Engineering and Science of Ceramic and Glass

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Chapter 1

Ceramic Materials

Ceramic Si_3N_4 bearing parts

Ceramic materials are inorganic, non-metallic materials and things made from them. They may be crystalline or partly crystalline. They are formed by the action of heat and

subsequent cooling. Clay was one of the earliest materials used to produce ceramics, but many different ceramic materials are now used in domestic, industrial and building products.

Types of ceramic materials

A ceramic material may be defined as any inorganic crystalline oxide material. It is solid and inert. Ceramic materials are brittle, hard, strong in compression, weak in shearing and tension. They withstand chemical erosion that occurs in an acidic or caustic environment. In many cases withstanding erosion from the acid and bases applied to it. Ceramics generally can withstand very high temperatures such as temperatures that range from 1,000 °C to 1,600 °C (1,800 °F to 3,000 °F). Exceptions include inorganic materials that do not have oxygen such as silicon carbide. Glass by definition is not a ceramic because it is an amorphous solid (non-crystalline). However, glass involves several steps of the ceramic process and its mechanical properties behave similarly to ceramic materials.

Traditional ceramic raw materials include clay minerals such as kaolinite, more recent materials include aluminium oxide, more commonly known as alumina. The modern ceramic materials, which are classified as advanced ceramics, include silicon carbide and tungsten carbide. Both are valued for their abrasion resistance, and hence find use in applications such as the wear plates of crushing equipment in mining operations. Advanced ceramics are also used in the medicine, electrical and electronics industries.

Crystalline ceramics

Crystalline ceramic materials are not amenable to a great range of processing. Methods for dealing with them tend to fall into one of two categories - either make the ceramic in the desired shape, by reaction in situ, or by "forming" powders into the desired shape, and then sintering to form a solid body. Ceramic forming techniques include shaping by hand (sometimes including a rotation process called "throwing"), slip casting, tape casting (used for making very thin ceramic capacitors, etc.), injection moulding, dry pressing, and other variations. A few methods use a hybrid between the two approaches.

Non-crystalline ceramics

Non-crystalline ceramics, being glasses, tend to be formed from melts. The glass is shaped when either fully molten, by casting, or when in a state of toffee-like viscosity, by methods such as blowing to a mold. If later heat-treatments cause this class to become partly crystalline, the resulting material is known as a glass-ceramic.

Properties of ceramics

The physical properties of any ceramic substance are a direct result of its crystalline structure and chemical composition. Solid state chemistry reveals the fundamental

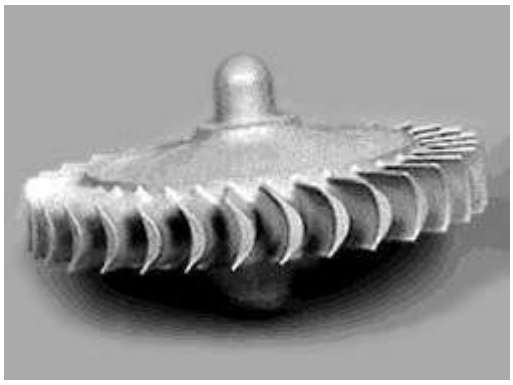
connection between microstructure and properties such as localized density variations, grain size distribution, type of porosity and second-phase content, which can all be correlated with ceramic properties such as mechanical strength σ by the Hall-Petch equation, hardness, toughness, dielectric constant, and the optical properties exhibited by transparent materials.

Physical properties of chemical compounds which provide evidence of chemical composition include odor, color, volume, density (mass / volume), melting point, boiling point, heat capacity, physical form at room temperature (solid, liquid or gas), hardness, porosity, and index of refraction.

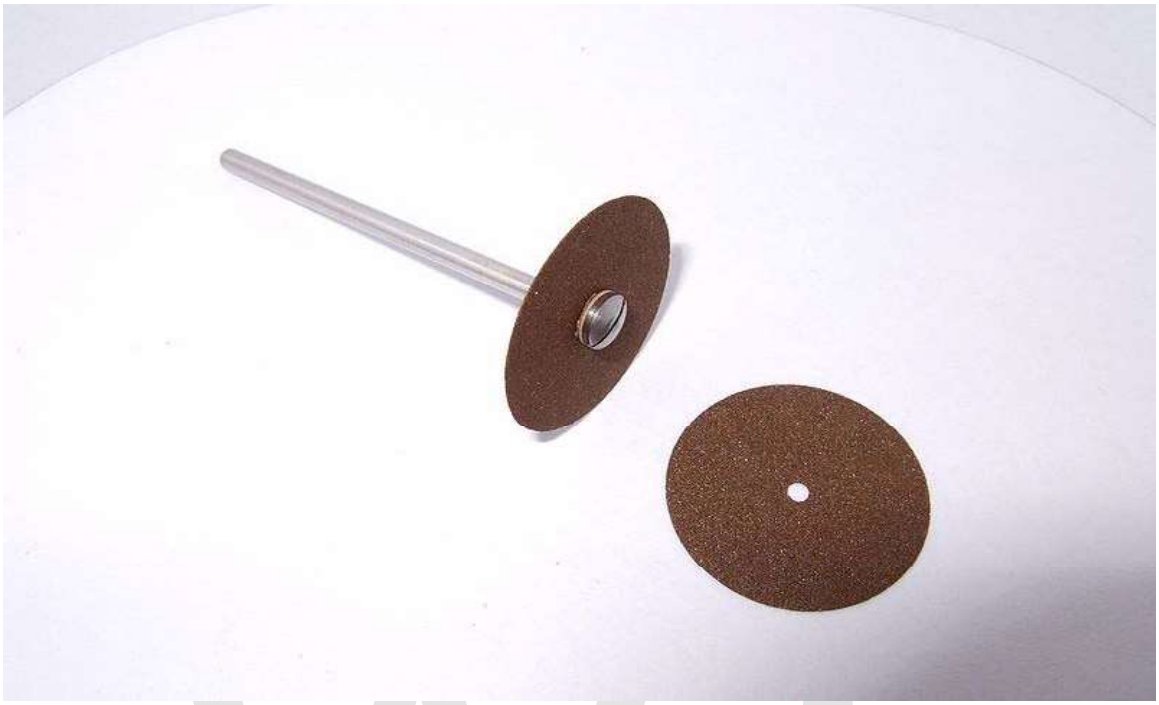
Ceramography is the art and science of preparation, examination and evaluation of ceramic microstructures. Evaluation and characterization of ceramic microstructures is often implemented on similar spatial scales to that used commonly in the emerging field of nanotechnology: from tens of angstroms (A) to tens of micrometers (μm). This is typically somewhere between the minimum wavelength of visible light and the resolution limit of the naked eye.

The microstructure includes most grains, secondary phases, grain boundaries, pores, micro-cracks, structural defects and hardness microindentions. Most bulk mechanical, optical, thermal, electrical and magnetic properties are significantly affected by the observed microstructure. The fabrication method and process conditions are generally indicated by the microstructure. The root cause of many ceramic failures is evident in the cleaved and polished microstructure. Physical properties which constitute the field of materials science and engineering include the following:

Mechanical properties



Radial rotor made from Si_3N_4 for a gas turbine engine



Cutting disks made of SiC

The Porsche Carrera GT's carbon-ceramic (silicon carbide) disc brake

Mechanical properties are important in structural and building materials as well as textile fabrics. They include the many properties used to describe the strength of materials such as: elasticity / plasticity, tensile strength, compressive strength, shear strength, fracture toughness & ductility (low in brittle materials), and indentation hardness.

Fracture mechanics is the field of mechanics concerned with the study of the formation and subsequent propagation of microcracks in materials. It uses methods of analytical solid mechanics to calculate the thermodynamic driving force on a crack and the methods of experimental solid mechanics to characterize the material's resistance to fracture and catastrophic failure.

In modern materials science, fracture mechanics is an important tool in improving the mechanical performance of materials and components. It applies the physics of stress and strain, in particular the theories of elasticity and plasticity, to the microscopic crystallographic defects found in real materials in order to predict the macroscopic mechanical failure of bodies. Fractography is widely used with fracture mechanics to understand the causes of failures and also verify the theoretical failure predictions with real life failures.

Thus, since cracks and other microstructural defects can lower the strength of a structure beyond that which might be predicted by the theory of crystalline objects, a different property of the material—above and beyond conventional strength—is needed to describe the fracture resistance of engineering materials. This is the reason for the need for fracture mechanics: the evaluation of the strength of flawed structures.

In this context, Fracture toughness is a property which describes the ability of a material containing a crack to resist fracture, and is one of the most important properties of any material for virtually all design applications. Fracture toughness is a quantitative way of expressing a material's resistance to brittle fracture when a crack is present. If a material has a large value of fracture toughness it will probably undergo ductile fracture. Brittle fracture is very characteristic of materials with a low fracture toughness value. Fracture mechanics, which leads to the concept of fracture toughness, was largely based on the work of A. A. Griffith who, amongst other things, studied the behaviour of cracks in brittle materials.

Ceramic materials are usually ionic or covalent bonded materials, and can be crystalline or amorphous. A material held together by either type of bond will tend to fracture before any plastic deformation takes place, which results in poor toughness in these materials. Additionally, because these materials tend to be porous, the pores and other microscopic imperfections act as stress concentrators, decreasing the toughness further, and reducing the tensile strength. These combine to give catastrophic failures, as opposed to the normally much more gentle failure modes of metals.

These materials do show plastic deformation. However, due to the rigid structure of the crystalline materials, there are very few available slip systems for dislocations to move, and so they deform very slowly. With the non-crystalline (glassy) materials, viscous flow

is the dominant source of plastic deformation, and is also very slow. It is therefore neglected in many applications of ceramic materials.

Electrical properties

Semiconductors

Some ceramics are semiconductors. Most of these are transition metal oxides that are II-VI semiconductors, such as zinc oxide.

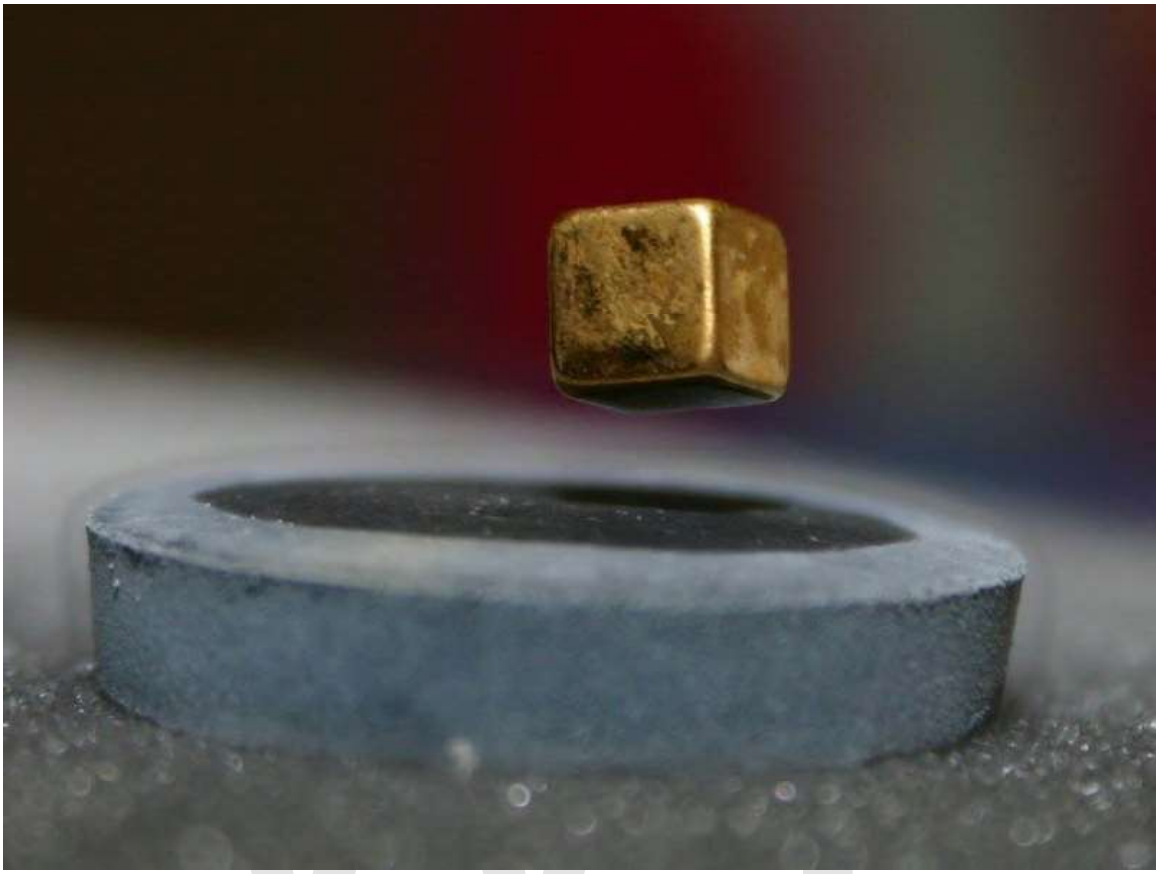
While there are prospects of mass producting blue LEDs from zinc oxide, ceramicists are most interested in the electrical properties that show grain boundary effects.

One of the most widely used of these is the varistor. These are devices that exhibit the property that resistance drops sharply at a certain threshold voltage. Once the voltage across the device reaches the threshold, there is a breakdown of the electrical structure in the vicinity of the grain boundaries, which results in its electrical resistance dropping from several megohms down to a few hundred ohms. The major advantage of these is that they can dissipate a lot of energy, and they self reset — after the voltage across the device drops below the threshold, its resistance returns to being high.

This makes them ideal for surge-protection applications. As there is control over the threshold voltage and energy tolerance, they find use in all sorts of applications. The best demonstration of their ability can be found in electrical substations, where they are employed to protect the infrastructure from lightning strikes. They have rapid response, are low maintenance, and do not appreciably degrade from use, making them virtually ideal devices for this application.

Semiconducting ceramics are also employed as gas sensors. When various gases are passed over a polycrystalline ceramic, its electrical resistance changes. With tuning to the possible gas mixtures, very inexpensive devices can be produced.

Superconductivity



The Meissner effect demonstrated by levitating a magnet above a cuprate superconductor, which is cooled by liquid nitrogen

Under some conditions, such as extremely low temperature, some ceramics exhibit high temperature superconductivity. The exact reason for this is not known, but there are two major families of superconducting ceramics.

Ferroelectricity and supersets

Piezoelectricity, a link between electrical and mechanical response, is exhibited by a large number of ceramic materials, including the quartz used to measure time in watches and other electronics. Such devices use both properties of piezoelectrics, using electricity to produce a mechanical motion (powering the device) and then using this mechanical motion to produce electricity (generating a signal). The unit of time measured is the natural interval required for electricity to be converted into mechanical energy and back again.

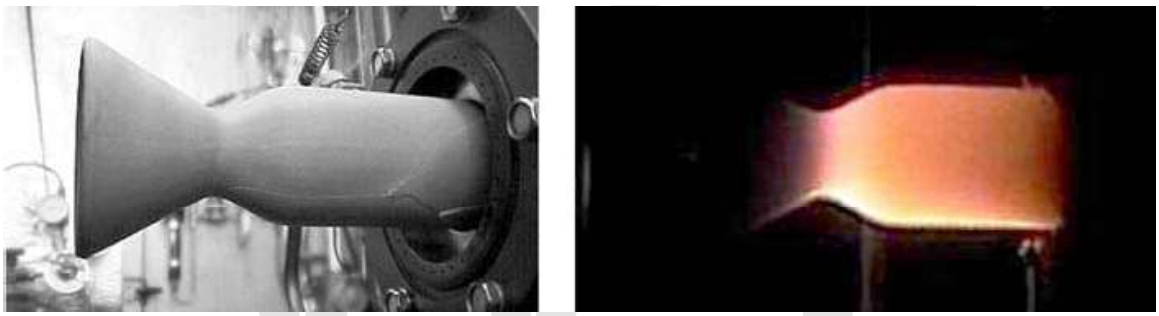
The piezoelectric effect is generally stronger in materials that also exhibit pyroelectricity, and all pyroelectric materials are also piezoelectric. These materials can be used to inter convert between thermal, mechanical, and/or electrical energy; for instance, after

synthesis in a furnace, a pyroelectric crystal allowed to cool under no applied stress generally builds up a static charge of thousands of volts. Such materials are used in motion sensors, where the tiny rise in temperature from a warm body entering the room is enough to produce a measurable voltage in the crystal.

In turn, pyroelectricity is seen most strongly in materials which also display the ferroelectric effect, in which a stable electric dipole can be oriented or reversed by applying an electrostatic field. Pyroelectricity is also a necessary consequence of ferroelectricity. This can be used to store information in ferroelectric capacitors, elements of ferroelectric RAM.

The most common such materials are lead zirconate titanate and barium titanate. Aside from the uses mentioned above, their strong piezoelectric response is exploited in the design of high-frequency loudspeakers, transducers for sonar, and actuators for atomic force and scanning tunneling microscopes.

Positive thermal coefficient



Silicon nitride rocket thruster. Left: Mounted in test stand. Right: Being tested with H_2/O_2 propellants

Increases in temperature can cause grain boundaries to suddenly become insulating in some semiconducting ceramic materials, mostly mixtures of heavy metal titanates. The critical transition temperature can be adjusted over a wide range by variations in chemistry. In such materials, current will pass through the material until joule heating brings it to the transition temperature, at which point the circuit will be broken and current flow will cease. Such ceramics are used as self-controlled heating elements in, for example, the rear-window defrost circuits of automobiles.

At the transition temperature, the material's dielectric response becomes theoretically infinite. While a lack of temperature control would rule out any practical use of the material near its critical temperature, the dielectric effect remains exceptionally strong even at much higher temperatures. Titanates with critical temperatures far below room temperature have become synonymous with "ceramic" in the context of ceramic capacitors for just this reason.

Optical properties

Cermax xenon arc lamp with synthetic sapphire output window

Optically transparent materials focus on the response of a material to incoming lightwaves of a range of wavelengths. Frequency selective optical filters can be utilized to alter or enhance the brightness and contrast of a digital image. Guided lightwave transmission via frequency selective waveguides involves the emerging field of fiber optics and the ability of certain glassy compositions as a transmission medium for a range of frequencies simultaneously (multi-mode optical fiber) with little or no interference between competing wavelengths or frequencies. This resonant mode of energy and data transmission via electromagnetic (light) wave propagation, though low powered, is virtually lossless. Optical waveguides are used as components in Integrated optical circuits (e.g. light-emitting diodes, LEDs) or as the transmission medium in local and long haul optical communication systems. Also of value to the emerging materials scientist is the sensitivity of materials to radiation in the thermal infrared (IR) portion of the electromagnetic spectrum. This heat-seeking ability is responsible for such diverse optical phenomena as Night-vision and IR luminescence.

Thus, there is an increasing need in the military sector for high-strength, robust materials which have the capability to transmit light (electromagnetic waves) in the visible (0.4 – 0.7 micrometers) and mid-infrared (1 – 5 micrometers) regions of the spectrum. These materials are needed for applications requiring transparent armor, including next-generation high-speed missiles and pods, as well as protection against improvised explosive devices (IED).

In the 1960s, scientists at General Electric (GE) discovered that under the right manufacturing conditions, some ceramics, especially aluminium oxide (alumina), could be made translucent. These translucent materials were transparent enough to be used for containing the electrical plasma generated in high-pressure sodium street lamps. During

the past two decades, additional types of transparent ceramics have been developed for applications such as nose cones for heat-seeking missiles, windows for fighter aircraft, and scintillation counters for computed tomography scanners.

In the early 1970s, Thomas Soules pioneered computer modeling of light transmission through translucent ceramic alumina. His model showed that microscopic pores in ceramic, mainly trapped at the junctions of microcrystalline grains, caused light to scatter and prevented true transparency. The volume fraction of these microscopic pores had to be less than 1% for high-quality optical transmission.

This is basically a particle size effect. Opacity results from the incoherent scattering of light at surfaces and interfaces. In addition to pores, most of the interfaces in a typical metal or ceramic object are in the form of grain boundaries which separate tiny regions of crystalline order. When the size of the scattering center (or grain boundary) is reduced below the size of the wavelength of the light being scattered, the scattering no longer occurs to any significant extent.

In the formation of polycrystalline materials (metals and ceramics) the size of the crystalline grains is determined largely by the size of the crystalline particles present in the raw material during formation (or pressing) of the object. Moreover, the size of the grain boundaries scales directly with particle size. Thus a reduction of the original particle size below the wavelength of visible light (~ 0.5 micrometers for shortwave violet) eliminates any light scattering, resulting in a transparent material.

Recently, Japanese scientists have developed techniques to produce ceramic parts that rival the transparency of traditional crystals (grown from a single seed) and exceed the fracture toughness of a single crystal. In particular, scientists at the Japanese firm Konoshima Ltd., a producer of ceramic construction materials and industrial chemicals, have been looking for markets for their transparent ceramics.

Livermore researchers realized that these ceramics might greatly benefit high-powered lasers used in the National Ignition Facility (NIF) Programs Directorate. In particular, a Livermore research team began to acquire advanced transparent ceramics from Konoshima to determine if they could meet the optical requirements needed for Livermore's Solid-State Heat Capacity Laser (SSHCL). Livermore researchers have also been testing applications of these materials for applications such as advanced drivers for laser-driven fusion power plants.

Examples of ceramics materials

Porcelain high-voltage insulator

Silicon carbide is used for inner plates of ballistic vests

Ceramic BN crucible

Until the 1950s, the most important ceramic materials were (1) pottery, bricks and tiles, (2) cements and (3) glass. A composite material of ceramic and metal is known as cermet.

- Barium titanate (often mixed with strontium titanate) displays ferroelectricity, meaning that its mechanical, electrical, and thermal responses are coupled to one another and also history-dependent. It is widely used in electromechanical

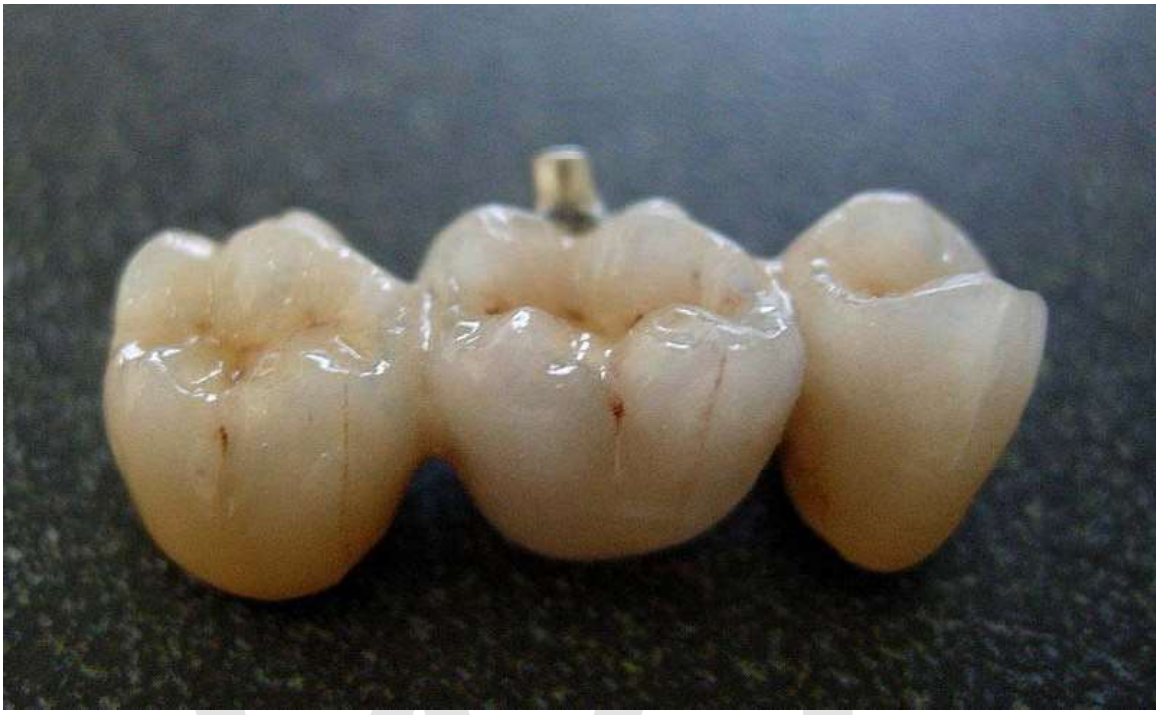
transducers, ceramic capacitors, and data storage elements. Grain boundary conditions can create PTC effects in heating elements.

- Bismuth strontium calcium copper oxide, a high-temperature superconductor
- Boron nitride is structurally isoelectronic to carbon and takes on similar physical forms: a graphite-like one used as a lubricant, and a diamond-like one used as an abrasive.
- Earthenware used for domestic ware such as plates and mugs.
- Ferrite is used in the magnetic cores of electrical transformers and magnetic core memory.
- Lead zirconate titanate (PZT) was developed at the United States National Bureau of Standards in 1954. PZT is used as an ultrasonic transducer, as its piezoelectric properties greatly exceed those of Rochelle salt.
- Magnesium diboride (MgB_2) is an unconventional superconductor.
- Porcelain is used for a wide range of household and industrial products.
- Sialon (Silicon Aluminium Oxynitride) has high strength; high thermal, shock, chemical and wear resistance, and low density. These ceramics are used in non-ferrous molten metal handling, weld pins and the chemical industry.
- Silicon carbide (SiC) is used as a susceptor in microwave furnaces, a commonly used abrasive, and as a refractory material.
- Silicon nitride (Si_3N_4) is used as an abrasive powder.
- Steatite (magnesium silicates) is used as an electrical insulator.
- Titanium carbide Used in space shuttle re-entry shields and scratchproof watches.
- Uranium oxide (UO_2), used as fuel in nuclear reactors.
- Yttrium barium copper oxide ($YBa_2Cu_3O_{7-x}$), another high temperature superconductor.
- Zinc oxide (ZnO), which is a semiconductor, and used in the construction of varistors.
- Zirconium dioxide (zirconia), which in pure form undergoes many phase changes between room temperature and practical sintering temperatures, can be chemically "stabilized" in several different forms. Its high oxygen ion conductivity recommends it for use in fuel cells. In another variant, metastable structures can impart transformation toughening for mechanical applications; most ceramic knife blades are made of this material.
- Partially stabilised zirconia (PSZ) is much less brittle than other ceramics and is used for metal forming tools, valves and liners, abrasive slurries, kitchen knives and bearings subject to severe abrasion.

Ceramic

18th century (Qing dynasty) Chinese porcelain vase

Fire test furnace insulated with firebrick and ceramic fibre insulation



Fixed partial denture, or "bridge"

A **ceramic** is an inorganic, non-metallic solid prepared by the action of heat and subsequent cooling. Ceramic materials may have a crystalline or partly crystalline structure, or may be amorphous (e.g., a glass). Because most common ceramics are crystalline, the definition of ceramic is often restricted to inorganic crystalline materials, as opposed to the non-crystalline glasses.

The earliest ceramics were pottery objects made from clay, either by itself or mixed with other materials, hardened in fire. Later ceramics were glazed and fired to create a colored, smooth surface. Ceramics now include domestic, industrial and building products and art objects. In the 20th century, new ceramic materials were developed for use in advanced ceramic engineering; for example, in semiconductors.

The word *ceramic* comes from the Greek word "κεραμικός" (*keramikos*), "of pottery" or "for pottery", from "κέραμος" (*keramos*), "potter's clay, tile, pottery" which is said to derive from the Indo-European word **cheros* (unattested), meaning heat. The earliest mention on the word "ceramic" is the Mycenaean Greek *ke-ra-me-we*, "workers of ceramics", written in Linear b syllabic script. *Ceramic* may be used as an adjective describing a material, product or process; or as a singular noun, or, more commonly, as a plural noun, *ceramics*.

Types of ceramic products

For convenience, ceramic products are usually divided into four sectors; these are shown below with some examples:

- *Structural*, including bricks, pipes, floor and roof tiles
- *Refractories*, such as kiln linings, gas fire radiants, steel and glass making crucibles
- *Whitewares*, including tableware, wall tiles, pottery products, and sanitary ware
- *Technical*, is also known as Engineering, Advanced, Special, and in Japan, Fine Ceramics. Such items include tiles used in the Space Shuttle program, gas burner nozzles, ballistic protection, nuclear fuel uranium oxide pellets, bio-medical implants, jet engine turbine blades, and missile nose cones. Frequently the raw materials do not include clays.

Examples of whiteware ceramics

- Earthenware, which is often made from clay, quartz and feldspar.
- Stoneware
- Porcelain, which are often made from kaolin
- Bone china

Classification of technical ceramics

Technical ceramics can also be classified into three distinct material categories:

- Oxides: Alumina, zirconia
- Non-oxides: Carbides, borides, nitrides, silicides
- Composites: Particulate reinforced, combinations of oxides and non-oxides.

