Vanadium diboride	VB_2 [12007-37-3] 72.564	Hexagonal *a* = 299.8 pm *c* = 305.7 pm C32, *hP3*, P6/mmm, AlB_2 type (Z = 1)	5070	23	n.a.	n.a.	n.a.	2450–2747	42.3	647.43	7.6–8.3	268								(HM 8–9)	Wear-resistant and semiconductive films	
Zirconium diboride	ZrB_2 [12045-64-6] 112.846	Hexagonal *a* = 316.9 pm *c* = 353.0 pm C32, *hP3*, P6/mmm, AlB_2 type (Z = 1)	6085	9.2	n.a.	n.a.	n.a.	3060–3245	57.9	392.54	5.5–8.3	343–506	220	n.a.	0.15	n.a.	305	n.a.	n.a.	18.63–33.34 (HM 8)	Gray metallic crystals, excellent thermal shock resistance, greatest oxidation inertness of all refractory hardmetals. Hot-pressed crucible for handling molten metals such as Zn, Mg, Fe, Cu, Zn, Cd, Sn, Pb, Rb, Bi, Cr, brass, carbon steel, cast irons, and molten cryolithe, yttria, zirconia, and alumina. Readily corroded by liquid metals such as Si, Cr, Mn, Co, Ni, Nb, Mo, Ta and attacked by molten salts such as Na_2O, alkali carbonates, and NaOH. Severe oxidation in air occurs above 1100–1400°C. Stable above 2000°C in inert or reducing atmosphere.	

Zirconium dodecaboride	ZrB_{12} 283.217	Cubic $a = 740.8$ pm $D2_f$, *cF52*, Fm3m, UB_{12} type ($Z = 4$)	3630	60–80	n.a.	n.a.	n.a.	2680		523														–	
Carbides																									
Aluminum carbide	Al_4C_3 [1299-86-1] 143.959	Trigonal (rhombohedral) a = 333 pm c = 2494 pm D71	2360	n.a.	n.a.	n.a.	n.a.	2798	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Decomposes in water with evolution of CH_4
Beryllium hemicarbide	Be_2C [506-66-1] 30.035	Cubic $a = 433$ pm C1, *cF12*, Fm3m, CaF_2 type ($Z = 4$)	1900	n.a.	n.a.	n.a.	n.a.	2100	21.0	1397	10.5	314.4	n.a.	96.5	0.100	155	n.a.	723	n.a.	23.63 HK	Brick-red or yellowish-red octahedra. Nuclear reactor cores.
Boron carbide (Norbide®)	B_4C [12069-32-8] 55.255	Hexagonal $a = 560$ pm $c = 1212$ pm $D1_g$, *hR15*, R3m, B_4C type	2512	4500	n.a.	n.a.	n.a.	2350–2427	27	1854	2.63–5.6	448–470	184	490	0.207	310–350	n.a.	1400–2900	3.2–4.2	31.38–34.32 HK (HM 9.32)	Hard black shiny crystals, fourth hardest material known after diamond, cubic boron nitride, and boron oxide. Does not burn in an O_2 flame if temperature is maintained below 983°C. Maximum operating temperature 2000°C (inert, reducing) or 600°C (oxidizing). Not attacked by hot HF or chromic acid. Used as abrasive, crucible container for molten salts except molten alkali hydroxides. In form of molded shape, used for pressure-blast nozzles, wire-drawing dies, and bearing surfaces for gauges. For grinding and lapping application available mesh sizes cover range 240 to 800.
Chromium carbide	Cr_3C_2 400.005	Hexagonal $a = 1398.02$ pm c = 453.20 pm	6992	109.0	n.a.	n.a.	n.a.	1665	n.a.	n.a.	11.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	13.10	Resists oxidation in range 800–1000°C. Corroded by molten metals Ni and Zn.
Chromium carbide	Cr_3C_2 [12012-35-0] 180.010	Orthorombic $a = 282$ pm $b = 553$ pm $c = 1147$ pm $D5_{10}$, *oP20*, Pbnm, Cr_3C_2 type ($Z = 4$)	6680	75.0	n.a.	n.a.	n.a.	1895	19.2	n.a.	10.3	386	n.a.	0.78	0.280	n.a.	n.a.	1041–1350	n.a.	25.99	Corroded by molten metals Ni, Zn, Cu, Cd, Al, Mn, and Fe. Corrosion resistant in molten Sn and Bi.

Table 10.22. *(continued)*

IUPAC name (synonyms, common trade names)	Theoretical chemical formula, [CAS RN], relative molecular mass ($^{12}C = 12.000$)	Crystal system, lattice parameters, structure type, Strukturbericht, Pearson, space group, structure type (Z)	Density (ρ/kg.m^{-3})	Electrical resistivity (ρ/μΩ.cm)	Dielectric permittivity [1MHz] (ε_r / nil)	Dielectric field strength (E_d/MV.m^{-1})	Dissipation or tangent loss factor ($tan\delta$)	Melting point ($m.p.$/°C)	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})	Coeff. linear thermal expansion (α/10^{-6}K^{-1})	Young's or elastic modulus (E/GPa)	Coulomb's or shear modulus (G/GPa)	Bulk or compression modulus (K/GPa)	Poisson ratio (ν)	Ultimate tensile strength (σ_{UTS}/MPa)	Flexural strength (π/MPa)	Compressive strength (σ/MPa)	Fracture toughness (K_{1C}/MPa.m$^{1/2}$)	Vickers or Knoop Hardness (HV or HK/GPa) (/HM)	Other physicochemical Properties, oxidation and corrosion resistance, and major uses.
Diamond	C [7782-40-3] 12.011	Cubic a = 356.683 pm A4, *cF8*, Fd3m, diamond type (Z =8)	3515.24	>10^{16} (I, IIa) >10^{5} (IIb)	n.a.	n.a.	n.a.	3550	900 (I) 2400 (IIa)	n.a.	2.16	930	n.a.	n.a.	n.a.	n.a.	n.a.	7000	n.a.	5.3– 6.7	78.45 HK (HM 10)	Exists in two major varieties: those bearing nitrogen as an impurity (Type I) and those without nitrogen (Type II). These two subgroups are further subdivided into Types Ia, Ib, IIa, and IIb. Type Ia diamonds are the most common type of naturally occurring diamond; they exhibit 0.1 to 0.2 wt.% nitrogen present in small aggregates, including platelets. By contrast, nitrogen in Type Ib diamonds is dispersed substitutionally. Of the two Type II diamond types, Type IIb is a semiconductor due to minute amounts of boron impurities and exhibits a blue color, whereas Type IIa diamonds are comparatively pure. Electric insulator (E_g = 7 eV.). Burns in oxygen.
Graphite	C [7782-42-5] 12.011	Hexagonal a = 246 pm b = 428 pm c = 671 pm A9, *hP4*,P6$_3$/mmc, graphite type (Z =4)	2250	1385	n.a.	n.a.	n.a.	3650	n.a.	n.a.	0.6– 4.3	6.9	n.a.	n.a.	n.a.	28	n.a.	n.a.	n.a.	n.a.	(HM 2)	High-temperature lubricant, crucible container for handling molten metals such as Mg, Al, Zn, Ga, Sb, and Bi
Hafnium carbide	HfC [12069-85-1] 190.501	Cubic a = 446.0 pm B1, *cF8*, Fm3m, rock salt type (Z = 4)	12,670	45.0	n.a.	n.a.	n.a.	3890– 3950	22.15	n.a.	6.3	424	179	n.a.	0.17	n.a.	n.a.	n.a.	n.a.	18.34– 28.44	Dark gray brittle solid, most refractory binary material known. Controls rods in nuclear reactors, crucible container for melting HfO_2 and other oxides. Corrosion resistant to liquid metals such as Nb, Ta, Mo, and W. Severe oxidation in air above 1100–1400°C and stable up to 2000°C in helium.	

Lanthanum dicarbide	LaC_2 [12071-15-7] 162.928	Tetragonal $a = 394.00$ pm $c = 657.20$ pm C11a, *tI6*, I4/mmm, CaC_2 type ($Z = 2$)	5290	68.0	n.a.	n.a.	2360–2438	n.a.	12.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Decomposed by H_2O
Molybdenum hemicarbide	β–Mo_2C [12069-89-5] 203.891	Hexagonal $a = 300.20$ pm $c = 427.40$ pm L'3, *hP3*, $P6_3/mmc$, Fe_2N type ($Z = 1$)	9180	71.0	n.a.	n.a.	2687	n.a.	29.4	7.8	221	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	14.70 (HM>7)	Gray powder. Wear-resistant film. Oxidized in air at 700–800°C. Corroded in molten metals Al, Mg, V, Cr, Mn, Fe, Ni, Cu, Zn, and Nb. Corrosion resistant in molten Cd, Sn, and Ta
Molybdenum carbide	MoC [12011-97-1] 107.951	Hexagonal $a = 290$ pm $c = 281$ pm B_3, $P6_3/mmc$, BN type ($Z = 4$)	9150	50.0	n.a.	n.a.	2577	n.a.	5.76	197	n.a.	n.a.	0.204	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	17.65 (HM>9)	Oxidized in air at 700–800°C
Niobium hemicarbide	Nb_2C [12011-99-3] 197.824	Hexagonal $a = 312.70$ pm $c = 497.20$ pm L'3, *hP3*, $P6_3/mmc$, Fe_2N type ($Z = 1$)	7800	n.a.	n.a.	n.a.	3090	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	20.82	
Niobium carbide	NbC [12069-94-2] 104.917	Cubic $a = 447.71$ pm B1, *cF8*, Fm3m, rock salt type ($Z = 4$)	7820	51.1–74.0	n.a.	n.a.	3760	14.2	n.a.	6.84	340	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	24.22 (HM>9)	Lavender gray powder, soluble in HF-HNO_3 mixture. Wear-resistant film, coating graphite in nuclear reactors. Oxidation in air becomes severe only above 1000°C.
Silicon carbide (Carbolon®, Crystolon®, Carborundum®)	β–SiC [409-21-2] 40.097	Cubic $a = 435.90$ pm B3, *cF8*, F43m, ZnS type ($Z = 4$)	3160	107–200	n.a.	n.a.	2093–2400	135	1205	4.5	262–468	168	414	0.192	550	n.a.	1000	3.1	26.48–32.85 (HM 9.5)	Green to bluish black, iridescent crystals. Soluble in fused alkali hydroxides. Abrasives best suited for grinding low-tensile-strength materials such as cast iron, brass, bronze, marble, concrete, stone and glass, optical structural, and wear-resistant components. Corroded by molten metals such as Na, Mg, Al, Zn, Fe, Sn, Rb, and Bi. Resistant to oxidation in air up to 1650°C. Maximum operating temperature of 2000°C in reducing or inert atmosphere.
Silicon carbide (moissanite, Carbolon®, Crystolon®, Carborundum®)	α–SiC [409-21-2] 40.097	Hexagonal $a = 308.10$ pm $c = 503.94$ pm B4, *hP4*, $P6_3/mmc$, wurtzite type ($Z = 2$)	3160	410,000	10.2	n.a.	n.a.	2093 trans.	42.5	690–715	4.3–4.6	386–414	179	n.a.	0.16	450–520	359	500	3.1	23.54–24.52 (HM 9.2)	Semiconductor (Eg=3.03 eV) soluble in fused alkali hydroxides

Table 10.22. *(continued)*

IUPAC name (synonyms, common trade names)	Theoretical chemical formula, [CAS RN], relative molecular mass ($^{12}C = 12.000$)	Crystal system, lattice parameters, structure type, Strukturbericht, Pearson, space group, structure type (Z)	Density (ρ/kg.m^{-3})	Electrical resistivity (ρ/μΩ.cm)	Dielectric permittivity [1MHz] (ε_r / nil)	Dielectric field strength (E_d/MV.m^{-1})	Dissipation or tangent loss factor ($tan\delta$)	Melting point ($m.p.$/°C)	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})	Coeff. linear thermal expansion (α/10^{-6}K^{-1})	Young's or elastic modulus (E/GPa)	Coulomb's or shear modulus (G/GPa)	Bulk or compression modulus (K/GPa)	Poisson ratio (ν)	Ultimate tensile strength (σ_{UTS}/MPa)	Flexural strength (π/MPa)	Compressive strength (σ/MPa)	Fracture toughness (K_{1C}/MPa.m$^{1/2}$)	Vickers or Knoop Hardness (HV or HK/GPa) (/HM)	Other physicochemical Properties, oxidation and corrosion resistance, and major uses.	
Tantalum hemicarbide	Ta,C [12070-07-4] 373.907	Hexagonal a = 310.60 pm c = 493.00 pm L'3, *hP3*, $P6_3/mmc$, Fe_2N type (Z = 1)	15,100	80.0	n.a.	n.a.	n.a.	3327	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	16.80–19.61		
Tantalum carbide	TaC [12070-06-3] 194.955	Cubic a = 445.55 pm B1, *cF8*, Fm3m, rock salt type (Z = 4)	14,800	30–42.1	n.a.	n.a.	n.a.	3880–3920	22.2	190	6.64–8.4	364	n.a.	n.a.	0.172	n.a.	n.a.	n.a.	n.a.	n.a.	15.68–17.65 (HM 9–10)	Golden brown crystals, soluble in HF-HNO_3 mixture. Crucible container for melting ZrO and similar oxides with high melting point. Corrosion resistant to molten metals such as Ta and Re. Readily corroded by liquid metals such as Nb, Mo, and Sn. Burning occurs in pure oxygen above 800°C. Severe oxidation in air above 1100–1400°C. Maximum operating temperature of 3760°C in helium	
Thorium dicarbide	α–ThC_2 [12071-31-7] 256.060	Tetragonal a = 585 pm c = 528 pm C11a, *tI6*, I4/mmm, CaC_2 type (Z = 2)	8960–9600	30.0	n.a.	n.a.	n.a.	2655	23.9	n.a.	8.46	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	5.88	α–β transition at 1427°C and β–γ at 1497°C. Decomposed by H_2O with evolution of C_2H_6	
Thorium carbide	ThC [12012-16-7] 244.049	Cubic a = 534.60 pm B1, *cF8*, Fm3m, rock salt type (Z = 4)	10,670	25.0	n.a.	n.a.	n.a.	2621	28.9	n.a.	6.48	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	9.807	Readily hydrolyzes in water evolving C_2H_6.	
Titanium carbide	TiC [12070-08-5] 59.878	Cubic a = 432.8 pm B1, *cF8*, Fm3m, rock salt type (Z = 4)	4938	52.5	n.a.	n.a.	n.a.	2940–3160	17–21	841	7.5–7.7	310–462	172	0.854	0.182	275–450	n.a.	1310	1.7–3.8	25.69–31.38 (HM 9–10)	Gray crystals. Superconducting at 1.1 K. Soluble in HNO_3 and aqua regia. Resistant to oxidation in air up to 450°C. Maximum operating temperature 3000°C in helium. Crucible container for handling molten metals such as Na, Bi, Zn, Pb, Sn, Bi, Rb, and Cd. Corroded by liquid metals Mg, Al, Si, Ti, Zr, V, Nb, Ta, Cr, Mo, Mn, Fe, Co, and Ni. Attacked by molten NaOH	

