

Ceramics Refractories and Engineering

Ceramics

The main properties of **ceramic refractories** include the capacity to withstand high temperatures without melting or decomposing and the capacity to remain unreactive and inert when exposed to severe environments.

Refractory materials, by definition, are supposed to be resistant to heat and are exposed to different degrees of mechanical stress and strain, thermal stress and strain, corrosion/erosion from the solids, liquids and gases, gas diffusion, and mechanical abrasion at various temperatures. Different refractories are designed and manufactured so that the properties of the refractories will be appropriate for their applications.

Refractories are mostly used (70%) in **basic metal industries**. In iron and steel making in integrated plants, iron is made in the blast furnace. Here iron is formed from the reduction of iron ore by carbon in the presence of limestone, which helps in forming the slag. Inside the blast furnace, the refractories experience abrasion in the upper part and intense heat and molten slag and metal contacts in the lower region. Thus, the properties of the trough of blast furnace should be that it resists the impact and splashing of the molten iron and slag.

In other primary metal industries such as aluminum, the refractory properties requirements are quite different than steel making. Although the temperature of aluminum refining and alloying process is much lower than steel, it has the unique problem of penetration in the refractories. Hence, the refractory should be designed so that it has a nonwetting characteristic to the aluminum molten. The nonwetting properties are introduced in the refractories by special additives.

In the **hydrocarbon industries**, the property requirements of the refractories are different than those of metal industries. Although the temperature in petrochemical refining is much lower than in metal industries, the refractories suffer a high rate of abrasion due to the flow of high-velocity particles at a continuous rate. Hence, the major characteristic requirement of these refractories is abrasion resistance. Also, the refractories need to be able to conserve heat. Hence, there are defined ranges of thermal conductivity for different regions of the process so that the processes conserve energy during the conversion processes.

In **glass-making process**, the refractories in the glass tank are in constant contact with the molten glass, and this poses different kinds of requirements for the refractory. Since glass in the molten state is quite fluid and tends to go through the refractory pores, the most needed characteristic should be nonporous refractories, and hence fused refractories are used in molten glass contact areas. It is obvious

that the property requirements of refractories vary significantly according to the application and use in different processes. Hence, the individual refractories need to be designed with characteristic properties for specific systems since the requirements vary with different high-temperature processes.

Refractories are broadly divided into two categories—**shaped** (**bricks** and **cast shapes**) and **unshaped** (**monolithic**) refractories. There are two kinds of shaped refractories—the primary kind is like brick or similar shapes and the other kind is the shapes made from monolithic refractories, where they are dictated by the properties of monolithic refractories. For shaped refractories (like brick making), attaining maximum density after the shapes are formed is the goal of the process.

Refractory properties can be classified as follows: **Physical and mechanical** like density, porosity, strength and abrasion. **Thermal** like thermal shock, thermal conductivity and thermal diffusivity. **Chemical** like corrosion and erosion.

Physical property requirements for shaped and unshaped refractories are different. For shaped refractories, the main requirements are their density and porosity and dimensional tolerance. Monolithic (unshaped) refractories, on the other hand, workability and aging, rammability with proper compaction and flowability is the main requirement.

The values of density and porosity determined by standard methods are used to recommend or predict the use of refractories for specific uses. In general, the higher the density, the lower the porosity. Also, other physical properties, such as the strength, abrasion, and gas permeability, are often related to the density and porosity of the refractory.

The **physical strengths**, in both cold and hot conditions, are often characterized as measures of the use of a refractory. Cold strengths indicate the handling and installation of the refractory, whereas hot strengths indicate how refractory will perform when used at elevated temperatures. Strengths of refractories are measured as cold and hot compressive strength, cold modulus of rupture, or hot modulus of rupture. Hot modulus of rupture provides the best indication of performance of a refractory material in use.

Abrasion resistance is a measure of the resistance of a refractory material when high-velocity particles abrade the surface of the refractory. It measures the strength of the bond and the refractory particles and its resistance to the flow of high-velocity particles across its surface.

The need for good abrasion resistance of refractory materials is most evident in the petrochemical industries where fine particles impinge the refractory surface at high velocities at moderately elevated temperatures.

On the other hand, **thermal properties** involved thermal expansion, thermal shock, thermal conductivity and thermal diffusivity. **Thermal expansion** is a measure of the refractory about its linear stability when it is exposed to different ranges of high temperatures and then cooled to the room temperatures. It is defined as a permanent linear change and is measured by the changes in the longest linear dimensions.