Each one of these classes can develop unique material properties because ceramics tend to be crystalline.

Other applications of ceramics

- Ceramics are used in the manufacture of knives. The blade of a ceramic knife will stay sharp for much longer than that of a steel knife, although it is more brittle and can be snapped by dropping it on a hard surface.

- Ceramics are increasingly used in motor sports, where a series of durable and lightweight insulatory coatings have become necessary, for example on exhaust manifolds.

- Ceramics such as alumina and boron carbide have been used in ballistic armored vests to repel large-calibre rifle fire. Such plates are known commonly as Small Arms Protective Inserts (SAPI). Similar material is used to protect cockpits of some military airplanes, because of the low weight of the material.

- Ceramic balls can be used to replace steel in ball bearings. Their higher hardness means that they are much less susceptible to wear and can offer more than triple lifetimes. They also deform less under load meaning they have less contact with

the bearing retainer walls and can roll faster. In very high speed applications, heat from friction during rolling can cause problems for metal bearings; problems which are reduced by the use of ceramics. Ceramics are also more chemically resistant and can be used in wet environments where steel bearings would rust. In many cases their electrically insulating properties may also be valuable in bearings. The two major drawbacks to using ceramics is a significantly higher cost, and susceptibility to damage under shock loads.

- In the early 1980s, Toyota researched production of an adiabatic ceramic engine which can run at a temperature of over 6000 °F (3300 °C). Ceramic engines are made of lighter materials and do not require a cooling system and hence allow a major weight reduction. Fuel efficiency of the engine is also higher at high temperature, as shown by Carnot's theorem. In a conventional metallic engine, much of the energy released from the fuel must be dissipated as waste heat in order to prevent a meltdown of the metallic parts. Despite all of these desirable properties, such engines are not in production because the manufacturing of ceramic parts in the requisite precision and durability is difficult. Imperfection in the ceramic leads to cracks, which can lead to potentially dangerous equipment failure. Such engines are possible in laboratory settings, but mass-production is not feasible with current technology.

- Work is being done in developing ceramic parts for gas turbine engines. Currently, even blades made of advanced metal alloys used in the engines' hot section require cooling and careful limiting of operating temperatures. Turbine engines made with ceramics could operate more efficiently, giving aircraft greater range and payload for a set amount of fuel.

- Recently, there have been advances in ceramics which include bio-ceramics, such as dental implants and synthetic bones. Hydroxyapatite, the natural mineral component of bone, has been made synthetically from a number of biological and chemical sources and can be formed into ceramic materials. Orthopedic implants made from these materials bond readily to bone and other tissues in the body without rejection or inflammatory reactions. Because of this, they are of great interest for gene delivery and tissue engineering scaffolds. Most hydroxyapatite ceramics are very porous and lack mechanical strength and are used to coat metal orthopedic devices to aid in forming a bond to bone or as bone fillers. They are also used as fillers for orthopedic plastic screws to aid in reducing the inflammation and increase absorption of these plastic materials. Work is being done to make strong, fully dense nano crystalline hydroxyapatite ceramic materials for orthopedic weight bearing devices, replacing foreign metal and plastic orthopedic materials with a synthetic, but naturally occurring, bone mineral. Ultimately these ceramic materials may be used as bone replacements or with the incorporation of protein collagens, synthetic bones.

- High-tech ceramic is used in watchmaking for producing watch cases. The material is valued by watchmakers for its light weight, scratch-resistance,

durability and smooth touch. IWC is one of the brands that initiated the use of ceramic in watchmaking. The case of the IWC 2007 Top Gun edition of the Pilot's Watch Double chronograph is crafted in black ceramic.

Types of ceramic materials

A ceramic material is often understood as restricted to inorganic *crystalline* oxide material. It is solid and inert. Ceramic materials are brittle, hard, strong in compression, weak in shearing and tension. They withstand chemical erosion that occurs in other materials subjected to acidic or caustic environment. Ceramics generally can withstand very high temperatures such as temperatures that range from 1,000 °C to 1,600 °C (1,800 °F to 3,000 °F). Exceptions include inorganic materials that do not include oxygen such as silicon carbide or silicon nitride. A glass is often not understood as a ceramic because of its amorphous (*non*-crystalline) character. However, glass making involves several steps of the ceramic process and its mechanical properties are similar to ceramic materials.

Traditional ceramic raw materials include clay minerals such as kaolinite, whereas more recent materials include aluminium oxide, more commonly known as alumina. The modern ceramic materials, which are classified as advanced ceramics, include silicon carbide and tungsten carbide. Both are valued for their abrasion resistance, and hence find use in applications such as the wear plates of crushing equipment in mining operations. Advanced ceramics are also used in the medicine, electrical and electronics industries.

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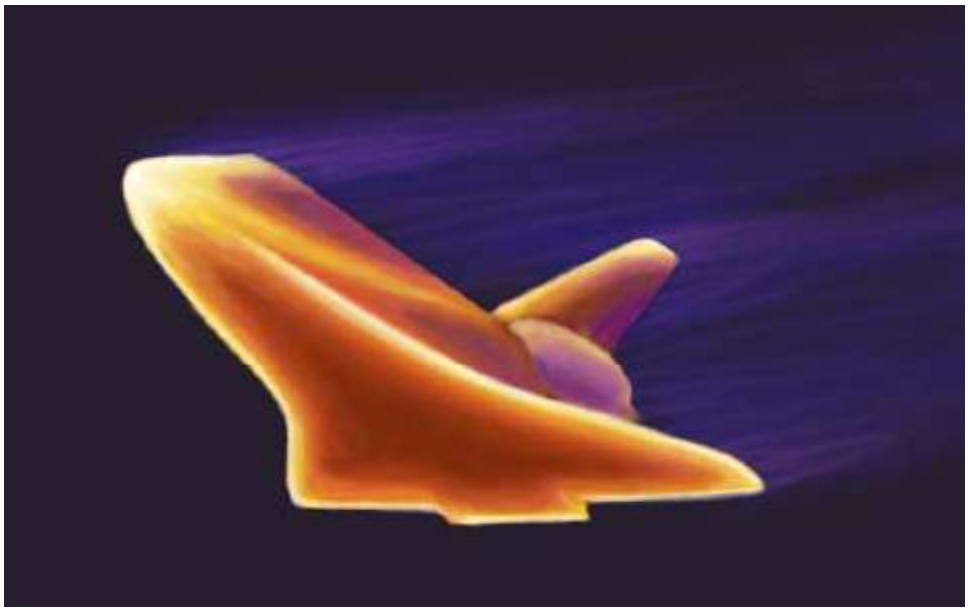
Chapter 2

Ceramic Engineering



Simulation of the outside of the Space Shuttle as it heats up to over 1,500 °C (2,730 °F) during re-entry into the Earth's atmosphere

Ceramic engineering is the science and technology of creating objects from inorganic, non-metallic materials. This is done either by the action of heat, or at lower temperatures using precipitation reactions from high purity chemical solutions. The term includes the purification of raw materials, the study and production of the chemical compounds concerned, their formation into components and the study of their structure, composition and properties.

Ceramic materials may have a crystalline or partly crystalline structure, with long-range order on atomic scale. Glass ceramics may have an amorphous or glassy structure, with limited or short-range atomic order. They are either formed from a molten mass that

solidifies on cooling, formed and matured by the action of heat, or chemically synthesized at low temperatures using, for example, hydrothermal or sol-gel synthesis.

The special character of ceramic materials gives rise to many applications in materials engineering, electrical engineering, chemical engineering and mechanical engineering. As ceramics are heat resistant, they can be used for many tasks that materials like metal and polymers are unsuitable for. Ceramic materials are used in a wide range of industries, including mining, aerospace, medicine, refinery, food and chemical industries, packaging science, electronics, industrial and transmission electricity, and guided lightwave transmission.

Bearing components made from 100% silicon nitride Si_3N_4

Ceramic bread knife

History

The word "ceramic" is derived from the Greek word κεραμικός (*keramikos*) meaning pottery. It is related to the older Indo-European language root "to burn", "Ceramic" may be used as a noun in the singular to refer to a ceramic material or the product of ceramic manufacture, or as an adjective. The plural "ceramics" may be used to refer the making of things out of ceramic materials. Ceramic engineering, like many sciences, evolved from a different discipline by today's standards. Materials science engineering is grouped with ceramics engineering to this day.

Leo Morandi's tile glazing line (circa 1945)

Abraham Darby first used coke in 1709 in Shropshire, England, to improve the yield of a smelting process. Coke is now widely used to produce carbide ceramics. Potter Josiah Wedgwood opened the first modern ceramics factory in Stoke-on-Trent, England, in 1759. Austrian chemist Karl Bayer, working for the textile industry in Russia, developed a process to separate alumina from bauxite ore in 1888. The Bayer process is still used to purify alumina for the ceramic and aluminum industries. Brothers Pierre and Jacques Curie discovered piezoelectricity in Rochelle salt circa 1880. Piezoelectricity is one of the key properties of electroceramics.

E.G. Acheson heated a mixture of coke and clay in 1893, and invented carborundum, or synthetic silicon carbide. Henri Moissan also synthesized SiC and tungsten carbide in his electric arc furnace in Paris about the same time as Acheson. Karl Schröter used liquid-phase sintering to bond or "cement" Moissan's tungsten carbide particles with cobalt in 1923 in Germany. Cemented (metal-bonded) carbide edges greatly increase the durability of hardened steel cutting tools. W.H. Nernst developed cubic-stabilized zirconia in the 1920s in Berlin. This material is used as an oxygen sensor in exhaust systems. The main limitation on the use of ceramics in engineering is brittleness.

Military

Soldiers pictured during the 2003 Iraq War seen through IR transparent Night Vision Goggles

The military requirements of World War II (1939–1945) encouraged developments, which created a need for high-performance materials and helped speed the development of ceramic science and engineering. Throughout the 1960s and 1970s, new types of ceramics were developed in response to advances in atomic energy, electronics, communications, and space travel. The discovery of ceramic superconductors in 1986 has spurred intense research to develop superconducting ceramic parts for electronic devices, electric motors, and transportation equipment.

There is an increasing need in the military sector for high-strength, robust materials which have the capability to transmit light around the visible (0.4–0.7 micrometers) and mid-infrared (1–5 micrometers) regions of the spectrum. These materials are needed for applications requiring transparent armor. Transparent armor is a material or system of materials designed to be optically transparent, yet protect from fragmentation or ballistic impacts. The primary requirement for a transparent armor system is to not only defeat the designated threat but also provide a multi-hit capability with minimized distortion of surrounding areas. Transparent armor windows must also be compatible with night vision equipment. New materials that are thinner, lightweight, and offer better ballistic performance are being sought. Such solid-state components have found widepread use for various applications in the electro-optical field including: optical fibers for guided lightwave transmission, optical switches, laser amplifiers and lenses, hosts for solid-state lasers and optical window materials for gas lasers, and infrared (IR) heat seeking devices for missile guidance systems and IR night vision.

Education

Czech Republic

- The Secondary Technical School Of Ceramics was founded in 1872 in Znojmo. In 1922 it moved to Karlovy Vary.
- The Ceramic Technical School At Bechyne was founded in 1884.

Japan - The Ceramic Society of Japan was founded in 1891 in Tokyo.

Germany

- The Ceramic Society Of Germany was founded in Berlin in 1919.
- Staatliche Fachschule fur Porzellan (Government Technical College for Porcelain) was founded in Selb in 1908. In 1973 it was transferred to Nuremberg Polytechnic, when it was incorporated into a professional training organisation for ceramics which also includes the Staatliche Fachschule fur Keramtechnik and a college for block release courses in ceramic trades, testing and laboratory work.

Poland – the Bunzlau Ceramic Technical College operated from 1887 to 1945.

Spain

- The 'Official Ceramic School' open in Madrid in 1911.
- The Ceramic School Of Manises – was founded in 1914.

United States - the first ceramic engineering course and department in the USA were established by Edward Orton, Jr., a professor of geology and mining engineering, at the Ohio State University in 1894. Orton and eight other refractory professionals founded the American Ceramic Society (ACerS) at the 1898 National Brick Manufacturers' Association convention in Pittsburgh. Orton was the first ACerS General Secretary, and his office at OSU served as the society headquarters in the beginning. Charles F. Binns established the New York State School of Clay-Working and Ceramics, now Alfred University, in 1900. Binns was the third ACerS president, and Orton the 32nd.

Modern industry

U.S. Army soldiers wearing bulletproof ballistic vests with an armored M3 Bradley

Now a multi-billion dollar a year industry, ceramic engineering and research has established itself as an important field of science. Applications continue to expand as researchers develop new kinds of ceramics to serve different purposes.

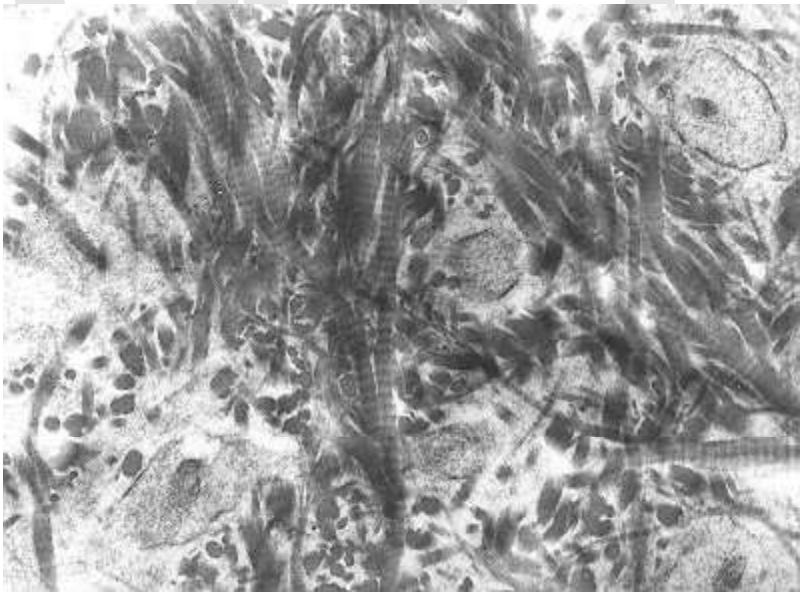
- Zirconium dioxide ceramics are used in the manufacture of knives. The blade of the ceramic knife will stay sharp for much longer than that of a steel knife, although it is more brittle and can be snapped by dropping it on a hard surface.

- Ceramics such as alumina, boron carbide and silicon carbide have been used in bulletproof vests to repel large-caliber rifle fire. Such plates are known commonly as small-arms protective inserts (SAPI). Similar material is used to protect cockpits of some military airplanes, because of the low weight of the material.

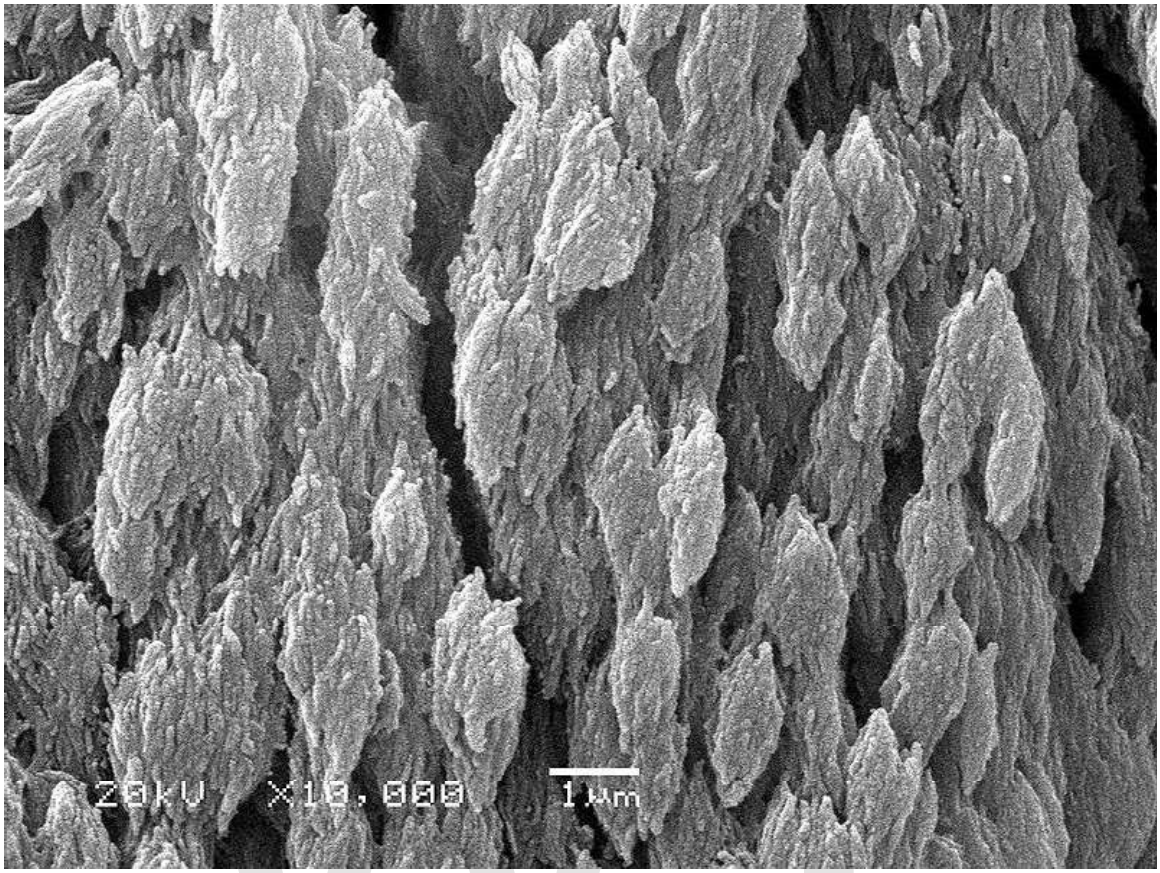
- Silicon nitride parts are used in ceramic ball bearings. Their higher hardness means that they are much less susceptible to wear and can offer more than triple lifetimes. They also deform less under load meaning they have less contact with the bearing retainer walls and can roll faster. In very high speed applications, heat from friction during rolling can cause problems for metal bearings; problems which are reduced by the use of ceramics. Ceramics are also more chemically resistant and can be used in wet environments where steel bearings would rust. The major drawback to using ceramics is a significantly higher cost. In many cases their electrically insulating properties may also be valuable in bearings.

- In the early 1980s, Toyota researched production of an adiabatic ceramic engine which can run at a temperature of over 6000 °F (3300 °C). Ceramic engines do not require a cooling system and hence allow a major weight reduction and therefore greater fuel efficiency. Fuel efficiency of the engine is also higher at high temperature, as shown by Carnot's theorem. In a conventional metallic engine, much of the energy released from the fuel must be dissipated as waste heat in order to prevent a meltdown of the metallic parts. Despite all of these desirable properties, such engines are not in production because the manufacturing of ceramic parts in the requisite precision and durability is difficult. Imperfection in the ceramic leads to cracks, which can lead to potentially dangerous equipment failure. Such engines are possible in laboratory settings, but mass-production is not feasible with current technology.

- Work is being done in developing ceramic parts for gas turbine engines. Currently, even blades made of advanced metal alloys used in the engines' hot section require cooling and careful limiting of operating temperatures. Turbine engines made with ceramics could operate more efficiently, giving aircraft greater range and payload for a set amount of fuel.



Collagen fibers of woven bone



SEM 10,000x magnification of crystalline bone mineral

- Recently, there have been advances in ceramics which include bio-ceramics, such as dental implants and synthetic bones. Hydroxyapatite, the natural mineral component of bone, has been made synthetically from a number of biological and chemical sources and can be formed into ceramic materials. Orthopedic implants made from these materials bond readily to bone and other tissues in the body without rejection or inflammatory reactions. Because of this, they are of great interest for gene delivery and tissue engineering scaffolds. Most hydroxy apatite ceramics are very porous and lack mechanical strength and are used to coat metal orthopedic devices to aid in forming a bond to bone or as bone fillers. They are also used as fillers for orthopedic plastic screws to aid in reducing the inflammation and increase absorption of these plastic materials. Work is being done to make strong, fully dense nano crystalline hydroxyapatite ceramic materials for orthopedic weight bearing devices, replacing foreign metal and plastic orthopedic materials with a synthetic, but naturally occurring, bone mineral. Ultimately these ceramic materials may be used as bone replacements or with the incorporation of protein collagens, synthetic bones.

- High-tech ceramic is used in watchmaking for producing watch cases. The material is valued by watchmakers for its light weight, scratch-resistance, durability and smooth touch. IWC is one of the brands that initiated the use of

ceramic in watchmaking. The case of the IWC 2007 Top Gun edition of the Pilot's Watch Double chronograph is crafted in high-tech black ceramic.

Glass-ceramics

A high strength glass-ceramic cooktop with negligible thermal expansion

Glass-ceramic materials share many properties with both glasses and ceramics. Glass-ceramics have an amorphous phase and one or more crystalline phases and are produced by a so called "controlled crystallization", which is typically avoided in glass manufacturing. Glass-ceramics often contain a crystalline phase which constitutes anywhere from 30% [m/m] to 90% [m/m] of its composition by volume, yielding an array of materials with interesting thermomechanical properties.

In the processing of glass-ceramics, molten glass is cooled down gradually before reheating and annealing. In this heat treatment the glass partly crystallizes. In many cases, so-called 'nucleation agents' are added in order to regulate and control the crystallization process. Because there is usually no pressing and sintering, glass-ceramics do not contain the volume fraction of porosity typically present in sintered ceramics.

The term mainly refers to a mix of lithium and aluminosilicates which yields an array of materials with interesting thermomechanical properties. The most commercially important of these have the distinction of being impervious to thermal shock. Thus, glass-ceramics have become extremely useful for countertop cooking. The negative thermal expansion coefficient (TEC) of the crystalline ceramic phase can be balanced with the positive TEC of the glassy phase. At a certain point (~70% crystalline) the glass-ceramic has a net TEC near zero. This type of glass-ceramic exhibits excellent mechanical properties and can sustain repeated and quick temperature changes up to 1000 °C.

Processing steps

The traditional ceramic process generally follows this sequence: Milling → Batching → Mixing → Forming → Drying → Firing → Assembly

Ball mill

- **Milling** is the process by which materials are reduced from a large size to a smaller size. Milling may involve breaking up cemented material (in which case individual particles retain their shape) or pulverization (which involves grinding the particles themselves to a smaller size). Milling is generally done by mechanical means, including *attrition* (which is particle-to-particle collision that results in agglomerate break up or particle shearing), *compression* (which applies a forces that results in fracturing), and *impact* (which employs a milling medium or the particles themselves to cause fracturing). Attrition milling equipment includes the wet scrubber (also called the planetary mill or wet attrition mill), which has paddles in water creating vortexes in which the material collides and break up. Compression mills include the jaw crusher, roller crusher and cone crusher. Impact mills include the ball mill, which has media that tumble and fracture the material. Shaft impactors cause particle-to particle attrition and compression.

- **Batching** is the process of weighing the oxides according to recipes, and preparing them for mixing and drying.

- **Mixing** occurs after batching and is performed with various machines, such as dry mixing ribbon mixers (a type of cement mixer), Mueller mixers, and pug mills. Wet mixing generally involves the same equipment.

- **Forming** is making the mixed material into shapes, ranging from toilet bowls to spark plug insulators. Forming can involve: (1) Extrusion, such as extruding "slugs" to make bricks, (2) Pressing to make shaped parts, (3) Slip casting, as in making toilet bowls, wash basins and ornamentals like ceramic statues. Forming produces a "green" part, ready for drying. Green parts are soft, pliable, and over time will lose shape. Handling the green product will change its shape. For example, a green brick can be "squeezed", and after squeezing it will stay that way.

- **Drying** is removing the water or binder from the formed material. Spray drying is widely used to prepare powder for pressing operations. Other dryers are tunnel

dryers and periodic dryers. Controlled heat is applied in this two-stage process. First, heat removes water. This step needs careful control, as rapid heating causes cracks and surface defects. The dried part is smaller than the green part, and is brittle, necessitating careful handling, since a small impact will cause crumbling and breaking.

- **Firing** is where the dried parts pass through a controlled heating process, and the oxides are chemically changed to cause sintering and bonding. The fired part will be smaller than the dried part.

Forming methods

Ceramic forming techniques include throwing, slipcasting, tape casting, injection molding, dry pressing, isostatic pressing, hot isostatic pressing (HIP) and others. Methods for forming ceramic powders into complex shapes are desirable in many areas of technology. Such methods are required for producing advanced, high-temperature structural parts such as heat engine components and turbines. Materials other than ceramics which are used in these processes may include: wood, metal, water, plaster and epoxy—most of which will be eliminated upon firing.

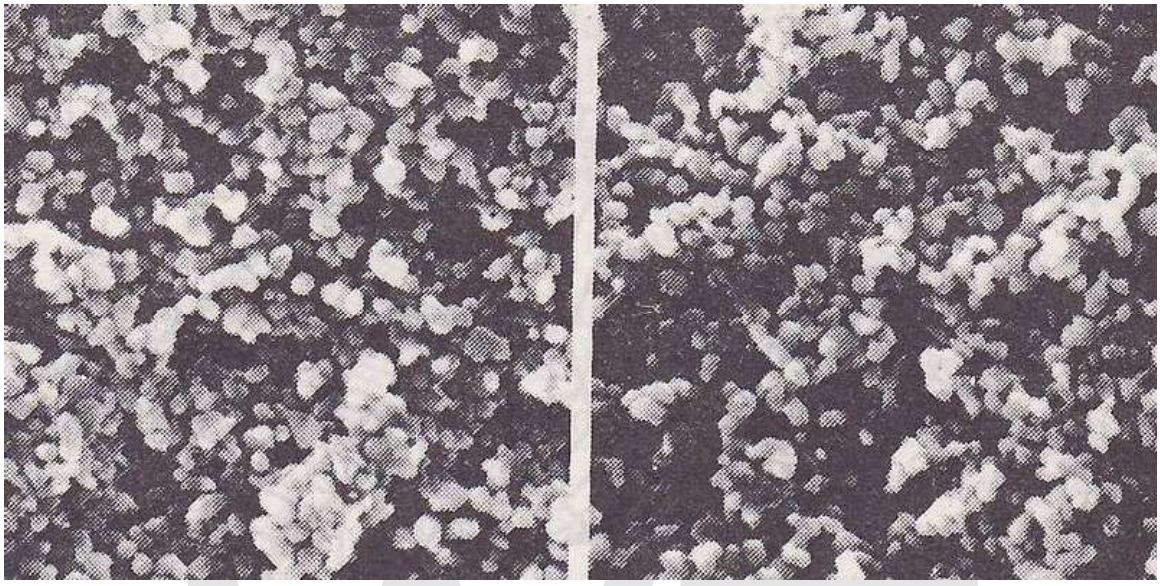
These forming techniques are well known for providing tools and other components with dimensional stability, surface quality, high (near theoretical) density and microstructural uniformity. The increasing use and diversity of specialty forms of ceramics adds to the diversity of process technologies to be used.

Thus, reinforcing fibers and filaments are mainly made by polymer, sol-gel, or CVD processes, but melt processing also has applicability. The most widely used specialty form is layered structures, with tape casting for electronic substrates and packages being preeminent. Photolithography is of increasing interest for precise patterning of conductors and other components for such packaging. Tape casting or forming processes are also of increasing interest for other applications, ranging from open structures such as fuel cells to ceramic composites.

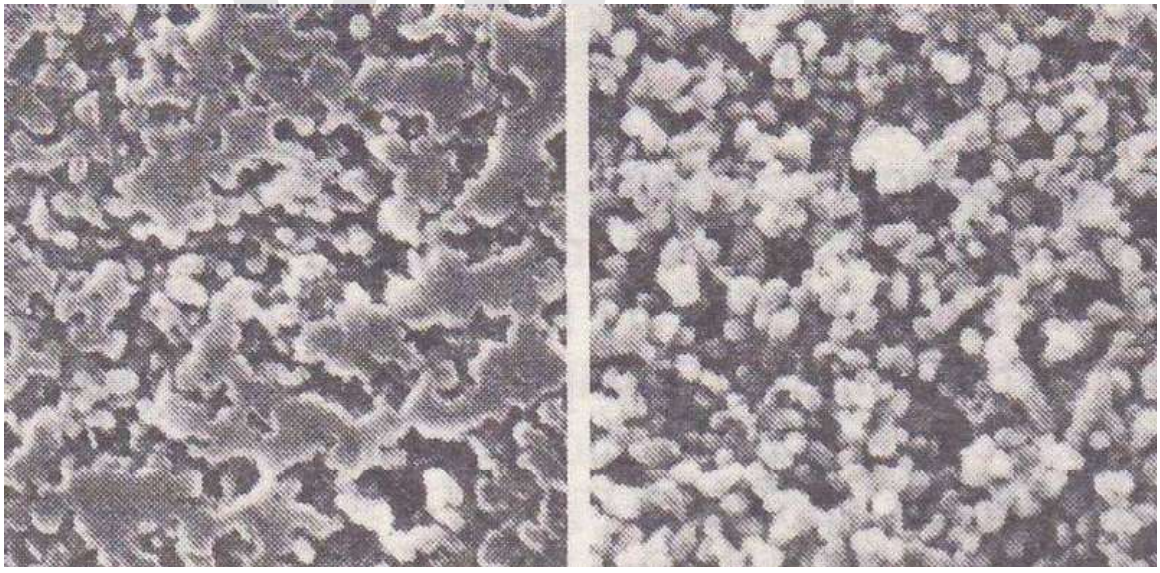
The other major layer structure is coating, where melt spraying is very important, but chemical and physical vapor deposition and chemical (e.g., sol-gel and polymer pyrolysis) methods are all seeing increased use. Besides open structures from formed tape, extruded structures, such as honeycomb catalyst supports, and highly porous structures, including various foams, for example, reticulated foam, are of increasing use.