Tungsten carbide (Widia®)	WC [12070-12-1] 195.851	Hexagonal $a = 290.63$ pm $c = 283.86$ pm L'3, *hP3*, $P6_3/mmc$, Fe_2N type ($Z = 1$)	15,630	19.2	n.a.	n.a.	2870	121	n.a.	6.9	710	n.a.	0.58	0.26	n.a.	n.a.	530	7.5–8.9	26.48 (HM>9)	Gray powder, dissolved by HF-HNO_3 mixture. Cutting tools, wear-resistant semiconductor film. Corroded by molten metals Mg, Al, V, Cr, Mn, Ni, Cu, Zn, Nb, and Mo. Corrosion resistant to molten Sn and Ta	
Tungsten hemicarbide	W_2C [12070-13-2] 379.691	Hexagonal $a = 299.82$ pm $c = 472.20$ pm L'3, *hP3*, $P6_3/mmc$, Fe_2N type ($Z = 2$)	17,340	81.0	n.a.	n.a.	2730	n.a.	n.a.	3.84	421	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	29.42	Black. Resistant to oxidation in air up to 700°C. Corrosion resistant to Mo	
Uranium carbide	U_2C_3 [12076-62-9]	Cubic $a = 808.89$ pm D5c, *cI40*, I43d, Pu_2C_3 type ($Z = 8$)	12,880	n.a.	n.a.	n.a.	1777	n.a.	n.a.	11.4	179–221	n.a.	n.a.	n.a.	n.a.	n.a.	434	n.a.	n.a.		
Uranium dicarbide	UC_2 [12071-33-9] 262.051	Tetragonal $a = 352.24$ pm $c = 599.62$ pm C11a, *tI6*, I4/mmm, CaC_2 type ($Z = 2$)	11,280	n.a.	n.a.	n.a.	2350–2398	32.7	147	14.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	5.88	Transition tetragonal to cubic at 1765°C. Decomposes in H_2O, slightly soluble in alcohol. Used in microsphere pellets to fuel nuclear reactors	
Uranium carbide	UC [12070-09-6] 250.040	Cubic $a = 496.05$ pm B1, *cF8*, Fm3m, rock salt type ($Z = 4$)	13,630	50.0	n.a.	n.a.	2370–2790	23.0	n.a.	11.4	172.4	66.9	n.a.	0.29	n.a.	n.a.	351.6	7.35–9.17 (HM>7)	Gray crystals with metallic appearance, reacts with oxygen. Corroded by molten metals Be, Si, Ni, and Zr		
Vanadium hemicarbide	V_2C [12012-17-8] 113.89	Hexagonal $a = 286$ pm $c = 454$ pm L'3, *hP3*, $P6_3/mmc$, Fe_2N type ($Z = 2$)	5750	n.a.	n.a.	n.a.	2166	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	29.42	Corroded by molten Nb, Mo, and Ta	
Vanadium carbide	VC [12070-10-9] 62.953	Cubic $a = 413.55$ pm B1, *cF8*, Fm3m, rock salt type ($Z = 4$)	5770	65.0–98.0	n.a.	n.a.	2810	24.8	n.a.	4.9	614	435	n.a.	n.a.	790–825	n.a.	613	n.a.	20.50	Black crystals soluble in HNO_3 with decomposition. Wear-resistant film, cutting tools. Resistant to oxidation in air up to 300°C	
Zirconium carbide	ZrC [12020-14-3] 103.235	Cubic $a = 469.83$ pm B1, *cF8*, Fm3m, rock salt type ($Z = 4$)	6730	68	n.a.	n.a.	3540–3560	20.61	205	6.82	345	123	338	0.257	110	n.a.	1641	n.a.	17.95–28.73 (HM >8)	Dark gray brittle solid, soluble in HF solutions containing nitrate or peroxide ions. UC-nuclear power reactor, crucible container for handling molten metals such as Bi, Cd, Pb, Sn, Rb, and molten zirconia ZrO_2. Corroded by liquid metals Mg, Al, Si, V, Nb, Ta, Cr, Mo, Mn, Fe, Co, Ni, and Zn. In air oxidizes rapidly above 500°C. Maximum operating temperature of 2350°C in helium	

Table 10.22. *(continued)*

IUPAC name (synonyms, common trade names)	Theoretical chemical formula, [CAS RN], relative molecular mass ($^{12}C = 12.000$)	Crystal system, lattice parameters, structure type, Strukturbericht, Pearson, space group, structure type (Z)	Density (ρ/kg.m^{-3})	Electrical resistivity (ρ/μΩ.cm)	Dielectric permittivity [1MHz] (ε_r / nil)	Dielectric field strength (E_d/MV.m^{-1})	Dissipation or tangent loss factor ($tan\delta$)	Melting point (*m.p.*/°C)	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})	Coeff. linear thermal expansion (α/10^{-6}K^{-1})	Young's or elastic modulus (E/GPa)	Coulomb's or shear modulus (G/GPa)	Bulk or compression modulus (K/GPa)	Poisson ratio (ν)	Ultimate tensile strength (σ_{UTS}/MPa)	Flexural strength (π/MPa)	Compressive strength (σ/MPa)	Fracture toughness (K_{1C}/MPa.m$^{1/2}$)	Vickers or Knoop Hardness (HV or HK/GPa) (/HM)	Other physicochemical Properties, oxidation and corrosion resistance, and major uses.
Nitrides																						
Aluminum nitride	AlN [24304-00-5] 40.989	Hexagonal a = 311.0 pm c = 497.5 pm B4, *hP8*, $P6_3mc$, wurtzite type (Z = 2)	3255	10^{17}	n.a.	n.a.	n.a.	2230	29.96	820	5.3	346	n.a.	0.28	n.a.	270	n.a.	2068	2.79	11.77 (HM 9–10)	Insulator (E_g=4.26 eV). Decomposes with water, acids, and alkalis to $Al(OH)_3$ and NH_3. Crucible container for GaAs crystal growth
Beryllium nitride	α-Be_3N_2 [1304-54-7] 55.050	Cubic a = 814 pm $D5_3$, *c80*, Ia3, Mn_2O_3 type (Z = 16)	2710	n.a.	n.a.	n.a.	n.a.	2200	n.a.	1221	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Hard white or grayish crystal. Oxidizes in air above 600°C. Slowly decomposes in water, quickly in acids and alkalis with evolution of NH_3
Boron nitride	BN [10043-11-5] 24.818	Hexagonal a = 250.4 pm c = 666.1 pm B_3, *hP8*, $P6_3/mmc$, BN type (Z = 2)	2250	10^{19}	n.a.	n.a.	0.0002	2730 (dec.)	15.41	711	7.54	85.5	n.a.	0.11	n.a.	41–62	n.a.	310	5.0	2.26 (HM 2.0)	Insulator (E_g=7.5 eV). Crucibles for melting molten metals such as Na, B, Fe, Ni, Al, Si, Cu, Mg, Zn, In, Bi, Rb, Cd, Ge, and Sn. Corroded by molten metals U, Pt, V, Ce, Be, Mo, Mn, Cr, V, and Al. Attacked by molten salts PbO_2, Sb_2O_3, AsO_3, Bi_2O_3, KOH, and K_2CO_3. Used in furnace insulation-diffusion masks and passivation layers
Boron nitride (Borazon®, CBN)	BN 24.818	Cubic a = 361.5 pm	3430	1900 (2000°C)	2.54	n.a.	0.0002	1540	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	7000	n.a.	46.09–49.00 (HM 10)	Tiny reddish to black grains. Used as abrasive for grinding tool and die steels and high-alloy steels when chemical reactivity of diamonds is a problem
Chromium heminitride	Cr_2N [12053-27-9] 117.999	Hexagonal a = 274 pm c = 445 pm L'3, *hP3*, $P6_3/mmc$, Fe_2N type (Z = 1)	6800	76	n.a.	n.a.	n.a.	1661	22.5	630	9.36	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	11.77–15.40	
Chromium nitride	CrN [24094-93-7] 66.003	Cubic a = 415.0 pm B1, *cF8*, Fm3m, rock salt type (Z = 4)	6140	640	n.a.	n.a.	n.a.	1499 (dec.)	12.1	795	2.34	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	10.69	

Hafnium nitride	HfN [25817-87-2] 192.497	Cubic $a = 451.8$ pm B1, *cF8*, Fm3m, rock salt type ($Z = 4$)	13,840	33	n.a.	n.a.	3310	21.6	210	6.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	16.08 (HM 8–9)	Most refractory of all nitrides
Molybdenum heminitride	Mo_2N [12033-31-7] 205.887	Cubic $a = 416$ pm L'1, *cP5*, Pm3m, Fe_4N type ($Z = 2$)	9460	19.8	n.a.	n.a.	760–899	17.9	293	6.12	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	16.68	Temperature transition at 5.0 K
Molybdenum nitride	MoN [12033-19-1] 109.947	Hexagonal $a = 572.5$ pm $c = 560.8$ pm B_h, *hP2*, P6/mmm, WC type ($Z = 1$)	9180	n.a.	n.a.	n.a.	1749	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	650	
Niobium nitride	NbN [24621-21-4] 106.913	Cubic $a = 438.8$ pm B1, *cF8*, Fm3m, rock salt type ($Z = 4$)	8470	78	n.a.	n.a.	2575	3.63	n.a.	10.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	13.73 (HM>8)	Dark gray crystals. Transition temperature 15.2 K. Insoluble in HCL, HNO_3, and H_2SO_4 but attacked by hot caustic, lime, or strong alkalis evolving NH_3
Silicon nitride	β-Si_3N_4 [12033-89-5] 140.284	Hexagonal $a = 760.8$ pm $c = 291.1$ pm P6/3m	3170	10^6	n.a.	n.a.	1850	28	713	2.25	55	n.a.	0.25	n.a.	850	n.a.	6.1	n.a.	7.0–8.3	n.a.	n.a.	17 (HM>9)	Gray amorphous powder or crystals. Resistant to thermal shock. Good oxidation resistance up to 1500°C but decomposes into nitrogen and silicon above 1850°C. Excellent corrosion resistance to molten nonferrous metals such as Al, Pb, Zn, Cd, Bi, Rb, and Sn, and molten salts like NaCl-KCl, NaF, and silicate glasses. However, corroded by molten Mg, Ti, V, Cr, Fe, and Co, cryolite, KOH, and Na_2O
Silicon nitride (Nitrasil®)	α-Si_3N_4 [12033-89-5] 140.284	Hexagonal $a = 775.88$ pm $c = 561.30$ pm P31c	3184	10^{19}	9.4	n.a.	1900 (sub.)	17	700	2.5–3.3	304	n.a.	n.a.	0.26	400–580	750	n.a.	26–35 (HM>9)					
Tantalum heminitride	Ta_2N 375.901	Hexagonal $a = 306$ pm $c = 496$ pm L'3, *hP3*, $P6_3/mmc$, Fe_2N type (Z=1)	15,600	263	n.a.	n.a.	2980	10.04	126	5.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	31.38					Decomposed by KOH with evolution of NH_3
Tantalum nitride (ε)	TaN [12033-62-4] 194.955	Hexagonal $a = 519.1$ pm $c = 290.6$ pm	13,800	128–135	n.a.	n.a.	3093	8.31	210	3.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	10.89 (HM>8)					Bronze or black crystals. Transition temperature 1.8 K. Insoluble in water, slowly attacked by aqua regia, HF, and HNO_3
Thorium nitride	ThN [12033-65-7] 246.045	Cubic a = 515.9 B1, *cF8*, Fm3m, rock salt type ($Z = 4$)	11,560	20	n.a.	n.a.	2820	7.38	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	5.88					Gray solid; slowly hydrolyzed by water