Most refractory materials expand when heated. Hence, when refractories are installed at room temperatures, the whole structure tightens up when heated. But if the temperature reaches higher than the softening temperature of the bonding system, the structure may distort or collapse. Hence, refractory systems should always be designed in such a way that the maximum temperature attainable in the system is lower than the softening or melting temperature of the refractory ingredients (grains and bonding system). Often cracks are observed in monolithic refractory systems when cooled, but, in most cases, the apparent cracks visible on cooling close up after the system is heated up.

Thermal Shock is measure of the refractory property when the refractory is exposed to alternate heating and cooling. It is an important property for a refractory material. Most high-temperature processes experience heating and cooling. Both refractory grains and the bonding system expand while being heated and

contract during cooling. Having similar grains in the structure, the thermal shock resistance depends on the matrix bonding of the grains.

Thermal conductivity is a measure of the refractory regarding its ability to conduct heat from the hot to the cold face when it is exposed to high temperatures. There are three different methods of determining thermal conductivity of refractory materials. The ASTM C-210 is the standard method for determining thermal conductivity of the refractories; ASTM C-202 is the standard method for determining thermal conductivity of refractory brick; and ASTM C-1113 is the standard method for determining thermal conductivity of refractories by hot wire.

The thermal conductivity tests are particularly important for insulating refractories where the thermal gradients from the hot face to the cold face dictate the use of a refractory material for the specific uses.

Thermal diffusivity is the thermal conductivity divided by density and the specific heat capacity at constant pressure. It measures the ability of a material to conduct the thermal energy relative to its ability to store the thermal energy. The high diffusivity means heat transfers rapidly. It describes the rate of temperature spread through a material.

Finally, **The chemical properties** of a refractory are defined by the chemical analysis of the refractory grains, by the nature of the bonding, and also by the ability of the refractory to resist the action of liquids when exposed to the high temperatures. The chemical properties of a refractory material are primarily dictated by the chemical composition of refractory.

The bonding system of the refractory plays a vital role in dictating its properties. When refractories are exposed to corrosive liquids at high temperatures, the extent of corrosion/erosion depends on the refractory grains and the chemical bonding system of the refractory. Refractory corrosion may be caused by mechanisms such as dissolution in contact with liquid, a vapor–liquid or solid-phase reactions. It may also occur due to penetration of the vapor or liquid in the pores, resulting in an alternate zone. In most cases, corrosion is the result of some combination of these factors.

A concentration gradient occurs in the refractory composition at the boundary region when the refractory comes in contact with the molten slag. The refractory components diffuse through the interfacial film and dissolve in the liquid. The interfacial film influences the rate of dissolution. The larger the concentration gradient, the faster the dissolution rate and thus the refractory dissolves more readily. Corrosion/erosion resistance is one of the most important characteristics of refractories, which are exposed to

molten metal and slag. Hence, the design of the tests closely simulating the conditions that the refractories experience during use is of great importance.

Fracture of Refractories

Fracture is one of the two most common modes of failure for the refractory linings of modern industrial processing vessels. The other is chemical attack, or corrosion by the material that the refractories are containing within the process vessel, often molten metals or glasses at very high temperatures. With molten metals, a unique corrosion process is also common from the slags protecting the liquid metals from the atmosphere.

Often these (slag/refractory) reactions are so intense and so problematical that special types of refractories, different from those in the rest of the process vessel lining, must be employed at the slag lines of metallurgical vessels. Fracture failures of refractories are of several varieties, including simple mechanical overload as may develop from impact during the loading of the process vessel with scrap metal.

Thermal stress fracture during cooling or heating, particularly the initial heat-up of a vessel or during rapid thermal cycling between heats, is another type of failure. These fractures may be catastrophic and result in the complete loss of the refractory lining. Sometimes thermal shock simply causes the surface spalling and a significant

reduction of lifetime, or campaign, of the lining. However, fracture need not always be disastrous; it may just result in the development of a crack pattern in the process vessel lining. Those crack surfaces may be held together and closed by the vessel lining compressive stresses that develop from thermal expansion when the vessel is heated to operating temperatures.

Classification of Ceramic Refractory Materials

Ceramics Refractories are classified in multiple ways, based on: Chemical composition, method of manufacture, fusion temperature, refractoriness and thermal conductivity.