Densification of consolidated powder bodies continues to be achieved predominantly by (pressureless) sintering. However, the use of pressure sintering by hot pressing is increasing, especially for non-oxides and parts of simple shapes where higher quality (mainly microstructural homogeneity) is needed, and larger size or multiple parts per pressing can be an advantage.

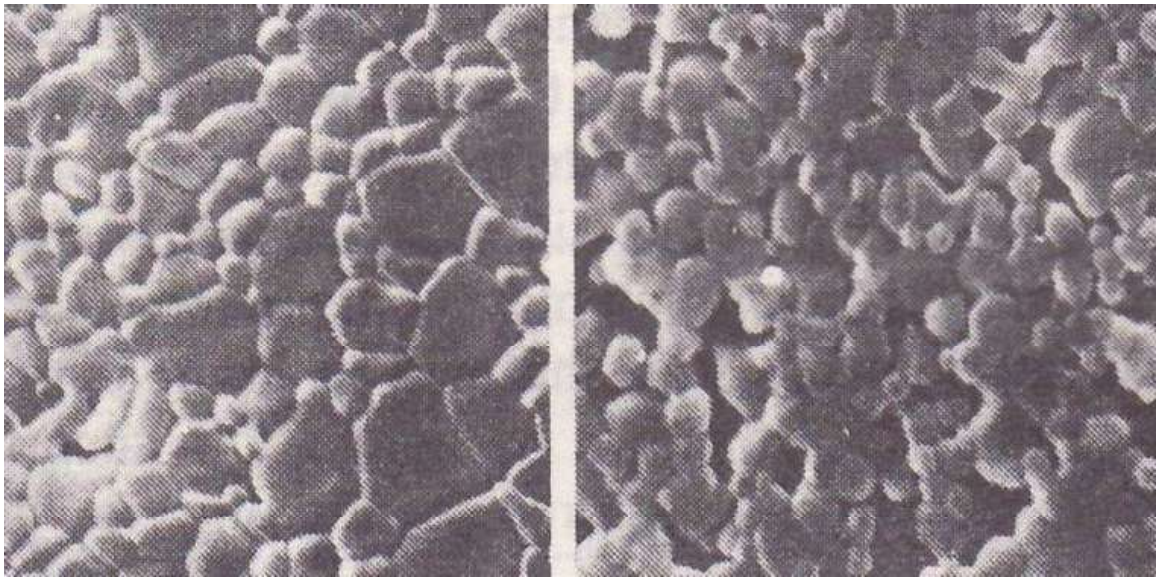
The sintering process



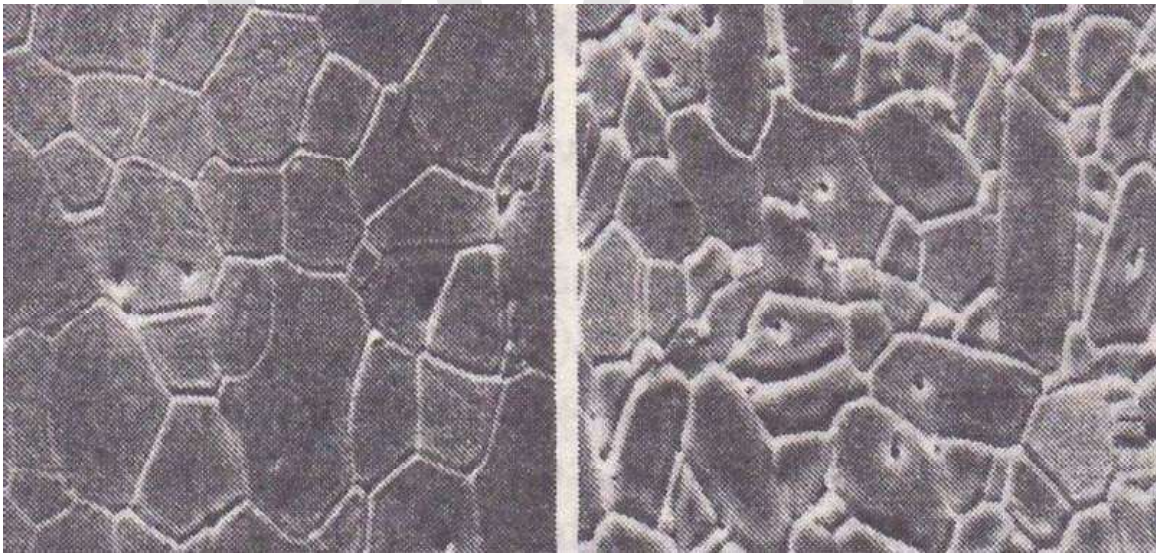
Scanning electron micrographs (SEM) of room temperature Al_2O_3 fine powder compact formed using a) colloidal processing and b) slip casting techniques. *Note: Mean particle diameter = 0.6 microns.



Scanning electron micrographs (SEM) of Al_2O_3 fine powder compact formed using a) colloidal processing and b) slip casting techniques and sintered to 1200°C. *Note: Mean cluster size = 3 microns.



Scanning electron micrographs (SEM) of Al_2O_3 fine powder compact formed using a) colloidal processing and b) slip casting techniques and sintered to 1400°C. *Note: Mean grain size = 2 microns.



Scanning electron micrographs (SEM) of fully densified Al_2O_3 ceramic formed using a) colloidal processing and b) slip casting techniques and sintered to 1600°C. *Note: Mean grain size = 3 microns.

The principles of sintering-based methods are simple ("sinter" has roots in the English "cinder"). The firing is done at a temperature below the melting point of the ceramic. Once a roughly-held-together object called a "green body" is made, it is baked in a kiln, where atomic and molecular diffusion processes give rise to significant changes in the primary microstructural features. This includes the gradual elimination of porosity, which is typically accompanied by a net shrinkage and overall densification of the component.

Thus, the pores in the object may close up, resulting in a denser product of significantly greater strength and fracture toughness.

Another major change in the body during the firing or sintering process will be the establishment of the polycrystalline nature of the solid. This change will introduce some form of grain size distribution, which will have a significant impact on the ultimate physical properties of the material. The grain sizes will either be associated with the initial particle size, or possibly the sizes of aggregates or particle clusters which arise during the initial stages of processing.

The ultimate microstructure (and thus the physical properties) of the final product will be limited by and subject to the form of the structural template or precursor which is created in the initial stages of chemical synthesis and physical forming. Ergo the importance of chemical powder and polymer processing as it pertains to the synthesis of industrial ceramics, glasses and glass-ceramics.

There are numerous possible refinements of the sintering process. Some of the most common involve pressing the green body to give the densification a head start and reduce the sintering time needed. Sometimes organic binders such as polyvinyl alcohol are added to hold the green body together; these burn out during the firing (at 200–350 °C). Sometimes organic lubricants are added during pressing to increase densification. It is common to combine these, and add binders and lubricants to a powder, then press. (The formulation of these organic chemical additives is an art in itself. This is particularly important in the manufacture of high performance ceramics such as those used by the billions for electronics, in capacitors, inductors, sensors, etc.)

A slurry can be used in place of a powder, and then cast into a desired shape, dried and then sintered. Indeed, traditional pottery is done with this type of method, using a plastic mixture worked with the hands. If a mixture of different materials is used together in a ceramic, the sintering temperature is sometimes above the melting point of one minor component - a *liquid phase* sintering. This results in shorter sintering times compared to solid state sintering.

Strength of ceramics

A material's strength is dependent on its microstructure. The engineering processes to which a material is subjected can alter this microstructure. The variety of strengthening mechanisms that alter the strength of a material include the mechanism of grain boundary strengthening. Thus, although yield strength is maximized with decreasing grain size, ultimately, very small grain sizes make the material brittle. Considered in tandem with the fact that the yield strength is the parameter that predicts plastic deformation in the material, one can make informed decisions on how to increase the strength of a material depending on its microstructural properties and the desired end effect.

The relation between yield stress and grain size is described mathematically by the Hall-Petch equation which is

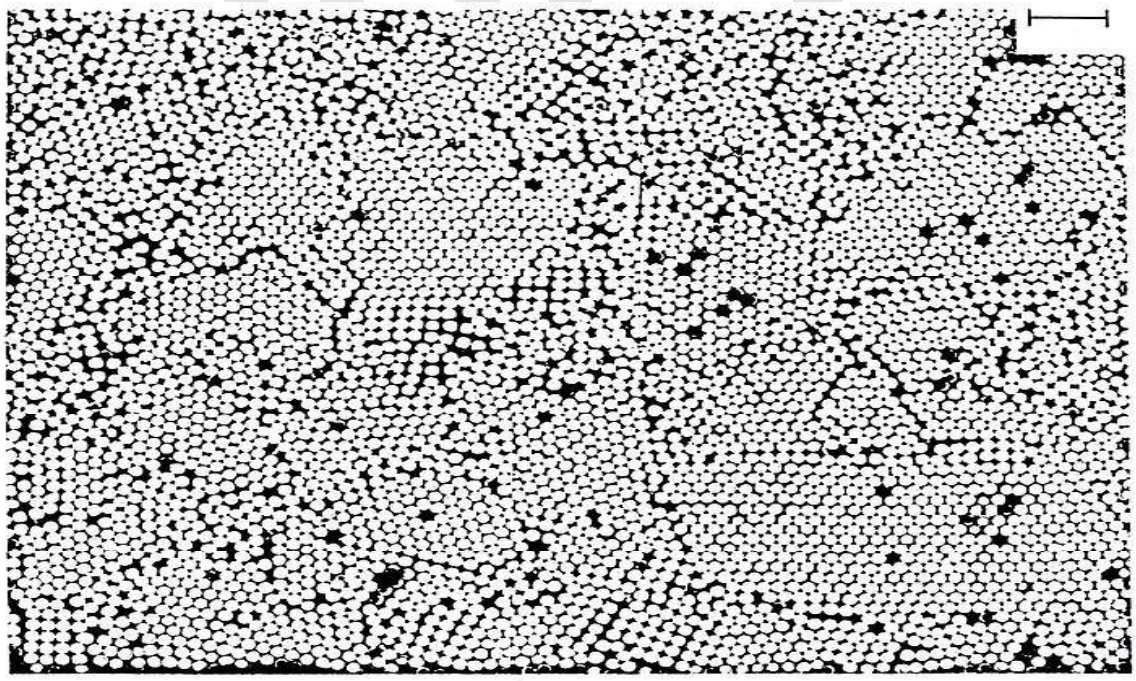
$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$$

where k_y is the strengthening coefficient (a constant unique to each material), σ_o is a materials constant for the starting stress for dislocation movement (or the resistance of the lattice to dislocation motion), d is the grain diameter, and σ_y is the yield stress.

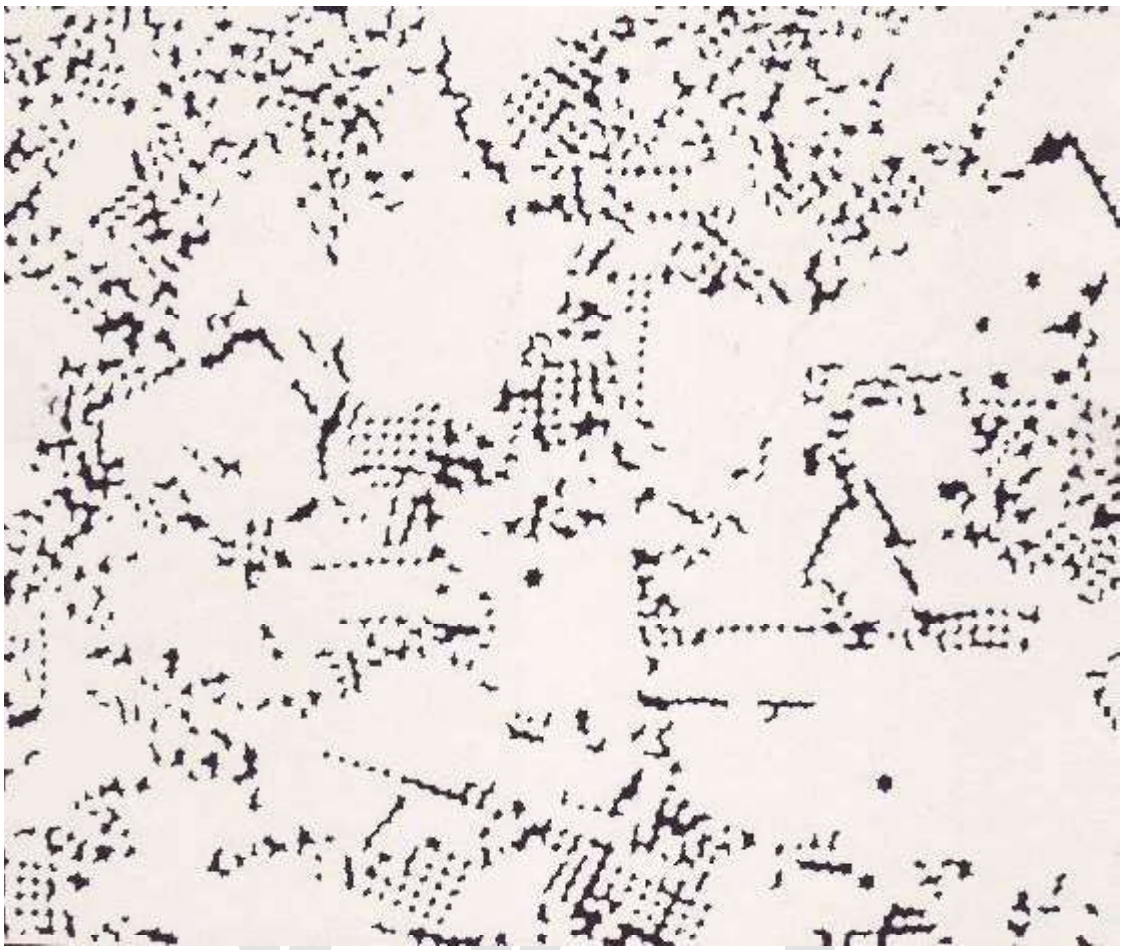
Theoretically, a material could be made infinitely strong if the grains are made infinitely small. This is, unfortunately, impossible because the lower limit of grain size is a single unit cell of the material. Even then, if the grains of a material are the size of a single unit cell, then the material is in fact amorphous, not crystalline, since there is no long range order, and dislocations can not be defined in an amorphous material. It has been observed experimentally that the microstructure with the highest yield strength is a grain size of about 10 nanometers, because grains smaller than this undergo another yielding mechanism, grain boundary sliding. Producing engineering materials with this ideal grain size is difficult because of the limitations of initial particle sizes inherent to nanomaterials and nanotechnology.

Theory of chemical processing

Microstructural uniformity



SEM micrograph of surface of colloidal solid. Structure and morphology consists of ordered domains with both interdomain and intradomain lattice defects.(Amorphous colloidal silica particles of average particle diameter 600 nm).



Manual highlighting reveals microstructural defects and domains in the above image

In the processing of fine ceramics, the irregular particle sizes and shapes in a typical powder often lead to non-uniform packing morphologies that result in packing density variations in the powder compact. Uncontrolled agglomeration of powders due to attractive van der Waals forces can also give rise to in microstructural inhomogeneities.

Differential stresses that develop as a result of non-uniform drying shrinkage are directly related to the rate at which the solvent can be removed, and thus highly dependent upon the distribution of porosity. Such stresses have been associated with a plastic-to-brittle transition in consolidated bodies, and can yield to crack propagation in the unfired body if not relieved.

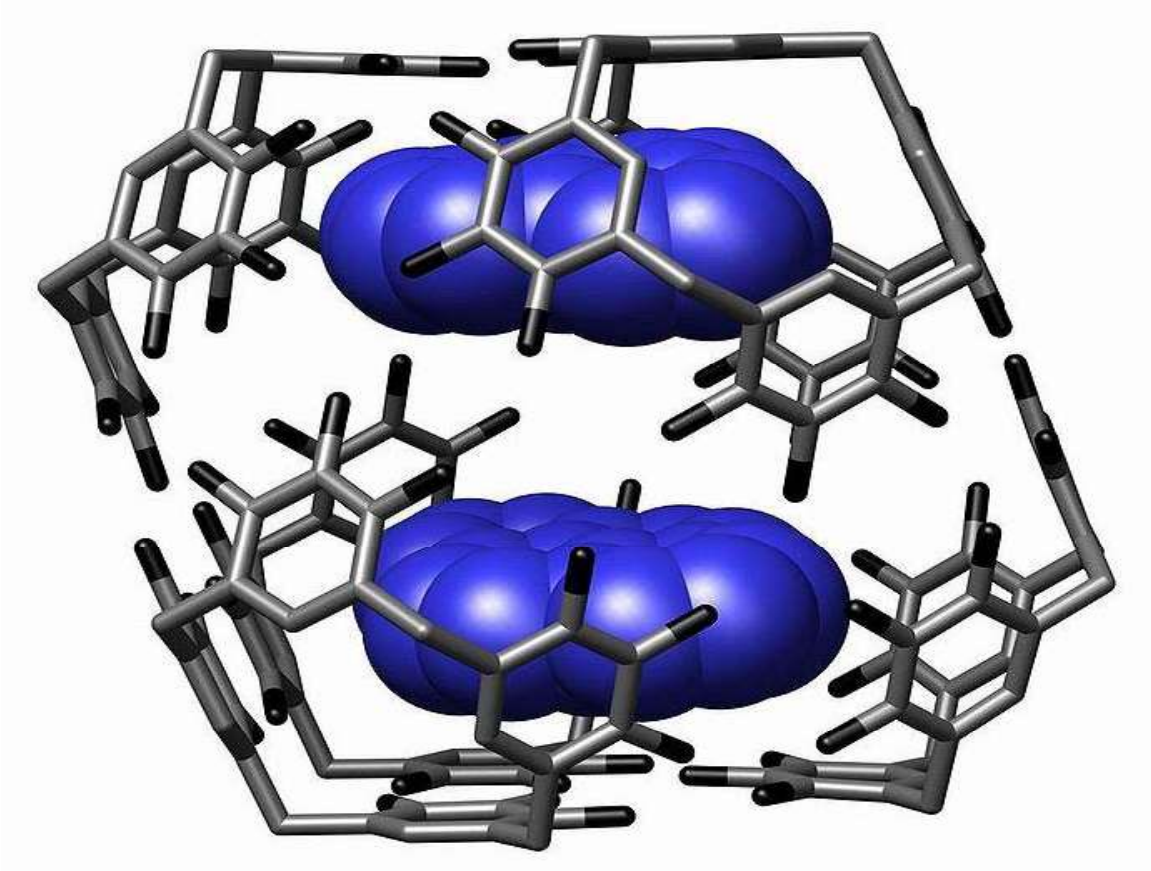
In addition, any fluctuations in packing density in the compact as it is prepared for the kiln are often amplified during the sintering process, yielding inhomogeneous densification. Some pores and other structural defects associated with density variations have been shown to play a detrimental role in the sintering process by growing and thus limiting end-point densities. Differential stresses arising from inhomogeneous densification have also been shown to result in the propagation of internal cracks, thus becoming the strength-controlling flaws.

It would therefore appear desirable to process a material in such a way that it is physically uniform with regard to the distribution of components and porosity, rather than using particle size distributions which will maximize the green density. The containment of a uniformly dispersed assembly of strongly interacting particles in suspension requires total control over particle-particle interactions. Monodisperse colloids provide this potential.

Monodisperse powders of colloidal silica, for example, may therefore be stabilized sufficiently to ensure a high degree of order in the colloidal crystal or polycrystalline colloidal solid which results from aggregation. The degree of order appears to be limited by the time and space allowed for longer-range correlations to be established.

Such defective polycrystalline colloidal structures would appear to be the basic elements of submicrometer colloidal materials science, and, therefore, provide the first step in developing a more rigorous understanding of the mechanisms involved in microstructural evolution in inorganic systems such as polycrystalline ceramics.

Self-assembly



An example of a supramolecular assembly

"Self-assembly" is the most common term in use in the modern scientific community to describe the spontaneous aggregation of particles (atoms, molecules, colloids, micelles, etc.) without the influence of any external forces. Large groups of such particles are known to assemble themselves into thermodynamically stable, structurally well-defined arrays, quite reminiscent of one of the 7 crystal systems found in metallurgy and mineralogy (e.g. face-centered cubic, body-centered cubic, etc.). The fundamental difference in equilibrium structure is in the spatial scale of the unit cell (or lattice parameter) in each particular case.

Thus, self-assembly is emerging as a new strategy in chemical synthesis and nanotechnology. Molecular self-assembly has been observed in various biological systems and underlies the formation of a wide variety of complex biological structures. Thus, self-assembly is also emerging as a new strategy in chemical synthesis and nanotechnology. Molecular crystals, liquid crystals, colloids, micelles, emulsions, phase-separated polymers, thin films and self-assembled monolayers all represent examples of the types of highly ordered structures which are obtained using these techniques. The distinguishing feature of these methods is self-organization in the absence of any external forces.

In addition, the principal mechanical characteristics and structures of biological ceramics, polymer composites, elastomers, and cellular materials are being re-evaluated, with an emphasis on bioinspired materials and structures. Traditional approaches focus on design methods of biological materials using conventional synthetic materials. This includes an emerging class of mechanically superior biomaterials based on microstructural features and designs found in nature. The new horizons have been identified in the synthesis of bioinspired materials through processes that are characteristic of biological systems in nature. This includes the nanoscale self-assembly of the components and the development of hierarchical structures.

Alternative methods

Melt processing

Several methods for making ceramics either use no powders at all, or do not directly make the ceramic from powder. The most extensive of these are the various melt processing methods, of which melt casting produces by far the largest volumes and individual sizes. Arc melting using graphite electrodes predominates, but some induction melting is used, directly coupling to the ceramic to be melted, usually after heating part of the mass by other means to about 1000 °C for sufficient coupling. (e.g. the growth of single crystals of cubic zirconia) for the jewelry trade in a skull crucible).

In either case, the method is predominantly skull melting, in which the melt is contained within a layer of the same ceramic that is kept unmelted by a water-cooled shell. Non-oxide materials that melt can be processed by arc or electron beam melting. However, melting is predominantly applied to oxides, such as alumina (Al_2O_3) and zirconia (ZrO_2). A solid ingot which is then crushed into grain for the manufacture of refractories, or into

powder for plasma spraying. The advantage of melt-derived powders for plasma spraying lies in multi-constituent powders, since better compositional homogeneity is generally achieved.

Ceramic components cast from the melt, usually into graphite molds, typically have much (10-1000-fold) larger grains and substantial porosity (10-20%) compared to sintered ceramics. Grain sizes on the surface of such cast pieces will typically be finer than in the interior due to rapid surface chilling, especially in single-phase materials. However, even the surface grain size will typically be at least an order of magnitude or greater than typical sintered grain sizes.

While some porosity can arise due to extrinsic entrapped gases, as well as evolution of some dissolved gases during solidification, much of it arises intrinsically from the substantially smaller volume of the solidified material relative to its melt for oxide materials. The intrinsic porosity, as well as much of the extrinsic porosity, forms at the solid/liquid interface.

Directional solidification, as used in growing single crystals, can eliminate entrapment of any of the intrinsic porosity, and be used to give potentially beneficial eutectic structures. In order to minimize problems due to extrinsic porosity from trapped volatile species, most single crystals are grown from material that has previously been melted at least once, and commonly twice. Most ceramic castings are designed to result in a solidification front that in term results in the solidification porosity being located in regions where it is less detrimental to performance.

Melt processing is also one of the most widely used methods for making ceramic coatings, and can be done over sizable areas. This is most commonly done by feeding appropriate size powders, for example, spray dried agglomerates a few tens of micrometers in diameter, into a chemically (e.g., oxyacetylene) or electrically (e.g., plasma) derived flame. Such melt spray coatings, although used considerably in the past, have often suffered from variable quality and too much porosity. While some porosity is intrinsic in the process (and increases with subsequent heat treatment in materials such as Al_2O_3, that are quenched in unstable, lower density phases), denser coatings have been obtained in recent years by using chambers for spraying at reduced pressure for higher particle velocities. Chamber spraying also allows cleaner, more reliable surfaces to be obtained, for example, by sputtering, for better, more reliable adhesion. Computer control of spray parameters is leading to significant improvements in reproducibility.

Chemical vapor deposition

Plasma (violet) enhances the growth of carbon nanotubes in plasma-enhanced chemical vapor deposition.

Another non-powder-base method is that of chemical vapor deposition (CVD). While used for making ceramic powders, this method is also used quite extensively for making ceramic coatings, as well as monolithic components. Typically, inorganic and related precursors, which are substantially less expensive, are utilized for bulk, as in structural bodies, with processing temperatures commonly in the 1000 - 1500 °C range. Organometallic precursors, typically much more expensive, can be used, for example, for coatings for electronics, with depositions at temperatures from a few to several hundred degrees Celsius. CVD has played a key role in the development of fiber optics by producing high-purity boules from which the fibers are drawn.

Under appropriate conditions, deposition rates as high as tens of micrometers per minute can be achieved for moderate process costs. CVD can produce some of the largest individual technical ceramic components. Another important advantage of CVD is that it can fairly readily produce a variety of quite important non-oxide materials, such as silicon carbide, silicon nitride, boron carbide, and boron nitride, which otherwise require very high temperatures to produce and typically can only be produced from powder by using additives that may ultimately limit performance (especially at high temperatures). For example, CVD deposited SiC or silicon nitride have substantially higher creep resistance at elevated temperatures than do bodies made by densifying powders that require additives.

The challenges of CVD are mainly control of microstructure and residual stresses. CVD commonly results in substantial grain sizes (from a few tens to a few hundreds of micrometers), development of growth cones (colonies of similarly oriented grains) usually growing at a much higher rate perpendicular to the growth surface rather than parallel with it, or both. Large grains typically result in less optimal mechanical properties. Other disadvantages include rough surfaces that require more machining and may limit the surface finish quality.

Residual stresses can be a very serious problem for CVD, as for any deposition process. Some stresses arise due to differential expansion between the material being deposited and the substrate- usually graphite for producing freestanding bodies, since it is easily removed, is relatively modest in cost, and allows a fair range of accommodation of thermal expansion. However, the major sources of residual stresses are apparently variations in stoichiometry and resultant lattice strains, since some stresses can actually substantially distort or destroy a component at deposition temperature, where there is little or no strain differential between the component and the surface onto which it is being deposited.

Control of both residual stress and microstructure is a common reason for CVD being conducted at relatively modest deposition rates, that is, reduced temperatures, pressures, and flow rates. However, the issue appears in part to be one of controlling appropriate nucleation, which should be addressable more fundamentally by chemical and physical means. There appears to be no intrinsic reason why one cannot utilize the cost advantages of high deposition rates while achieving acceptable microstructures and residual stresses. This will likely be in an area for important research and development.

Physical vapor deposition

Various methods of physical vapor deposition (PVD) are also used. These include evaporation (e.g., electron beam), sputtering, and reaction process (e.g., reactive sputtering). Since the deposition rates are quite low, such processes are restricted to thin coatings.

Coatings for wear applications, especially for many cutting and related tools-for example, with TiN by reactive deposition-are now widely done on an industrial scale. An important

opportunity presented by PVD, as well as CVD and probably some other deposition processes, is to learn to control preferred orientations in coatings. If one can obtain coatings with proper preferred orientation of some anisotropic ceramics, much better matching of ceramic coating and substrate thermal expansions can be achieved.

A number of ceramics can also be deposited by electrochemical means which, in principle, could be used for producing monolithic components as well as coatings as with CVD. However, there has been only limited investigation of this technique for coating purposes. The vehicle for deposition is usually a molten salt, which in itself presents a substantial challenge of temperature and corrosion, as does the problem of small pockets of the bath being incorporated in the coating, limiting coating quality. Much more development of the process is needed, ranging from basic chemistry to control of factors influencing film microstructure.

