

**Ceramics:** Important clays and feldspar, ceramic, their types and manufacture. High technology ceramics and their applications, superconducting and semiconducting oxides, fullerenes carbon nanotubes and carbon fiber.

**Ceramic materials** are inorganic, nonmetallic compounds, usually oxides like  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and non-oxides such as carbides, nitrides, and borides. Both ionic and covalent bonds, or combination of them, can be found in ceramic materials.

Although different types of ceramics can have very different properties, in general ceramics are corrosion-resistant and hard, but brittle. Most ceramics are also good insulators and can withstand high temperatures. These properties have led to their use in virtually every aspect of modern life.

Ceramic materials may occur in the form of single crystal and in the form of polycrystalline material (polycrystals). These polycrystals are oriented with respect to each other in more or less completely random way. They are also called “grains”. When the grains have a different composition, the ceramic material is of multiphase. The grains in the monolithic material are of single phase.

**Clay:** A hydrated aluminium silicates with other oxides. e.g.  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$

**Feldspar:** A naturally occurring industrial important, network silicate with a low melting temperature. It becomes glass upon firing and bonds the refractory components together. Some  $\text{Si}^{+4}$  ions are replaced with  $\text{Al}^{+3}$  in substitutional positions and some  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$  ions are interstitial positions. e.g.  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ .

**Silica:**  $\text{SiO}_2$  is a polymorphic compound (quartz, tridymite and cristobalite are some of its forms). It acts as the refractory component of traditional ceramics. Common examples are earthenware, porcelain, and brick.

The **two main categories** of ceramics are **traditional and advanced**. Traditional ceramics include objects made of clay and cements that have been hardened by heating at high temperatures. Traditional ceramics are used in dishes, crockery, flowerpots, and roof and wall tiles. Advanced ceramics include carbides, such as silicon carbide,  $\text{SiC}$ ; oxides, such as aluminum oxide,  $\text{Al}_2\text{O}_3$ ; nitrides, such as silicon nitride,  $\text{Si}_3\text{N}_4$ ; and many other materials, including the mixed oxide ceramics that can act as superconductors. Advanced ceramics require modern processing

techniques, and the development of these techniques has led to advances in medicine and engineering.

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The classification of ceramics is shown below.

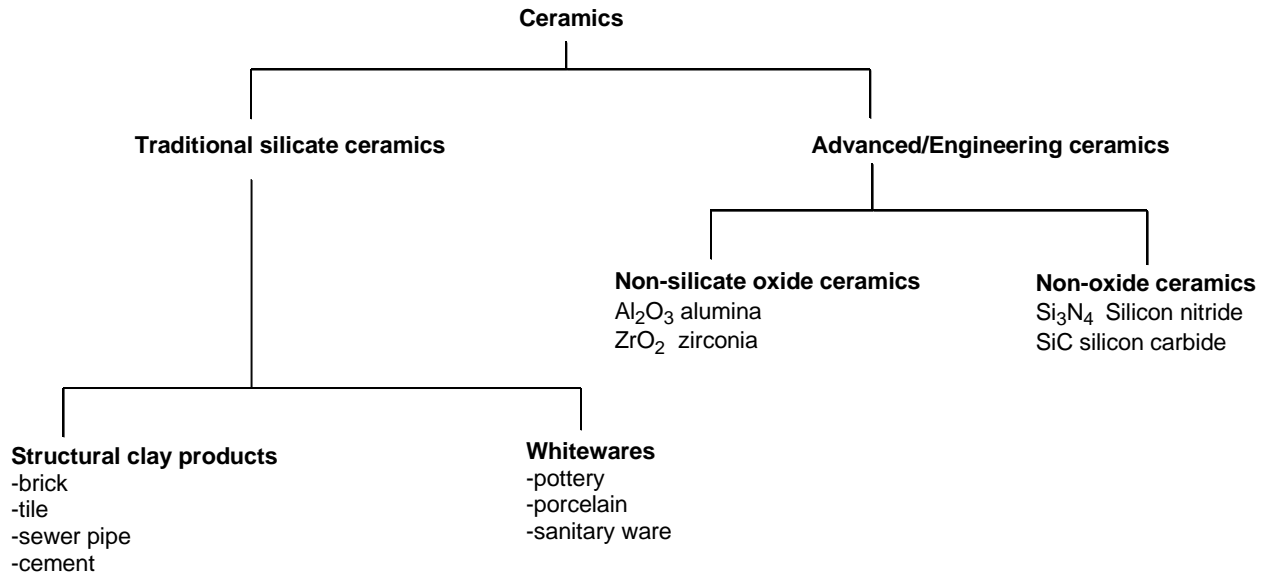


Figure 1 shows a typical cross-section of ceramic material. It is composed of an assembly of irregularly shaped grains and pores. The solid-solid interfaces are called "grain boundaries" and the solid-gas interfaces are called "free surfaces". Grain boundaries and free surfaces constitute the microstructure of the ceramic material.