Table 10.22. *(continued)*

IUPAC name (synonyms, common trade names)	Theoretical chemical formula, [CAS RN], relative molecular mass ($^{12}C = 12.000$)	Crystal system, lattice parameters, structure type, Strukturbericht, Pearson, space group, structure type (Z)	Density (ρ/kg.m^{-3})	Electrical resistivity (ρ/μΩ.cm)	Dielectric permittivity [1MHz] (ε_r / nil)	Dielectric field strength (E_d/MV.m^{-1})	Dissipation or tangent loss factor ($tan\delta$)	Melting point ($m.p.$/°C)	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})	Coeff. linear thermal expansion (α/10^{-6}K^{-1})	Young's or elastic modulus (E/GPa)	Coulomb's or shear modulus (G/GPa)	Bulk or compression modulus (K/GPa)	Poisson ratio (ν)	Ultimate tensile strength (σ_{UTS}/MPa)	Flexural strength (π/MPa)	Compressive strength (σ/MPa)	Fracture toughness (K_{1C}/MPa.m$^{1/2}$)	Vickers or Knoop Hardness (HV or HK/GPa) (/HM)	Other physicochemical Properties, oxidation and corrosion resistance, and major uses.
Thorium nitride	Th_3N_4 [12033-90-8]	Hexagonal a = 388 pm c = 618 pm $D5_{13}$, *hP5*, 3m1, La_2O_3 type (Z = 1)	10,400	n.a.	n.a.	n.a.	n.a.	1750	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
Titanium nitride	TiN [25583-20-4] 61.874	Cubic a = 424.6 pm B1, *cF8*, Fm3m, rock salt type (Z = 4)	5430	21.7	n.a.	n.a.	n.a.	2930 (dec.)	29.1	586	9.35	248	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	972	5.0	18.63 (HM 8–9)	Bronze powder. Transition temperature 4.2 K. Corrosion resistant to molten metals such as Al, Pb, Mg, Zn, Cd, and Bi. Corroded by molten Na, Rb, Ti, V, Cr, Mn, Sn, Ni, Cu, Fe, and Co. Dissolved by boiling aqua regia, decomposed by boiling alkalis evolving NH_3
Tungsten dinitride	WN_2 [60922-26-1] 211.853	Hexagonal a = 289.3 pm c = 282.6 pm	7700	n.a.	n.a.	n.a.	n.a.	600 (dec.)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Brown crystals
Tungsten heminitride	W_2N [12033-72-6] 381.687	Cubic a = 412 pm L'1, *cP5*, Pm3m, Fe_4N type (Z = 2)	17,700	n.a.	n.a.	n.a.	n.a.	982	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Gray crystals
Tungsten nitride	WN [12058-38-7]	Hexagonal	15,940	n.a.	n.a.	n.a.	n.a.	593	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
Uranium nitride	UN [25658-43-9] 252.096	Cubic a = 489.0 pm B1, *cF8*, Fm3m, rock salt type (Z = 4)	14,320	208	n.a.	n.a.	n.a.	2900	12.5	188	9.72	149	60	n.a.	0.24	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
Uranium nitride	U_3N_4 [12033-83-9] 518.259	Cubic a = 1070 pm $D5_3$, *cI80*, Ia3, Mn_2O_3 type (Z = 16)	11,240	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4.46		
Vanadium nitride	VN [24646-85-3] 64.949	Cubic a = 414.0 pm B1, *cF8*, Fm3m, rock salt type (Z = 4)	6102	86	n.a.	n.a.	n.a.	2360	11.25	586	8.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	14.91 (HM 9–10)	Black powder. Transition temperature 7.5 K. Soluble in aqua regia

Zirconium nitride	ZrN [25658-42-8] 105.231	Cubic $a = 457.7$ pm B1, *cF8*, Fm3m, rock salt type ($Z = 4$)	7349	13.6	n.a.	n.a.	n.a.	2980	20.9	377	7.24	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	979	n.a.	14.51 (HM>8)	Yellow solid. Transition temperature 9 K. Corrosion resistant to steel, basic slag, and cryolithe and molten metals such as Al, Pb, Mg, Zn, Cd, and Bi. Corroded by molten Be, Na, Rb, Ti, V, Cr, Mn, Sn, Ni, Cu, Fe, and Co. Soluble in concentrated HF, slowly soluble in hot H_2SO_4
Silicides																						
Chromium disilicide	$CrSi_2$ [12018-09-6] 108.167	Hexagonal a =442 pm $c = 635$ pm C40, *hP9*, P6$_2$22, $CrSi_2$ type ($Z = 3$)	4910	1400	n.a.	n.a.	n.a.	1490–1550	106	n.a.	13.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	9.77–11.08		
Chromium silicide	Cr_3Si [12018-36-9] 184.074	Cubic $a = 456$ pm A15, *cP8*, Pm3n, Cr_3Si type ($Z = 2$)	6430	45.5	n.a.	n.a.	n.a.	1770	n.a.	n.a.	10.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	9.86		
Hafnium disilicide	$HfSi_2$ [12401-56-8] 234.66	Orthorhombic $a = 369$ pm $b = 1446$ pm $c = 364$ pm C49, *oC12*, Cmcm, $ZrSi_2$ type ($Z = 4$)	8030	n.a.	n.a.	n.a.	n.a.	1699	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	8.48–9.12		
Molybdenum disilicide	$MoSi_2$ [12136-78-6] 152.11	Tetragonal $a = 319$ pm $c = 783$ pm C11b, *tI6*, I4/mmm, $MoSi_2$ type ($Z = 2$)	6260	21.5	n.a.	n.a.	n.a.	1870	58.9	n.a.	8.12	407	163	0.344	0.165	276	n.a.	2068–2415	n.a.	12.36	The compound is thermally stable in air up to 1000°C. Corrosion resistant to molten metals such as Zn, Pd, Ag, Bi, and Rb. Corroded by liquid metals Mg, Al, Si, V, Cr, Mn, Fe, Ni, Cu, Mo, and Ce	
Niobium disilicide	$NbSi_2$ [12034-80-9] 149.77	Hexagonal $a = 479$ pm $c = 658$ pm C40, *hP9*, P6$_2$22, $CrSi_2$ type ($Z = 3$)	5290	50.4	n.a.	n.a.	n.a.	2160	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	10.30		
Tantalum disilicide	$TaSi_2$ [12039-79-1] 237.119	Hexagonal $a = 477$ pm $c = 655$ pm C40, *hP9*, P6$_2$22, $CrSi_2$ type ($Z = 3$)	9140	8.5	n.a.	n.a.	n.a.	2299	n.a.	n.a.	8.8–9.54	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	11.77–15.69	Corroded by molten Ni	
Tantalum silicide	Ta_5Si_3 [12067-56-0] 988.992	Hexagonal $a = 747.4$ pm $c = 522.5$ pm $P6_3/mcm$	13,060		n.a.	n.a.	n.a.	2499	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	11.77–14.71	The compound is thermally stable in air up to 400°C	

Table 10.22. *(continued)*

IUPAC name (synonyms, common trade names)	Theoretical chemical formula, [CAS RN], relative molecular mass ($^{12}C = 12.000$)	Crystal system, lattice parameters, structure type, Strukturbericht, Pearson, space group, structure type (Z)	Density (ρ/kg.m^{-3})	Electrical resistivity (ρ/μΩ.cm)	Dielectric permittivity [1MHz] (ε_r / nil)	Dielectric field strength (E_d/MV.m^{-1})	Dissipation or tangent loss factor ($tan\delta$)	Melting point ($m.p.$/°C)	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})	Coeff. linear thermal expansion (α/10^{-6}K^{-1})	Young's or elastic modulus (E/GPa)	Coulomb's or shear modulus (G/GPa)	Bulk or compression modulus (K/GPa)	Poisson ratio (ν)	Ultimate tensile strength (σ_{UTS}/MPa)	Flexural strength (π/MPa)	Compressive strength (σ/MPa)	Fracture toughness (K_{1C}/MPa.m$^{1/2}$)	Vickers or Knoop Hardness (HV or HK/GPa) (/HM)	Other physicochemical Properties, oxidation and corrosion resistance, and major uses.	
Thorium disilicide	$ThSi_2$ [12067-54-8] 288.209	Tetragonal a =413 pm c =1435 pm Cc, tI12, I4/amd, $ThSi_2$ type ($Z = 4$)	7790	n.a.	n.a.	n.a.	n.a.	1850	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	10.98	Corrosion resistant to molten Cu; corroded by molten Ni	
Titanium disilicide	$TiSi_2$ [12039-83-7] 104.051	Orthorhombic a = 360pm b = 1376 pm c = 360 pm C49, *oC12*, Cmcm, $ZrSi_2$ type ($Z = 4$)	4150	123	n.a.	n.a.	n.a.	1499	n.a.	n.a.	10.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	10.19		
Titanium trisilicide	Ti_5Si_3 [12067-57-1] 323.657	Hexagonal a = 747 pm c = 516 pm $D8_8$, *hP16*, $P6_3/mcm$, Mn_5Si_3 type ($Z = 2$)	4320	55	n.a.	n.a.	n.a.	2120	n.a.	n.a.	11.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	9.67		
Tungsten disilicide	WSi_2 [12039-88-2] 240.01	Tetragonal a = 320 pm c = 781 pm C11b, *tI6*, I4/mmm, $MoSi_2$ type ($Z = 2$)	9870	33.4	n.a.	n.a.	n.a.	2165	n.a.	n.a.	8.28	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	10.69		
Tungsten silicide	W_5Si_3 [12039-95-1] 1003.46	Hexagonal a = 719 pm c = 485 pm $P6_3/mcm$	12,210	n.a.	n.a.	n.a.	n.a.	2320	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	7.55	Corroded by molten Ni	
Uranium disilicide	USi_2 294.200	Tetragonal a = 397 pm c = 1371 pm Cc, *tI12*, I4/amd, $ThSi_2$ type ($Z = 4$)	9250	n.a.	n.a.	n.a.	n.a.	1700	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	6.86		
Uranium silicide	β–U_3Si_2 770.258	Tetragonal a = 733 pm c = 390 pm D5a, *tP10*, P4/mbm, U_3Si_2 type ($Z = 2$)	12,200	150	n.a.	n.a.	n.a.	1666	14.7	n.a.	14.8	77.9	33.1	n.a.	0.170	n.a.	n.a.	n.a.	n.a.	n.a.	7.81		
Vanadium disilicide	VSi_2 [12039-87-1] 107.112	Hexagonal a = 456 pm c = 636 pm C40, *hP9*, $P6_222$, $CrSi_2$ type ($Z = 3$)	5100	9.5	n.a.	n.a.	n.a.	1699	n.a.	n.a.	11.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	13.73		

Vanadium silicide	V_3Si [12039-76-8] 180.9085	Cubic $a = 471$ pm A15, *cP8*, Pm3n, Cr_3Si type ($Z = 2$)	5740	203	n.a.	n.a.	1732	n.a.	35.6–39	795.5–880	8.0.	7.1–8.3	365–416	162–184	234–496	0.231–0.254	206–255	282–1084	2549–3103	3.5–5.0	20.59–29.42 (HM 9)				
Zirconium disilicide	$ZrSi_2$ [12039-90-6] 147.395	Orthorhombic $a = 372$ pm $b = 1469$ pm $c = 366$ pm C49, *oC12*, Cmcm, $ZrSi_2$ type ($Z = 4$)	4880	161	n.a.	n.a.	1604	n.a.	n.a.	n.a.	8.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	10.10				
Oxides																									
Aluminum sesquioxide (alumina, corundum, saphir)	α–Al_2O_3 [1344-28-1] [1302-74-5] 101.961	Trigonal (rhombohedral) $a = 475.91$ pm $c = 1298.94$ pm $D5_1$, *hR10*, R-3*c*, corundum type (Z=2)	3987	$2 \infty 10^{23}$	9.1–9.8	28–47	0.0005	2054													White and translucent hard material used as abrasive for grinding. Excellent electric insulator and also wear resistant. Insoluble in water and in strong mineral acids, readily soluble in strong alkali hydroxides, attacked by HF or NH_4HF_2. Owing to its corrosion resistance, in inert atmosphere, in molten metals such as Mg, Ca, Sr, Ba, Mn, Sn, Pb, Ga, Bi, As, Sb, Hg, Mo, W, Co, Ni, Pd, Pt, and U it is used as crucible container for these liquid metals. Alumina is readily attacked in an inert atmosphere by molten metals such as Li, Na, Be, Al, Si, Ti, Zr, Nb, Ta, and Cu. Maximum service temperature 1950°C				
Beryllium monoxide (berrylia)	BeO [1304-56-9] 25.011	Trigonal (hexagonal) $a = 270$ pm $c = 439$ pm B4, *hP4*, $P6_3mc$, wurtzite type ($Z = 2$)	3008–3030	$1.0 \infty 10^{22}$	6.8–7.66	11.8	0.0004	2550–2565	245–250	996.5	7.5–9.7	296.5–345	n.a.	n.a.	0.340	103.4	241–250	1551	3.68	14.71 (HM 9)	It is the only material with diamond that combines both excellent thermal shock resistance, high electrical resistivity, and high thermal conductivity, and hence is used for heat sinks in electronics. Beryllia is very soluble in water, but slowly in concentrated acids and alkalis. Highly toxic. Exhibits outstanding corrosion resistance to liquid metals Li, Na, Al, Ga, Pb, Ni, and Ir. Readily attacked by molten metals such as Be, Si, Ti, Zr, Nb, Ta, Mo, and W. Maximum service temperature 2400°C.				