Polymer pyrolysis

One of the newest nonpowder-based methods of preparing ceramics or ceramic coatings is polymer pyrolysis. Here, one obtains a ceramic by the pyrolysis of an appropriate metal organic polymer, in direct analogy with the fabrication of glassy carbon or graphite fibers by pyrolysis of appropriate organic polymers. While this method is applicable to some oxides, it is predominantly for non-oxides. The preparation of SiC from Si-C-based polymers and Si_3N_4 from Si-N-based polymers has been demonstrated and progress has been made toward obtaining B_4C and BN-based ceramics from appropriate polymeric precursors.

The term "based" is used to denote the fact that one typically does not obtain exact stoichiometry of the desired ceramic or the precursor polymer. Instead, an excess of one constituent or a mixture of products is generally obtained. It is common to obtain mixtures of Si_3N_4 and SiC, or to produce Si_3N_4 with excess Si (which can be converted to Si_3N_4 by pyrolyzing in a nitrogen producing atmosphere, such as N, or NH_3).

The weight yield of the resultant ceramic from the polymer must typically be in the range of SO-80% for a practical process. However, for some systems yields as high as 90% have been calculated theoretically and approached very closely experimentally with the appropriate precursor, one that results in essentially exclusive loss of hydrogen in the forming of the final ceramic product. Substantial shrinkage and/or cracking, as well as porosity, are the typical mechanisms by which the substantial differences in densities between the starting polymer and the resultant ceramic composition are accommodated.

One basic limitation of polymer pyrolysis is that it cannot produce fully dense ceramic materials unless at least one dimension is small, on the order of micrometers. Typical resultant porosities of bulk bodies from pyrolysis are in the range of 20-40%, at least for pieces a few mm thick. Thicker pieces may have more porosity, and thus the achievable sizes are limited. Nevertheless, glassy carbon parts at least 30 cm long have been produced. The process is potentially most widely applicable for fabrication of coatings or fibers, for which it is already in commercial production, as well as composites.

Sol-gel processing is also of interest for composites. Melt processing is used extensively for producing oxide fibers. Industrially, this includes fibers for fiber optics, reinforcement (fiber-glass composites), and insulation fibers for products ranging from home to high-temperature furnace applications.

Insulation fibers are typically formed by blowing molten streams, while optical and reinforcement fibers are drawn. Previously, only quite viscous melts, such as silicate, could be used, otherwise surface tensions would result in droplet formation. However, the development of inviscid melt spinning has relaxed this limitation. This is accomplished by extruding the molten fiber into a chamber where the hot fiber acts as a substrate for CVD (commonly of graphite, from CH_4, for example) such that sufficiently rapid CVD coating onto the fiber prevents its breakup into droplets. New glass compositions for fibers are of interest, including halides for low-loss IR fibers, and oxynitride or oxycarbide compositions for higher stiffness.

Ceramic composites

The Porsche Carrera GT's carbon-ceramic (silicon carbide) composite disc brake

Substantial interest has arisen in recent years in fabricating ceramic composites. While there is considerable interest in composites with one or more non-ceramic constituents,

the greatest attention is on composites in which all constituents are ceramic. These typically comprise two ceramic constituents: a continuous matrix, and a dispersed phase of ceramic particles, whiskers, or short (chopped) or continuous ceramic fibers. The challenge, as in wet chemical processing, is to obtain a uniform or homogeneous distribution of the dispersed particle or fiber phase.

Consider first the processing of particulate composites. The particulate phase of greatest interest is tetragonal zirconia because of the toughening that can be achieved from the phase transformation from the metastable tetragonal to the monoclinic crystalline phase, aka transformation toughening. There is also substantial interest in dispersion of hard, non-oxide phases such as SiC, TiB, TiC, boron, carbon and especially oxide matrices like alumina and mullite. There is also interest too incorporating other ceramic particulates, especially those of highly anisotropic thermal expansion. Examples include Al_2O_3, TiO_2, graphite, and boron nitride.

In processing particulate composites, the issue is not only homogeneity of the size and spatial distribution of the dispersed and matrix phases, but also control of the matrix grain size. However, there is some built-in self-control due to inhibition of matrix grain growth by the dispersed phase. Particulate composites, though generally offer increased resistance to damage, failure, or both, are still quite sensitive to inhomogeneities of composition as well as other processing defects such as pores. Thus they need good processing to be effective.

Particulate composites have been made on a commercial basis by simply mixing powders of the two constituents. Although this approach is inherently limited in the homogeneity that can be achieved, it is the most readily adaptable for existing ceramic production technology. However, other approaches are of interest.

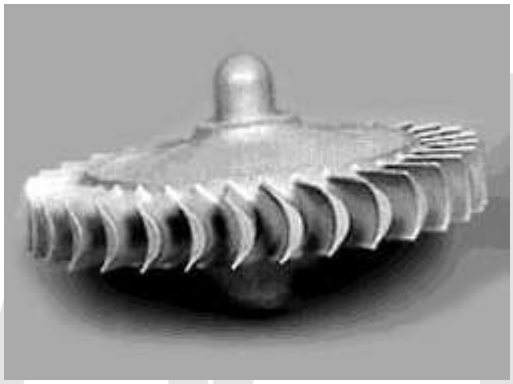
From the technological standpoint, a particularly desirable approach to fabricating particulate composites is to coat the matrix or its precursor onto fine particles of the dispersed phase with good control of the starting dispersed particle size and the resultant matrix coating thickness. One should in principle be able to achieve the ultimate in homogeneity of distribution and thereby optimize composite performance. This can also have other ramifications, such as allowing more useful composite performance to be achieved in a body having porosity, which might be desired for other factors, such as limiting thermal conductivity.

There are also some opportunities to utilize melt processing for fabrication of ceramic, particulate, whisker and short-fiber, and continuous-fiber composites. Clearly, both particulate and whisker composites are conceivable by solid-state precipitation after solidification of the melt. This can also be obtained in some cases by sintering, as for precipitation-toughened, partially stabilized zirconia. Similarly, it is known that one can directionally solidify ceramic eutectic mixtures and hence obtain uniaxially aligned fiber composites. Such composite processing has typically been limited to very simple shapes and thus suffers from serious economic problems due to high machining costs.

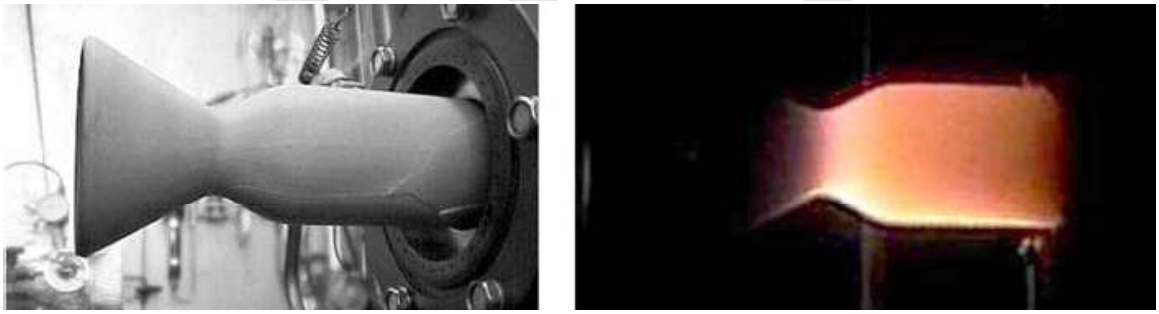
Clearly, there are possibilities of using melt casting for many of these approaches. Potentially even more desirable is using melt-derived particles. In this method, quenching is done in a solid solution or in a fine eutectic structure, in which the particles are then processed by more typical ceramic powder processing methods into a useful body. There have also been preliminary attempts to use melt spraying as a means of forming composites by introducing the dispersed particulate, whisker, or fiber phase in conjunction with the melt spraying process.

Besides many process improvements, the first of two major needs for fiber composites is lower fiber costs. The second major need is fiber compositions or coatings, or composite processing, to reduce degradation that results from high-temperature composite exposure under oxidizing conditions.

Applications



Radial rotor made from Si_3N_4 for a gas turbine engine



Silicon nitride thruster. Left: Mounted in test stand. Right: Being tested with H_2/O_2 propellants

The products of technical ceramics include tiles used in the Space Shuttle program, gas burner nozzles, ballistic protection, nuclear fuel uranium oxide pellets, bio-medical implants, jet engine turbine blades, and missile nose cones.

Its products are often made from materials other than clay, chosen for their particular physical properties. These may be classified as follows:

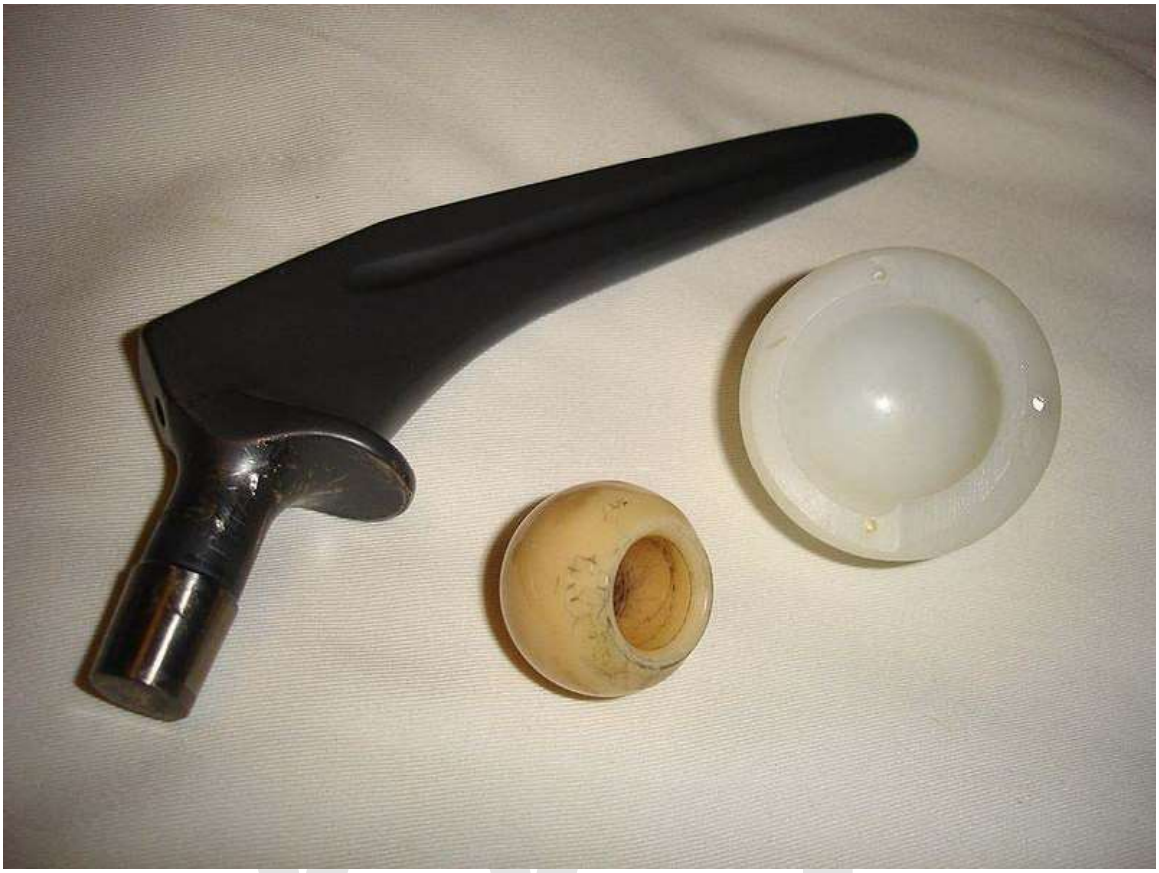
- Oxides: silica, alumina, zirconia
- Non-oxides: carbides, borides, nitrides, silicides
- Composites: particulate or whisker reinforced matrices, combinations of oxides and non-oxides (e.g. polymers).

Ceramics can be used in many technological industries. One application are the ceramic tiles on NASA's Space Shuttle, used to protect it and the future supersonic space planes from the searing heat of reentry into the Earth's atmosphere. They are also used widely in electronics and optics. In addition to the applications listed here, ceramics are also used as a coating in various engineering cases. An example would be a ceramic bearing coating over a titanium frame used for an airplane. Recently the field has come to include the studies of single crystals or glass fibers, in addition to traditional polycrystalline materials, and the applications of these have been overlapping and changing rapidly.

Aerospace

- Engines; Shielding a hot running airplane engine from damaging other components.
- Airframes; Used as a high-stress, high-temp and lightweight bearing and structural component.
- Missile nose-cones; Shielding the missile internals from heat.
- Space Shuttle tiles
- Space-debris ballistic shields -- Ceramic fiber woven shields offer better protection to hypervelocity (~7 km/s) particles than aluminum shields of equal weight.
- Rocket Nozzles; Withstands and focuses the exhaust of the rocket booster.

Biomedical



A titanium hip prosthesis, with a ceramic head and polyethylene acetabular cup

- Artificial bone; Dentistry applications, teeth.
- Biodegradable splints; Reinforcing bones recovering from osteoporosis
- Implant material

Electronics

- Capacitors
- Integrated Circuit packages
- Transducers
- Insulators

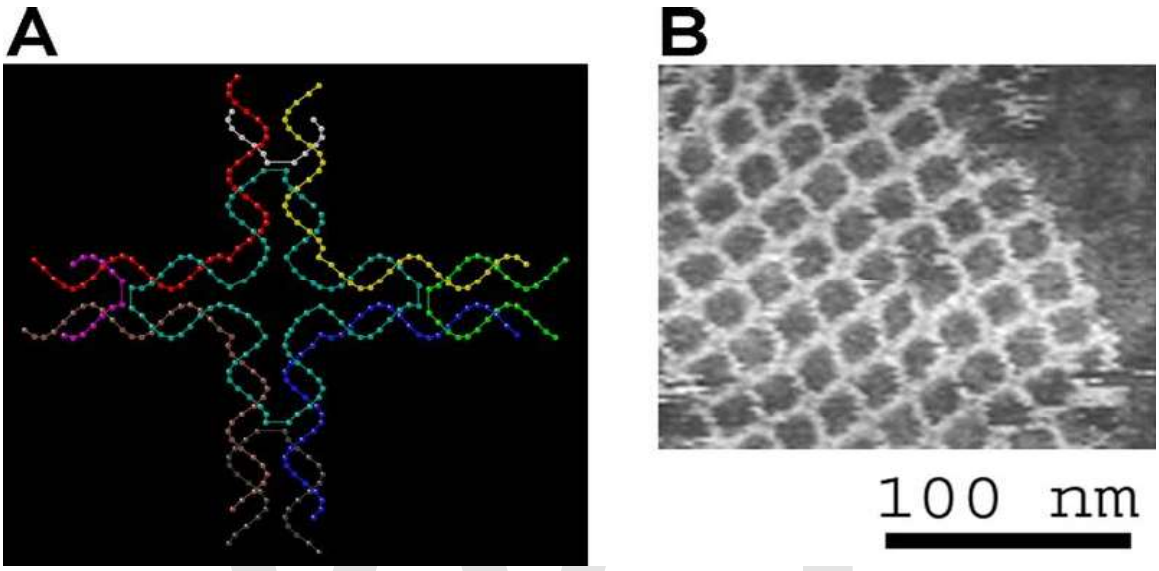
Optical

- Optical fibers; Guided Lightwave Transmission
- Switches
- Laser amplifiers
- Lenses
- Infrared Heat Seeking Devices

Automotive

- Heat shield
- Exhaust Heat Management

Biomaterials



The DNA structure at left (schematic shown) will self-assemble into the structure visualized by atomic force microscopy at right.

Silicification is quite common in the biological world and occurs in bacteria, single-celled organisms, plants, and animals (invertebrates and vertebrates). Crystalline minerals formed in such environment often show exceptional physical properties (e.g. strength, hardness, fracture toughness) and tend to form hierarchical structures that exhibit microstructural order over a range of length or spatial scales. The minerals are crystallized from an environment that is undersaturated with respect to silicon, and under conditions of neutral pH and low temperature (0-40 °C). Formation of the mineral may occur either within or outside of the cell wall of an organism, and specific biochemical reactions for mineral deposition exist that include lipids, proteins and carbohydrates. The significance of the cellular machinery cannot be overemphasized, and it is with advances in experimental techniques in cellular biology and the capacity to mimic the biological environment that significant progress is currently being reported.

Most natural (or biological) materials are complex composites whose mechanical properties are often outstanding, considering the weak constituents from which they are assembled. These complex structures, which have risen from hundreds of million years of evolution, are inspiring the design of novel materials with exceptional physical properties for high performance in adverse conditions. Their defining characteristics such as hierarchy, multifunctionality, and the capacity for self-healing, are currently being investigated.

The basic building blocks begin with the 20 amino acids and proceed to polypeptides, polysaccharides, and polypeptides–saccharides. These, in turn, compose the basic proteins, which are the primary constituents of the 'soft tissues' common to most biominerals. With well over 1000 proteins possible, current research emphasizes the use of collagen, chitin, keratin, and elastin. The 'hard' phases are often strengthened by crystalline minerals, which nucleate and grow in a biomediated environment that determines the size, shape and distribution of individual crystals. The most important mineral phases have been identified as hydroxyapatite, silica, and aragonite. Using the classification of Wegst and Ashby, the principal mechanical characteristics and structures of biological ceramics, polymer composites, elastomers, and cellular materials have been presented. Selected systems in each class are being investigated with emphasis on the relationship between their microstructure over a range of length scales and their mechanical response.

Thus, the crystallization of inorganic materials in nature generally occurs at ambient temperature and pressure. Yet the vital organisms through which these minerals form are capable of consistently producing extremely precise and complex structures. Understanding the processes in which living organisms control the growth of crystalline minerals such as silica could lead to significant advances in the field of materials science, and open the door to novel synthesis techniques for nanoscale composite materials, or nanocomposites.

The iridescent nacre inside a Nautilus shell

High-resolution SEM observations were performed of the microstructure of the mother-of-pearl (or nacre) portion of the abalone shell. Those shells exhibit the highest mechanical strength and fracture toughness of any non-metallic substance known. The nacre from the shell of the abalone has become one of the more intensively studied biological structures in materials science. Clearly visible in these images are the neatly stacked (or ordered) mineral tiles separated by thin organic sheets along with a macrostructure of larger periodic growth bands which collectively form what scientists are currently referring to as a hierarchical composite structure. (The term hierarchy simply implies that there are a range of structural features which exist over a wide range of length scales).

Future developments reside in the synthesis of bio-inspired materials through processing methods and strategies that are characteristic of biological systems. These involve nanoscale self-assembly of the components and the development of hierarchical structures.

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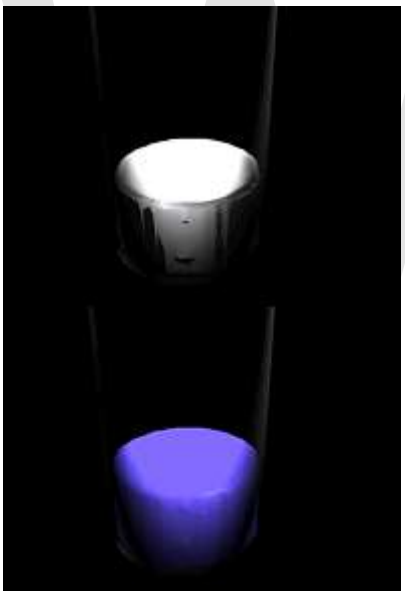
Chapter 3

Viscosity

Viscosity



Clear liquid above has lower viscosity than the substance below

SI symbol:	μ, η
SI unit:	Pa·s = kg/(s·m)
Derivations from other quantities:	μ = G·t

Viscosity is a measure of the resistance of a fluid which is being deformed by either shear stress or tensile stress. In everyday terms (and for fluids only), viscosity is "thickness" or "internal friction". Thus, water is "thin", having a lower viscosity, while honey is "thick", having a higher viscosity. Put simply, the less viscous the fluid is, the greater its ease of movement (fluidity).

Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction. For example, high-viscosity felsic magma will create a tall, steep stratovolcano, because it cannot flow far before it cools, while low-viscosity mafic lava will create a wide, shallow-sloped shield volcano. All real fluids (except superfluids) have some resistance to stress and therefore are **viscous**, but a fluid which has no resistance to shear stress is known as an **ideal fluid** or **inviscid fluid**.

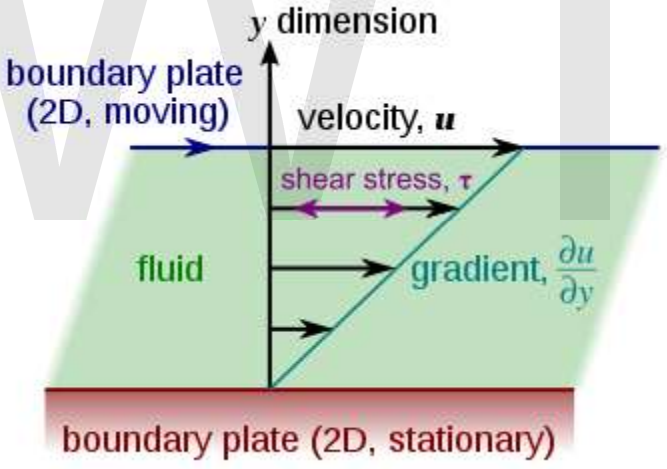
The study of flowing matter is known as rheology, which includes viscosity and related concepts.

Etymology

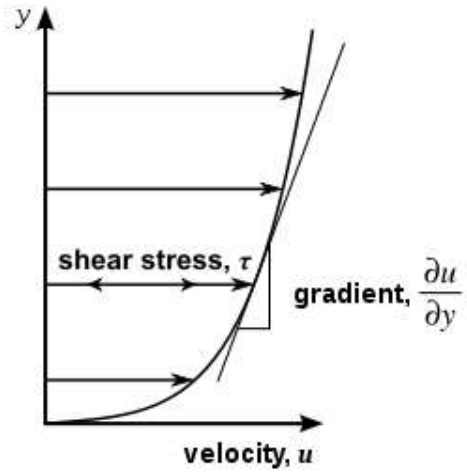
The word "viscosity" derives from the Latin word "viscum alba" for mistletoe. A viscous glue called birdlime was made from mistletoe berries and used for lime-twigs to catch birds.

Properties and behavior

Overview



Laminar shear of fluid between two plates. Friction between the fluid and the moving boundaries causes the fluid to shear. The force required for this action is a measure of the fluid's viscosity. This type of flow is known as a Couette flow.



Laminar shear, the non-constant gradient, is a result of the geometry the fluid is flowing through (e.g. a pipe).

In general, in any flow, layers move at different velocities and the fluid's viscosity arises from the shear stress between the layers that ultimately opposes any applied force.

The relationship between the shear stress and the velocity gradient can be obtained by considering two plates closely spaced at a distance *y*, and separated by a homogeneous substance. Assuming that the plates are very large, with a large area *A*, such that edge effects may be ignored, and that the lower plate is fixed, let a force *F* be applied to the upper plate. If this force causes the substance between the plates to undergo shear flow with a velocity gradient *u* (as opposed to just shearing elastically until the shear stress in the substance balances the applied force), the substance is called a fluid.

The applied force is proportional to the area and velocity gradient in the fluid and inversely proportional to the distance between the plates. Combining these three relations results in the equation:

$$F = \mu A \frac{u}{y},$$

where μ is the proportionality factor called *viscosity*.

This equation can be expressed in terms of shear stress $\tau = \frac{F}{A}$. Thus as expressed in differential form by Isaac Newton for straight, parallel and uniform flow, the shear stress between layers is proportional to the velocity gradient in the direction perpendicular to the layers:

$$\tau = \mu \frac{\partial u}{\partial y}$$

Hence, through this method, the relation between the shear stress and the velocity gradient can be obtained.

$$\frac{u}{y}$$

Note that the *rate of shear deformation* is $\frac{u}{y}$ which can be also written as a *shear velocity*, $\frac{du}{dy}$.

James Clerk Maxwell called viscosity *fugitive elasticity* because of the analogy that elastic deformation opposes shear stress in solids, while in viscous fluids, shear stress is opposed by *rate* of deformation.

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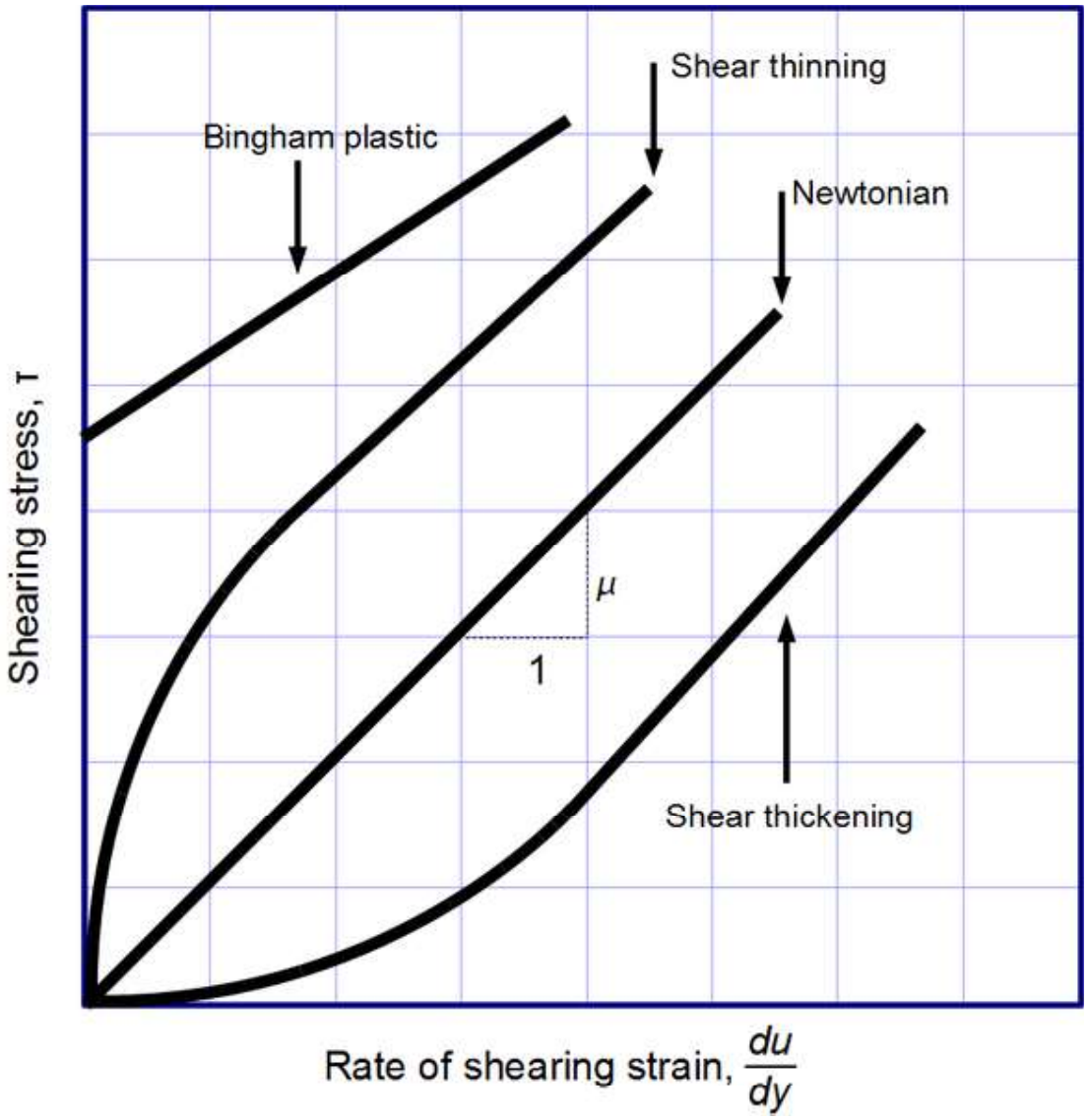
Types of viscosity



Viscosity, the slope of each line, varies among materials

Newton's law of viscosity, given above, is a constitutive equation (like Hooke's law, Fick's law, Ohm's law). It is not a fundamental law of nature but an approximation that holds in some materials and fails in others. Non-Newtonian fluids exhibit a more complicated relationship between shear stress and velocity gradient than simple linearity. Thus there exist a number of forms of viscosity:

- **Newtonian**: fluids, such as water and most gases which have a constant viscosity.
- **Shear thickening**: viscosity *increases* with the rate of shear.
- **Shear thinning**: viscosity *decreases* with the rate of shear. Shear thinning liquids are very commonly, but misleadingly, described as thixotropic.

- **Thixotropic**: materials which become *less* viscous over time when shaken, agitated, or otherwise stressed.
- **Rheopectic**: materials which become *more* viscous over time when shaken, agitated, or otherwise stressed.
- A **Bingham plastic** is a material that behaves as a solid at low stresses but flows as a viscous fluid at high stresses.
- A **magnetorheological fluid** is a type of "smart fluid" which, when subjected to a magnetic field, greatly increases its apparent viscosity, to the point of becoming a viscoelastic solid.