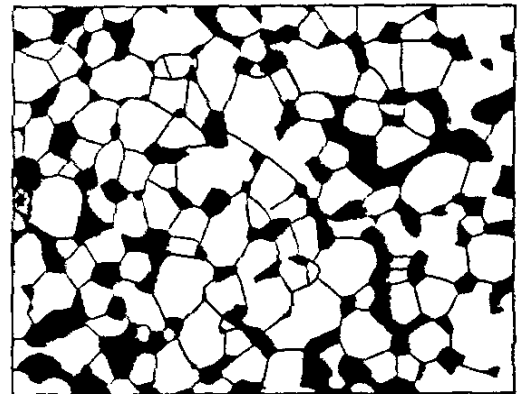


Figure 1

To obtain polycrystalline ceramic material, a compressed fine-grained powder is subjected to a high temperature around (65-75)% of its melting point. The process is called "sintering"; in which the powder compact shrinks during heating, and its bulk density increases to form the ceramic body. The densification of the powder compact is accompanied by coarsening of primary grains "grain growth" and elimination or decrease in volume of intergranular voids "pore shrinkage". The evolution and rate of these microstructure changes are referred to as "microstructure development" of the sintered ceramic body.

The mechanical and physical properties of ceramics are depending on their **microstructure**. The mechanical properties are correlated to the **grain size** (the diameter of the sphere of the same grain volume) while the thermal, magnetic and electrical properties are influenced by the existence of the interfaces (grain boundaries and free surfaces). The correlation between the properties of ceramics and their microstructure reflects the importance of sintering studies. Normally, these studies attempt to attain high density and controlled grain size of the product.

Semiconductors are subgroup of ceramics; they are covalently bonded solids that, in addition to well-known Si and Ge, include GaAs, CdTe, and InP ...etc. Other semiconductors outside the electronic materials are SiC, TiO<sub>2</sub>, ZnO, and others.

The arrangement of atoms in solids, in general, and ceramics, in particular, will exhibit **long-range order**, only **short-range order**, or a combination of both. Solids that exhibit long-range order are referred to as **crystalline** solids, while those in which that periodicity is lacking are known as **amorphous**, **glassy**, or **noncrystalline** solids.

#### Composition

Some ceramics are composed of only two elements. For example, alumina is aluminum oxide, Al<sub>2</sub>O<sub>3</sub>; zirconia is zirconium oxide, ZrO<sub>2</sub>; Ceramics are good insulators and can withstand high temperatures. A popular use of ceramics is in artwork. silicon dioxide, SiO<sub>2</sub>. Other ceramic materials, including many minerals, have complex and even variable compositions. For example, the ceramic mineral feldspar, one of the components of granite, has the formula KAlSi<sub>3</sub>O<sub>8</sub>. The chemical bonds in ceramics can be covalent, ionic, or polar covalent, depending on the chemical composition of the ceramic. When the components of the ceramic are a metal and a nonmetal, the bonding is primarily ionic; examples are magnesium oxide (magnesia), MgO, and barium titanate, BaTiO<sub>3</sub>. In ceramics composed of a metalloid and a nonmetal, bonding is primarily covalent; examples are boron nitride, BN, and silicon carbide, SiC. Most ceramics have a highly crystalline structure, in which a three-dimensional unit, called a unit cell, is repeated throughout the material. For example, magnesium oxide crystallizes in the rock salt structure. In this structure, Mg<sup>2+</sup> ions alternate with O<sup>2-</sup> ions along each perpendicular axis.

## **Manufacture of Traditional Ceramics**

Traditional ceramics are made from natural materials such as clay that have been hardened by heating at high temperatures (driving out water and allowing strong chemical bonds to form between the flakes of clay). In fact, the word "ceramic" comes from the Greek *keramos*, whose original meaning was "burnt earth." When artists make ceramic works of art, they first mold clay, often mixed with other raw materials, into the desired shape. Special ovens called kilns are used to "fire" (heat) the shaped object until it hardens.