A. Based on Chemical Composition

1- Acidic refractories are generally impervious to acidic materials but easily attacked by basic materials, and are thus used with acidic slag in acidic environments. They include substances such as silica, alumina, and fire clay brick refractories. Notable reagents that can attack both alumina and silica are hydrofluoric acid, phosphoric acid, and fluorinated gases. At high temperatures, acidic refractories may also react with limes and basic oxides.

Silica refractories are refractories containing more than 93% silicon oxide (SiO_2). They are acidic, have high resistance to thermal shock, flux and slag resistance, and high spalling resistance. Silica bricks are

often used in the iron and steel industry as furnace materials. An important property of silica brick is its ability to maintain hardness under high loads until its fusion point.

Silica Refractories are usually cheaper hence easily disposable. New technologies that provide higher strength and more casting duration with less silicon oxide (SiO_2) 90% when mixed with organic resins have been developed.

Zirconia refractories are refractories primarily composed of the zirconium oxide (ZrO_2). They are often used for glass furnaces because they have low thermal conductivity, are not easily wetted by molten glass and have low reactivity with molten glass. These refractories are also useful for applications in high temperature construction materials.

Aluminosilicate refractories mainly consist of alumina (Al_2O_3) and silica (SiO_2). Aluminosilicate refractories can be semiacidic, fireclay composite, or high alumina content composite.

2- Basic refractories are used in areas where slags and atmosphere are basic. They are stable to alkaline materials but can react to acids. The main raw materials belong to the RO group, of which magnesia (MgO) is a common example. Other examples include dolomite and chrome-magnesia. For the first half of the twentieth century, the steel making process used artificial periclase (roasted magnesite) as a furnace lining material.

Magnesite refractories are composed of $\geq 85\%$ magnesium oxide. They have high slag resistance to lime and iron-rich slags, strong abrasion and corrosion resistance, and high refractoriness under load, and are typically used in metallurgical furnaces.

Dolomite refractories are mainly consist of calcium magnesium carbonate. Typically, dolomite refractories are used in converter and refining furnaces.

Magnesia-chrome refractories are mainly consist of magnesium oxide (MgO) and chromium oxide (Cr_2O_3). These refractories have high refractoriness and have a high tolerance for the corrosive environments.

3- Neutral refractories are used in areas where slags and atmosphere are either acidic or basic and are chemically stable to both acids and bases. The most common examples of these ceramics materials are alumina (Al_2O_3), chromia (Cr_2O_3) and carbon. **Carbon graphite refractories** mainly consist of carbon.

These refractories are often used in highly reducing environments, and their properties of high refractoriness allow them excellent thermal stability and resistance to slags. **Chromite refractories** are composed of sintered magnesia and chromia. They have constant volume at high temperatures, high refractoriness, and high resistance

to slags. **Alumina refractories** are composed of $\geq 50\%$ alumina (Al_2O_3).

B. Based on Method of Manufacture

These include dry press process, fused cast, hand molded, Formed (normal, fired bricks or chemically bonded) and the un-formed (monolithic-plastic, ramming and gunning mass, castables, mortars, dry vibrating cements).

C. Based on Fusion Temperature

Refractory materials are classified into three types based on fusion temperature (melting point). **Normal refractories** have a fusion temperature of $1580\text{--}1780\text{ }^\circ\text{C}$ (Fire clay). **High refractories** have a fusion temperature of $1780\text{--}2000\text{ }^\circ\text{C}$ (Chromite). Super refractories have a fusion temperature of $> 2000\text{ }^\circ\text{C}$ (e.g. Zirconia).

D. Based on Refractoriness

Refractoriness is the property of a refractory's multiphase to reach a specific softening degree at high temperature without load, and is measured with a pyrometric cone equivalent (PCE) test. Refractories are classified as **Super duty**: PCE value of 33–38, **High duty**: PCE value of 30–33, **Intermediate duty**: PCE value of 28–30 and **Low duty**: PCE value of 19–28.

E. Based on Thermal Conductivity

Refractories may be classified by thermal conductivity as either conducting, nonconducting, or insulating. Examples of conducting refractories are SiC and ZrC, whereas examples of nonconducting refractories are silica and alumina. Insulating refractories include calcium silicate materials, kaolin, and zirconia.

Insulating ceramics refractories are used to reduce the rate of heat loss through furnace walls. These ceramics refractories have low thermal conductivity due to a high degree of porosity, with a desired porous structure of small, uniform pores evenly distributed throughout the refractory brick in order to minimize the thermal conductivity. Insulating refractories can be further classified into four types.