Viscosity coefficients

Viscosity coefficients can be defined in two ways:

- **Dynamic viscosity**, also **absolute viscosity**, the more usual one (typical units Pa·s, Poise, P);
- **Kinematic viscosity** is the *dynamic viscosity* divided by the density (typical units m^2/s, Stokes, St).

Viscosity is a tensorial quantity that can be decomposed in different ways into two independent components. The most usual decomposition yields the following viscosity coefficients:

- **Shear viscosity**, the most important one, often referred to as simply **viscosity**, describing the reaction to applied shear stress; simply put, it is the ratio between the pressure exerted on the surface of a fluid, in the lateral or horizontal direction, to the change in velocity of the fluid as you move down in the fluid (this is what is referred to as a velocity gradient).
- **Volume viscosity** (also called **bulk viscosity** or **second viscosity**) becomes important only for such effects where fluid compressibility is essential. Examples would include shock waves and sound propagation. It appears in the Stokes' law (sound attenuation) that describes propagation of sound in Newtonian liquid.

Alternatively,

- **Extensional viscosity**, a linear combination of shear and bulk viscosity, describes the reaction to elongation, widely used for characterizing polymers. For example, at room temperature, water has a dynamic shear viscosity of about 1.0×10^{-3} Pa·s and motor oil of about 250×10^{-3} Pa·s.

Viscosity measurement

Viscosity is measured with various types of viscometers and rheometers. A rheometer is used for those fluids which cannot be defined by a single value of viscosity and therefore

require more parameters to be set and measured than is the case for a viscometer. Close temperature control of the fluid is essential to accurate measurements, particularly in materials like lubricants, whose viscosity can double with a change of only 5 °C.

For some fluids, viscosity is a constant over a wide range of shear rates (Newtonian fluids). The fluids without a constant viscosity (non-Newtonian fluids) cannot be described by a single number. Non-Newtonian fluids exhibit a variety of different correlations between shear stress and shear rate.

One of the most common instruments for measuring kinematic viscosity is the glass capillary viscometer.

In paint industries, viscosity is commonly measured with a Zahn cup, in which the efflux time is determined and given to customers. The efflux time can also be converted to kinematic viscosities (centistokes, cSt) through the conversion equations.

Also used in paint, a Stormer viscometer uses load-based rotation in order to determine viscosity. The viscosity is reported in Krebs units (KU), which are unique to Stormer viscometers.

A Ford viscosity cup measures the rate of flow of a liquid. This, under ideal conditions, is proportional to the kinematic viscosity.

Vibrating viscometers can also be used to measure viscosity. These models such as the *Dynatrol* use vibration rather than rotation to measure viscosity.

Extensional viscosity can be measured with various rheometers that apply extensional stress.

Volume viscosity can be measured with an acoustic rheometer.

Apparent viscosity is a calculation derived from tests performed on drilling fluid used in oil or gas well development. These calculations and tests help engineers develop and maintain the properties of the drilling fluid to the specifications required.

Units

Dynamic viscosity

The usual symbol for dynamic viscosity used by mechanical and chemical engineers — as well as fluid dynamicists — is the Greek letter mu (μ). The symbol η is also used by chemists, physicists, and the IUPAC.

The SI physical unit of dynamic viscosity is the pascal-second (Pa·s), (equivalent to $N \cdot s/m^2$, or kg/(m·s)). If a fluid with a viscosity of one Pa·s is placed between two plates,

and one plate is pushed sideways with a shear stress of one pascal, it moves a distance equal to the thickness of the layer between the plates in one second.

The cgs physical unit for dynamic viscosity is the *poise* (P), named after Jean Louis Marie Poiseuille. It is more commonly expressed, particularly in ASTM standards, as *centipoise* (cP). Water at 20 °C has a viscosity of 1.0020 cP or 0.001002 kg/(m·s).

$1\ \mathrm{P} = 1\ \mathrm{g \cdot cm^{-1} \cdot s^{-1}}$.
$1\ \mathrm{Pa \cdot s} = 1\ \mathrm{kg \cdot m^{-1} \cdot s^{-1}} = 10\ \mathrm{P}$.

The relation to the SI unit is

$1\ \mathrm{P} = 0.1\ \mathrm{Pa \cdot s}$,
$1\ \mathrm{cP} = 1\ \mathrm{mPa \cdot s} = 0.001\ \mathrm{Pa \cdot s}$.

Kinematic viscosity

In many situations, we are concerned with the ratio of the inertial force to the viscous force (i.e. the Reynolds number, $Re = VD / \nu$) , the former characterized by the fluid density ρ. This ratio is characterized by the *kinematic viscosity* (Greek letter nu, ν), defined as follows:

$$\nu = \frac{\mu}{\rho}$$

The SI unit of ν is $\mathrm{m^2/s}$. The SI unit of ρ is $\mathrm{kg/m^3}$.

The cgs physical unit for kinematic viscosity is the *stokes* (St), named after George Gabriel Stokes. It is sometimes expressed in terms of *centiStokes* (cSt). In U.S. usage, *stoke* is sometimes used as the singular form.

$1\ \mathrm{St} = 1\ \mathrm{cm^2 \cdot s^{-1}} = 10^{-4}\ \mathrm{m^2 \cdot s^{-1}}$.
$1\ \mathrm{cSt} = 1\ \mathrm{mm^2 \cdot s^{-1}} = 10^{-6}\mathrm{m^2 \cdot s^{-1}}$.

Water at 20 °C has a kinematic viscosity of about 1 cSt.

The kinematic viscosity is sometimes referred to as **diffusivity of momentum**, because it has the same unit as and is comparable to diffusivity of heat and diffusivity of mass. It is therefore used in dimensionless numbers which compare the ratio of the diffusivities.

Fluidity

The reciprocal of viscosity is *fluidity*, usually symbolized by $\varphi = 1 / \mu$ or $F = 1 / \mu$, depending on the convention used, measured in *reciprocal poise* ($\mathrm{cm \cdot s \cdot g^{-1}}$), sometimes called the *rhe*. *Fluidity* is seldom used in engineering practice.

The concept of fluidity can be used to determine the viscosity of an ideal solution. For two components *a* and *b*, the fluidity when *a* and *b* are mixed is

$$F \approx \chi_a F_a + \chi_b F_b,$$

which is only slightly simpler than the equivalent equation in terms of viscosity:

$$\mu \approx \frac{1}{\chi_a/\mu_a + \chi_b/\mu_b},$$

where χ_a and χ_b is the mole fraction of component *a* and *b* respectively, and μ_a and μ_b are the components pure viscosities.

Non-standard units

The Reyn is a British unit of dynamic viscosity.

Viscosity index is a measure for the change of kinematic viscosity with temperature. It is used to characterise lubricating oil in the automotive industry.

At one time the petroleum industry relied on measuring kinematic viscosity by means of the Saybolt viscometer, and expressing kinematic viscosity in units of *Saybolt Universal Seconds* (SUS). Other abbreviations such as SSU (*Saybolt Seconds Universal*) or SUV (*Saybolt Universal Viscosity*) are sometimes used. Kinematic viscosity in centistoke can be converted from SUS according to the arithmetic and the reference table provided in ASTM D 2161.

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Molecular origins

Pitch has a viscosity approximately 230 billion (2.3×10^{11}) times that of water.

The viscosity of a system is determined by how molecules constituting the system interact. There are no simple but correct expressions for the viscosity of a fluid. The simplest exact expressions are the Green–Kubo relations for the linear shear viscosity or the Transient Time Correlation Function expressions derived by Evans and Morriss in 1985. Although these expressions are each exact in order to calculate the viscosity of a dense fluid, using these relations requires the use of molecular dynamics computer simulations.

Gases

Viscosity in gases arises principally from the molecular diffusion that transports momentum between layers of flow. The kinetic theory of gases allows accurate prediction of the behavior of gaseous viscosity.

Within the regime where the theory is applicable:

- Viscosity is independent of pressure and
- Viscosity increases as temperature increases.

James Clerk Maxwell published a famous paper in 1866 using the kinetic theory of gases to study gaseous viscosity. To understand why the viscosity is independent of pressure consider two adjacent boundary layers (A and B) moving with respect to each other. The internal friction (the viscosity) of the gas is determined by the probability a particle of layer A enters layer B with a corresponding transfer of momentum. Maxwell's calculations showed him that the viscosity coefficient is proportional to both the density, the mean free path and the mean velocity of the atoms. On the other hand, the *mean free path* is inversely proportional to the density. So an increase of pressure doesn't result in any change of the viscosity.

Relation to mean free path of diffusing particles

In relation to diffusion, the kinematic viscosity provides a better understanding of the behavior of mass transport of a dilute species. Viscosity is related to shear stress and the rate of shear in a fluid, which illustrates its dependence on the mean free path, λ, of the diffusing particles.

From fluid mechanics, for a Newtonian fluid, the shear stress, τ, on a unit area moving parallel to itself, is found to be proportional to the rate of change of velocity with distance perpendicular to the unit area:

$$\tau = \mu \frac{du_x}{dy}$$

for a unit area parallel to the x-z plane, moving along the x axis. We will derive this formula and show how μ is related to λ.

Interpreting shear stress as the time rate of change of momentum, p, per unit area A (rate of momentum flux) of an arbitrary control surface gives

$$\tau = \frac{\dot{p}}{A} = \frac{\dot{m}\langle u_x \rangle}{A}.$$

where $\langle u_x \rangle$ is the average velocity along x of fluid molecules hitting the unit area, with respect to the unit area.

Further manipulation will show

$$\dot{m} = \rho \bar{u} A$$
$$\langle u_x \rangle = \frac{1}{2} \lambda \frac{du_x}{dy}$$

, assuming that molecules hitting the unit area come from all distances between 0 and λ (equally distributed), and that their average velocities change linearly with distance (always true for small enough λ). From this follows:

$$\tau = \underbrace{\frac{1}{2} \rho \bar{u} \lambda}_{\mu} \cdot \frac{du_x}{dy} \quad \Rightarrow \quad \nu = \frac{\mu}{\rho} = \tfrac{1}{2} \bar{u} \lambda,$$

where

$\dot{m}$ is the rate of fluid mass hitting the surface,
ρ is the density of the fluid,
$\bar{u}$ is the average molecular speed ($\bar{u} = \sqrt{\langle u^2 \rangle}$),
μ is the dynamic viscosity.

Effect of temperature on the viscosity of a gas

Sutherland's formula can be used to derive the dynamic viscosity of an ideal gas as a function of the temperature:

$$\mu = \mu_0 \frac{T_0 + C}{T + C} \left(\frac{T}{T_0} \right)^{3/2}$$

This in turn is equal to

$$\lambda \cdot \frac{T^{3/2}}{T + C}, \text{where} \quad \lambda = \frac{\mu_0 (T_0 + C)}{T_0^{3/2}} \text{ which is a constant.}$$

in Sutherland's formula:

- μ = dynamic viscosity in (Pa·s) at input temperature T,
- μ_0 = reference viscosity in (Pa·s) at reference temperature T_0,
- T = input temperature in kelvins,
- T_0 = reference temperature in kelvins,
- C = Sutherland's constant for the gaseous material in question.

Valid for temperatures between $0 < T < 555$ K with an error due to pressure less than 10% below 3.45 MPa.

Sutherland's constant and reference temperature for some gases

Gas	C [K]	T_0 [K]	μ_0 [μPa s]
air	120	291.15	18.27
nitrogen	111	300.55	17.81
oxygen	127	292.25	20.18
carbon dioxide	240	293.15	14.8
carbon monoxide	118	288.15	17.2
hydrogen	72	293.85	8.76
ammonia	370	293.15	9.82
sulfur dioxide	416	293.65	12.54
helium	79.4	273	19

Viscosity of a dilute gas

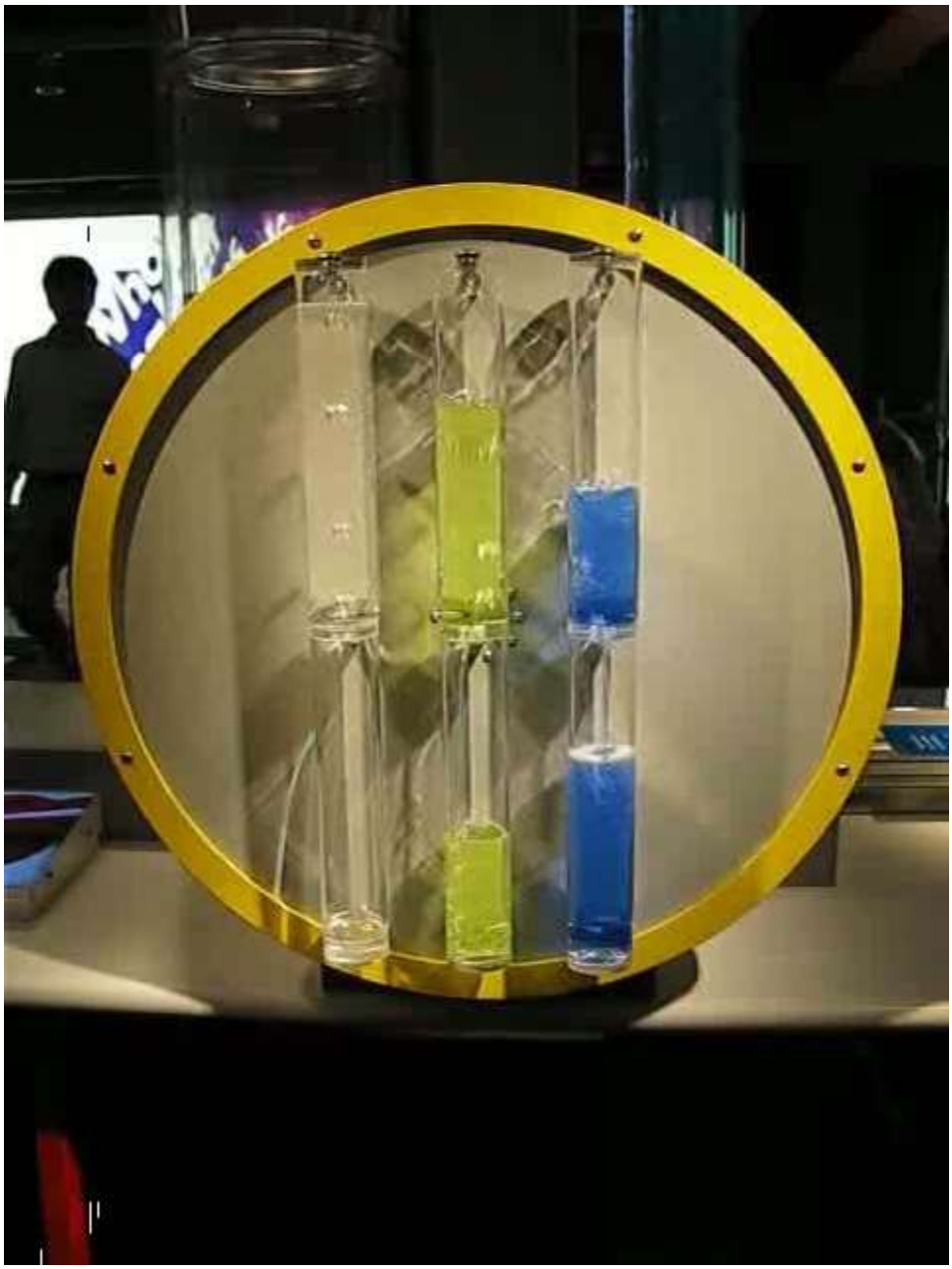
The Chapman-Enskog equation may be used to estimate viscosity for a dilute gas. This equation is based on a semi-theoretical assumption by Chapman and Enskog. The equation requires three empirically determined parameters: the collision diameter (σ), the maximum energy of attraction divided by the Boltzmann constant (ϵ/κ) and the collision integral ($\omega(T^*)$).

$$\mu_0 \times 10^6 = 2.6693 \frac{(MT)^{1/2}}{\sigma^2 \omega(T^*)},$$

with

- $T^* = \kappa T/\varepsilon$ — reduced temperature (dimensionless),
- μ_0 = viscosity for dilute gas (μPa.s),
- M = molecular mass (g/mol),
- T = temperature (K),
- σ = the collision diameter (Å),
- ε / κ = the maximum energy of attraction divided by the Boltzmann constant (K),
- ω_μ = the collision integral.

Liquids



Three liquids with different Viscosities

In liquids, the additional forces between molecules become important. This leads to an additional contribution to the shear stress though the exact mechanics of this are still controversial. Thus, in liquids:

- Viscosity is independent of pressure (except at very high pressure); and

- Viscosity tends to fall as temperature increases (for example, water viscosity goes from 1.79 cP to 0.28 cP in the temperature range from 0 °C to 100 °C).

The dynamic viscosities of liquids are typically several orders of magnitude higher than dynamic viscosities of gases.

Viscosity of blends of liquids

The viscosity of the blend of two or more liquids can be estimated using the Refutas equation. The calculation is carried out in three steps.

The first step is to calculate the Viscosity Blending Number (VBN) (also called the Viscosity Blending Index) of each component of the blend:

$$\text{VBN} = 14.534 \times \ln\left[\ln(v + 0.8)\right] + 10.975 \quad (1)$$

where v is the kinematic viscosity in centistokes (cSt). It is important that the kinematic viscosity of each component of the blend be obtained at the same temperature.

The next step is to calculate the VBN of the blend, using this equation:

$$\text{VBN}_{\text{Blend}} = [x_A \times \text{VBN}_A] + [x_B \times \text{VBN}_B] + \cdots + [x_N \times \text{VBN}_N] \quad (2)$$

where x_X is the mass fraction of each component of the blend.

Once the viscosity blending number of a blend has been calculated using equation (2), the final step is to determine the kinematic viscosity of the blend by solving equation (1) for v:

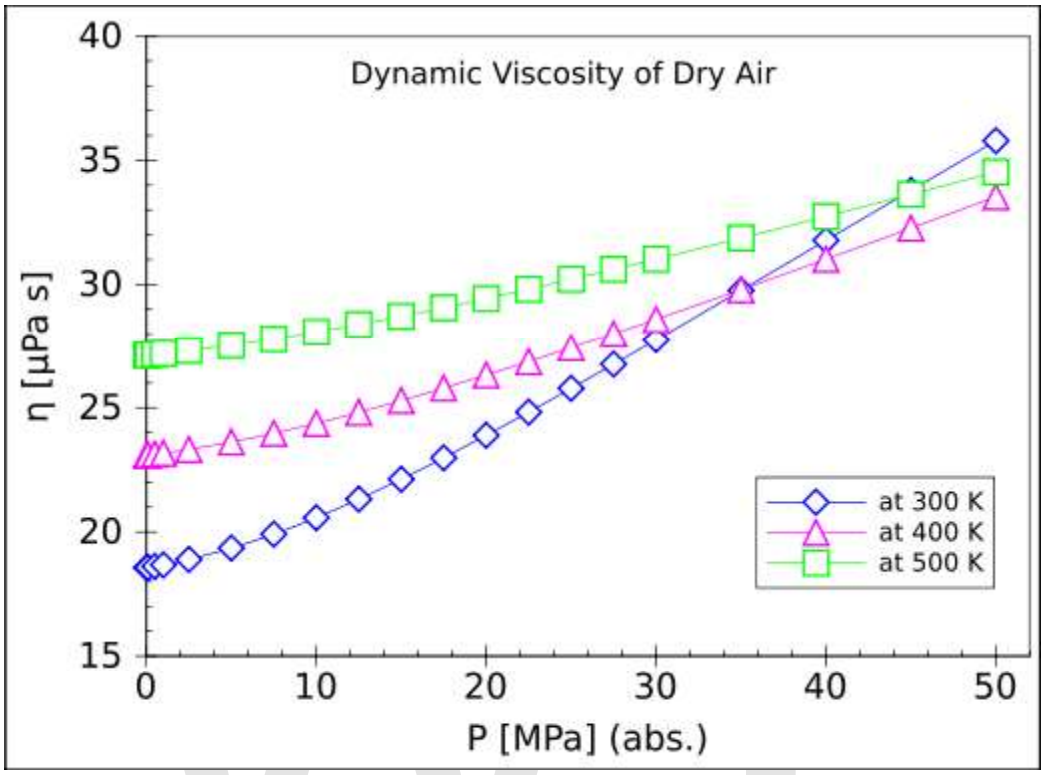
$$v = \exp\left(\exp\left(\frac{\text{VBN}_{\text{Blend}} - 10.975}{14.534}\right)\right) - 0.8, \quad (3)$$

where VBN_{Blend} is the viscosity blending number of the blend.

Viscosity of selected substances

The viscosity of air and water are by far the two most important materials for aviation aerodynamics and shipping fluid dynamics. Temperature plays the main role in determining viscosity.

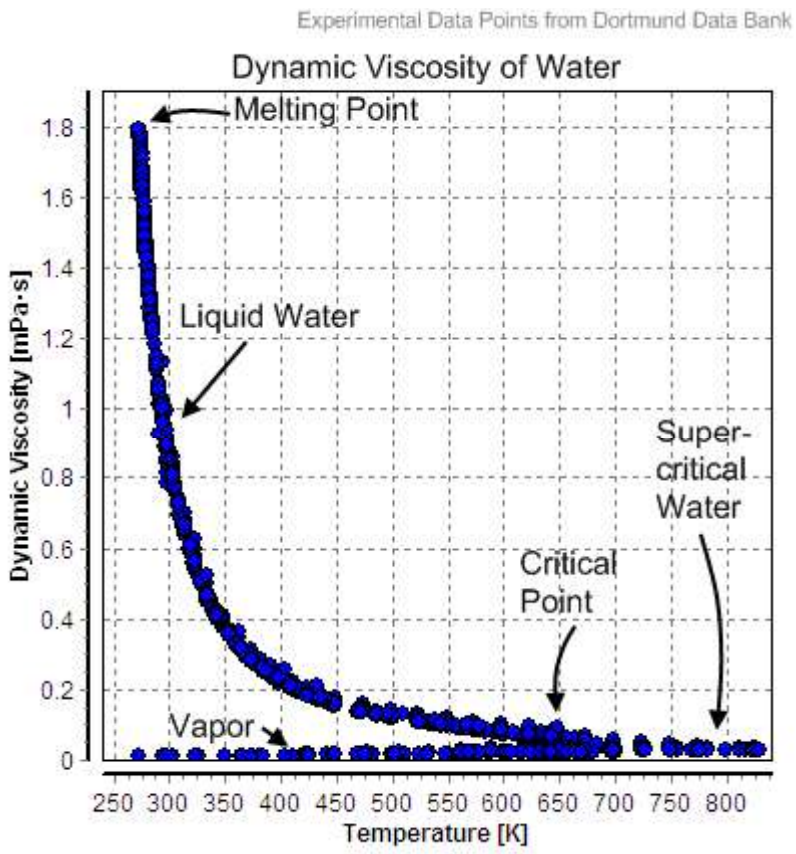
Viscosity of air



Pressure dependence of the dynamic viscosity of dry air at the temperatures of 300, 400 and 500 K

The viscosity of air depends mostly on the temperature. At 15.0 °C, the viscosity of air is 1.78×10^{-5} kg/(m·s), 17.8 μPa.s or 1.78×10^{-5} Pa.s.. One can get the viscosity of air as a function of temperature from the Gas Viscosity Calculator

Viscosity of water



Dynamic Viscosity of Water

The dynamic viscosity of water is 8.90×10^{-4} Pa·s or 8.90×10^{-3} dyn·s/cm^2 or 0.890 cP at about 25 °C.
Water has a viscosity of 0.0091 poise at 25 °C, or 1 centipoise at 20 °C.
As a function of temperature T (K): (Pa·s) = $A \times 10^{B/(T-C)}$
where A=2.414×10^{-5} Pa·s ; B = 247.8 K ; and C = 140 K.

Viscosity of liquid water at different temperatures up to the normal boiling point is listed below.

Temperature [°C]	Viscosity [mPa·s]
10	1.308
20	1.002
30	0.7978
40	0.6531

50	0.5471
60	0.4668
70	0.4044
80	0.3550
90	0.3150
100	0.2822

Viscosity of various materials

Example of the viscosity of milk and water. Liquids with higher viscosities will not make such a splash when poured at the same velocity.

Honey being drizzled.

Peanut butter is a semi-solid and can therefore hold peaks.

Some dynamic viscosities of Newtonian fluids are listed below:

Viscosity of selected gases at 100 kPa, [µPa·s]		
Gas	**at 0 °C (273 K)**	**at 27 °C (300 K)**
air	17.4	18.6
hydrogen	8.4	9.0
helium		20.0
argon		22.9
xenon	21.2	23.2
carbon dioxide		15.0
methane		11.2
ethane		9.5

Viscosity of liquids at 25 °C		
Liquid ():	**Viscosity** [Pa·s]	**Viscosity** [cP=mPa.s]
acetone	3.06×10^{-4}	0.306
benzene	6.04×10^{-4}	0.604
blood (37 °C)	$(3–4)\times10^{-3}$	3–4
castor oil	0.985	985
corn syrup	1.3806	1380.6
ethanol	1.074×10^{-3}	1.074
ethylene glycol	1.61×10^{-2}	16.1
glycerol	1.2 (at 20 °C)	1200
HFO-380	2.022	2022
mercury	1.526×10^{-3}	1.526
methanol	5.44×10^{-4}	0.544
Motor oil SAE 10 (20 °C)	0.065	65
Motor oil SAE 40 (20 °C)	0.319	319
nitrobenzene	1.863×10^{-3}	1.863
liquid nitrogen @ 77K	1.58×10^{-4}	0.158
propanol	1.945×10^{-3}	1.945
olive oil	.081	81
pitch	2.3e8	2.3e11
quark–gluon plasma	5e11	5e14
sulfuric acid	2.42×10^{-2}	24.2
water	8.94×10^{-4}	0.894

Viscosity of fluids with variable compositions		
Fluid	**Viscosity** [Pa·s]	**Viscosity** [cP]
honey	2–10	2,000–10,000
molasses	5–10	5,000–10,000
molten glass	10–1,000	10,000–1,000,000
chocolate syrup	10–25	10,000–25,000
molten chocolate*	45–130	45,000–130,000
ketchup*	50–100	50,000–100,000
peanut butter*	c. 250	c. 250,000

shortening*	c. 250	250,000

* These materials are highly non-Newtonian.

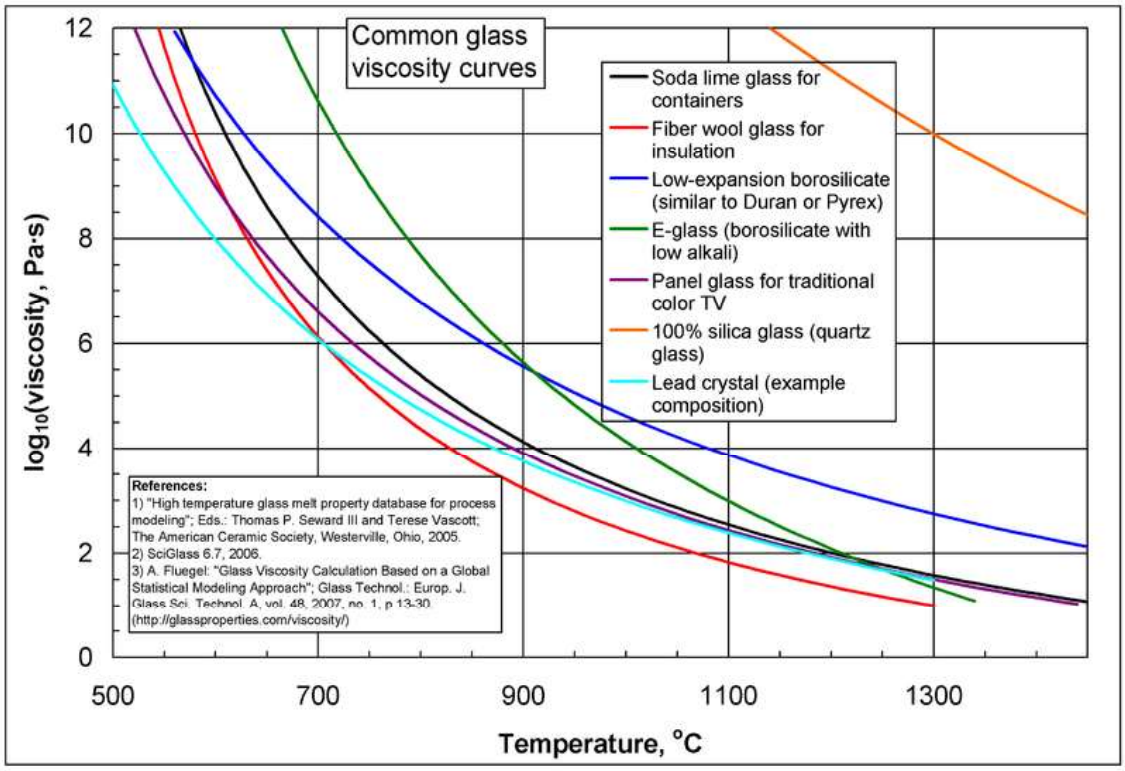
Viscosity of solids

On the basis that all solids such as granite flow to a small extent in response to small shear stress, some researchers have contended that substances known as amorphous solids, such as glass and many polymers, may be considered to have viscosity. This has led some to the view that solids are simply "liquids" with a very high viscosity, typically greater than 10^{12} Pa·s. This position is often adopted by supporters of the widely held misconception that glass flow can be observed in old buildings. This distortion is the result of the undeveloped glass making process of earlier eras, and not due to the viscosity of glass.