Clay consists of a large number of very tiny flat plates, stacked together but separated by thin layers of water. The water allows the plates to cling together, but also acts as a lubricant, allowing the plates to slide past one another. As a result, clay is easily molded into shapes. High temperatures drive out water and allow bonds to form between plates, holding them in place and promoting the formation of a hard solid. Binders such as bone ash are sometimes added to the clay to promote strong bond formation, which makes the ceramic resistant to breakage. The common clay used to make flowerpots and roof tiles is usually red-orange because of the presence of iron oxides. White ceramics are made from rarer (and thus more expensive) white clays, primarily kaolin.

The oldest known ceramics made by humans are figurines found in the former Czechoslovakia that are thought to date from around 27,000 B.C.E. It was determined that the figurines were made by mixing clay with bone, animal fat, earth, and bone ash (the ash that results when animal bones are heated to a high temperature), molding the mixture into a desired shape, and heating it in a domed pit. The manufacture of functional objects such as pots, dishes, and storage vessels, was developed in ancient Greece and Egypt during the period 9000 to 6000 B.C.E.

An important advance was the development of white porcelain. Porcelain is a hard, tough ceramic that is less brittle than the ceramics that preceded it. Its strength allows it to be fashioned into beautiful vessels with walls so thin they can even be translucent. It is made from kaolin mixed with china stone, and the mixture is heated to a very high temperature (1,300°C, or 2,372°F). Porcelain was developed in China around C.E. 600 during the T'ang dynasty and was perfected during the Ming dynasty, famous for its blue and white porcelain. The porcelain process was

introduced to the Arab world in the ninth century; later Arabs brought porcelain to Spain, from where the process spread throughout Europe.

Bone china has a composition similar to that of porcelain, but at least 50 percent of the material is finely powdered bone ash. Like porcelain, bone china is strong and can be formed into dishes with very thin, translucent walls. Stoneware is a dense, hard, gray or tan ceramic that is less expensive than bone china and porcelain, but it is not as strong. As a result, stoneware dishes are usually thicker and heavier than bone china or porcelain dishes.

### **Manufacture of Advanced Ceramics**

The preparation of an advanced ceramic material usually begins with a finely divided powder that is mixed with an organic binder to help the powder consolidate, so that it can be molded into the desired shape. Before it is fired, the ceramic body is called "green." The green body is first heated at a low temperature in order to decompose or oxidize the binder. It is then heated to a high temperature until it is "sintered," or hardened, into a dense, strong ceramic. At this time, individual particles of the original powder fuse together as chemical bonds form between them. During sintering the ceramic may shrink by as much as 10 to 40 percent. Because shrinkage is not uniform, additional machining of the ceramic may be required in order to obtain a precise shape.

Sol-gel technology allows better mixing of the ceramic components at the molecular level, and hence yields more homogeneous ceramics, because the ions are mixed while in solution. In the sol-gel process, a solution of an organometallic compound is hydrolyzed to produce a "sol," a colloidal suspension of a solid in a liquid. Typically the solution is a metal alkoxide such as tetramethoxysilane in an alcohol solvent. The sol forms when the individual formula units polymerize (link together to form chains and networks). The sol can then be spread into a thin film, precipitated into tiny uniform spheres called microspheres, or further processed to form a gel inside a mold that will yield a final ceramic object in the desired shape. The many crosslinks between the formula units result in a ceramic that is less brittle than typical ceramics.

Although the sol-gel process is very expensive, it has many advantages, including low temperature

requirements; the ceramist's ability to control porosity and to form films, spheres, and other structures that are difficult to form in molds; and the attainment of specialized ceramic compositions and high product purity. Porous ceramics are made by the sol-gel process. These ceramics have spongelike structures, with many porelike lacunae, or openings, that can make up from 25 to 70 percent of the volume. The pore size can be large, or as small as 50 nanometers ( $2 \times 10^{-6}$  inches) in diameter. Because of the large number of pores, porous ceramics have enormous surface areas (up to 500 square meters, or 5,382 square feet, per gram of ceramic), and so can make excellent catalysts. For example, zirconium oxide is a ceramic oxygen sensor that monitors the air-to-fuel ratio in the exhaust systems of automobiles.