Table 10.22. *(continued)*

IUPAC name (synonyms, common trade names)	Theoretical chemical formula, [CAS RN], relative molecular mass ($^{12}C = 12.000$)	Crystal system, lattice parameters, structure type, Strukturbericht, Pearson, space group, structure type (Z)	Density (ρ/kg.m^{-3})	Electrical resistivity (ρ/μΩ.cm)	Dielectric permittivity [1MHz] (ε_r / nil)	Dielectric field strength (E_d/MV.m^{-1})	Dissipation or tangent loss factor ($tan\delta$)	Melting point (*m.p.*/°C)	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})	Coeff. linear thermal expansion (α/10^{-6}K^{-1})	Young's or elastic modulus (E/GPa)	Coulomb's or shear modulus (G/GPa)	Bulk or compression modulus (K/GPa)	Poisson ratio (ν)	Ultimate tensile strength (σ_{UTS}/MPa)	Flexural strength (π/MPa)	Compressive strength (σ/MPa)	Fracture toughness (K_{1C}/MPa.m$^{1/2}$)	Vickers or Knoop Hardness (HV or HK/GPa) (/HM)	Other physicochemical Properties, oxidation and corrosion resistance, and major uses.
Calcium oxide (calcia, lime)	CaO [1305-78-8] 56.077	Cubic a = 481.08 pm B2, *cP2*, Pm3m, CsCl type (Z=1)	3320	1.0 ∞ 10^{14}	11.1	n.a.	n.a.	2927	8–16	753.1	3.88	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	5.49 (HM 4.5)	White or grayish ceramics. Readily absorbs CO_2 and water from air to form spent lime and calcium carbonate. Reacts readily with water to give $Ca(OH)_2$. Volumic expansion coefficient 0.225 × 10^{-9}.K^{-1}. Exhibits outstanding corrosion resistance to liquid metals Li and Na
Cerium dioxide (ceria, cerianite)	CeO_2 [1306-38-3] 172.114	Cubic a = 541.1 pm C1, *cF12*, Fm3m, fluorite type (Z = 4)	7650	10^{10}	n.a.	n.a.	n.a.	2340	n.a.	389	10.6	181	70.3	n.a.	0.311	n.a.	n.a.	n.a.	n.a.	n.a.	(HM 6)	Pale yellow cubic crystals. Abrasive for polishing glass, interference filters, antireflection coating. Insoluble in water, soluble in H_2SO_4 and HNO_3 but insoluble in diluted acid
Chromium oxide (eskolaite)	Cr_2O_3 [1308-38-9] 151.990	Trigonal (rhombohedral) a = 538 pm, 54°50′ $D5_3$, *hR10*, R3c, corundum type (Z = 2)	5220	1.3 ∞ 10^{9} (346°C)	n.a.	n.a.	n.a.	2330	n.a.	921.1	10.90	103	n.a.	n.a.	n.a.	n.a.	268	n.a.	3.9	29 (HM >8)	
Dysprosium oxide (dysprosia)	Dy_2O_3 [1308-87-8] 373.00	Cubic $D5_3$, *cI80*, Ia3, Mn_2O_3 type (Z = 16)	8300	n.a.	n.a.	n.a.	n.a.	2408	n.a.	n.a.	7.74.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
Europium oxide (europia)	Eu_2O_3 [1308-96-9] 351.928	Cubic $D5_3$, *cI80*, Ia3, Mn_2O_3 type (Z = 6)	7422	n.a.	n.a.	n.a.	n.a.	2350	n.a.	n.a.	7.02.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
Gadolinium oxide (gadolinia)	Gd_2O_3 [12064-62-9] 362.50	Cubic $D5_3$, *cI80*, Ia3, Mn_2O_3 type (Z = 16)	7630	n.a.	n.a.	n.a.	n.a.	2420	n.a.	276	10.44	124	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4.71	
Hafnium dioxide (hafnia)	HfO_2 [12055-23-1] 210.489	Monoclinic [1790°C] a = 511.56 pm b = 517.22 pm c = 529.48 pm C43, *mP12*, $P2_1/c$, baddeleyite type (Z = 4)	9680	5 ∞10^{15}	n.a.	n.a.	n.a.	2900	1.14	121	5.85	57	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	7.65–10.30	Monoclinic (baddeleyite) below 1790°C, tetragonal above 1790°C

Lanthanum dioxide (lanthania)	La_2O_3 [1312-81-8] 325.809	Trigonal (hexagonal) $D5_3$, *hP5*, P3m1), lanthania type ($Z = 1$)	6510	$1 \infty 10^{14}$ (550°C)	n.a.	n.a.	2315	n.a.	288.89	11.9	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Insoluble in water, soluble in diluted strong mineral acids
Magnesium monoxide (magnesia, periclase)	MgO [1309-48-4] 40.304	Cubic $a = 420$ pm B1, *cF8*, Fm3m, rock salt type ($Z = 4$)	3581	$1.3 \infty 10^{15}$	9.65–9.8	n.a.	2852	50–75	962.3	11.52	303.4	117–130	n.a.	0.33–0.36	200–300	441	1300–1379	1.8	7.35 (HM 5.5–6)	White ceramics, with a high reflective index in the visible and near-UV regions. Used as linings in steel furnaces. Crucible container for fluoride melts. Very slowly soluble in pure water but soluble in diluted strong mineral acids. Exhibits outstanding corrosion resistance in liquid metals Mg, Li, and Na. Readily attacked by molten metals Be, Si, Ti, Zr, Nb, and Ta. MgO reacts with water, CO_2, and diluted acids. Maximum service temperature 2400°C. Transmittance of 80% and n=1.75 in IR region 7 to 300 μm
Niobium pentaoxide (columbite, niobia)	Nb_2O_5 [1313-96-8] 265.810	Trigonal (rhombohedral) $a = 211.6$ pm $b = 382.2$ pm $c = 193.5$ pm columbite type	4470	$5.5 \infty 10^{12}$	n.a.	n.a.	1520	n.a.	502.41	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	14.71	Dielectric used in film supercapacitors. Insoluble in water, soluble in HF and in hot concentrated H_2SO_4
Samarium oxide (samaria)	Sm_2O_3 [12060-58-1] 348.72	Cubic $D5_3$, *cI80*, Ia3, Mn_2O_3 type ($Z = 16$)	7620	n.a.	n.a.	n.a.	n.a.	2.07	331	10.3	183	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4.30	
Silicium dioxide (silica, α–quartz)	α–SiO_2 [7631-86-9] [14808-60-7] 60.085	Trigonal (rhombohedral) $a = 491.27$ pm $c = 540.46$ pm C8, *hP9*, R-3c, α–quartz type (Z=3)	2202–2650	$1 \infty 10^{20}$	3.79	50	0.0002	1.38	787	0.55	72.95	29.9	n.a.	0.170	69–276	310	690–1380	0.9–1.2	5.39–12.36 (HM 7)	Colorless amorphous (i.e., fused silica) or crystalline (i.e., quartz) material having a low thermal expansion coefficient and excellent optical transmittance in far UV. Silica is insoluble in strong mineral acids and alkalis except HF, concentrated H_3PO_4, NH_4HF_2, concentrated alkali metal hydroxides. Owing to its good corrosion resistance to liquid metals such as Si, Ge, Sn, Pb, Ga, In, Tl, Rb, Bi, and Cd, it is used as crucible container for melting these metals, while silica is readily attacked in an inert atmosphere by molten metals such as Li, Na, K Mg, and Al. Quartz crystals are piezoelectric and pyroelectric. Maximum service temperature 1090°C

Table 10.22. *(continued)*

IUPAC name (synonyms, common trade names)	Theoretical chemical formula, [CAS RN], relative molecular mass ($^{12}C = 12.000$)	Crystal system, lattice parameters, structure type, Strukturbericht, Pearson, space group, structure type (Z)	Density (ρ/kg.m^{-3})	Electrical resistivity (ρ/μΩ.cm)	Dielectric permittivity [1MHz] (ε_r / nil)	Dielectric field strength (E_d/MV.m^{-1})	Dissipation or tangent loss factor ($tan\delta$)	Melting point (*m.p.*/°C)	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})	Coeff. linear thermal expansion (α/10^{-6}K^{-1})	Young's or elastic modulus (E/GPa)	Coulomb's or shear modulus (G/GPa)	Bulk or compression modulus (K/GPa)	Poisson ratio (ν)	Ultimate tensile strength (σ_{UTS}/MPa)	Flexural strength (π/MPa)	Compressive strength (σ/MPa)	Fracture toughness (K_{1C}/MPa.m$^{1/2}$)	Vickers or Knoop Hardness (HV or HK/GPa) (/HM)	Other physicochemical Properties, oxidation and corrosion resistance, and major uses.
Tantalum pentaoxide (tantalite, tantala)	Ta_2O_5 [1314-61-0] 441.893	Trigonal (rhombohedral) columbite type	8200	$1.0 \infty 10^{12}$	n.a.	n.a.	n.a.	1882	n.a.	301.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.9	n.a.	Dielectric used in film supercapacitors. Tantalum oxide is a high-refractive-index, low-absorption material used in making optical coatings in the near-UV (350 nm) to IR (8 μm). Insoluble in most chemicals except HF, HF-HNO_3 mixtures, oleum, fused alkali hydroxides (e.g., NaOH, KOH), and molten pyrosulfates
Thorium dioxide (thoria, thorianite)	ThO_2 [1314-20-1] 264.037	Cubic a = 559.52 pm C1, *cF12*, Fm3m, fluorite type (Z= 4)	9860	$4 \infty 10^{19}$	n.a.	n.a.	n.a.	3390	14.19	272.14	9.54	144.8	94.2	n.a.	0.280	96.5	n.a.	n.a.	1475	1.07	9.27 (HM 6.5)	Corrosion-resistant container material for molten metals Na, Hf, Ir, Ni, Mo, Mn, Th, and U. Corroded by liquid metals Be, Si, Ti, Zr, Nb, and Bi. Radioactive
Titanium dioxide (Anatase)	TiO_2 [13463-67-7] [1317-70-0] 79.866	Tetragonal a = 379.3 pm c = 951.2 pm C5, *tI12*, I4$_1$/amd, Anatase type (Z = 4) Ti-O: 191pm (2) 195 pm (4) Packing fraction: 70%	3900 [3890]	n.a.	n.a.	n.a.	n.a.	700°C (rutile)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	(HM 5.5–6)	Metastable over long periods of time despite being less thermodynamically stable than rutile. However, above 700°C, the irreversible and rapid monotropic conversion of anatase to rutile occurs. It exhibits a greater transparency in the near-UV than rutile. With an absorption edge at 385 nm, anatase absorbs less light at the blue end of the visible spectrum and has a blue tone
Titanium dioxide (brookite)	TiO_2 [13463-67-7] [12188-41-9] 79.866	Orthorhombic a = 545.6 pm b = 918.2 pm c = 514.3 pm C21, *oP24*, Pbca brookite type, Z = 8 Ti-O: 184 pm – 203 pm	4130					1750													(HM 5.5–6.0)	

Titanium dioxide (rutile, titania)	TiO_2 [13463-67-7] [1317-80-2] 79.866	Tetragonal $a = 459.37$ pm $c = 296.18$ pm C4, *tP6*, P4/mnm rutile type ($Z = 2$) Ti-O: 194.4 pm (4) 198.8 pm (2), packing fraction 77%	4240 [4250]	10^{9}	110–117	769	n.a.	1847	10.4 (// c) 7.4 (⊥ c)	711	7.14	248–282	111	206–282	0.278	69–103	340	800–940	2.8	10.89 (HM 7–7.5)	White solid that exhibits a high refractive index, even higher than that of diamond. Transparent from visible to near-infrared radiation (i.e., 408 nm to 5000 nm). On the blue end of the visible spectrum the strong absorption band at 385 nm renders rutile powder slightly brighter than anatase, explaining its typical yellow undertone. When heated in air to 900°C the powdered material becomes lemon-yellow and exhibits a maximum absorption edge at 476 nm but coloring disappears on cooling. Doped rutile is phototropic, i.e., it exhibits a reversible darkening when exposed to light. Readily soluble in HF and in concentrated H_2SO_4. Reacts rapidly in molten alkali hydroxides and fused alkali carbonates. Corrosion resistant to liquid Ni and Mo. Readily attacked in an inert atmosphere by molten Be, Si, Ti, Zr, Nb, and Ta	
Titanium monoxide (hongquiite)	TiO [12137-20-1] 63.6694	Cubic $a = 417$ pm B1, *cF8*, Fm3m rock salt type ($Z = 4$)	4888					1750		628	9.19									Gold-bronze solid. Prepared by mixing stoichiometric amounts of Ti and TiO_2 heated in a Mo-crucible at 1600°C or by the reduction of TiO_2 with H_2 under pressure at 130 atm and 2000°C. Slightly paramagnetic solid with $\chi_m = +88 \times 10^{-6}$ emu	
Titanium sesquioxide	Ti_2O_3 [1344-54-3] 143.3382	Trigonal (rhombohedral) $a = 515.5$ pm $c = 1361$ pm $D5_1$, *hR10*, R-3c corundum type (Z=2)	4486					1839		679										Dark-violet to purple-violet solid. It can be prepared by mixing stoichiometric amounts of Ti and TiO_2 heated in a Mo-crucible at 1600°C. Slightly paramagnetic solid with $\chi_m = +63 \times 10^{-6}$ emu	