However, others argue that solids are, in general, elastic for small stresses while fluids are not. Even if solids flow at higher stresses, they are characterized by their low-stress behavior. This distinction is muddled if measurements are continued over long time periods, such as the Pitch drop experiment. Viscosity may be an appropriate characteristic for solids in a plastic regime. The situation becomes somewhat confused as the term *viscosity* is sometimes used for solid materials, for example Maxwell materials, to describe the relationship between stress and the rate of change of strain, rather than rate of shear.

These distinctions may be largely resolved by considering the constitutive equations of the material in question, which take into account both its viscous and elastic behaviors. Materials for which both their viscosity and their elasticity are important in a particular range of deformation and deformation rate are called *viscoelastic*. In geology, earth materials that exhibit viscous deformation at least three times greater than their elastic deformation are sometimes called rheids.

Viscosity of amorphous materials



Common glass viscosity curves.

Viscous flow in amorphous materials (e.g. in glasses and melts) is a thermally activated process:

$$\mu = A \cdot e^{Q/RT},$$

where Q is activation energy, T is temperature, R is the molar gas constant and A is approximately a constant.

The viscous flow in amorphous materials is characterized by a deviation from the Arrhenius-type behavior: Q changes from a high value Q_H at low temperatures (in the glassy state) to a low value Q_L at high temperatures (in the liquid state). Depending on this change, amorphous materials are classified as either

- strong when: $Q_H - Q_L < Q_L$ or
- fragile when: $Q_H - Q_L \geq Q_L$.

The fragility of amorphous materials is numerically characterized by the Doremus' fragility ratio:

$$R_D = \frac{Q_H}{Q_L}$$

and strong material have $R_D < 2$ whereas fragile materials have $R_D \geq 2$.

The viscosity of amorphous materials is quite exactly described by a two-exponential equation:

$$\mu = A_1 \cdot T \cdot \left[1 + A_2 \cdot e^{B/RT}\right] \cdot \left[1 + C \cdot e^{D/RT}\right],$$

with constants A_1, A_2, B, C and D related to thermodynamic parameters of joining bonds of an amorphous material.

Not very far from the glass transition temperature, T_g, this equation can be approximated by a Vogel-Fulcher-Tammann (VFT) equation.

If the temperature is significantly lower than the glass transition temperature, $T < T_g$, then the two-exponential equation simplifies to an Arrhenius type equation:

$$\mu = A_L T \cdot e^{Q_H/RT}$$

with:

$$Q_H = H_d + H_m,$$

where H_d is the enthalpy of formation of broken bonds (termed configuron s) and H_m is the enthalpy of their motion. When the temperature is less than the glass transition temperature, $T < T_g$, the activation energy of viscosity is high because the amorphous materials are in the glassy state and most of their joining bonds are intact.

If the temperature is highly above the glass transition temperature, $T > T_g$, the two-exponential equation also simplifies to an Arrhenius type equation:

$$\mu = A_H T \cdot e^{Q_L/RT},$$

with:

$$Q_L = H_m.$$

When the temperature is higher than the glass transition temperature, $T > T_g$, the activation energy of viscosity is low because amorphous materials are melt and have most of their joining bonds broken which facilitates flow.

Eddy viscosity

In the study of turbulence in fluids, a common practical strategy for calculation is to ignore the small-scale *vortices* (or *eddies*) in the motion and to calculate a large-scale motion with an *eddy viscosity* that characterizes the transport and dissipation of energy in the smaller-scale flow. Values of eddy viscosity used in modeling ocean circulation may be from 5×10^4 to 10^6 Pa·s depending upon the resolution of the numerical grid.

The linear viscous stress tensor

Viscous forces in a fluid are a function of the rate at which the fluid velocity is changing over distance. The velocity at any point ***r*** is specified by the velocity field ***v***(***r***). The velocity at a small distance *d**r*** from point ***r*** may be written as a Taylor series:

$$\mathbf{v}(\mathbf{r} + d\mathbf{r}) = \mathbf{v}(\mathbf{r}) + \frac{d\mathbf{v}}{d\mathbf{r}} d\mathbf{r} + \ldots,$$

where *d**v*** / *d**r*** is shorthand for the dyadic product of the del operator and the velocity:

$$\frac{d\mathbf{v}}{d\mathbf{r}} = \begin{bmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_x}{\partial y} & \frac{\partial v_x}{\partial z} \\ \frac{\partial v_y}{\partial x} & \frac{\partial v_y}{\partial y} & \frac{\partial v_y}{\partial z} \\ \frac{\partial v_z}{\partial x} & \frac{\partial v_z}{\partial y} & \frac{\partial v_z}{\partial z} \end{bmatrix}.$$

This is just the Jacobian of the velocity field.

Viscous forces are the result of relative motion between elements of the fluid, and so are expressible as a function of the velocity field. In other words, the forces at ***r*** are a function of ***v***(***r***) and all derivatives of ***v***(***r***) at that point. In the case of linear viscosity, the viscous force will be a function of the Jacobian tensor alone. For almost all practical situations, the linear approximation is sufficient.

If we represent *x*, *y*, and *z* by indices 1, 2, and 3 respectively, the *i*,*j* component of the Jacobian may be written as $\partial_i v_j$ where ∂_i is shorthand for $\partial/\partial x_i$. Note that when the first and higher derivative terms are zero, the velocity of all fluid elements is parallel, and there are no viscous forces.

Any matrix may be written as the sum of an antisymmetric matrix and a symmetric matrix, and this decomposition is independent of coordinate system, and so has physical significance. The velocity field may be approximated as:

$$v_j(\mathbf{r} + d\mathbf{r}) = v_j(\mathbf{r}) + \frac{1}{2}\left(\partial_i v_j - \partial_j v_i\right) dr_i + \frac{1}{2}\left(\partial_i v_j + \partial_j v_i\right) dr_i,$$

where Einstein notation is now being used in which repeated indices in a product are implicitly summed. The second term from the right is the asymmetric part of the first derivative term, and it represents a rigid rotation of the fluid about ***r*** with angular velocity ω where:

$$\omega = \frac{1}{2}\nabla \times \mathbf{v} = \frac{1}{2}\begin{bmatrix} \partial_2 v_3 - \partial_3 v_2 \\ \partial_3 v_1 - \partial_1 v_3 \\ \partial_1 v_2 - \partial_2 v_1 \end{bmatrix}.$$

For such a rigid rotation, there is no change in the relative positions of the fluid elements, and so there is no viscous force associated with this term. The remaining symmetric term is responsible for the viscous forces in the fluid. Assuming the fluid is isotropic (i.e. its properties are the same in all directions), then the most general way that the symmetric term (the rate-of-strain tensor) can be broken down in a coordinate-independent (and therefore physically real) way is as the sum of a constant tensor (the rate-of-expansion tensor) and a traceless symmetric tensor (the rate-of-shear tensor):

$$\frac{1}{2}\left(\partial_i v_j + \partial_j v_i\right) = \underbrace{\frac{1}{3}\partial_k v_k \delta_{ij}}_{\text{rate-of-expansion tensor}} + \underbrace{\left(\frac{1}{2}\left(\partial_i v_j + \partial_j v_i\right) - \frac{1}{3}\partial_k v_k \delta_{ij}\right)}_{\text{rate-of-shear tensor}},$$

where δ_{ij} is the unit tensor. The most general linear relationship between the stress tensor ***σ*** and the rate-of-strain tensor is then a linear combination of these two tensors:

$$\sigma_{\text{visc};ij} = \zeta \partial_k v_k \delta_{ij} + \mu\left(\partial_i v_j + \partial_j v_i - \frac{2}{3}\partial_k v_k \delta_{ij}\right),$$

where ς is the coefficient of bulk viscosity (or "second viscosity") and μ is the coefficient of (shear) viscosity.

The forces in the fluid are due to the velocities of the individual molecules. The velocity of a molecule may be thought of as the sum of the fluid velocity and the thermal velocity. The viscous stress tensor described above gives the force due to the fluid velocity only. The force on an area element in the fluid due to the thermal velocities of the molecules is just the hydrostatic pressure. This pressure term ($-p\,\delta_{ij}$) must be added to the viscous stress tensor to obtain the total stress tensor for the fluid.

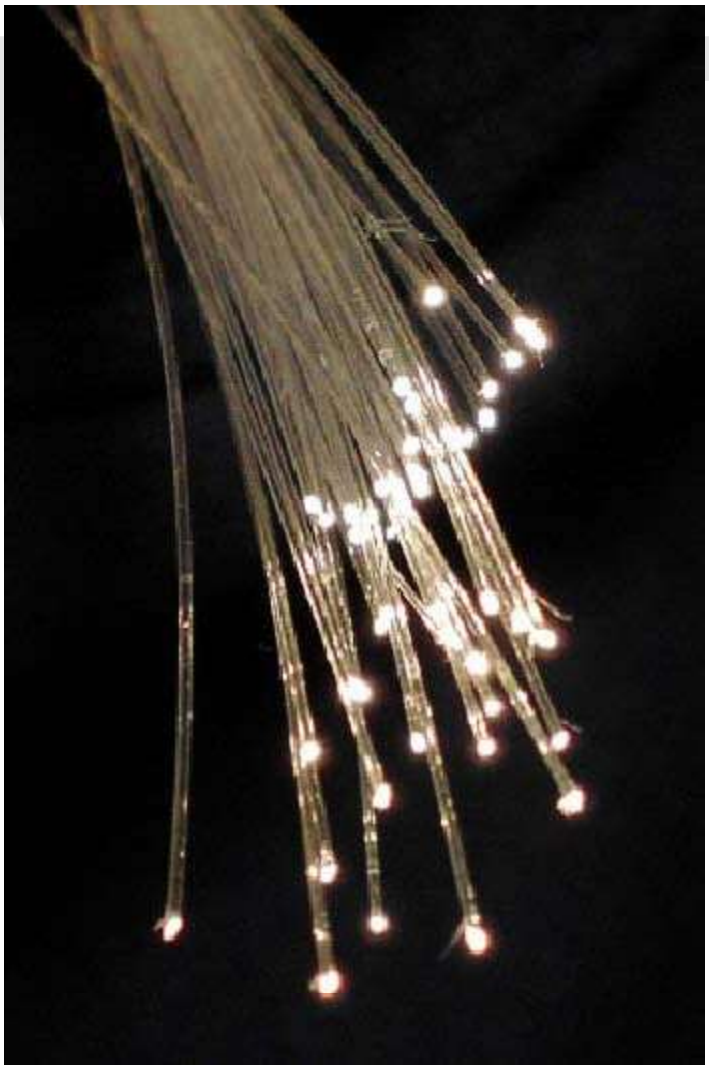
$$\sigma_{ij} = -p\delta_{ij} + \sigma_{\text{visc};ij}.$$

The infinitesimal force dF_i on an infinitesimal area dA_i is then given by the usual relationship:

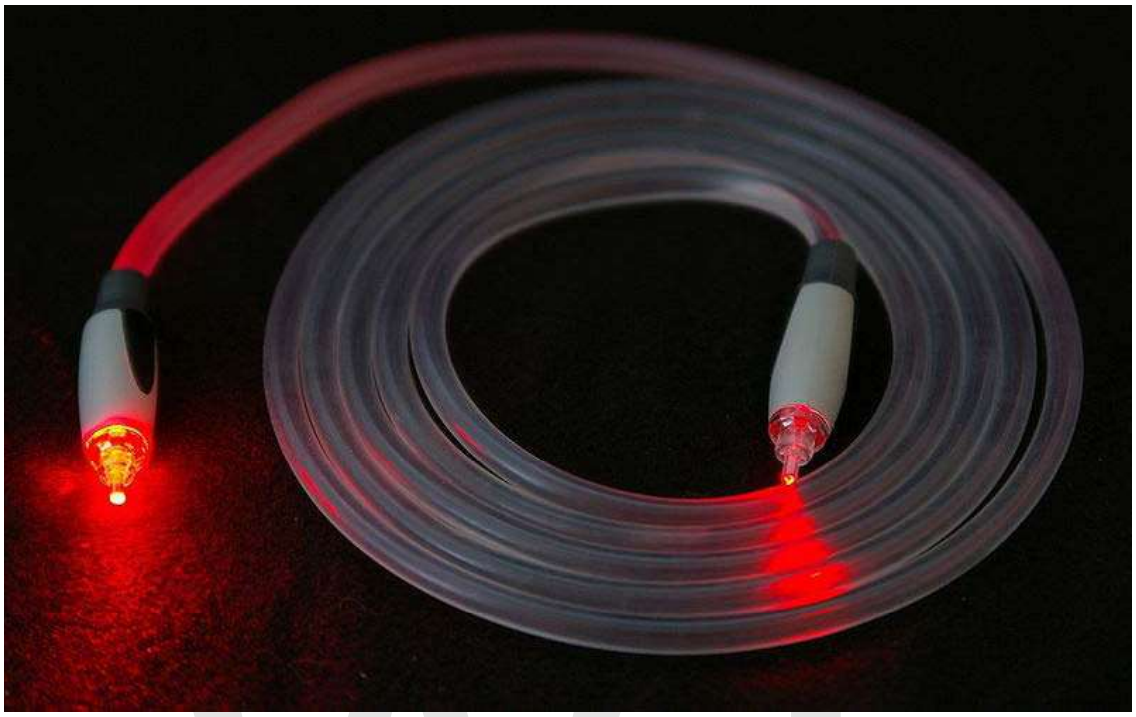
$$dF_i = \sigma_{ij}\, dA_j.$$

Chapter 4

Optical Fiber



A bundle of optical fibers



A TOSLINK fiber optic audio cable being illuminated at one end

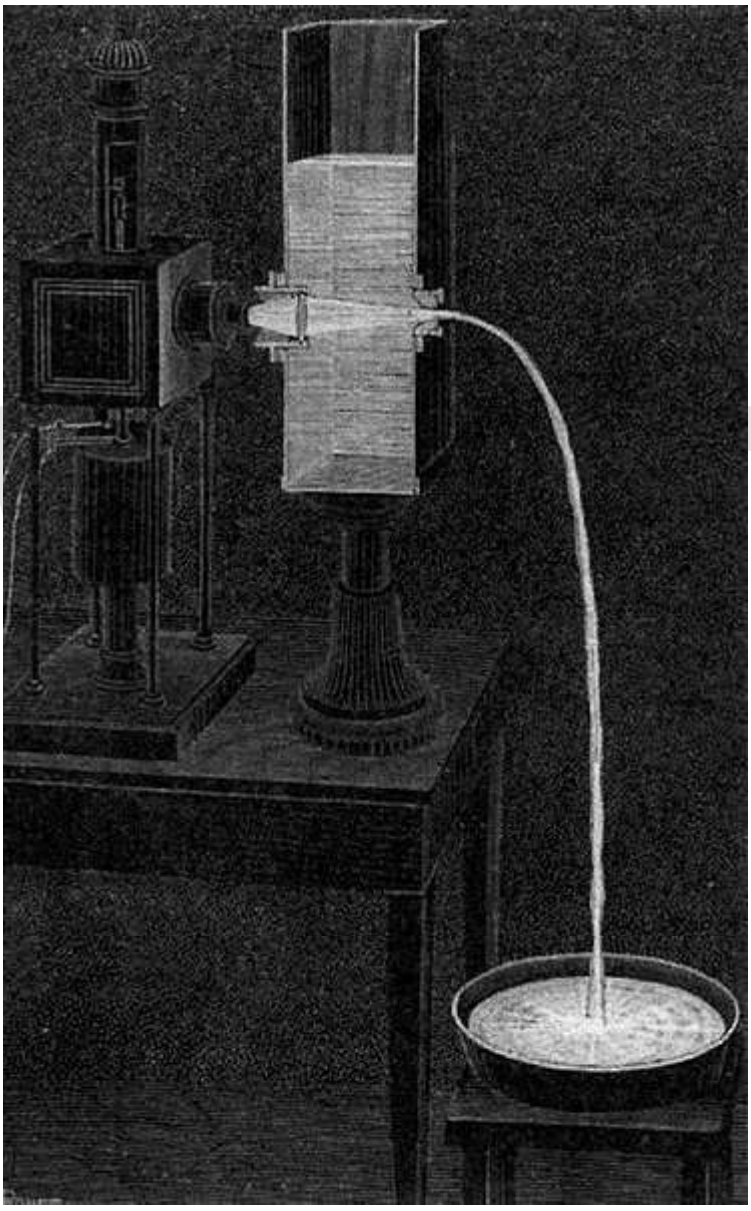
An **optical fiber** or **optical fibre** is a thin, flexible, transparent fiber that acts as a waveguide, or "light pipe", to transmit light between the two ends of the fiber. The field of applied science and engineering concerned with the design and application of optical fibers is known as **fiber optics**. Optical fibers are widely used in fiber-optic communications, which permits transmission over longer distances and at higher bandwidths (data rates) than other forms of communication. Fibers are used instead of metal wires because signals travel along them with less loss and are also immune to electromagnetic interference. Fibers are also used for illumination, and are wrapped in bundles so they can be used to carry images, thus allowing viewing in tight spaces. Specially designed fibers are used for a variety of other applications, including sensors and fiber lasers.

Optical fiber typically consists of a transparent core surrounded by a transparent cladding material with a lower index of refraction. Light is kept in the core by total internal reflection. This causes the fiber to act as a waveguide. Fibers which support many propagation paths or transverse modes are called multi-mode fibers (MMF), while those which can only support a single mode are called single-mode fibers (SMF). Multi-mode fibers generally have a larger core diameter, and are used for short-distance communication links and for applications where high power must be transmitted. Single-mode fibers are used for most communication links longer than 1,050 meters (3,440 ft).

Joining lengths of optical fiber is more complex than joining electrical wire or cable. The ends of the fibers must be carefully cleaved, and then spliced together either

mechanically or by fusing them together with heat. Special optical fiber connectors are used to make removable connections.

History



Daniel Colladon first described this "light fountain" or "light pipe" in an 1842 article titled *On the reflections of a ray of light inside a parabolic liquid stream*. This particular illustration comes from a later article by Colladon, in 1884.

Fiber optics, though used extensively in the modern world, is a fairly simple and old technology. Guiding of light by refraction, the principle that makes fiber optics possible,

was first demonstrated by Daniel Colladon and Jacques Babinet in Paris in the early 1840s. John Tyndall included a demonstration of it in his public lectures in London a dozen years later. Tyndall also wrote about the property of total internal reflection in an introductory book about the nature of light in 1870: "When the light passes from air into water, the refracted ray is bent *towards* the perpendicular... When the ray passes from water to air it is bent *from* the perpendicular... If the angle which the ray in water encloses with the perpendicular to the surface be greater than 48 degrees, the ray will not quit the water at all: it will be *totally reflected* at the surface.... The angle which marks the limit where total reflection begins is called the limiting angle of the medium. For water this angle is 48°27', for flint glass it is 38°41', while for diamond it is 23°42'."

Practical applications, such as close internal illumination during dentistry, appeared early in the twentieth century. Image transmission through tubes was demonstrated independently by the radio experimenter Clarence Hansell and the television pioneer John Logie Baird in the 1920s. The principle was first used for internal medical examinations by Heinrich Lamm in the following decade. In 1952, physicist Narinder Singh Kapany conducted experiments that led to the invention of optical fiber. Modern optical fibers, where the glass fiber is coated with a transparent cladding to offer a more suitable refractive index, appeared later in the decade. Development then focused on fiber bundles for image transmission. The first fiber optic semi-flexible gastroscope was patented by Basil Hirschowitz, C. Wilbur Peters, and Lawrence E. Curtiss, researchers at the University of Michigan, in 1956. In the process of developing the gastroscope, Curtiss produced the first glass-clad fibers; previous optical fibers had relied on air or impractical oils and waxes as the low-index cladding material. A variety of other image transmission applications soon followed.

In the late 19th and early 20th centuries, light was guided through bent glass rods to illuminate body cavities. Alexander Graham Bell invented a 'Photophone' to transmit voice signals over an optical beam.

Jun-ichi Nishizawa, a Japanese scientist at Tohoku University, also proposed the use of optical fibers for communications in 1963, as stated in his book published in 2004 in India. Nishizawa invented other technologies which contributed to the development of optical fiber communications, such as the graded-index optical fiber as a channel for transmitting light from semiconductor lasers. Charles K. Kao and George A. Hockham of the British company Standard Telephones and Cables (STC) were the first to promote the idea that the attenuation in optical fibers could be reduced below 20 decibels per kilometer (dB/km), allowing fibers to be a practical medium for communication. They proposed that the attenuation in fibers available at the time was caused by impurities, which could be removed, rather than fundamental physical effects such as scattering. They correctly and systematically theorized the light-loss properties for optical fiber, and pointed out the right material to manufacture such fibers — silica glass with high purity. This discovery led to Kao being awarded the Nobel Prize in Physics in 2009.

NASA used fiber optics in the television cameras sent to the moon. At the time such use in the cameras was 'classified confidential' and only those with the right security

clearance or those accompanied by someone with the right security clearance were permitted to handle the cameras.

The crucial attenuation limit of 20 dB/km was first achieved in 1970, by researchers Robert D. Maurer, Donald Keck, Peter C. Schultz, and Frank Zimar working for American glass maker Corning Glass Works, now Corning Incorporated. They demonstrated a fiber with 17 dB/km attenuation by doping silica glass with titanium. A few years later they produced a fiber with only 4 dB/km attenuation using germanium dioxide as the core dopant. Such low attenuation ushered in optical fiber telecommunication. In 1981, General Electric produced fused quartz ingots that could be drawn into fiber optic strands 25 miles (40 km) long.

Attenuation in modern optical cables is far less than in electrical copper cables, leading to long-haul fiber connections with repeater distances of 70–150 kilometers (43–93 mi). The erbium-doped fiber amplifier, which reduced the cost of long-distance fiber systems by reducing or eliminating optical-electrical-optical repeaters, was co-developed by teams led by David N. Payne of the University of Southampton and Emmanuel Desurvire at Bell Labs in 1986. Robust modern optical fiber uses glass for both core and sheath and is therefore less prone to aging processes. It was invented by Gerhard Bernsee of Schott Glass in Germany in 1973.

The emerging field of photonic crystals led to the development in 1991 of photonic-crystal fiber which guides light by diffraction from a periodic structure, rather than by total internal reflection. The first photonic crystal fibers became commercially available in 2000. Photonic crystal fibers can carry higher power than conventional fibers and their wavelength-dependent properties can be manipulated to improve performance.

Applications

Optical fiber communication

Optical fiber can be used as a medium for telecommunication and networking because it is flexible and can be bundled as cables. It is especially advantageous for long-distance communications, because light propagates through the fiber with little attenuation compared to electrical cables. This allows long distances to be spanned with few repeaters. Additionally, the per-channel light signals propagating in the fiber have been modulated at rates as high as 111 gigabits per second by NTT, although 10 or 40 Gbit/s is typical in deployed systems. Each fiber can carry many independent channels, each using a different wavelength of light (wavelength-division multiplexing (WDM)). The net data rate (data rate without overhead bytes) per fiber is the per-channel data rate reduced by the FEC overhead, multiplied by the number of channels (usually up to eighty in commercial dense WDM systems as of 2008). The current laboratory fiber optic data rate record, held by Bell Labs in Villarceaux, France, is multiplexing 155 channels, each carrying 100 Gbit/s over a 7000 km fiber. Nippon Telegraph and Telephone Corporation have also managed 69.1 Tbit/s over a single 240 km fiber (multiplexing 432 channels,

equating to 171 Gbit/s per channel). Bell Labs also broke a 100 Petabit per second *kilometer* barrier (15.5 Tbit/s over a single 7000 km fiber).

For short distance applications, such as creating a network within an office building, fiber-optic cabling can be used to save space in cable ducts. This is because a single fiber can often carry much more data than many electrical cables, such as 4 pair Cat-5 Ethernet cabling. Fiber is also immune to electrical interference; there is no cross-talk between signals in different cables and no pickup of environmental noise. Non-armored fiber cables do not conduct electricity, which makes fiber a good solution for protecting communications equipment located in high voltage environments such as power generation facilities, or metal communication structures prone to lightning strikes. They can also be used in environments where explosive fumes are present, without danger of ignition. Wiretapping is more difficult compared to electrical connections, and there are concentric dual core fibers that are said to be tap-proof.

Fiber optic sensors

Fibers have many uses in remote sensing. In some applications, the sensor is itself an optical fiber. In other cases, fiber is used to connect a non-fiberoptic sensor to a measurement system. Depending on the application, fiber may be used because of its small size, or the fact that no electrical power is needed at the remote location, or because many sensors can be multiplexed along the length of a fiber by using different wavelengths of light for each sensor, or by sensing the time delay as light passes along the fiber through each sensor. Time delay can be determined using a device such as an optical time-domain reflectometer.

Optical fibers can be used as sensors to measure strain, temperature, pressure and other quantities by modifying a fiber so that the quantity to be measured modulates the intensity, phase, polarization, wavelength or transit time of light in the fiber. Sensors that vary the intensity of light are the simplest, since only a simple source and detector are required. A particularly useful feature of such fiber optic sensors is that they can, if required, provide distributed sensing over distances of up to one meter.

Extrinsic fiber optic sensors use an optical fiber cable, normally a multi-mode one, to transmit modulated light from either a non-fiber optical sensor, or an electronic sensor connected to an optical transmitter. A major benefit of extrinsic sensors is their ability to reach places which are otherwise inaccessible. An example is the measurement of temperature inside aircraft jet engines by using a fiber to transmit radiation into a radiation pyrometer located outside the engine. Extrinsic sensors can also be used in the same way to measure the internal temperature of electrical transformers, where the extreme electromagnetic fields present make other measurement techniques impossible. Extrinsic sensors are used to measure vibration, rotation, displacement, velocity, acceleration, torque, and twisting. A solid state version of the gyroscope using the interference of light has been developed. The fiber optic gyroscope (FOG) has no moving parts and exploits the Sagnac effect to detect mechanical rotation.

A common use for fiber optic sensors are in advanced intrusion detection security systems, where the light is transmitted along the fiber optic sensor cable, which is placed on a fence, pipeline or communication cabling, and the returned signal is monitored and analysed for disturbances. This return signal is digitally processed to identify if there is a disturbance, and if an intrusion has occurred an alarm is triggered by the fiber optic security system.

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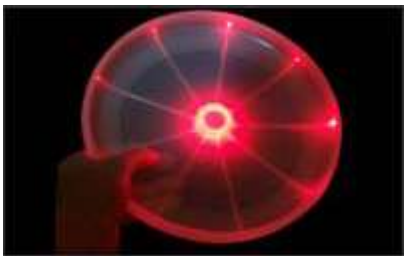
Other uses of optical fibers



A frisbee illuminated by fiber optics

Light reflected from optical fiber illuminates exhibited model

Fiber optic front sight on a hand gun

Fibers are widely used in illumination applications. They are used as light guides in medical and other applications where bright light needs to be shone on a target without a clear line-of-sight path. In some buildings, optical fibers are used to route sunlight from the roof to other parts of the building. Optical fiber illumination is also used for decorative applications, including signs, art, and artificial Christmas trees. Swarovski boutiques use optical fibers to illuminate their crystal showcases from many different angles while only employing one light source. Optical fiber is an intrinsic part of the light-transmitting concrete building product, LiTraCon.

Optical fiber is also used in imaging optics. A coherent bundle of fibers is used, sometimes along with lenses, for a long, thin imaging device called an endoscope, which is used to view objects through a small hole. Medical endoscopes are used for minimally invasive exploratory or surgical procedures (endoscopy). Industrial endoscopes are used for inspecting anything hard to reach, such as jet engine interiors.

In spectroscopy, optical fiber bundles are used to transmit light from a spectrometer to a substance which cannot be placed inside the spectrometer itself, in order to analyze its composition. A spectrometer analyzes substances by bouncing light off of and through

them. By using fibers, a spectrometer can be used to study objects that are too large to fit inside, or gasses, or reactions which occur in pressure vessels.

An optical fiber doped with certain rare earth elements such as erbium can be used as the gain medium of a laser or optical amplifier. Rare-earth doped optical fibers can be used to provide signal amplification by splicing a short section of doped fiber into a regular (undoped) optical fiber line. The doped fiber is optically pumped with a second laser wavelength that is coupled into the line in addition to the signal wave. Both wavelengths of light are transmitted through the doped fiber, which transfers energy from the second pump wavelength to the signal wave. The process that causes the amplification is stimulated emission.