Heat-resistant insulating materials with the application temperatures $\leq 1100\text{ }^{\circ}\text{C}$. **Refractory** insulating materials with the application temperatures $\leq 1400\text{ }^{\circ}\text{C}$. **High refractory** insulating materials with application temperatures $\leq 1700\text{ }^{\circ}\text{C}$. **Ultra-high refractory** insulating materials with application temperatures $\leq 2000\text{ }^{\circ}\text{C}$.

Engineering ceramics are structured and functional ceramics used in applications differing from those employing classical utility ceramics to advanced ceramic applications. However, the differentiation is not only made in terms of the applications, but also material. Oxidic,

non-oxidic and mixed ceramics such as aluminium oxide, zirconium oxide or silicon carbide that classified as engineering or technical ceramics which are designated to suit the majority of industrial and advance engineering applications.

Engineering ceramics are widely used in electronic, structural, and machine applications. They are characterized by high strength and fracture toughness, which are achieved in part by reducing the number and size distribution of microcracks in the finished part. Aluminas, silicon carbides and nitrides, sialons, and stabilized zirconias are the most prominent of this category. They are used in applications where heat resistance, hardness, fracture toughness, and strength are essential, e.g., for bearings, engine and turbine parts, cutting tools, and where wear resistant surfaces are required. In general, the main groups of **engineering ceramics** are oxides, nitrides, carbides, and borides.

1. Alumina

Alumina (Al_2O_3) is one of the most important ceramic materials, both pure and as a ceramic and glass component. The usefulness of alumina derives from a variety of its properties. It has a high melting point of the 2054°C , and is chemically very stable and unreactive, leading to applications as high-temperature components, catalyst substrates, and biomedical implants. The hardness, strength, and the abrasion resistance of alumina are among the highest for oxides,

making it useful for abrasive materials, bearings, and cutting tools. The electrical resistance of alumina is high, so it is used pure and as a component in the electrical insulators and components. Alumina has excellent optical transparency, and along with the additives such as the chromium and titanium, it is important as a gem stone like (the sapphires and rubies).

Alumina is produced primarily from bauxite rocks treated through Bayer process. Bauxite is the name of the ore that is the primary source of alumina; bauxite contains the gibbsite, $\gamma\text{-Al}(\text{OH})_3$, which is the stable phase of the $\text{Al}(\text{OH})_3$ at ambient temperature and pressure, in which these hydroxides are dissolved in the sodium hydroxide to separate them from other unwanted constituents of the bauxite. The dissolution reactions are carried out at about 285°C and 200 atm. The solution containing $\text{NaAl}(\text{OH})_4$ is separated from the unwanted solid impurities by sedimentation and filtration, and the solute is cooled to about (55°C) to precipitate aluminum hydroxides from the solution.

The stable phase of alumina at all temperatures and ambient pressure is corundum ($\alpha\text{-Al}_2\text{O}_3$) which belongs to the rhombohedral system with the most tightly bonded compound, resulting in very high hardness, high melting point and high density. Alumina also exists in several different polymorphs, metastable phases (γ , η , θ , κ , δ and χ) as well as the thermally stable α -phase. The metastable phases are also known as transition phases of alumina.

The differences in properties between phases make them important in different applications. For example, α and κ phases are widely used as wear resistant coatings due to their high hardness and thermal stability, while γ and θ phases are more suited for catalytic applications due to their lower surface energies, leading to larger active surface areas available for catalytic reactions.

The γ -phase in particular is one of transition phases of alumina with numerous applications. It commonly used as catalyst and catalyst support due to its low cost, good thermal stability, high specific surface area, surface acidity and interaction with deposited transitional metals, also it can be transformed into a different phase under heat treatment.

Solid polycrystalline alumina is made from alumina powder by sintering process. The traditional sintering methods for ceramics involve forming a powder into “green” ware, partially drying it at low temperatures, possibly calcining it at intermediate temperatures (900°C – 1100°C), and firing it to a dense solid at high temperature, for alumina above 1400°C . The time and temperature required to form the desired degree of porosity in the dense solid depend mainly on particle size of the alumina powder.