Table 10.22. *(continued)*

IUPAC name (synonyms, common trade names)	Theoretical chemical formula, [CAS RN], relative molecular mass ($^{12}C = 12.000$)	Crystal system, lattice parameters, structure type, Strukturbericht, Pearson, space group, structure type (Z)	Density (ρ/kg.m^{-3})	Electrical resistivity (ρ/μΩ.cm)	Dielectric permittivity [1MHz] (ε_r / nil)	Dielectric field strength (E_d/MV.m^{-1})	Dissipation or tangent loss factor ($tan\delta$)	Melting point ($m.p.$/°C)	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})	Coeff. linear thermal expansion (α/10^{-6}K^{-1})	Young's or elastic modulus (E/GPa)	Coulomb's or shear modulus (G/GPa)	Bulk or compression modulus (K/GPa)	Poisson ratio (ν)	Ultimate tensile strength (σ_{UTS}/MPa)	Flexural strength (π/MPa)	Compressive strength (σ/MPa)	Fracture toughness (K_{1C}/MPa.m$^{1/2}$)	Vickers or Knoop Hardness (HV or HK/GPa) (/HM)	Other physicochemical Properties, oxidation and corrosion resistance, and major uses.
Trititanium pentoxide (anasovite)	Ti_3O_5 [12065-65-5] 223.0070	Dimorphic (120°C) Low temperature: anasovite type monoclinic C2/m (Z = 4) mC32 a = 975.2 pm b = 380.2 pm c = 944.2 pm β = 91.55° High temperature: pseudobrookite orthorhombic Cc mC32	4900					1777														Dark blue crystals. Anasovite Type II is similar to that identified in titania slags.[29] Can be stabilized at room temperature with a small amount of iron
Uranium dioxide (uraninite)	UO_2 [1344-57-6] 270.028	Cubic a = 546.82 pm C1, *cF12*, Fm3m, fluorite type (Z= 4)	10,960	3.8×10^{10}	n.a.	n.a.	n.a.	2880	10.04	234.31	11.2	145	74.2	n.a.	0.302	n.a.	n.a.	n.a.	5.88 (HM 6–7)	Used in nuclear power reactors as nuclear-fuel-sintered element containing either natural or enriched uranium
Yttrium oxide (yttria)	Y_2O_3 [1314-36-9] 225.81	Trigonal (Hexagonal) $D5_3$, *hP5*, P3m1, lanthania type (Z = 1)	5030	n.a.	n.a.	n.a.	n.a.	2439	n.a.	439.62	8.10	114.5	48.3	n.a.	0.186	n.a.	n.a.	393	0.71	6.86	Yttria is a medium-refractive-index, low-absorption material used for optical coating in the near-UV (300 nm) to IR (12 μm) regions and hence used to protect Al and Ag mirrors. Used for crucibles containing molten lithium
Zirconium dioxide (baddeleyite, monoclinic zirconia)	ZrO_2 [1314-23-4] [12036-23-6] 123.223	Monoclinic a = 514.54 pm b = 520.75 pm c = 531.07 pm 99.23° C43, *mP12*, $P2_1/c$, baddeleyite type (Z = 4)	5850	2.3×10^{10}	n.a.	n.a.	n.a.	2710	n.a.	711	7.56	241	97	n.a.	0.337	n.a.	2068	9.2	11.77 (HM 6.5)	Monoclinic zirconia (baddeleyite structure) stable below 1197°C, tetragonal zirconia (rutile structure) stable between 1197 and 2300°C, cubic zirconia (fluorine structure) stable above 2300°C or at lower temperature if stabilized by addition of magnesia, calcia or yttria. Maximum service temperature 2400°C. Zirconia starts to act as an oxygen anion conductor at 1200°C. Highly
Zirconium dioxide [tetragonal zirconia phase (TZP), > 1170°C]	ZrO_2 [1314-23-4] 123.223	Tetragonal C4, *tP6* $P4_2/mnm$, rutile type (Z=2)	5680–6050	7.7×10^7	n.a.	n.a.	n.a.	2710	n.a.	n.a.	10–11	200–210	n.a.	n.a.	0.310	n.a.	800–1200	>2900	7–12	12.5	

Zirconium dioxide [yttria-stabilized zirconia (YSZ) with 8–10 mol.% Y_2O_3]	ZrO_2 [1314-23-4] [64417-98-7] 123.223	Cubic C1, *cF12*, Fm3m, fluorite type (Z= 4)	6045	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	corrosion resistant to molten metals such as Bi, Hf, Ir, Pt, Fe, Ni, Mo, Pu, and V. Strongly attacked by liquid metals Be, Li, Na, K, Si, Ti, Zr, and Nb. Insoluble in water, but slowly soluble in HCl and HNO_3; soluble in boiling concentrated H_2SO_4 and alkali hydroxides but readily attacked by HF
Zirconium dioxide [partially stabilized zirconia (PSZ) with MgO]	ZrO_2 [1314-23-4] [64417-98-7] 123.223	Cubic C1, *cF12*, Fm3m, fluorite type (Z = 4)	5800–6045	n.a.	24.7	400–480	n.a.	2710	1.8	400	10.1	200	n.a.	n.a.	0.230	700	690	1850	9.0–9.5	15.69	
Zirconium dioxide TTZ (stabilized Y_2O_3)	ZrO_2 [1314-23-4] [64417-98-7] 123.223	Cubic C1, *cF12*, Fm3m, fluorite type (Z = 4)	6045	n.a.	n.a.	n.a.	n.a.	2710	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	9.2–10	n.a.	

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10.9 Glasses

10.9.1 Definitions

Glass is, from a thermodynamic point of view, a ***supercooled liquid***, i.e., a molten liquid cooled at a rate sufficiently rapid to fix the random microscopic organization of a liquid and avoid the crystallization process to operate. Therefore, by contrast with crystallized solids, glasses do not exhibit a clear melting temperature and the structural change is only reported by an inflection in the temperature-time curve. This change is called the ***glass transition temperature***. As a general rule, glasses are amorphous inorganic solids usually made of silicates, but other inorganic or organic compounds can exhibit a vitreous structure (e.g., sulfides, polymers). As a general rule, commercial glasses are hard but both brittle and thermal-shock-sensitive materials, excellent electrical insulators, optically transparent media, and exhibit for certain particular chemical compositions (e.g., ***Vycor®*** and borosilicated glasses, such as ***Pyrex®***) an excellent corrosion resistance to a wide range of chemicals except hydrofluoric acid, ammonium fluoride, and strong alkali-metal hydroxides and other strong alkalis. Owing to their good transmission in the visible range, glasses are extensively used for optical lenses, sight lenses, and windows. while corrosion-resistant glasses are widely used for cookware and laboratory glassware. The basic components of silicate glasses are silica, SiO_2 (e.g., from siliceous sand), lime, CaO (i.e., from fired limestone, $CaCO_3$), and soda, Na_2O (i.e., from soda ash, Na_2CO_3). Other oxides are used for special purposes such as boric acid (B_2O_3), potash (K_2O), baria (BaO), and lithia (Li_2O), while colored glasses require minute additions of transition-metal oxides (e.g., FeO, Co_2O_3).

Silicate glasses can be grouped into the following categories: **A-glass** (i.e., high alkali or soda-lime), **C-glass** (i.e., chemical resistant), **E-glass** (i.e., calcium alumino borosilicate or borosilicated glasses), and **S-glass** (i.e., high strength magnesium alumino silicate).

10.9.2 Physical Properties of Glasses

See Table 10.23, pages 672–675.

10.9.3 Glassmaking Processes

The majority of industrial glass is produced by continuous melting processes, while batch-type processes are restricted to customized formulations for special purposes.

Large-scale production of industrial glasses utilizes huge melting crucibles with a rectangular shape called glass tanks that are heated from the bottom and sidewalls by natural gas or oil burners; sometimes auxiliary electric heaters immersed in the melt (i.e., booster electrodes) are used to provide additional heat. The temperature of the melt can be as high as 1660°C to ensure the complete melting of alumina-rich raw materials (Ca-feldspars); the specific energy consumption is about 2.8 kWh/kg of glass. Commercial glass tanks can hold up to 1200 tonnes of molten glass. The thick bottom and sidewalls are built with refractory materials, usually mullite bricks, while electrofused alumina-silica-zirconia bricks are used for the inner layer, which is in direct contact with the melt. The vault or cupola is usually made of silica bricks. The glass tank is divided into two distinct sections called the ***melting end*** where the feed (i.e., cullet and raw materials) is introduced, while in the second section, called the ***working or refining end***, the molten glass reaches its working viscosity. The division between the two sections can be either permanent with a refractory barrier or using mobile baffles.

Table 10.23. Physical properties of selected commercial glasses

Glass trade name	Chemical composition (wt.%)	Density (kg.m^{-3})	Young's modulus (E/GPa)	Poisson ratio (ν/nil)	Knoop hardness (HK)[30]	Thermal conductivity (k/W.m^{-1}.K^{-1})	Specific heat capacity (c_p/J.kg^{-1}.K^{-1})	Coefficient linear thermal expansion (0–300°C) (10^{-6}K^{-1})	Strain point (/°C)[31]	Annealing point (°C)[32]	Softening point (°C)[33]	Working point (°C)[34]	Continuous operating temperature (°C)	Refractive index at 589.3nm (n_D/nil)	Relative permittivity at 1MHz (ε_r/nil)	Dielectric field strength (E_d/MV.m^{-1})	Loss factor (tanδ/nil)	Electrical volume resistivity (Ω.m)
Corning® 0080 (light bulb)	$73SiO_2$-$17Na_2O$-$5CaO$-$4MgO$-$1Al_2O_3$	2470	71	0.22	465	n.a.		9.35	473	514	696	1005	110	1.512	7.2	n.a.	0.009	$10^{12.8}$
Corning® 0120 (potash soda lead glass)	$56SiO_2$-$29PbO$-$9K_2O$-$4Na_2O$-$2Al_2O_3$	3050	59	0.22	382			8.95	395	435	630	985		1.560	6.7		0.008	10^{17}
Corning® 0137 (potash soda lead glass)	$52.5SiO_2$-$28PbO$-$13K_2O$-$5SrO$-$1Al_2O_3$-$0.5Na_2O$	3180	n.a.	0.22				9.70	436	478	661	977		1.570				
Corning® 0138 (potash soda lead glass)	$54SiO_2$-$23PbO$-$8K_2O$-$6Na_2O$-$5SrO$-$2Al_2O_3$-$3CaO$-$2MgO$	3020	n.a.	0.22				9.85	450	490	670			1.563				
Corning® 0160 (crystal glass)	$56SiO_2$-$31PbO$-$8Na_2O$-$5SrO$-$4K_2O$-$1Al_2O_3$-$1Li_2O$-$1Sb_2O_3$-$1As_2O_3$	3090	n.a.	0.22				9.30	367	405	583			1.569				
Corning® 0281 (glassware)	$74SiO_2$-$14Na_2O$-$9CaO$-$1Al_2O_3$-$1B_2O_3$-$0.3Sb_2O_3$-$0.1As_2O_3$	2570		0.22				8.7	500	540	719			1.515				
Corning® 0317 (aircraft window)	$61SiO_2$-$17Al_2O_3$-$13Na_2O$-$3K_2O$-$3MgO$-$1TiO_2$-$1As_2O_3$-$0.4CaO$	2480	73	0.22				8.7	574	624	871			1.506				
Corning® 0320 (tape reel)	$63SiO_2$-$12Al_2O_3$-$13B_2O_3$-$6Na_2O$-$5Li_2O$	2450		0.22				7.07	463	493	638							
Corning® 0331 (centrifuge tubes)	$66SiO_2$-$21Al_2O_3$-$9Na_2O$-$4Li_2O$-$1MgO$-$0.2K_2O$	2380		0.22				7.55	510	548								
Corning® 6720 (tableware)	$60SiO_2$-$10Al_2O_3$-$10ZnO$-$8Na_2O$-$5CaO$-$2K_2O$-$1B_2O_3$	2410																
Corning® 7570 (high leaded glass)	$74PbO$-$12B_2O_3$-$11Al_2O_3$-$3SiO_2$	5420	56	0.28	n.a.	n.a.		8.40	342	363	440	558	100	1.860	15		0.0022	10^{17}

Corning® 8078 (ophthalmic glass)	$44SiO_2$-$24PbO$-$21BaO$-$6Na_2O$-$4ZnO$-$1CaO$-$5ZrO2$-$3TiO_2$-$2La_2O_3$-$0.1Sb_2O_3$-$0.1As_2O_3$																	
E-Glass (electrical glass)	$54SiO_2$-$14Al_2O_3$-$10B_2O_3$-$17.5CaO$-$4.5MgO$	2600	72					5.0					600		6.1			
C-Glass (chemically resistant glass)	$65SiO_2$-$4Al_2O_3$-$5.5B_2O_3$-$14CaO$-$3MgO$-$8Na_2O$-$0.5K_2O$																	
S-Glass (high-strength glass)	$65SiO_2$-$25Al_2O_3$-$10MgO$	2490	87					5.6					760		5.2			
Corning® 9025 (cathodic ray tube panel)	$68SiO_2$-$12B_2O_3$-$4Al_2O_3$-$6K_2O$-$5Na_2O$-$3Li_2O$-$1TiO_2$-$1CeO_2$																	
Corning® 9068 (color TV panel)	$65SiO_2$-$10SrO$-$9K_2O$-$7Na_2O$-$2Al_2O_3$-$2CaO$-$2BaO$-$2PbO$-$1MgO$-$1TiO_2$-$1CeO_2$																	
Float glass (soda lime glass)	$74SiO_2$-$15Na_2O$-$5CaO$-$4MgO$-$1Al_2O_3$	2530	72	0.23	n.a.	0.937		8.90	514	546	726	n.a.	230	1.523	n.a.	n.a.	n.a.	n.a.
Kimble®EG11	Leaded glass	2850	n.a	n.a.	n.a.			10.80	394	434	626	980	n.a.	1.540	n.a.	n.a.	n.a.	10^9
Macor® (machinable glass)	$46SiO_2$-$17MgO$-$16Al_2O_3$-$10K_2O$-$7B_2O_3$-$4F$ (55 wt.% fluorophlogopite and 45 wt.% borosilicate glass)	2520	66.9	0.29		1.46	790	9.30					800 (1000)		6.03	9.40	0.0047	10^{16}
Pyrex® 0211 (microsheet glass)	$65SiO_2$-$2Al_2O_3$-$5.9CaO$-$7ZnO$-$9B_2O_3$-$7Na_2O$-$7K_2O$-$3TiO_2$	2570	76	0.22	593	0.98		7.38	508	550	720	1008		1.523	6.7		0.005	
Pyrex® 7059 (substrate glass)	$49SiO_2$-$25BaO$-$15B_2O_3$-$10Al_2O_3$-$1As_2O_3$	2760						4.60	593	639	844			1.533				
Pyrex® 7070	$72SiO_2$-$25B_2O_3$-$1Al_2O_3$-$1K_2O$-$0.5Li_2O$-$0.5Na_2O$	2130	52	0.22	n.a.			3.20	456	496	n.a.	n.a.	230	1.469	4.1	n.a.	0.006	10^{17}
Pyrex®7740 (Labware)	$80.6SiO_2$-$13B_2O_3$-$4Na_2O$-$2.3Al_2O_3$-$0.1K_2O$	2230	76	0.20	418	1.13		3.25	510	560	821	1252	230	1.474	4.6	n.a.	0.005	10^{17}
Pyrex®7789	$81SiO_2$-$13B_2O_3$-$3Na_2O$-$2Al_2O_3$-$1K_2O$	2220	64.3	n.a.	n.a.	n.a.		3.25	510	560	815	n.a.	n.a.	1.474				
Pyrex®7799	$70SiO_2$-$10B_2O_3$-$9Na_2O$-$6Al_2O_3$-$2BaO$-$1K_2O$-$1CaO$-$0.5MgO$-$0.5ZnO$	2470						6.20	525	560	740							
Pyrex®7800 (pharmaceutical glass)	$72SiO_2$-$11B_2O_3$-$7Na_2O$-$6Al_2O_3$-$2CaO$-$1K_2O$-$1BaO$	2340	n.a.	n.a.														