Optical fibers doped with a wavelength shifter are used to collect scintillation light in physics experiments.

Optical fiber can be used to supply a low level of power (around one watt) to electronics situated in a difficult electrical environment. Examples of this are electronics in high-powered antenna elements and measurement devices used in high voltage transmission equipment.

A growing trend in iron sights for arms, is the use of short pieces of optical fiber for contrast enhancement dots, made in such a way that ambient light falling on the length of the fiber is concentrated at the tip, making the dots slightly brighter than the surroundings. This method is most commonly used in front sights, but many makers offer sights that use fiber optics on front and rear sights. Fiber optic sights can now be found on handguns, rifles, and shotguns, both as aftermarket accessories and a growing number of factory guns.

Principle of operation

An optical fiber is a cylindrical dielectric waveguide (nonconducting waveguide) that transmits light along its axis, by the process of total internal reflection. The fiber consists of a *core* surrounded by a cladding layer, both of which are made of dielectric materials. To confine the optical signal in the core, the refractive index of the core must be greater than that of the cladding. The boundary between the core and cladding may either be abrupt, in *step-index fiber*, or gradual, in *graded-index fiber*.

Index of refraction

The index of refraction is a way of measuring the speed of light in a material. Light travels fastest in a vacuum, such as outer space. The speed of light in a vacuum is about 300,000 kilometres (186 thousand miles) per second. Index of refraction is calculated by dividing the speed of light in a vacuum by the speed of light in some other medium. The index of refraction of a vacuum is therefore 1, by definition. The typical value for the cladding of an optical fiber is 1.46. The core value is typically 1.48. The larger the index of refraction, the slower light travels in that medium. From this information, a good rule

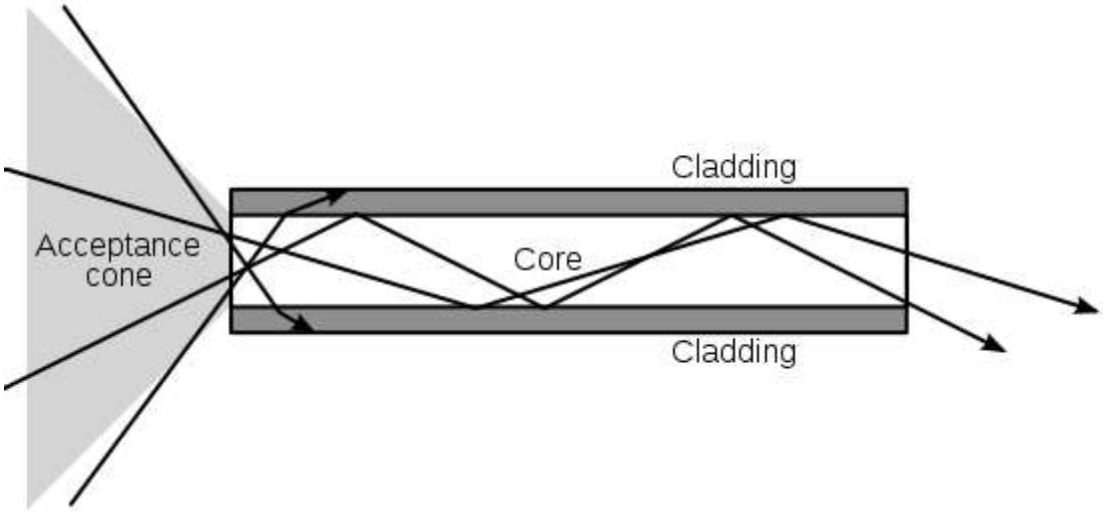
of thumb is that signal using optical fiber for communication will travel at around 200 million meters per second. Or to put it another way, to travel 1000 kilometers in fiber, the signal will take 5 milliseconds to propagate. Thus a phone call carried by fiber between Sydney and New York, a 12000 kilometer distance, means that there is an absolute minimum delay of 60 milliseconds (or around 1/16th of a second) between when one caller speaks to when the other hears. (Of course the fiber in this case will probably travel a longer route, and there will be additional delays due to communication equipment switching and the process of encoding and decoding the voice onto the fiber).

Total internal reflection

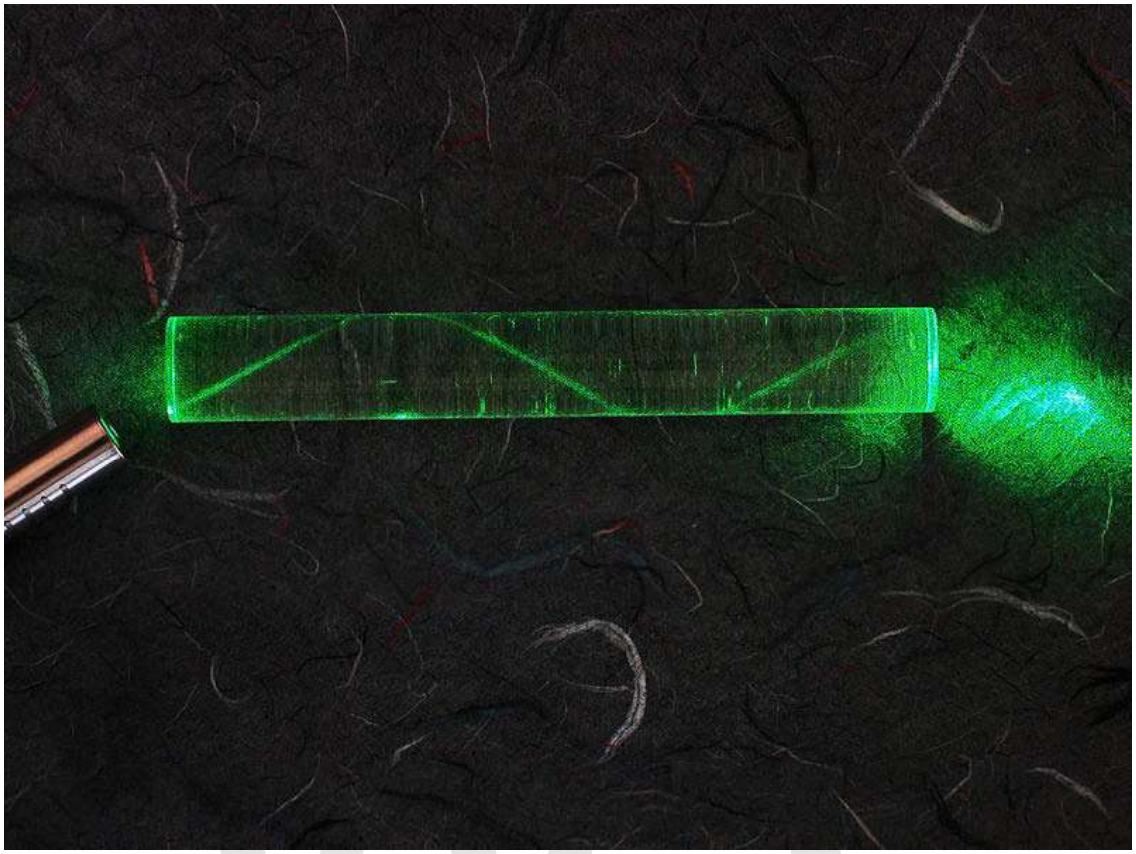
When light traveling in a dense medium hits a boundary at a steep angle (larger than the "critical angle" for the boundary), the light will be completely reflected. This effect is used in optical fibers to confine light in the core. Light travels along the fiber bouncing back and forth off of the boundary. Because the light must strike the boundary with an angle greater than the critical angle, only light that enters the fiber within a certain range of angles can travel down the fiber without leaking out. This range of angles is called the acceptance cone of the fiber. The size of this acceptance cone is a function of the refractive index difference between the fiber's core and cladding.

In simpler terms, there is a maximum angle from the fiber axis at which light may enter the fiber so that it will propagate, or travel, in the core of the fiber. The sine of this maximum angle is the numerical aperture (NA) of the fiber. Fiber with a larger NA requires less precision to splice and work with than fiber with a smaller NA. Single-mode fiber has a small NA.

Multi-mode fiber

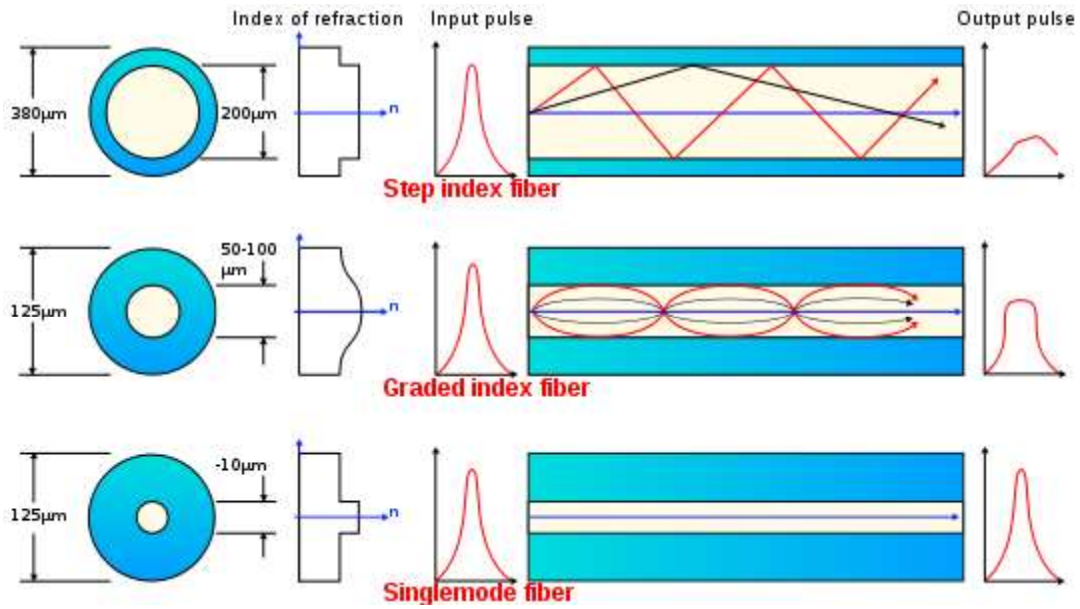


The propagation of light through a multi-mode optical fiber.



A laser bouncing down an acrylic rod, illustrating the total internal reflection of light in a multi-mode optical fiber.

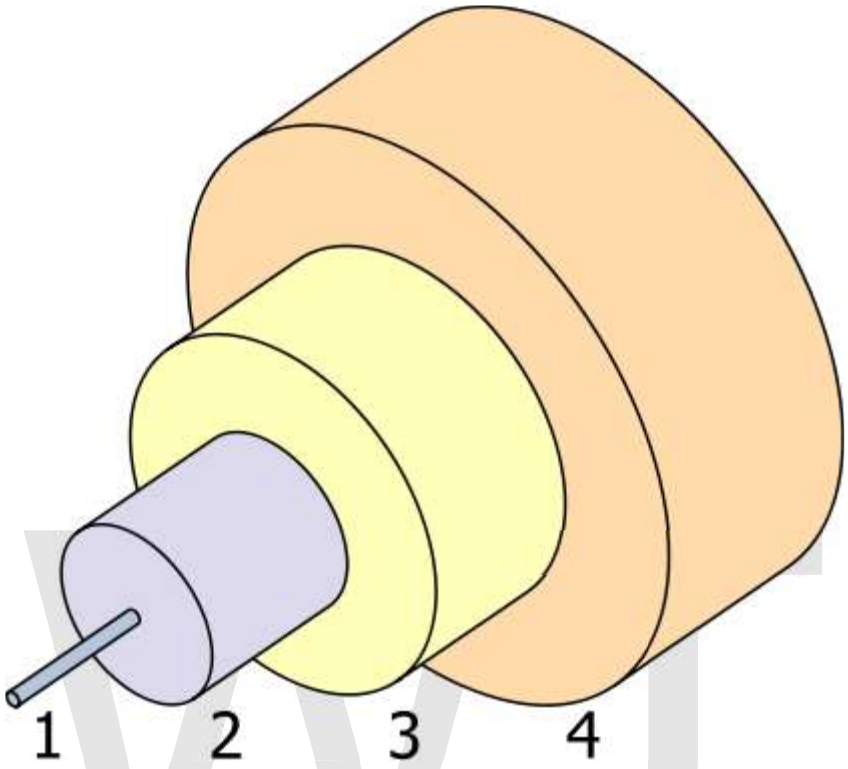
Fiber with large core diameter (greater than 10 micrometers) may be analyzed by geometrical optics. Such fiber is called *multi-mode fiber*, from the electromagnetic analysis. In a step-index multi-mode fiber, rays of light are guided along the fiber core by total internal reflection. Rays that meet the core-cladding boundary at a high angle (measured relative to a line normal to the boundary), greater than the critical angle for this boundary, are completely reflected. The critical angle (minimum angle for total internal reflection) is determined by the difference in index of refraction between the core and cladding materials. Rays that meet the boundary at a low angle are refracted from the core into the cladding, and do not convey light and hence information along the fiber. The critical angle determines the acceptance angle of the fiber, often reported as a numerical aperture. A high numerical aperture allows light to propagate down the fiber in rays both close to the axis and at various angles, allowing efficient coupling of light into the fiber. However, this high numerical aperture increases the amount of dispersion as rays at different angles have different path lengths and therefore take different times to traverse the fiber.



Optical fiber types.

In graded-index fiber, the index of refraction in the core decreases continuously between the axis and the cladding. This causes light rays to bend smoothly as they approach the cladding, rather than reflecting abruptly from the core-cladding boundary. The resulting curved paths reduce multi-path dispersion because high angle rays pass more through the lower-index periphery of the core, rather than the high-index center. The index profile is chosen to minimize the difference in axial propagation speeds of the various rays in the fiber. This ideal index profile is very close to a parabolic relationship between the index and the distance from the axis.

Single-mode fiber



The structure of a typical single-mode fiber.
1. Core: 8 µm diameter
2. Cladding: 125 µm dia.
3. Buffer: 250 µm dia.
4. Jacket: 400 µm dia.

Fiber with a core diameter less than about ten times the wavelength of the propagating light cannot be modeled using geometric optics. Instead, it must be analyzed as an electromagnetic structure, by solution of Maxwell's equations as reduced to the electromagnetic wave equation. The electromagnetic analysis may also be required to understand behaviors such as speckle that occur when coherent light propagates in multi-mode fiber. As an optical waveguide, the fiber supports one or more confined transverse modes by which light can propagate along the fiber. Fiber supporting only one mode is called *single-mode* or *mono-mode fiber*. The behavior of larger-core multi-mode fiber can also be modeled using the wave equation, which shows that such fiber supports more than one mode of propagation (hence the name). The results of such modeling of multi-mode fiber approximately agree with the predictions of geometric optics, if the fiber core is large enough to support more than a few modes.

The waveguide analysis shows that the light energy in the fiber is not completely confined in the core. Instead, especially in single-mode fibers, a significant fraction of the energy in the bound mode travels in the cladding as an evanescent wave.

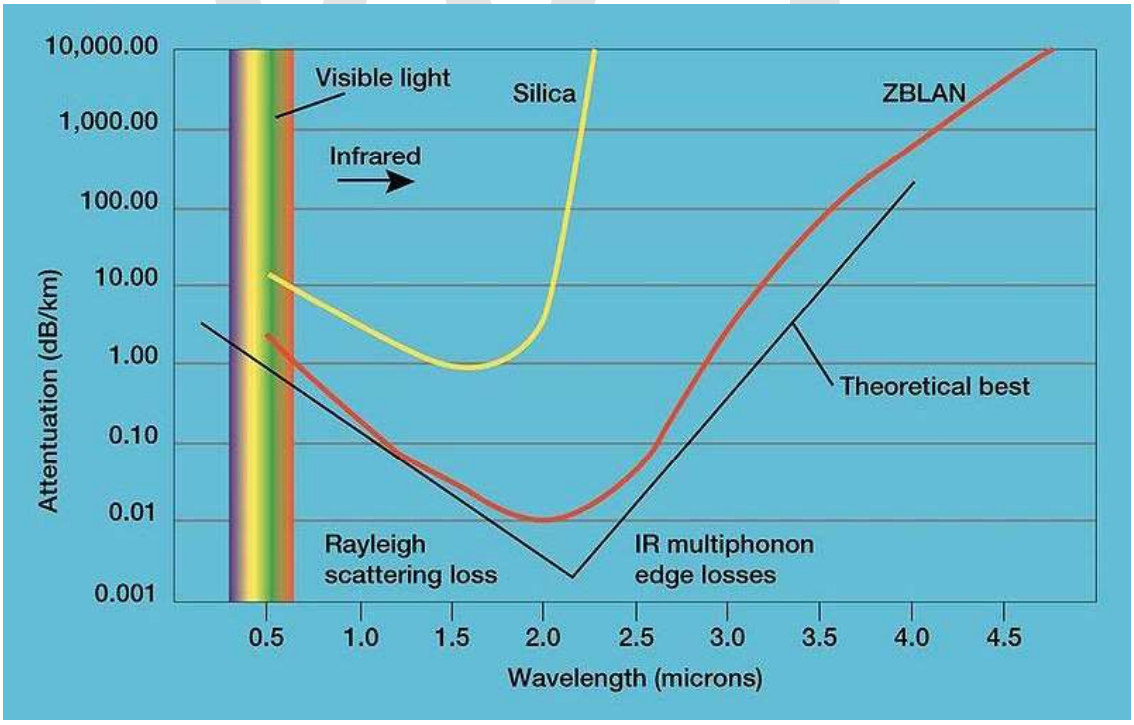
The most common type of single-mode fiber has a core diameter of 8–10 micrometers and is designed for use in the near infrared. The mode structure depends on the wavelength of the light used, so that this fiber actually supports a small number of additional modes at visible wavelengths. Multi-mode fiber, by comparison, is manufactured with core diameters as small as 50 micrometers and as large as hundreds of micrometers. The normalized frequency V for this fiber should be less than the first zero of the Bessel function J_0 (approximately 2.405).

Special-purpose fiber

Some special-purpose optical fiber is constructed with a non-cylindrical core and/or cladding layer, usually with an elliptical or rectangular cross-section. These include polarization-maintaining fiber and fiber designed to suppress whispering gallery mode propagation.

Photonic-crystal fiber is made with a regular pattern of index variation (often in the form of cylindrical holes that run along the length of the fiber). Such fiber uses diffraction effects instead of or in addition to total internal reflection, to confine light to the fiber's core. The properties of the fiber can be tailored to a wide variety of applications.

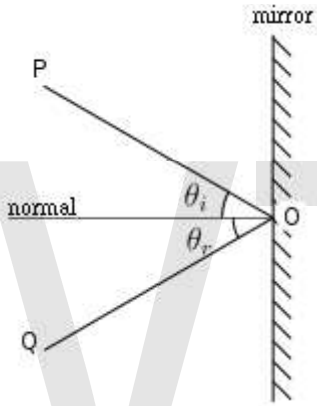
Mechanisms of attenuation



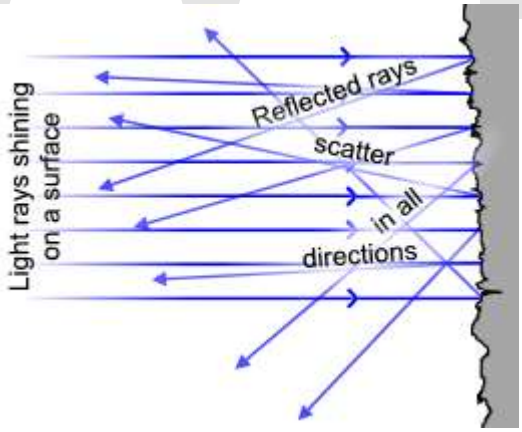
Light attenuation by ZBLAN and silica fibers

Attenuation in fiber optics, also known as transmission loss, is the reduction in intensity of the light beam (or signal) with respect to distance traveled through a transmission medium. Attenuation coefficients in fiber optics usually use units of dB/km through the medium due to the relatively high quality of transparency of modern optical transmission media. The medium is usually a fiber of silica glass that confines the incident light beam to the inside. Attenuation is an important factor limiting the transmission of a digital signal across large distances. Thus, much research has gone into both limiting the attenuation and maximizing the amplification of the optical signal. Empirical research has shown that attenuation in optical fiber is caused primarily by both scattering and absorption.

Light scattering



Specular reflection



Diffuse reflection

The propagation of light through the core of an optical fiber is based on total internal reflection of the lightwave. Rough and irregular surfaces, even at the molecular level, can cause light rays to be reflected in random directions. This is called diffuse reflection or scattering, and it is typically characterized by wide variety of reflection angles.

Light scattering depends on the wavelength of the light being scattered. Thus, limits to spatial scales of visibility arise, depending on the frequency of the incident light-wave and the physical dimension (or spatial scale) of the scattering center, which is typically in the form of some specific micro-structural feature. Since visible light has a wavelength of the order of one micrometre (one millionth of a meter) scattering centers will have dimensions on a similar spatial scale.

Thus, attenuation results from the incoherent scattering of light at internal surfaces and interfaces. In (poly)crystalline materials such as metals and ceramics, in addition to pores, most of the internal surfaces or interfaces are in the form of grain boundaries that separate tiny regions of crystalline order. It has recently been shown that when the size of the scattering center (or grain boundary) is reduced below the size of the wavelength of the light being scattered, the scattering no longer occurs to any significant extent. This phenomenon has given rise to the production of transparent ceramic materials.

Similarly, the scattering of light in optical quality glass fiber is caused by molecular level irregularities (compositional fluctuations) in the glass structure. Indeed, one emerging school of thought is that a glass is simply the limiting case of a polycrystalline solid. Within this framework, "domains" exhibiting various degrees of short-range order become the building blocks of both metals and alloys, as well as glasses and ceramics. Distributed both between and within these domains are micro-structural defects which will provide the most ideal locations for the occurrence of light scattering. This same phenomenon is seen as one of the limiting factors in the transparency of IR missile domes.

At high optical powers, scattering can also be caused by nonlinear optical processes in the fiber.

UV-Vis-IR absorption

In addition to light scattering, attenuation or signal loss can also occur due to selective absorption of specific wavelengths, in a manner similar to that responsible for the appearance of color. Primary material considerations include both electrons and molecules as follows:

1) At the electronic level, it depends on whether the electron orbitals are spaced (or "quantized") such that they can absorb a quantum of light (or photon) of a specific wavelength or frequency in the ultraviolet (UV) or visible ranges. This is what gives rise to color.

2) At the atomic or molecular level, it depends on the frequencies of atomic or molecular vibrations or chemical bonds, how close-packed its atoms or molecules are, and whether or not the atoms or molecules exhibit long-range order. These factors will determine the capacity of the material transmitting longer wavelengths in the infrared (IR), far IR, radio and microwave ranges.

The design of any optically transparent device requires the selection of materials based upon knowledge of its properties and limitations. The lattice absorption characteristics observed at the lower frequency regions (mid IR to far-infrared wavelength range) define the long-wavelength transparency limit of the material. They are the result of the interactive coupling between the motions of thermally induced vibrations of the constituent atoms and molecules of the solid lattice and the incident light wave radiation. Hence, all materials are bounded by limiting regions of absorption caused by atomic and molecular vibrations (bond-stretching)in the far-infrared (>10 μm).

Thus, multi-phonon absorption occurs when two or more phonons simultaneously interact to produce electric dipole moments with which the incident radiation may couple. These dipoles can absorb energy from the incident radiation, reaching a maximum coupling with the radiation when the frequency is equal to the fundamental vibrational mode of the molecular dipole (e.g. Si-O bond) in the far-infrared, or one of its harmonics.

The selective absorption of infrared (IR) light by a particular material occurs because the selected frequency of the light wave matches the frequency (or an integer multiple of the frequency) at which the particles of that material vibrate. Since different atoms and molecules have different natural frequencies of vibration, they will selectively absorb different frequencies (or portions of the spectrum) of infrared (IR) light.

Reflection and transmission of light waves occur because the frequencies of the light waves do not match the natural resonant frequencies of vibration of the objects. When IR light of these frequencies strikes an object, the energy is either reflected or transmitted.

Manufacturing

Materials

Glass optical fibers are almost always made from silica, but some other materials, such as fluorozirconate, fluoroaluminate, and chalcogenide glasses as well as crystalline materials like sapphire, are used for longer-wavelength infrared or other specialized applications. Silica and fluoride glasses usually have refractive indices of about 1.5, but some materials such as the chalcogenides can have indices as high as 3. Typically the index difference between core and cladding is less than one percent.

Plastic optical fibers (POF) are commonly step-index multi-mode fibers with a core diameter of 0.5 millimeters or larger. POF typically have higher attenuation coefficients than glass fibers, 1 dB/m or higher, and this high attenuation limits the range of POF-based systems.

Silica

Silica exhibits fairly good optical transmission over a wide range of wavelengths. In the near-infrared (near IR) portion of the spectrum, particularly around 1.5 μm, silica can have extremely low absorption and scattering losses of the order of 0.2 dB/km. A high

transparency in the 1.4-μm region is achieved by maintaining a low concentration of hydroxyl groups (OH). Alternatively, a high OH concentration is better for transmission in the ultraviolet (UV) region.

Silica can be drawn into fibers at reasonably high temperatures, and has a fairly broad glass transformation range. One other advantage is that fusion splicing and cleaving of silica fibers is relatively effective. Silica fiber also has high mechanical strength against both pulling and even bending, provided that the fiber is not too thick and that the surfaces have been well prepared during processing. Even simple cleaving (breaking) of the ends of the fiber can provide nicely flat surfaces with acceptable optical quality. Silica is also relatively chemically inert. In particular, it is not hygroscopic (does not absorb water).

Silica glass can be doped with various materials. One purpose of doping is to raise the refractive index (e.g. with Germanium dioxide (GeO_2) or Aluminium oxide (Al_2O_3)) or to lower it (e.g. with fluorine or Boron trioxide (B_2O_3)). Doping is also possible with laser-active ions (for example, rare earth-doped fibers) in order to obtain active fibers to be used, for example, in fiber amplifiers or laser applications. Both the fiber core and cladding are typically doped, so that the entire assembly (core and cladding) is effectively the same compound (e.g. an aluminosilicate, germanosilicate, phosphosilicate or borosilicate glass).

Particularly for active fibers, pure silica is usually not a very suitable host glass, because it exhibits a low solubility for rare earth ions. This can lead to quenching effects due to clustering of dopant ions. Aluminosilicates are much more effective in this respect.

Silica fiber also exhibits a high threshold for optical damage. This property ensures a low tendency for laser-induced breakdown. This is important for fiber amplifiers when utilized for the amplification of short pulses.

Because of these properties silica fibers are the material of choice in many optical applications, such as communications (except for very short distances with plastic optical fiber), fiber lasers, fiber amplifiers, and fiber-optic sensors. The large efforts which have been put forth in the development of various types of silica fibers have further increased the performance of such fibers over other materials.

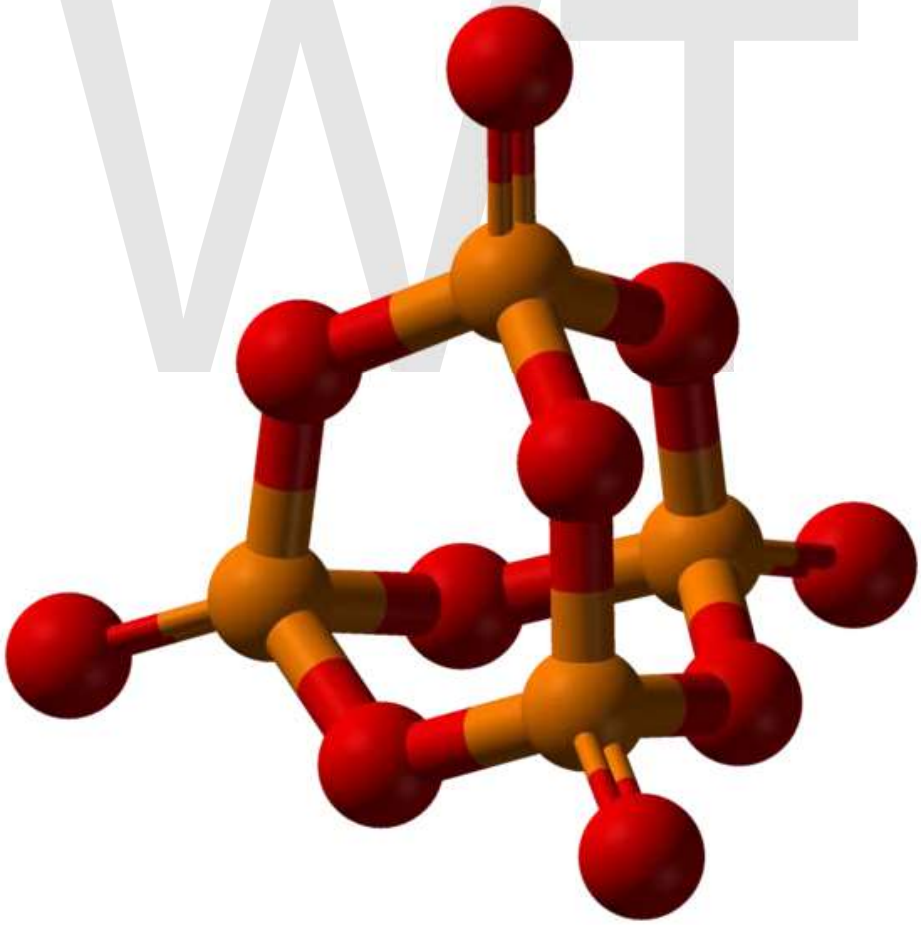
Fluorides

Fluoride glass is a class of non-oxide optical quality glasses composed of fluorides of various metals. Because of their low viscosity, it is very difficult to completely avoid crystallization while processing it through the glass transition (or drawing the fiber from the melt). Thus, although heavy metal fluoride glasses (HMFG) exhibit very low optical attenuation, they are not only difficult to manufacture, but are quite fragile, and have poor resistance to moisture and other environmental attacks. Their best attribute is that they lack the absorption band associated with the hydroxyl (OH) group (3200–3600 cm^{-1}), which is present in nearly all oxide-based glasses.