Aerogels are solid foams prepared by removing the liquid from the gel during a sol-gel process at high temperatures and low pressures. Because aerogels are good insulators, have very low densities, and do not melt at high temperatures, they are attractive for use in spacecraft.

***Applications of ceramic products:***

Ceramic materials have a wide range of applications. Some *modern* applications are:

1. Ceramic engines for transportation and turbines for energy production due to the refractoriness of ceramics and their ability to sustain high loads at high temperatures, together with their low densities
2. Optical communications such as fiber optics due to optical properties of a glass
3. Electrooptic applications like displays and transparent displays (semiconductive optical ceramics)
4. Laser materials (the active materials)
5. Substrates in electronic circuits; due to insulative properties, low-loss factors, and excellent thermal and environmental stability
6. Ceramic capacitors due to exceedingly large dielectric constants of the perovskite family
7. Magnetic ceramics based on the spinel ferrites
8. Piezoelectric ceramics for sensors and actuators
9. The nonlinear I-V characteristics for circuit protection
10. Ionically conducting ceramics for use as solid electrolytes in high-temperature fuel cells and as chemical sensors
11. Electrodes in photoelectrochemical devices or cells PEC, which are solar cells that produce electrical energy or hydrogen in a process similar to the electrolysis of water

12. A new revolution in silicate ceramics (Stone Age materials) is taking place to make them materials for the future. Alkali-activated cements and mortars (also called geopolymers) are an example.

In principle, the advantages of an all-ceramic engine are several and include lower weight, a higher operating temperature that translates to higher efficiencies, and less pollution. It is also predicted that such engines would not require cooling and maybe not even any lubrication, which once more would simplify the design of the engine, reducing the number of moving parts, and lowering the overall weight of the vehicle.

### **General Characteristics of Ceramics:**

Ceramic materials are generally:

- |                              |  |
|------------------------------|--|
| 1. Hard                      | 6. Electrically insulative                   |
| 2. Wear-resistant            | 7. Thermally insulative                      |
| 3. Brittle                   | 8. Refractory                                |
| 4. Nonmagnetic               | 9. Vulnerable (susceptible) to thermal shock |
| 5. Intrinsically transparent | 10. Oxidation-resistant, Chemically stable   |

The dominant characteristics of ceramics are summarized by the following:

- i. They are stable and resistant to chemical attack.
- ii. They are brittle, hard, and wear resistant.
- iii. They have high temperature strength.
- iv. They are good electrical insulators at room temperature.
- v. Their thermal conductivities lie between those of polymers and of metals.

### **Fullerenes carbon nanotubes and carbon fibers:**

In 1991 Iijima Sumio of NEC Corporation's Fundamental Research Laboratory, Tsukuba Science City, Japan, investigated material extracted from solids that grew on the tips of carbon electrodes after being discharged under  $C_{60}$  formation conditions. Iijima found that the solids consisted of tiny tubes made up of numerous concentric "graphene" cylinders, each cylinder wall consisting of a sheet of carbon atoms arranged in hexagonal rings. The cylinders usually had closed-off ends and ranged from 2 to 10 micrometres (millionths of a metre) in length and 5 to 40 nanometres (billionths of a metre) in diameter. High-resolution transmission electron

microscopy later revealed that these multiwalled carbon nanotubes (MWNTs) are seamless and that the spacings between adjacent layers is about 0.34 nanometre, close to the spacing observed between sheets of graphite. The number of concentric cylinders in a given tube ranged from 3 to 50, and the ends were generally capped by fullerene domes that included pentagonal rings (necessary for closure of the tubes). It was soon shown that single-walled nanotubes (SWNTs) could be produced by this method if a cobalt-nickel catalyst was used. In 1996 a group led by Smalley produced SWNTs in high purity by laser vaporization of carbon impregnated with cobalt and nickel. These nanotubes are essentially elongated fullerenes.

Individual carbon nanotubes may be metallic or semiconducting, depending on the helical orientation of the rows of hexagonal rings in the walls of the tubes. Rather than conducting electricity via electron transport, a diffusive process that results in electron scattering and conductive heating, SWNTs exhibit ballistic transport, a highly efficient and fast conduction process in which electrons, prevented from diffusing through the wall of the tube or around its circumference by the regular hexagonal array of carbon atoms, propagate rapidly along the axis of the tube. Open-ended SWNTs emit electrons at currents that attain approximately 100 nanoamperes (billionths of an ampere). Owing to such remarkable properties, electrical conductors made of bundles of nanotubes should exhibit zero energy loss. Aligned MWNTs show promise as field-emission devices with potential applications in electronic flat-panel displays. Nanotubes may also be used as highly resilient probe tips for scanning tunneling microscopes and atomic force microscopes.