In order to decrease the porosity of the final sintered solid, various other oxides have been added to alumina. An especially valuable finding by added (MgO) to pure alumina powder. The challenge is

to obtain a densified ceramic very close to the theoretical density with a well-controlled microstructure at lower sintering temperature contrary to high sintering temperatures which are expensive, energy consumption as well as in investment costs. The first way to decrease the sintering temperature is to use liquid phase sintering by additives that produce eutectics at low melting temperatures.

Toughened alumina. Numerous researchers have reported that the addition of a second phase, a process referred to as toughening process, can increase the strength and the toughness of alumina. The fracture strength and toughness of alumina can be increased by the additions of yttria and zirconia. Zirconia-toughened alumina ZTA consists of an alpha-alumina matrix with a dispersion of second phase of ZrO_2 particles.

2. Silica

Silica (SiO_2) is the most abundant mineral in the earth's crust, existing in a wide variety of crystalline and noncrystalline forms due to the flexibility of linkage among crystal structure, also silica defines as a polymorphic material found in the nature in an amorphous form (opal, pebbles) or in the crystallized form (quartz, cristobalite and tridymite).

A major source of silica is **sand**. In ceramics industry, high-quality silica sand with high SiO_2 content (>99.5%) is used. Sands have

various chemical compositions, determined by the type of rock being mined. The stable room temperature form of silica is **quartz**, which is itself a widely available mineral and ingredient in numerous commercial ceramics and glasses due to its properties that permit it to be used in the high temperature and corrosive environments and as abrasives, refractory materials, fillers in the paints, and the optical components.

Silica undergoes a series of phase transformation upon heating; the form in which silica is found determines the thermal properties of silicate ceramics. Under ambient conditions, **α -quartz** is the stable thermodynamically favored polymorph of the silica at the room temperature.

At 573 °C, α -quartz is transformed into **β -quartz**, generally similar in structure but with less distortion results from the volume change (about 2%) due to this transformation. This thermal transformation preserves the optical activity of quartz. Heating quartz to 867°C leads to transformation of β -quartz into **β -tridymite** with volume increase of (12%), involving breaking of (Si-O) bonds to allow the formation of hexagonal structure with lower density. Quartz-tridymite phase transformation involves a high activation energy process that results in loss of the optical activity of the quartz.

The heating of β -tridymite to (1470°C) gives the **β -cristobalite** with (FCC) crystal structure that represent the highest crystalline and

temperature polymorph of the silica with volume increase of about (5%). Further heating of cristobalite results in melting at 1723°C. All these changes are reversible under suitable conditions of slow cooling.

3. Zirconia

Zirconium dioxide (ZrO_2), sometimes known as the zirconia, is a white crystalline oxide of zirconium and very important industrial ceramic for structural applications because of its high toughness, which has proven to be superior to other ceramics. In addition, it has applications making use of its high ionic conductivity. Zirconia is chemically unreactive and have very high melting point about ($\approx 2880^\circ\text{C}$).

Zirconia is found in natural state in the form of baddeleyite, but is more frequently prepared from zirconium silicate (zircon : ZrSiO_4) by using high temperature heat treatments, accompanied by chemical treatments, which eliminate the siliceous fraction from zircon. Zirconia is also define as a polymorph material with three main phases are known: monoclinic phase $<1170^\circ\text{C}$, tetragonal ($1170\text{--}2370^\circ\text{C}$) and cubic $>2370^\circ\text{C}$. At high temperature, zirconia solidifies in cubic phase then transforms to tetragonal phase when ($T < 2370^\circ\text{C}$) and finally, below (1170°C), becomes monoclinical phase. This last transition ($t \rightarrow m$) is accompanied by considerable dimensional variations (increase in volume of $\approx 4\%$), which largely

exceed the maximum stress limit, resulting in a fragmentation of material. A zirconia part sintered at temperatures about 1500°C breaks up and is destroyed during cooling, during the ($t \rightarrow m$) transition. This means that “pure” zirconia can be used only in powder form. To produce zirconia sintered pieces, (ZrO_2) must be combined with other oxides known as “stabilizers” such as CaO , MgO or Y_2O_3 .

The intermediate-temperature of zirconia, which has a tetragonal structure, can be stabilized at room temperature by the addition of modest amounts (**below ~8 mol%**) of dopants. This doped zirconia has mechanical toughness values as high as 17 MPa.m^{1/2}. On the other hand, the high-temperature phase of zirconia, which has a cubic structure, can be stabilized at room temperature by the addition of significant amounts (**above ~8 mol%**) of dopants. This form of zirconia has one of the highest ionic conductivity values associated with ceramics, allowing the use of the material in oxygen sensors and solid oxide fuel cells.