Table 10.23. *(continued)*

Glass trade name	Chemical composition (wt.%)	Density ($kg.m^{-3}$)	Young's modulus (E/GPa)	Poisson ratio (ν/nil)	Knoop hardness (HK)[30]	Thermal conductivity (k/$W.m^{-1}.K^{-1}$)	Specific heat capacity (c_p/$J.kg^{-1}.K^{-1}$)	Coefficient linear thermal expansion (0–300°C) ($10^{-6}K^{-1}$)	Strain point (/°C)[31]	Annealing point (°C)[32]	Softening point (°C)[33]	Working point (°C)[34]	Continuous operating temperature (°C)	Refractive index at 589.3nm (n_D/nil)	Relative permittivity at 1MHz (ε_r/nil)	Dielectric field strength (E_d/$MV.m^{-1}$)	Loss factor (tanδ/nil)	Electrical volume resistivity (Ω.m)
Pyrex®7913 (Vycor® HT)	$96.5SiO_2$-$3B_2O_3$-$0.5Al_2O_3$	2180	89	0.19	487	0.19		0.552–0.75	890	1020	1530	n.a.	900	1.458	3.8		0.0015	10^{17}
Pyrex®plus		2302			438			5.70	467	502	676			1.492				
Robax® (fire-resistant glass)	Pyroceramics	2580	93	0.25	n.a.	1.6	800	0.5			n.a.		680					
Sapphire glass	fused Al_2O_3	3980	379	0.29	1500	16–23		n.a.							9–11		48	10^{18}
Schott®BaK1 (barium crown)		3190	73	0.252	530	0.795	687	8.60						1.5725				
Schott®BK1 (borosilicate crown)		2460	74	0.210	560	1.069	825	8.80						1.5101				
Schott®BK7 (borosilicate crown)		2510	82	0.206	610	1.114	858	8.30						1.5168				
Schott®FK3 (fluoro crown)		2270	46	0.243	380	0.90	840	9.40						1.4650				
Schott®FK5 (fluoro crown)		2450	62	0.232	520	0.925	808	10.00						1.4875				
Schott®FK51 (fluoro crown)		3730	81	0.293	430	0.911	636	15.30						1.4866				
Schott®FK52 (fluoro crown)		3640	78	0.291	400	0.861	716	16.00						1.4861				
Schott®FK54 (fluoro crown)		3180	76	0.286	390	n.a.	n.a.	16.50						1.4370				
Schott®K5 (crown)		2590	71	0.224	530	0.950	783	9.60						1.5225				

Schott®KF9 (crown flint)		2710	67	0.202	490	1.160	490	7.90						1.5474					
Schott®LaK9 (lanthanum flint)		3510	110	0.285	700	0.908	649	7.50						1.6910					
Schott®LF5 (lanthanum flint)		3220	59	0.223	450	0.866	657	10.60						1.5814					
Schott®PK3 (phosphate crown)		2590	84	0.209	640	1.193	779	8.30						1.5254					
Schott®PK50 (phosphate crown)		2590	66	0.235	430	0.772	812	10.30						1.5205					
Schott®PSK3 (heavy phosphate crown)		2910	84	0.226	630	0.990	682	7.30						1.5523					
Schott®SF11 (heavy flint)		4740	66	0.235	450	0.744	450	6.80						1.7845					
Schott®SF63 (heavy flint)		4620	58	0.235	390	0.744	431	9.00						1.7484					
Schott®SK2 (heavy crown)		3550	78	0.263	550	0.776	595	7.10						1.6074					
Schott®ZKN7		2490	70	0.214	530	1.042	770	5.20						1.5085					

[30] Microhardness 100-g-force load
[31] For a dynamic viscosity of $10^{15.5}$Pa.s
[32] For a dynamic viscosity of 10^{13}Pa.s
[33] For a dynamic viscosity of $10^{8.6}$Pa.s
[34] For a dynamic viscosity of 10^{4}Pa.s

Cardarelli, F. (2008) Materials Handbook. A Concise Desktop Reference, 2nd Edition. Springer London.

Float glass (annealed glass). Historically, two techniques were used to produce sheets of glass. **Flat glass** was obtained by extruding and rolling a softened mass of glass, while **cylinder glass** was obtained by blowing molten glass into a cylindrical iron mold. The ends were cut and removed while a cut was made on the overall length of the cylinder. The cut cylinder was then placed in an oven, where the cylinder bent flat into a glass sheet. In both processes, from an optical point of view, the surfaces were rarely parallel, leading to optical distortions. By contrast, today 90% of the flat glass produced worldwide is obtained by the ***float glass process*** invented in the 1950s by Sir Alastair Pilkington of Pilkington Glass Co. In the float glass process, molten glass exiting a melting furnace is poured onto a bath of molten tin metal. The glass floats on the specular surface of the molten tin and levels out as it spreads along the bath, providing a smooth finish on both sides. The glass cools and slowly solidifies as it travels over the molten tin and leaves the tin bath in a continuous ribbon. The glass is then fire-polished. The finished product has near-perfect parallel surfaces.The only drawback of annealed glass is that upon mechanical stress it breaks into large and sharp pieces that can cause serious injury. For that reason, building codes worldwide prohibit the use of annealed glass where there is a high risk of breakage and injury.

Tempered glass (toughened glass, safety glass). Tempered glass is obtained after applying a thermal tempering process to annealed glass. The glass is cut to the required size and any required processing such as polishing or drilling is carried out before the tempering process begins. The hot glass at 600°C coming from an annealing furnace is placed onto a roller table. The glass is then quenched with forced cold air convection. This rapidly cools the glass surface below its annealing point, causing it to harden and contract, while the inner core of the glass remains free to flow for a short time. The final contraction of the inner layer induces compressive stresses in the surface of the glass balanced by tensile stresses in the body of the glass. This typical pattern of cooling can be observed under polarized light. Tempered glass exhibits typically a mechanical strength six times that of annealed glass and hence it is also called ***toughened glass***. However, this increased mechanical strength has a drawback. Due to the balanced stresses in the glass, any damage to the glass edges will result in the glass shattering into small sized pieces, and for that reason it is also called ***safety glass*** under the tradename ***Securit®***. Therefore, the glass must be cut to size before toughening and cannot be reworked once tempered. Moreover, the toughened glass surface is less hard than annealed glass and more prone to scratching.

Laminated glass. This multilayered composite material was first invented in 1903 by the French chemist Edouard Benedictus, who had been inspired by the breaking resistance of a glass flask coated with a layer of cellulose nitrate. Today, laminated glass is currently produced by bonding two or more layers of ordinary annealed glass together with a plastic interlayer of polyvinyl butyral (PVB). The polymer is sandwiched by the glass, which is then heated to around 70°C and passed through rollers to expel any air pockets and form the initial bond. A typical laminate has a 3-mm layer of glass, 0.38-mm interlayer, and another 3-mm layer of glass. This gives a final product that would be referred to as 6.38 laminated glass. The plastic interlayer keeps the two sheets of glass tightly bound even when broken, and its high strength prevents the glass from breaking up into large sharp pieces. Multiple laminates and thicker glass increase the strength. Bulletproof glass panels, made up of thick glass and several interlayers, can be as thick as 50 mm. The plastic interlayer also gives the glass a much higher acoustic insulation rating due to the damping effect.

10.9.4 Further Reading

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10.10 Proppants

10.10.1 Fracturing Techniques in Oil-Well Production

Under the constant pressure of the market and the prediction of long-term depletion of oil resources, the oil and gas industry has constantly increased the productivity and injectivity of production wells. For instance, today, by increasing the drilling depth, it is possible to recover oil and natural gas from remote and shallow reservoirs. However, to recover fossil fuels more efficiently from existing or new oil fields exhibiting low original permeability, some additional techniques must be used for better results. Actually, in many cases including severe damage around well-bore, complex beds, layered unconnected reservoirs, or laminated reservoirs with low permeability, the best known techniques for the treatment of reservoir beds are the ***fracturing technologies***, which provide the only stimulation method possible. These techniques will be briefly described in the next several paragraphs. There are basically two methods in the industry to stimulate well production by extensive improvement of the inflow conditions in a reservoir bed[35]: ***hydraulic fracturing*** and, to a lesser extent, ***pressure acidizing***, which is restricted to carbonated rocks (e.g., limestones and dolomites). As mentioned previously, the aim of both types of stimulation is to improve the cumulative production versus time behavior of an oil well.

10.10.1.1 Hydraulic Fracturing

This technique was developed by the oil industry in the 1940s for opening up tight reservoir[36] rocks to improve product recovery. It consists in pumping and injecting a fluid into the production well until the hydrostatic pressure increases to a level sufficient to expand the strata and fracture the rock, which results in the creation of a network of cracks in the rock formation. The pumping rate is high enough to overcome the maximum rate of fluid loss in the medium to be fractured. The fractures produced are generally only a few millimeters wide, but they may be either horizontal or vertical depending on the path of least resistance. With a widening fracture, the oil increasingly migrates into the pore space of the rocks. Therefore, the presence of high-conductivity fractures affects the overall oil mass transfer efficiency, and they have a significant impact on reservoir performance. To insure the success of reservoir-bed treatment, a sufficient depth of penetration must be achieved originating at the well bore and extending into the rock mass. Usually, a penetration depth of 40 to 70 m is common. After the porous rock has been fractured, it is necessary to prop open the newly formed cracks to act against the closure stress in order to facilitate the continued flow of gas and oil and to avoid the catastrophic collapse of reservoir walls due to the elevated surrounding lithostatic pressure. If the cracks were not propped open, they would close under the overburden. The most common technique consist in pumping a slurry made of a mixture of viscous carrier fluid (i.e., frac fluid: water or brines) and solid particulate materials into the

[35] Rischmuller, H. (1993) *Resources of Oil and Gas*. In: *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A23. VCH, Weinheim, p. 183.
[36] The reservoir is the underground formation where oil and gas has accumulated. It consists of a porous rock to hold the oil or gas, and an impervious cap rock that prevents them to escape.

fractured formation. The particulate materials are called ***propping agent*** or, most commonly, ***proppants***. Note that at the end of the treatment, the proppant slurry is displaced from the well bore and tubing by a clean flush fluid. However, the volume of flush fluid must be accurately determined so as not to release the proppants into the reservoir. In conclusion, proppants are agents that keep cracks open against closure stresses, avoid the collapse of reservoir walls, and insure an efficient mass transfer for both oil and gas while the production well is moved to another location. Note that hydraulic fracturing is used not only in oil and gas industry but also in hydrogeology to improve the performance of aquifers.

10.10.1.2 Pressure Acidizing

This method uses an aqueous acidic solution instead of brines or water for creating unpropped fractures. To do this, a greater increase in permeability than with common hydraulic fracturing is achieved by chemical dissolution of a part of the carbonate matrix along the fracture walls. Obviously, this treatment can only be used in the case of carbonated formations, such as limestones or dolomites. The most common acidic agents are aqueous solutions of hydrochloric acid (5 to 15 wt.% HCl), hydrofluoric acid (1 to 6 wt.% HF), acetic acid, citric acid, and surfactants. The surfactants are used as dispersing agents to promote the dispersion of solids, to improve the wettability of the rock, and to prevent emulsification. To determine whether acidizing or fracturing will yield the greatest economic benefit, the current condition of the well must be known. This includes knowledge of the undamaged production capacity of the reservoir and the type of damage in existence including the severity and cause of the damage. Worldwide, acidizing has about a 50% success rate, which is believed to be due to a lack of knowledge about the true well condition. On the other hand, fracturing can result in substantially greater improvement in productivity than acidizing just to remove the skin damage, but at a much higher cost. Acidizing is a good stimulation candidate in moderate to high permeability reservoirs that show substantial damage after completion. If there is a damaged zone around the well bore where effective permeability is reduced, acidizing can increase productivity by as much as fivefold, depending on the degree and depth of damage. On the other hand, if acidizing is used to increase permeability above the average reservoir effective permeability, very little stimulation benefit results. Increasing near-well-bore permeability by even an order of magnitude results in a less than twofold productivity improvement.

In conclusion, these two techniques increase economically recoverable reserves and improve vertical communication in layered and unconnected reservoirs. Reserves can be increased either by increasing the flow capacity of an uneconomic well or by increasing the drainage radius of a well or by contacting producing layers that are not connected to the well through perforations. Economic benefit can also be obtained by accelerating production from low-permeability reservoirs. Sweep efficiency can be increased by forming line sources or sinks for injection or production.

10.10.2 Proppant and Frac Fluid Selection Criteria

10.10.2.1 Proppant Materials

As a general rule, not all materials can be used as efficient propping agents. Actually, due to the existing geothermal gradient (e.g., 30°C/km) and lithostatic pressure (e.g., 23 MPa/km) in sedimentary basins, a suitable proppant material must withstand both these harsh conditions (i.e., high bottom temperature and elevated pressure) encountered in deep wells (up to 6 km) and insure the good mass transfer of oil and gas. Hence, the critical characteristics and properties that must be taken into account for the proper selection of proppants are listed below:

- high crushing or compressive strength;
- both elevated hardness and fracture toughness;
- high gas and oil permeability;
- narrow particle-size distribution;
- low specific surface area;
- low bulk and tap densities;
- chemical inertness in hot acidic solutions and hot brines;
- good thermal stability;
- good flowability and rheology in frac fluids;
- low abrasiveness;
- low cost and large commercial availability.