Carbon nanotubes exhibit faster phonon transport than diamond, which was previously recognized as the best thermal conductor, and the electric current-carrying capacity of nanotubes is approximately four orders of magnitude higher than that of copper. The Young's modulus of MWNTs (a measure of their elasticity, or ability to recover from stretching or compression) is estimated by researchers to be greater than that of carbon fibres by a factor of 5 to 10. MWNTs are capable of readily absorbing loads via a sequence of reversible elastic deformations, such as buckling or kinking, in which the bonds between carbon atoms remain intact.

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Nanotubes can be “decapped” by oxidation and the resulting opened tubes filled with metals, such as lead, or even with buckyballs. Boron and nitrogen atoms may be incorporated into carbon



nanotube walls. Microscopic metal particles that would otherwise be rapidly oxidized may be stabilized in air by encapsulation in nanotube skins.

### **Potential Applications of Fullerenes:**

The discovery of C<sub>60</sub> has led to a paradigm shift in the understanding of graphite, in particular graphene sheets on a small scale. It is now known that the most stable form of a carbon aggregate, containing tens to several thousands of atoms, is a closed buckyball or nanotube. This new understanding is not restricted to pure carbon but also applies to other sheet-forming materials such as boron nitride, which can also form nanotubes. Closed fullerene structures, incorporating sulfides of such metals as tungsten and molybdenum, exhibit excellent solid-lubricant properties. Conducting carbon nanotubes may be coated with sheaths of metal sulfides to produce tiny insulated electrical wire.

Fullerenes and nanotubes have engendered much excitement, especially with regard to possible future applications, but so far such applications have been few and far between. Nanotubes in particular may well bring about a revolution in materials science. For example, if SWNTs can be made in bundles of 100 billion, then a material will be produced that may approach the limits of tensile strength possible for any known material involving the chemical bond. In practice, no material approaches its theoretical “intrinsic strength,” because of breakdowns brought on by the propagation of microscopic defects through the material. A bundle of nanotubes, however, may bypass this problem, as microscopic defects may anneal along the length of a particular tube and certainly should not propagate across the bundle—thus avoiding the problems that occur in conventional materials. Estimates of potential tensile strength vary, but it is predicted that a 1-metre rod may reach 50 to 100 times the strength of steel at one-sixth the weight. The impact of such a material on civil engineering, building construction, aircraft, and automobiles would be spectacular. In order to realize this potential, however, new processes will have to be discovered that can produce long (more than 1 metre), perfectly ordered bundles in which all 100 billion nanotubes preferably have the same diameter and atomic arrangement. At present the technology to achieve this does not exist; indeed, it is not even obvious what strategy might be used to reach this goal. More realistically, carbon-nanotube composite materials exhibiting improved behaviour over standard carbon-fibre composites are likely in the near term. In addition,

applications on a small scale should be feasible for medical purposes—for instance, the strength of individual nanotubes may prove useful in microsurgery or nanosurgery.

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**Carbon fibers** (alternatively CF, graphite fiber or graphite fibre) are fibers about 5–10 micrometres in diameter and composed mostly of carbon atoms. Carbon fibers have several advantages including high stiffness, high tensile strength, low weight, high chemical resistance, high temperature tolerance and low thermal expansion. These properties have made carbon fiber very popular in aerospace, civil engineering, military, and motorsports, along with other competition sports. However, they are relatively expensive when compared with similar fibers, such as glass fibers or plastic fibers.

To produce a carbon fiber, the carbon atoms are bonded together in crystals that are more or less aligned parallel to the long axis of the fiber as the crystal alignment gives the fiber high strength-to-volume ratio (in other words, it is strong for its size). Several thousand carbon fibers are bundled together to form a tow, which may be used by itself or woven into a fabric.

Carbon fibers are usually combined with other materials to form a composite. When impregnated with a plastic resin and baked it forms carbon-fiber-reinforced polymer (often referred to as carbon fiber) which has a very high strength-to-weight ratio, and is extremely rigid although somewhat brittle. Carbon fibers are also composited with other materials, such as graphite, to form reinforced carbon-carbon composites, which have a very high heat tolerance.

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