The stabilization of tetragonal phase at room temperature can result in the following common forms of zirconia: (1) **partially stabilized zirconia (PSZ)** – zirconia consisting of a matrix of a brittle ceramic and a dispersion of tetragonal precipitates within matrix when doped with CaO (Ca-PSZ) or MgO (Mg-PSZ); (2) **tetragonal zirconia polycrystals (TZP)** consisting of a matrix of stabilized ZrO_2 that has been stabilized in the tetragonal form by the addition of dopants

such as CeO_2 (Ce-TZP) and Y_2O_3 (Y-TZP). Fully stabilized zirconia (FSZ) refers to a ceramic material that has been completely stabilized in the cubic form.

4. Magnesia

A magnesia (MgO) is defined by the (ASTM) as “a dead-burned refractory material consisting mainly of crystalline magnesium oxide”. Also, ASTM defines “dead-burned” as a basic refractory material resulting from a heat treatment that yields a product resistant to the atmospheric hydration or recombination with carbon dioxide. Periclase is the mineral name for magnesium oxide and this mineral is rarely found in nature.

Magnesium oxide is produced by calcination process of magnesium carbonate or magnesium hydroxide. The latter is obtained by the treatment of magnesium chloride solutions, typically the seawater, with lime. Calcining at different temperatures produces magnesium oxide of different reactivity.

High temperatures ($1500-2000^\circ\text{C}$) diminish the available surface area and produces dead-burned magnesia, an unreactive form used as a refractory. Calcining temperatures ($1000-1500^\circ\text{C}$) produce hard-burned magnesia, which has limited reactivity and calcining at lower temperature, ($700-1000^\circ\text{C}$) produces light-burned magnesia, a reactive form, also known as caustic calcined magnesia.

Magnesium oxide has a very high melting point of 2800°C. This characteristic, together with its resistance to basic slags, ubiquity, and moderate cost, makes magnesium oxide products the choice for heat-intensive, metallurgical processes such as for the production of metals, cements, and glasses. Magnesia is physically and chemically stable at high temperatures. It has two useful attributes: high thermal conductivity and low electrical conductivity.

By far the largest consumer of magnesia worldwide is the refractory industry, which consumed about 56 % of magnesia in United States, the remaining (44 %) used in agricultural, chemical, construction, environmental, and other industrial applications. Also its used as additive ceramic material to enhance the properties of different sort of materials.

6. Titanium Dioxide

Titanium dioxide (TiO_2) is one of the high-melting (1840°C) and chemically inert transition metal oxide. Oxide ceramics based on titanium dioxide are very corrosion resistant, and also have a very low abrasion coefficient and high optical properties; thus, they are used as drawing dyes in the textile industry.

TiO_2 is by far the most important white pigment with a high light resistance. By doping rutile with other transition metal cations, different colors can be achieved. TiO_2 is used as a pigment additive

for coatings, plastics, and paper as well as thin films and sunscreen and UV blocking pigments.

As a mineral, titanium dioxide occurs in three modifications: **rutile**, **anatase** and the **brookite**. Under the normal conditions, rutile is the most stable form. When heated, both anatase and brookite transform irreversibly to rutile before melting at 1840 °C. For all applications, high-temperature rutile modification is used. As a pigment, the rutile form is superior to the anatase. In addition, nanosized titanium dioxide, particularly in the anatase form, exhibits photocatalytic activity under ultraviolet (UV) irradiation.

The most common mineral source is **ilmenite**. Ilmenite is converted into pigment grade titanium dioxide via either **sulfate process** or **chloride process**. Both sulfate and chloride processes produce the titanium dioxide pigment in the rutile crystal form, but the sulfate process can be adjusted to produce the anatase form. Anatase, being softer, is used in fiber and paper applications.

In the **sulfate process**, ilmenite is treated with the sulfuric acid to extract iron(II) sulfate pentahydrate. The resulting synthetic rutile is further processed according to the specifications of the end user, i.e. pigment grade or otherwise.

An alternative process, known as **chloride process** converts ilmenite or other titanium sources to titanium tetrachloride via reaction with

elemental chlorine, which is then purified by distillation, and reacted with oxygen to regenerate the chlorine and produce the titanium dioxide.