10.10.2.2 Frac Fluids

The above-mentioned proppants can only be used successfully when mixed with a viscous fluid to form a pumpable slurry; hence the carrying fluid also plays an important rheological role in the final fracturing job. Many fluids have been used in fracturing operations, including lease crude oil, water, brines, linear gels, foams, cross-linked polymer gels, emulsions, and even carbon dioxide. Most fracturing fluids used today are either linear or cross-linked aqueous polymer gels or foams. These fluids are extremely complex and exhibit rheological properties that are sensitive to several critical operating parameters. Some of their properties, such as their shear rate, are also time and temperature dependent. The most common fracturing fluids used today include guar cross-linked with borate or zirconium, carboxymethyl-hydroxypropyl guar (CMHPG) cross-linked with zirconium, foams of guar-based fluids and nitrogen or carbon dioxide for gas assist, and gelled oils made of phosphate esters and sodium aluminate. When pH adjustment is required, this can be achieved by adding sodium hydroxide (NaOH) or magnesium oxide (MgO) directly to the frac fluid. Other additives include fluid loss additives, breakers, and surfactants. Breakers are typically enzymes or oxidizers for guar-based products. For gelled oil, acids and bases are used to break the association polymer structure including magnesium oxide.

10.10.2.3 Properties and Characterization of Proppants

To select a suitable propping agent, the properties of the material must be characterized according to well-known standards, e.g., the standards edited by the American Petroleum Institute (API) or other professional societies involved in the oil and gas industry (e.g., IoP, IFP, or ASTM). The critical properties that must be measured to qualify a suitable propping agent with the explanation of the critical values are listed in Table 10.24.

10.10.2.4 Classification of Proppant Materials

The materials commonly used as proppants can be grouped into three main categories, listed in Table 10.25. The first proppant material used was rounded silica sand mined from glacial deposits. This material was initially selected owing to both its wide availability near production wells and its low cost, but since the early days several other industrial materials have been selected and used as proppants, and today we observe the increased use of synthetic materials, especially sintered and fused ceramics. The main impetus in focusing on ceramics was driven by the fact that ceramic materials offer suitable properties for use in modern deep wells today.

Table 10.24. Critical properties for proppants

Critical properties		Description	Requirements	Benefits
Mechanical properties	High crushing strength (σ_c/MPa)	The crushing strength is the compressive strength of a material, i.e., its ability to resist compaction or compression under axial load.	$\sigma_c > 35$ MPa	Insures prop of cracks and avoids the collapse of cap rock if crushing strength is above the lithostatic pressure at the given depth.
	Crushing resistance (wt.%)	A series of crushing resistance tests consists in determining the stress at which the proppant material shows excessive generation of fines. Tests are conducted on samples that have been sieved. Four specific stress levels (i.e., 7.5, 10, 12.5, and 15 ksi) are used in the recommended practice (see API RP-61).	Suggested fine limit (API): 12/20 25 wt.% 16/20 25 wt.% 20/40 10 wt.% 40/70 8 wt.% Suggested fine limit (Stim. Lab.) All 5 wt.%	The lower the fine generation, the better the permeability of the reservoir; moreover; this avoids fooling of cavities and porosities.
	Pycnometer density (ρ_{pyc}/kg.m^{-3})	The pycnometer density measures the true skeletal density including closed internal porosity. Its knowledge is required for the determination of the specific surface area. It is usually measured with a helium pycnometer because helium gas will penetrate all open pores and intricate channels.	$\rho_{pyc} < 2800$ kg.m^{-3}	A low-pycnometer-density material allows the use of low-viscosity carrying fluids, leading to both lower power consumption and pumping rates during well injection.
	Bulk density (ρ_{bulk}/kg.m^{-3})	The bulk density corresponds to the mass of proppants that fill a unit volume and includes both proppant and porosity void volume.	$\rho_{bulk} < 1600$ kg.m^{-3}	A low-bulk-density material leads to the use of less mass of proppant for a given volume of reservoir bed or storage tank to fill.
	Tap density (ρ_{tap}/kg.m^{-3})	The tap density corresponds to the volume occupied by a weighed powder after a set number of taps, usually 10, have been applied to the bottom of its container. As such, the tap density provides a measure of the compactability of a powder.	$\rho_{tap} < 1800$ kg.m^{-3}	A low-tap-density material allows one to use less mass of proppant for a given volume of reservoir bed to fill.
	Permeability coefficient (darcy)	Characterizes the volume flow rate of a fluid into a porous medium exhibiting a cross-section area, *A*, and a thickness, *l*, under a given pressure differential ΔP (see standard API RP-61). Conductivity is *kA/l*.	k > 340 darcies[37] P > 6 darcy-ft	A high permeability coefficient insures a good mass transfer of oil and gas into the fractured rock.

[37] The darcy corresponds to the volume flow rate of one cubic centimeter per second of a liquid having a dynamic viscosity of 1 centipoise, which flows through an area of one square centimeter of a porous medium in 1 s when it undergoes a pressure gradient of one atmosphere per centimeter of length. Hence, 1 darcy = $9.869232266 \times 10^{-13}$ m^2.

Table 10.24. *(continued)*

Critical properties		Description	Requirements	Benefits
Size and dimensions[38]	Particle size distribution (PSD)	Distribution of the particle size is determined by sieving according to ASTM C429-82(1996).	425 < D < 850μm (40 < mesh < 20)	A narrow grain size distribution insures a good intercalation of grains into tight fractures and excellent packing ability. The sizes used in hydraulic fracturing are typically in US mesh: 20/40, 16/20, and 16/30. Some 30/50 and 12/20 is used in specialty applications.
	Sphericity and roundness indices (*S, RI)*	Dimensionless quantities that measure the ellipsoidal shape and particle smoothness, respectively. It gives the ratio of the smaller diameter to the larger diameter, and the ratio of actual area to theoretical area.	$S > 0.9$ $RI > 0.9$	Beadlike particles allow a good flowability of the slurry during pumping operation.
	Porosity (ε/vol.%)	Dimensionless quantity equal to the void volume fraction, i.e., ratio of volume of voids to the overall volume of material.	ε < 30 vol.%	The lower the porosity, the better the crushing strength, the lower the brittleness.
Chemical properties	Chemical composition	Chemical composition of the dried solid, expressed as oxides or elements, indicates also the oxidation degree of multivalent species (e.g., Fe, Mn, Cr, Co, and V).	No hazardous substances, low Fe(II) and Fe(III).	Soluble hazardous substances must be avoided so as not to contaminate aquifers, and release of iron cations is not recommended for well control.
	Weight loss in acidic media and boiling water	Weight loss during dissolution of a representative sample in an acidic mixture of 12 wt.% HCl and 3 wt.% HF at a given temperature of 100°C and/or in boiling water.	Less than 2 wt.% in acid mixture, and no dissolution in boiling water.	Chemical inertness allows it to resist the dissolution of beads into acidic frac fluids, brines, and corrosive agents used in chemical fracturing (e.g., HCl, HF, etc.).
Other	Maximum operating temperature (°C)	Capability to withstand maximum temperatures encountered in the deepest production wells owing to the usual geothermal gradient encountered in sedimentary basins (i.e., 30°C/km)	At least above 250°C with no phase changes	Helps to avoid creep phenomena and softening of the material under permanent load.
	Price (US$/tonne)	Specific cost, i.e., cost per unit mass of material including raw material cost, production cost, and distribution cost.	Less than 500 US$/tonne	Allows for competitive product on the market.

[38] ASTM F1877-98 – Standard Practice for Characterization of Particles.

Table 10.25. Major materials used as proppants

Material	Description	Characteristics
Rounded silica sand (e.g., Arizona Sand, Badger Mining, Borden, Colorado Silica, Hepworth, Oglebay Norton, Uninim)	Naturally occurring sand usually mined from glacial deposits, sometimes called Ottawa sands. Silica sand is essentially made of quartz (SiO_2) grains.	**Pressure range:** $28 < \sigma_c < 35$ MPa ($4 < \sigma_c < 5$ ksi) **Advantages:** Low cost, low density, wide availability, and excellent chemical resistance in acidic media except those containing free HF **Drawbacks:** Low permeability, low crushing strength, and poor resistance to flow back
Resin-coated sand (e.g., Borden, Santrol, Hepworth)	The first application of a phenolic resin coating was to particles such as silica sand, glass beads, and ceramics. The concept was to inject a partially cured resin-coated proppant into a well and let the elevated bottom hole temperature finish the resin polymerization and bond the coated particles together, forming a down-hole filter. When a proppant is coated with a phenolic formaldehyde resin that is securely attached to the proppant surface by a silane or other coupling agent, the former brittle material becomes crush resistant. Actually, the resin coating helps to provide a smooth and round substrate surface. In addition, it reduces stress between grains and maintains particle integrity. The coated grains are less sensitive to embedment and generate fewer fines. Finally, it increases the chemical resistance of particles.	**Pressure range:** $35 < \sigma_c < 69$ MPa ($7 < \sigma_c < 10$ ksi) **Advantages:** Better resistance to flow back and improved crushing strength **Drawbacks:** Higher tendency to produce dust under high shear conditions (dust explosions)
Ceramics (e.g., Carbo-Ceramics Inc., Norton Alcoa, Sintex Minerals Inc.)	Synthetic materials made by sintering of bauxite and kaolinite clay. After processing, the final material mineralogical composition consists of a mixture of mullite and corundum. Sometimes less common ceramics are also used, e.g., carborundum, stabilized cubic zirconia, other oxides, and silicates.	**Pressure range:** σ_c up to 140 MPa (σ_c up to 20 ksi) **Advantages:** High crushing strength **Drawbacks:** High density, high cost

10.10.2.5 Production of Synthetic Proppants

All ceramic proppant producers use as feedstock essentially bauxite and, to a lesser extent, other industrial minerals with a high alumina content such as kaolin, nepheline syenite, wollastonite, talc, and feldspars. The final spherical shape is obtained by several processing routes currently used in the ceramics industry for producing beads and other particulate materials. The most common of these processes are pelletizing and sintering, atomization, fire polishing, and flame spraying.

Pelletizing and sintering. In this process, which is the most common among ceramic proppant producers, raw material with a high alumina content (i.e., bauxite, or kaolin clay) is ground to a final particle size of several micrometers by ball milling prior to formation of the pellets. Then the material is calcined at 1000°C to drive off moisture and water from hydratation and reground to less than a micrometer to obtain through granulation as high

a green density as possible. Afterwards, various pelletizing techniques can be used to agglomerate the material. Usually, ball forming consists in finely grounding the fired material and mixing it in a rotary dryer with water and a binder that gives them temporary cohesion and that does not affect the final strength of the material (e.g., molasses, starch, cellulose gum, polyvinyl alcohol, bentonite, sodium metasilicate, and sodium lignosulfonate). Until the final desired size of green pellets is obtained, the binder is continuously added. Finally, the green pellets are fired with a suitable parting agent (e.g., pure alumina powder) into a kiln between 1200 and 1650°C for a sufficient amount of time for vitrification to occur. After sintering the balls are made of alpha-alumina (i.e., corundum) and mullite grains with a diameter of 50 to 300 μm formed by crystalline growth during sintering together with a glassy phase. Hence sintered bauxite exhibits only a low residual porosity (<5%) because it has shrunk by 20%, and it is dense (>3550 $kg.m^{-3}$) and strong.

Atomization. This technique involves the melting at high temperatures (i.e., above 1800°C) of raw material particles together to obtain a molten bath of bulk liquid. Usually, the bulk liquid contains more than thousands of times the amount of raw material required to make a single product particle. A thin stream of molten material is atomized by dropping it into a disruptive air jet, subdividing the stream into fine, molten droplets. The droplets are then kept away from one another and from other objects until they have been cooled and solidified. Then they can be recovered as substantially discrete ellipsoidal glassy (i.e., amorphous) particles.

Fire polishing. In this techniques, discrete solid particles are heated to the softening or melting temperature of the material, usually between 1200 and 1650°C, while suspended and dispersed in a hot gaseous medium (e.g., fluidized bed). As particles become soft or molten, surface tension forms them into an ellipsoidal shape. If kept in suspension until cooled below softening temperature, the particles may be recovered as spherical grains.

Flame spraying. In this technique, finely ground raw particles are premixed with a combustible gas mixture, i.e., fuel and oxidant, and the mixture is then introduced into a burner. Hence, in the hot flame, the tiny particles melt or soften, and the surface tension leads them to exhibit an ellipsoidal shape. To prevent molten droplets or soften particles from contacting any surface before cooling, the flame must be allowed to move freely in a large combustion chamber. The droplets or softened particles are then kept away from one another and from the reactor walls until they have been cooled and solidified.

It is important to point out that, despite the wide availability of industrial minerals for preparing commercial ceramic proppants (e.g., bauxite, kaolin clay), all the major proppant producers must overcome technical issues for obtaining crush-resistant beads made of tough and hard corundum or mullite minerals. Actually all the above-mentioned processes require at least a comminution step and also a firing or sintering step conducted at high temperature. Hence, the overall process for obtaining suitable ceramic proppants is always energy demanding and accounts for 60% of the cost of the final product. Hence, the process represents a major pitfall for obtaining competitive ceramic proppants at low prices.

10.10.2.6 Properties of Commercial Proppants

The properties of most common commercial proppants measured according to standardized tests are summarized in Table 10.26.