5. Beryllium Oxide

Beryllium Oxide (**BeO**) or beryllia, has many characteristics that make it desirable for numerous applications. Foremost among these are applications where high thermal conductivity and electrical isolation are required. Pure beryllia exhibits a thermal conductivity higher than that of all metals except silver, gold, copper, and high purity aluminum. In addition, beryllia has excellent dielectric properties; outstanding resistance to wetting and corrosion by many metals and chemicals.

Beryllium oxide is cubic close-packed and the alpha form of BeO is stable to above 2050°C. BeO is stable in dry atmospheres and is inert to most materials. BeO reacts with graphite at high temperature, forming beryllium carbide. While beryllia in the pure form is perfectly safe, care must be taken when machining BeO, as the dust is toxic if inhaled.

6. Silicon Carbide

Silicon carbide exists in the form of a very large number of crystallographic varieties. The most widespread polytypes are the [β -SiC] (**cubic, low temperature**) and [α -SiC] (**hexagonal, high**

temperature) varieties. SiC powder is densified by reaction sintering reaction, natural or pressure sintering. Reaction sintering consists of compacting a mixture of silicon and carbon, which is then infiltrated with liquid silicon.

Industrially, the natural sintering is the most widely used. It requires introducing a small quantity of the additives, carbon and boron or carbon and aluminum. The mixture is formed, then the compact treated in inert atmosphere between **2000 and 2100°C**. The chemical reactions and the densification mechanisms are complex and vary with temperature and nature of sintering additives.

The use of pressure sintering or hot isostatic pressing is limited to the production of completely dense ceramic pieces with very low additive contents. Silicon carbide can also be densified between **2000 and 2100°C** in the presence of a liquid phase formed from additives, such as Y_2O_3 and Al_2O_3 .

The high sublimation temperature of SiC (**about 2700 °C**) makes it useful for bearings and furnace parts. Silicon carbide does not melt at any known temperature. It is also highly inert chemically. There is currently much interest in its use as a semiconductor material in electronics, where its high thermal conductivity, the high electric field breakdown strength and high maximum current density make SiC more promising than silicon for high-powered devices in the electronic technology.

Silicon carbide is a popular abrasive in modern industry due to the durability and the low cost. In manufacturing, it is used for its high hardness in the abrasive machining and in cutting tools.

7. Silicon Nitride

Silicon nitride with the formula (Si_3N_4) is a chemical compound of elements silicon and nitrogen,. It is a white, high-melting-point solid that is relatively chemically inert with high hardness. Silicon nitride can be sintered in five different methods: reaction sintering, natural sintering, pressure sintering, hot isostatic pressing and nitrogen gas pressure sintering. Apart from reaction sintering, all the other processes require sintering additives. This consists of nitriding powdery silicon compact at (1300–1350°C).

Silicon nitride exists under two crystalline structures of hexagonal symmetry: **low temperature** (α) variety, whose crystals are equiaxed and the **high temperature** (β) variety, generally in form of acicular crystals. The transformation ($\alpha \rightarrow \beta$) is not reversible. It is possible to modulate the microstructure (size and shape of crystals) in a broad domain according to desired properties or applications. Its widely used in automobile, bearing, medical, electronics and cutting tools applications. Silicon nitride exhibits high strength at elevated temperatures and excellent thermal shock, creep and oxidation resistance in the hostile environments, which makes it ideal for gas turbine and diesel engine applications.

8. Aluminum Nitride

There are several large-scale methods for producing AlN, two of which are currently used in industry. One method is direct nitridation of aluminum. Al powders are converted directly to the nitride at temperatures above the melting point of the metal. Careful process control is necessary to avoid coalescence of metal prior to nitridation. Reducing alumina using nitrogen or ammonia in the presence of carbon is another method to produce AlN.

The main vendors for AlN powders are refractory technologies and their properties depends on supplier, powder characteristics, and purity. Many of applications of AlN require it to be in consolidated in the form of substrates or crucibles. It is an electrical insulator and has a high thermal conductivity (better than Fe), which makes it attractive for electronic packaging. Aluminum nitride crucibles are widely used to contain metal melts and molten salts.

9. Zirconium Diboride

ZrB₂ is useful as a crucible material for metal melts because of its excellent corrosion resistance. Several different processes can be used to produce ZrB₂; these are similar to those used to form carbides and nitrides. Commercially, either a direct reaction between zirconium and boron carried out at high temperature in an inert atmosphere or in vacuum.