Table 10.26. Properties of commercial proppants

Proppant (trade name, producer)		Particle size distribution[39] (mesh)	Bulk and pycnometer densities (ρ/kg.m^{-3})		Crushed fraction (wt.%)	Weight loss HCl-HF 60°C (/wt.%)	Weight loss boiling water (wt.%)	Permeability (121°C) (k/D)	Conductivity (121°C) (k/D-ft)	Roundness index (RI)	Sphericity	Price (US$/tonne)
Rounded silica sand (Oglebay Norton)		8/16, 12/20, 16/30, **20/40**	1540	2650	2.0 ksi 0.68 3.0 ksi 1.99 4.0 ksi 6.70	0.9	Traces	2 ksi 249 4 ksi 119 6 ksi 58 8 ksi 0	2 ksi 4.592 4 ksi 2.051 6 ksi 0.952 8 ksi 0.000	0.6	0.9	50
Resin-coated sand	Precured resin-coated sand (Tempered Econoflex®, Santrol)	12/20, 16/30, **20/40** (620μm)	1490	2590	2 ksi 0.00 4 ksi 0.10 6 ksi 0.10 8 ksi 0.20 10 ksi 0.50 12 ksi 1.40	<0.3	Traces	4 ksi 263 6 ksi 248 8 ksi 210 10 ksi 144 12 ksi 107	4 ksi 5.049 6 ksi 4.679 8 ksi 3.881 10 ksi 2.564 12 ksi 1.811	0.9	0.9	200
	Precured resin-coated sand (Tempered HS®, Santrol)	12/20, 16/30, **20/40** (730μm)	1530	2530	6 ksi 0.40 8 ksi 0.60 10 ksi 2.30	<0.3	Traces	2 ksi 328 4 ksi 249 6 ksi 178 8 ksi 103 10 ksi 61	2 ksi 6.743 4 ksi 4.302 6 ksi 3.011 8 ksi 1.753 10 ksi 995	0.8	0.8	200
	Precured resin-coated sand (Tempered DC®, Santrol)	12/20, 16/30, **20/40** (710μm)	1540	2570	2 ksi 0.10 4 ksi 0.30 6 ksi 0.70 8 ksi 1.20 10 ksi 5.10	<0.3	Traces	2 ksi 301 4 ksi 229 6 ksi 166 8 ksi 89 10 ksi 46	2 ksi 6.432 4 ksi 4.038 6 ksi 3.033 8 ksi 1.446 10 ksi 742	0.8	0.8	200
	Precured resin-coated sand (Tempered LC®, Santrol)	12/20, 16/30, **20/40** (720μm)	1530	2600	2 ksi 0.20 4 ksi 0.40 6 ksi 1.90 8 ksi 4.50 10 ksi 10.70	<0.3	Traces	2 ksi 272 4 ksi 201 6 ksi 115 8 ksi 59 10 ksi 31	2 ksi 5.034 4 ksi 3.629 6 ksi 2.014 8 ksi 987 10 ksi 503	0.8	0.8	200

Resin-coated sand	Precured resin-coated sand (Tempered TF®, Santrol)	12/20, 16/30, **20/40** (570μm)	1540	2600	2 ksi 0.40 4 ksi 1.30 6 ksi 2.50 8 ksi 5.30 10 ksi 13.00	<0.3	Traces	2 ksi 146 4 ksi 117 6 ksi 68 8 ksi 29 10 ksi 16	2 ksi 2.804 4 ksi 2.072 6 ksi 1.180 8 ksi 472 10 ksi 254	0.8	0.8	200
Sintered ceramics	Lightweight (Naplite®, Norton-Alcoa)	12/18, 16/20, **20/40** (721μm)	1560	2600	5.0 ksi 0.5 7.5 ksi 2.4 10 ksi 7.7	3.2	Traces	2 ksi 465 4 ksi 401 6 ksi 300 8 ksi 181 10 ksi 111	2 ksi 9.507 4 ksi 7.999 6 ksi 5.840 8 ksi 3.434 10 ksi 2.055	0.9	0.9	422–556
	Lightweight (Valuprop®, Norton-Alcoa)	**20/40** (657μm), 30/50	1560	2600	5.0 ksi 1.2 7.5 ksi 4.0	3.2	Traces	2 ksi 356 4 ksi 302 6 ksi 212 8 ksi 150 10 ksi 106	2 ksi 6.936 4 ksi 5.723 6 ksi 3.911 8 ksi 2.683 10 ksi 1.843	0.9	0.9	422–556
	Low-cost and lightweight ceramics (Carbo-Econoprop®, CCI)	**20/40** (635μm), 30/50	1560	2700	5.0 ksi 0.8 7.5 ksi 2.8	1.7	Traces	2 ksi 340 4 ksi 320 6 ksi 220 8 ksi 130 10 ksi 70	2 ksi 3.300 4 ksi 2.900 6 ksi 2.000 8 ksi 1.100 10 ksi 0.500	0.9	0.9	422–556
	Lightweight and intermediate-strength ceramics (CarboLite®, CCI)	12/18, 16/20, **20/40** (730μm)	1570	2710	10.0 ksi 5.2 12.5 ksi 8.3	1.7	Traces	2 ksi 570 4 ksi 480 6 ksi 340 8 ksi 210 10 ksi 120	2 ksi 10.70 4 ksi 8.900 6 ksi 6.000 8 ksi 3.700 10 ksi 2.000	0.9	0.9	333–480
	Medium-density (Interprop®, Norton-Alcoa)	16/30, **20/40** 30/50	1880	3200	5.0 ksi 0.3 7.5 ksi 0.8 10 ksi 2.2 12.5 ksi 4.0	2.5	Traces	2 ksi 485 4 ksi 415 6 ksi 335 8 ksi 235 10 ksi 160 12 ksi 110	2 ksi 7.830 4 ksi 6.585 6 ksi 5.230 8 ksi 3.615 10 ksi 2.375 12 ksi 1.720	0.9	0.9	422–556

[39] ASTM C429-96 – Standard Test Method for Sieve Analysis of Raw Materials for Glass Manufacture.

Cardarelli, F. (2008) Materials Handbook. A Concise Desktop Reference, 2nd Edition. Springer London.

Table 10.26. *(continued)*

Proppant (trade name, producer)		Particle size distribution[39] (mesh)	Bulk and pycnometer densities (ρ/kg.m^{-3})		Crushed fraction (wt.%)	Weight loss HCl-HF 60°C (/wt.%)	Weight loss boiling water (wt.%)	Permeability (121°C) (k/D)	Conductivity (121°C) (k/D-ft)	Roundness index (RI)	Sphericity	Price (US$/tonne)
Sintered ceramics	Intermediate-strength ceramics (CarboProp®, CCI)	16/30, **20/40** (658μm), 30/60	1880	3270	10.0 ksi 2.2 12.5 ksi 5.1	4.5	Traces	2 ksi 385 4 ksi 345 6 ksi 290 8 ksi 250 10 ksi 200 12 ksi 150 14 ksi 100	2 ksi 6.180 4 ksi 5.430 6 ksi 4.450 8 ksi 3.720 10 ksi 2.890 12 ksi 2.145 14 ksi 1.445	0.9	0.9	333–480
	Sintered bauxite (Norton-Alcoa)	16/30, **20/40** (662μm), 30/50	2020	3450	7.5 ksi 0.4 10 ksi 1.1 12.5 ksi 2.2 15 ksi 4.0	2.0	Traces	2 ksi 472 4 ksi 408 6 ksi 352 8 ksi 299 10 ksi 217 12 ksi 173 14 ksi 141	2 ksi 4 ksi 6 ksi 8 ksi 10 ksi 12 ksi 14 ksi	0.9	0.9	422–556
	High-strength sintered bauxite ceramics (CarboHSP® 2000, CCI)	12/18, 16/20, 16/30, **20/40** (717μm), 30/60	2040	3560	10.0 ksi 0.7 12.5 ksi 1.4 15.0 ksi 2.7	3.5	Traces	2 ksi 539 4 ksi 440 6 ksi 370 8 ksi 302 10 ksi 246 12 ksi 204 14 ksi 166	2 ksi 8.168 4 ksi 6.595 6 ksi 5.368 8 ksi 4.283 10 ksi 3.405 12 ksi 2.719 14 ksi 2.140	0.9	0.9	650

10.10.2.7 Proppant Market

The world annual consumption of proppants is estimated at about 2.2 million tonnes per year. The international market share has been roughly 65% North Sea, 15% Africa, 10% Middle East, 5% Far East, and 5% South America including Mexico. As a general rule, the majority of fracturing jobs use rounded silica sand (i.e., Ottawa sand), which is the most popular fracturing proppant used in oil-well production owing to its low price (68 US$/tonne) and because of its large geological availability. Nevertheless, newly developed sintered and fused synthetic ceramic proppants represent today roughly 22% of the previous market (ca. 196,000 tonnes/year). Actually, over the last 20 years, ceramic proppants, despite their high cost of 650–750 US$/tonne, have become increasingly popular due to their improved properties, especially their high crushing strength, near-spherical shape, and excellent chemical inertness. On the other hand, resin-coated sands, which are priced 360 US$/tonne, fill the gap between sand and ceramics. The leading producing countries of ceramic proppants are mainly the United States and, to a lesser extent, Brazil. The leading company is Carbo-Ceramics (CCI), which produces 60% of all the ceramic proppants consumed worldwide. CCI is followed by Norton Alcoa, also located in the USA, the third company being Sintex in Brazil, which sells a sintered bauxite under the trade name Sinterball.

Table 10.27. Worldwide production of proppants (2006)

Proppant material	Worldwide production (tonnes/annum)
Sand	2,000,000
Resin-coated sand	180,000
Synthetic ceramics	200,000
Total =	2,380,000

10.10.2.8 Proppant Producers

Table 10.28. Ceramic proppant producers

Producer	Proppant trade names
Carbo Ceramics 6565 MacArthur Blvd., Suite 1050, Irving, TX 75039, USA Telephone: +1 (972) 401-0090 Fax: +1 (972) 401-0705 URL: http://www.carboceramics.com/	– Carbo HSP – Carbo Prop – Carbo Lite – Ceramax P – Ceramax I+SI – Ceramax I – Ceramax E
Norton Alcoa 11300 North Central Expressway, Suite 402, Dallas, TX 75243, USA Telephone: +1 (972) 233-0661 Fax: +1 (972) 233-1409 URL: http://www.nortonalcoa.com/	– Sintered bauxite – Inter Prop – Nap Lite – Valu Prop
Sintex Minerals & Services (Brazil) 29810 Southwest Freeway, Rosenberg, TX 77471, USA URL: http://www.sintexminerals.com/	– SinterBall – SinterProp

Table 10.29. Resin-coated sand producers

Producer	Proppant trade names
Borden Chemicals 180 E. Broad Street , Columbus, OH 43215-3799, USA Telephone: +1 (614) 225-4127 E-mail: anschutzda@bordenchem.com URL: http://www.bordenchem.com/	– Diamond Flex – Econo Flex- AcFrac CR – AcPack – SB Prime – PR-6000 – SB-Excel – PR-6000 – CR-4000
Santrol P.O. Box 639, 2727 FM 521, Fresno, TX 77545, USA Telephone: +1 (281) 431-0670 Fax: +1 (281) 431-0044 E-mail: sales@santrol.com URL: http://www.santrol.com/	AcFrac Black – Tempered HS – Tempered DC – Tempered LC – Tempered TF – Super HS – Super LC – Super TF- Super DC

Table 10.30. Rounded silica sand producers

Producer	Sand trade name
Fairmount Minerals Chardon, OH, USA E-mail: sales@fairmountminerals.com URL: http://www.fairmount-minerals.com/	Ottawa sand
Oglebay Norton Industrial Sands Phoenix Office, Suite 320, 410 North 44th Street, Phoenix, AZ 85008, USA Telephone: +1 (602) 389-4399 Fax: +1 (602) 389-4389 URL: http://www.oglebaynorton.com/	Brady sand
Unimin Corp. 258 Elm Street, New Canaan, CT 06840-5300, USA Telephone: (800) 243-9004 Fax: (800) 243-9005	Jordan sand
Wedron Silica Division of Fairmount Minerals, South Olive Street, Wedron, IL 60557, USA Telephone: +1 (815) 433-2449 Fax: +1 (815) 433-9393 E-mail: sales@wedronsilica.com URL: http://www.wedronsilica.com/	Round silica sand

Table 10.31. Proppant testing laboratories

Stim-Lab P.O. Box 1644, Duncan, OK 73534-1644, USA Telephone: +1 (580) 252-4309 Fax: +1 (580) 252-6979 E-mail: stimlab@stimlab.com URL: http://www.stimlab.com/
FracTech Unit 204, Bedfont Lakes Industrial Park, Challenge Road, Ashford, Middlesex, TW15 1AX, UK Telephone: (+44) (0) 1784 244100 Fax: (+44) (0) 1784 250544 URL: http://www.fractech.co.uk/
Fracture Technologies Aaron House, 6 Bardolph Rd, Richmond, Surrey, TW9 2LS, UK Telephone: (+44) (0) 20 8288 7405 Fax: (+44) (0) 20 8287 1802 E-mail: sales@wellwhiz.com URL: http://www.wellwhiz.com/

10.10.3 Further Reading

API Recommended Practice RP-56 (1998) *Recommended Practices for Evaluating Sand used in Hydraulic Fracturing Operations*. American Institute of Petroleum Engineers, Washington, D.C.

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MADER, D. (1989) *Hydraulic Proppant Fracturing and Gravel Packing.* In: Developments in Petroleum Science, Vol. 26. Elsevier, Amsterdam.

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VALKO, P.; ECONOMIDES, M.J. (1995) *Hydraulic Fracture Mechanics.* Wiley, London.

YEW, C.H. (1997) *Mechanics of Hydraulic Fracturing.* Gulf Professional Publishing.

Cardarelli, F. (2008) Materials Handbook. A Concise Desktop Reference, 2nd Edition. Springer London.