An example of a heavy metal fluoride glass is the ZBLAN glass group, composed of zirconium, barium, lanthanum, aluminium, and sodium fluorides. Their main technological application is as optical waveguides in both planar and fiber form. They are advantageous especially in the mid-infrared (2000–5000 nm) range.

HMFGs were initially slated for optical fiber applications, because the intrinsic losses of a mid-IR fiber could in principle be lower than those of silica fibers, which are transparent only up to about 2 μm. However, such low losses were never realized in practice, and the fragility and high cost of fluoride fibers made them less than ideal as primary candidates. Later, the utility of fluoride fibers for various other applications was discovered. These include mid-IR spectroscopy, fiber optic sensors, thermometry, and imaging. Also, fluoride fibers can be used for guided lightwave transmission in media such as YAG (yttria-alumina garnet) lasers at 2.9 μm, as required for medical applications (e.g. ophthalmology and dentistry).

Phosphates



The P_4O_{10} cagelike structure—the basic building block for phosphate glass.

Phosphate glass constitutes a class of optical glasses composed of metaphosphates of various metals. Instead of the SiO_4 tetrahedra observed in silicate glasses, the building block for this glass former is Phosphorus pentoxide (P_2O_5), which crystallizes in at least four different forms. The most familiar polymorph comprises molecules of P_4O_{10}.

Phosphate glasses can be advantageous over silica glasses for optical fibers with a high concentration of doping rare earth ions. A mix of fluoride glass and phosphate glass is fluorophosphate glass.

Chalcogenides

The chalcogens—the elements in group 16 of the periodic table—particularly sulfur (S), selenium (Se) and tellurium (Te)—react with more electropositive elements, such as silver, to form chalcogenides. These are extremely versatile compounds, in that they can be crystalline or amorphous, metallic or semiconducting, and conductors of ions or electrons.

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Process

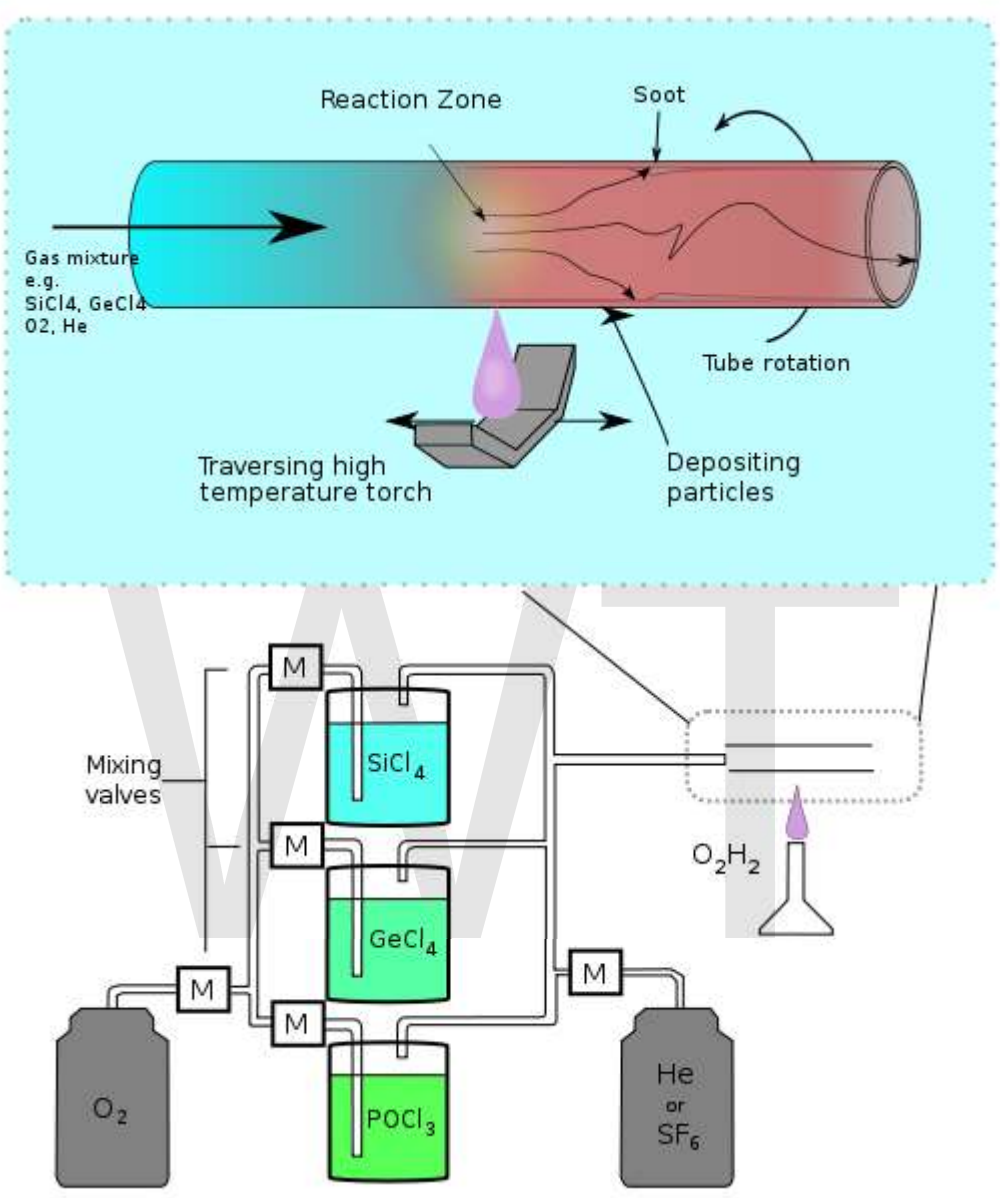

Illustration of the modified chemical vapor deposition (inside) process

Standard optical fibers are made by first constructing a large-diameter *preform*, with a carefully controlled refractive index profile, and then *pulling* the preform to form the long, thin optical fiber. The preform is commonly made by three chemical vapor deposition methods: *inside vapor deposition*, *outside vapor deposition*, and *vapor axial deposition*.

With *inside vapor deposition*, the preform starts as a hollow glass tube approximately 40 centimeters (16 in) long, which is placed horizontally and rotated slowly on a lathe. Gases such as silicon tetrachloride ($SiCl_4$) or germanium tetrachloride ($GeCl_4$) are

injected with oxygen in the end of the tube. The gases are then heated by means of an external hydrogen burner, bringing the temperature of the gas up to 1900 K (1600 °C, 3000 °F), where the tetrachlorides react with oxygen to produce silica or germania (germanium dioxide) particles. When the reaction conditions are chosen to allow this reaction to occur in the gas phase throughout the tube volume, in contrast to earlier techniques where the reaction occurred only on the glass surface, this technique is called *modified chemical vapor deposition (MCVD)*.

The oxide particles then agglomerate to form large particle chains, which subsequently deposit on the walls of the tube as soot. The deposition is due to the large difference in temperature between the gas core and the wall causing the gas to push the particles outwards (this is known as thermophoresis). The torch is then traversed up and down the length of the tube to deposit the material evenly. After the torch has reached the end of the tube, it is then brought back to the beginning of the tube and the deposited particles are then melted to form a solid layer. This process is repeated until a sufficient amount of material has been deposited. For each layer the composition can be modified by varying the gas composition, resulting in precise control of the finished fiber's optical properties.

In outside vapor deposition or vapor axial deposition, the glass is formed by *flame hydrolysis*, a reaction in which silicon tetrachloride and germanium tetrachloride are oxidized by reaction with water (H_2O) in an oxyhydrogen flame. In outside vapor deposition the glass is deposited onto a solid rod, which is removed before further processing. In vapor axial deposition, a short *seed rod* is used, and a porous preform, whose length is not limited by the size of the source rod, is built up on its end. The porous preform is consolidated into a transparent, solid preform by heating to about 1800 K (1500 °C, 2800 °F).

The preform, however constructed, is then placed in a device known as a drawing tower, where the preform tip is heated and the optic fiber is pulled out as a string. By measuring the resultant fiber width, the tension on the fiber can be controlled to maintain the fiber thickness.

Coatings

The light is "guided" down the core of the fiber by an optical "cladding" with a lower refractive index that traps light in the core through "total internal reflection."

The cladding is coated by a "buffer" that protects it from moisture and physical damage. The buffer is what gets stripped off the fiber for termination or splicing. These coatings are UV-cured urethane acrylate composite materials applied to the outside of the fiber during the drawing process. The coatings protect the very delicate strands of glass fiber—about the size of a human hair—and allow it to survive the rigors of manufacturing, proof testing, cabling and installation.

Today’s glass optical fiber draw processes employ a dual-layer coating approach. An inner primary coating is designed to act as a shock absorber to minimize attenuation

caused by microbending. An outer secondary coating protects the primary coating against mechanical damage and acts as a barrier to lateral forces. Sometimes a metallic armour layer is added to provide extra protection.

These fiber optic coating layers are applied during the fiber draw, at speeds approaching 100 kilometers per hour (60 mph). Fiber optic coatings are applied using one of two methods: wet-on-dry, in which the fiber passes through a primary coating application, which is then UV cured, then through the secondary coating application which is subsequently cured; and wet-on-wet, in which the fiber passes through both the primary and secondary coating applications and then goes to UV curing.

Fiber optic coatings are applied in concentric layers to prevent damage to the fiber during the drawing application and to maximize fiber strength and microbend resistance. Unevenly coated fiber will experience non-uniform forces when the coating expands or contracts, and is susceptible to greater signal attenuation. Under proper drawing and coating processes, the coatings are concentric around the fiber, continuous over the length of the application and have constant thickness.

Fiber optic coatings protect the glass fibers from scratches that could lead to strength degradation. The combination of moisture and scratches accelerates the aging and deterioration of fiber strength. When fiber is subjected to low stresses over a long period, fiber fatigue can occur. Over time or in extreme conditions, these factors combine to cause microscopic flaws in the glass fiber to propagate, which can ultimately result in fiber failure.

Three key characteristics of fiber optic waveguides can be affected by environmental conditions: strength, attenuation and resistance to losses caused by microbending. External fiber optic coatings protect glass optical fiber from environmental conditions that can affect the fiber's performance and long-term durability. On the inside, coatings ensure the reliability of the signal being carried and help minimize attenuation due to microbending.

Practical issues

Optical fiber cables

An optical fiber cable

In practical fibers, the cladding is usually coated with a tough resin *buffer* layer, which may be further surrounded by a *jacket* layer, usually glass. These layers add strength to the fiber but do not contribute to its optical wave guide properties. Rigid fiber assemblies sometimes put light-absorbing ("dark") glass between the fibers, to prevent light that leaks out of one fiber from entering another. This reduces cross-talk between the fibers, or reduces flare in fiber bundle imaging applications.

Modern cables come in a wide variety of sheathings and armor, designed for applications such as direct burial in trenches, high voltage isolation, dual use as power lines, installation in conduit, lashing to aerial telephone poles, submarine installation, and insertion in paved streets. The cost of small fiber-count pole-mounted cables has greatly decreased due to the high demand for fiber to the home (FTTH) installations in Japan and South Korea.

Fiber cable can be very flexible, but traditional fiber's loss increases greatly if the fiber is bent with a radius smaller than around 30 mm. This creates a problem when the cable is bent around corners or wound around a spool, making FTTX installations more complicated. "Bendable fibers", targeted towards easier installation in home environments, have been standardized as ITU-T G.657. This type of fiber can be bent with a radius as low as 7.5 mm without adverse impact. Even more bendable fibers have been developed. Bendable fiber may also be resistant to fiber hacking, in which the signal in a fiber is surreptitiously monitored by bending the fiber and detecting the leakage.

Another important feature of cable is cable withstanding against the horizontally applied force. It is technically called max tensile strength defining how much force can applied to the cable during the installation period.

Telecom Anatolia fiber optic cable versions are reinforced with aramid yarns or glass yarns as intermediary strength member. In commercial terms, usage of the glass yarns are more cost effective while no loss in mechanical durability of the cable. Glass yarns also protect the cable core against rodents and termites.

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Termination and splicing

ST connectors on multi-mode fiber.

Optical fibers are connected to terminal equipment by optical fiber connectors. These connectors are usually of a standard type such as *FC*, *SC*, *ST*, *LC*, or *MTRJ*.

Optical fibers may be connected to each other by connectors or by *splicing*, that is, joining two fibers together to form a continuous optical waveguide. The generally accepted splicing method is arc fusion splicing, which melts the fiber ends together with an electric arc. For quicker fastening jobs, a "mechanical splice" is used.

Fusion splicing is done with a specialized instrument that typically operates as follows: The two cable ends are fastened inside a splice enclosure that will protect the splices, and the fiber ends are stripped of their protective polymer coating (as well as the more sturdy outer jacket, if present). The ends are *cleaved* (cut) with a precision cleaver to make them perpendicular, and are placed into special holders in the splicer. The splice is usually inspected via a magnified viewing screen to check the cleaves before and after the splice. The splicer uses small motors to align the end faces together, and emits a small spark between electrodes at the gap to burn off dust and moisture. Then the splicer generates a larger spark that raises the temperature above the melting point of the glass, fusing the ends together permanently. The location and energy of the spark is carefully controlled so that the molten core and cladding do not mix, and this minimizes optical loss. A splice loss estimate is measured by the splicer, by directing light through the cladding on one side and measuring the light leaking from the cladding on the other side. A splice loss under 0.1 dB is typical. The complexity of this process makes fiber splicing much more difficult than splicing copper wire.

Mechanical fiber splices are designed to be quicker and easier to install, but there is still the need for stripping, careful cleaning and precision cleaving. The fiber ends are aligned and held together by a precision-made sleeve, often using a clear index-matching gel that enhances the transmission of light across the joint. Such joints typically have higher optical loss and are less robust than fusion splices, especially if the gel is used. All splicing techniques involve the use of an enclosure into which the splice is placed for protection afterward.

Fibers are terminated in connectors so that the fiber end is held at the end face precisely and securely. A fiber-optic connector is basically a rigid cylindrical barrel surrounded by a sleeve that holds the barrel in its mating socket. The mating mechanism can be "push and click", "turn and latch" ("bayonet"), or screw-in (threaded). A typical connector is installed by preparing the fiber end and inserting it into the rear of the connector body. Quick-set adhesive is usually used so the fiber is held securely, and a strain relief is secured to the rear. Once the adhesive has set, the fiber's end is polished to a mirror finish. Various polish profiles are used, depending on the type of fiber and the application. For single-mode fiber, the fiber ends are typically polished with a slight curvature, such that when the connectors are mated the fibers touch only at their cores. This is known as a "physical contact" (PC) polish. The curved surface may be polished at an angle, to make an "angled physical contact" (APC) connection. Such connections have higher loss than PC connections, but greatly reduced back reflection, because light that reflects from the angled surface leaks out of the fiber core; the resulting loss in signal strength is known as gap loss. APC fiber ends have low back reflection even when disconnected.

In the 1990s, terminating fiber optic cables was very labor intensive. The number of parts per connector, polishing of the fibers, and the need to oven-bake the epoxy in each connector made terminating fiber optic cables very difficult. Today, many different connectors are on the market and offer an easier, less labor intensive way of terminating the cables. Some of the most popular connectors have already been polished from the

factory and include a gel inside the connector and those two steps help save money on labor especially on large projects. A cleave is made at a required length in order to get as close to the polished piece already inside the connector, with the gel surrounding the point where the two piece meet inside the connector very little light loss is exposed.

Free-space coupling

It is often necessary to align an optical fiber with another optical fiber, or with an optoelectronic device such as a light-emitting diode, a laser diode, or a modulator. This can involve either carefully aligning the fiber and placing it in contact with the device, or can use a lens to allow coupling over an air gap. In some cases the end of the fiber is polished into a curved form that is designed to allow it to act as a lens.

In a laboratory environment, a bare fiber end is coupled using a fiber launch system, which uses a microscope objective lens to focus the light down to a fine point. A precision translation stage (micro-positioning table) is used to move the lens, fiber, or device to allow the coupling efficiency to be optimized. Fibers with a connector on the end make this process much simpler: the connector is simply plugged into a pre-aligned fiberoptic collimator, which contains a lens that is either accurately positioned with respect to the fiber, or is adjustable. To achieve the best injection efficiency into single-mode fiber, the direction, position, size and divergence of the beam must all be optimized. With good beams, 70 to 90% coupling efficiency can be achieved.

With properly polished single-mode fibers, the emitted beam has an almost perfect Gaussian shape—even in the far field—if a good lens is used. The lens needs to be large enough to support the full numerical aperture of the fiber, and must not introduce aberrations in the beam. Aspheric lenses are typically used.

Fiber fuse

At high optical intensities, above 2 megawatts per square centimeter, when a fiber is subjected to a shock or is otherwise suddenly damaged, a *fiber fuse* can occur. The reflection from the damage vaporizes the fiber immediately before the break, and this new defect remains reflective so that the damage propagates back toward the transmitter at 1–3 meters per second (4−11 km/h, 2–8 mph). The open fiber control system, which ensures laser eye safety in the event of a broken fiber, can also effectively halt propagation of the fiber fuse. In situations, such as undersea cables, where high power levels might be used without the need for open fiber control, a "fiber fuse" protection device at the transmitter can break the circuit to prevent any damage.

Example

Fiber connections can be used for various types of connections. For example, most high definition televisions offer a digital audio optical connection. This allows the streaming of audio over light, using the TOSLink protocol.

Electric power transmission

Optical fiber can be used to transmit electricity. While the efficiency is not nearly that of traditional copper wire, it is especially useful in situations where it is desirable to not have a metallic conductor as in the case of use near MRI machines which produce strong magnetic currents.

WT

Chapter 5

Radioactive Waste

Radioactive waste is a waste product containing radioactive material. It is usually the product of a nuclear process such as nuclear fission, though industries not directly connected to the nuclear power industry may also produce radioactive waste.

Radioactivity diminishes over time, so in principle the waste needs to be isolated for a period of time until it no longer poses a hazard. This can mean hours to years for some common medical or industrial radioactive wastes, or thousands of years for high-level wastes from nuclear power plants and nuclear weapons reprocessing.

The majority of radioactive waste is "low-level waste", meaning it has low levels of radioactivity per mass or volume.

The main approaches to managing radioactive waste to date have been segregation and storage for short-lived wastes, near-surface disposal for low and some intermediate level wastes, and deep burial or transmutation for the long-lived, high-level wastes.

A summary of the amounts of radioactive wastes and management approaches for most developed countries are presented and reviewed periodically as part of the IAEA Joint Convention on Safety of Spent Fuel Management and the Safety of Radioactive Waste Management.

The nature and significance of radioactive waste

Radioactive waste typically comprises a number of radioisotopes: unstable configurations of elements that decay, emitting ionizing radiation which can be harmful to humans and the environment. Those isotopes emit different types and levels of radiation, which last for different periods of time.

Physics

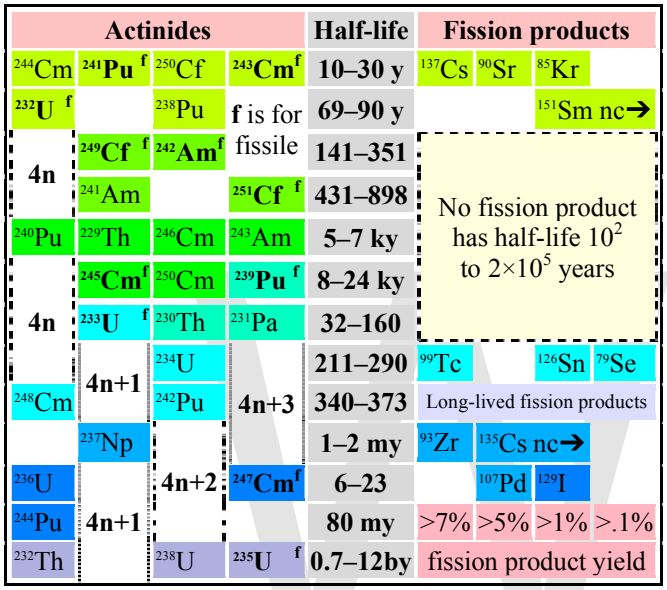
Long-lived fission products				
Prop:	**$t^{1/2}$**	**Yield**	**Q ***	**βγ**
Unit:	**Ma**	**%**	**KeV**	*****
^{99}Tc	0.211	6.1385	294	β
^{126}Sn	0.230	0.1084	4050	βγ
^{79}Se	0.327	0.0447	151	β
^{93}Zr	1.53	5.4575	91	βγ
^{135}Cs	2.3	6.9110	269	β
^{107}Pd	6.5	1.2499	33	β
^{129}I	15.7	0.8410	194	βγ

Medium-lived fission products				
Prop:	**$t^{1/2}$**	**Yield**	**Q ***	**βγ**
Unit:	**a**	**%**	**KeV**	*****
^{155}Eu	4.76	.0803	252	βγ
^{85}Kr	10.76	.2180	687	βγ
^{113m}Cd	14.1	.0008	316	β
^{90}Sr	28.9	4.505	2826	**β**
^{137}Cs	30.23	6.337	1176	βγ
^{121m}Sn	43.9	.00005	390	βγ
^{151}Sm	90	.5314	77	β

The radioactivity of all nuclear waste diminishes with time. All radioisotopes contained in the waste have a half-life—the time it takes for any radionuclide to lose half of its radioactivity—and eventually all radioactive waste decays into non-radioactive elements. Certain radioactive elements (such as plutonium-239) in "spent" fuel will remain hazardous to humans and other creatures for hundreds of thousands of years. Other radioisotopes remain hazardous for millions of years. Thus, these wastes must be shielded for centuries and isolated from the living environment for millennia. Some elements, such as iodine-131, have a short half-life (around 8 days in this case) and thus they will cease to be a problem much more quickly than other, longer-lived, decay products, but their activity is much greater initially. The two tables show some of the major radioisotopes, their half-lives, and their radiation yield as a proportion of the yield of fission of uranium-235.

The faster a radioisotope decays, the more radioactive it will be. The energy and the type of the ionizing radiation emitted by a pure radioactive substance are important factors in deciding how dangerous it is. The chemical properties of the radioactive element will determine how mobile the substance is and how likely it is to spread into the environment and contaminate humans. This is further complicated by the fact that many radioisotopes do not decay immediately to a stable state but rather to a radioactive decay product leading to decay chains.

Pharmacokinetics



Exposure to high levels of radioactive waste may cause serious harm or death. Treatment of an adult animal with radiation or some other mutation-causing effect, such as a cytotoxic anti-cancer drug, may cause cancer in the animal. In humans it has been calculated that a 5 sievert dose is usually fatal, and the lifetime risk of dying from radiation induced cancer from a single dose of 0.1 sieverts is 0.8%, increasing by the same amount for each additional 0.1 sievert increment of dosage. Ionizing radiation causes deletions in chromosomes. If a developing organism such as an unborn child is irradiated, it is possible a birth defect may be induced, but it is unlikely this defect will be in a gamete or a gamete forming cell. The incidence of radiation-induced mutations in humans is undetermined, due to flaws in studies done to date.

Depending on the decay mode and the pharmacokinetics of an element (how the body processes it and how quickly), the threat due to exposure to a given activity of a radioisotope will differ. For instance iodine-131 is a short-lived beta and gamma emitter, but because it concentrates in the thyroid gland, it is more able to cause injury than caesium-137 which, being water soluble, is rapidly excreted in urine. In a similar way, the alpha emitting actinides and radium are considered very harmful as they tend to have long biological half-lives and their radiation has a high linear energy transfer value. Because of such differences, the rules determining biological injury differ widely

according to the radioisotope, and sometimes also the nature of the chemical compound which contains the radioisotope.

Sources of waste

Radioactive waste comes from a number of sources. The majority of waste originates from the nuclear fuel cycle and nuclear weapons reprocessing. However, other sources include medical and industrial wastes, as well as naturally occurring radioactive materials (NORM) that can be concentrated as a result of the processing or consumption of coal, oil and gas, and some minerals, as discussed below.

Nuclear fuel cycle

Front end

Waste from the front end of the nuclear fuel cycle is usually alpha-emitting waste from the extraction of uranium. It often contains radium and its decay products.

Uranium dioxide (UO_2) concentrate from mining is not very radioactive - only a thousand or so times as radioactive as the granite used in buildings. It is refined from yellowcake (U_3O_8), then converted to uranium hexafluoride gas (UF_6). As a gas, it undergoes enrichment to increase the U-235 content from 0.7% to about 4.4% (LEU). It is then turned into a hard ceramic oxide (UO_2) for assembly as reactor fuel elements.

The main by-product of enrichment is depleted uranium (DU), principally the U-238 isotope, with a U-235 content of ~0.3%. It is stored, either as UF_6 or as U_3O_8. Some is used in applications where its extremely high density makes it valuable, such as the keels of yachts, and anti-tank shells. It is also used with plutonium for making mixed oxide fuel (MOX) and to dilute, or downblend, highly enriched uranium from weapons stockpiles which is now being redirected to become reactor fuel.

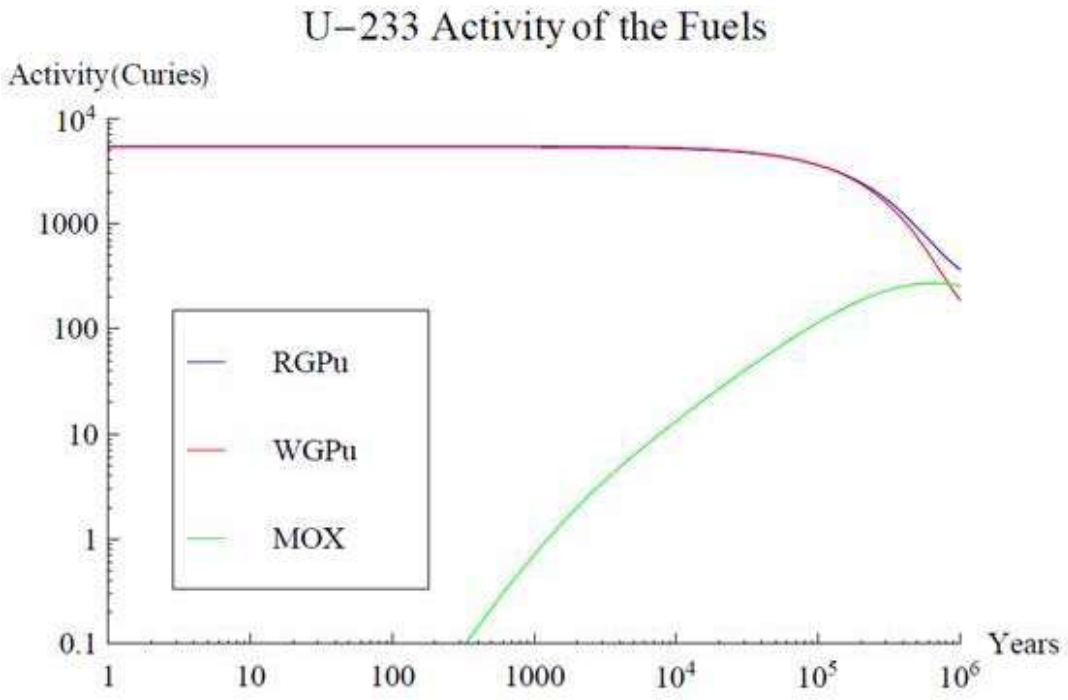
Back end

The back end of the nuclear fuel cycle, mostly spent fuel rods, contains fission products that emit beta and gamma radiation, and actinides that emit alpha particles, such as uranium-234, neptunium-237, plutonium-238 and americium-241, and even sometimes some neutron emitters such as californium (Cf). These isotopes are formed in nuclear reactors.

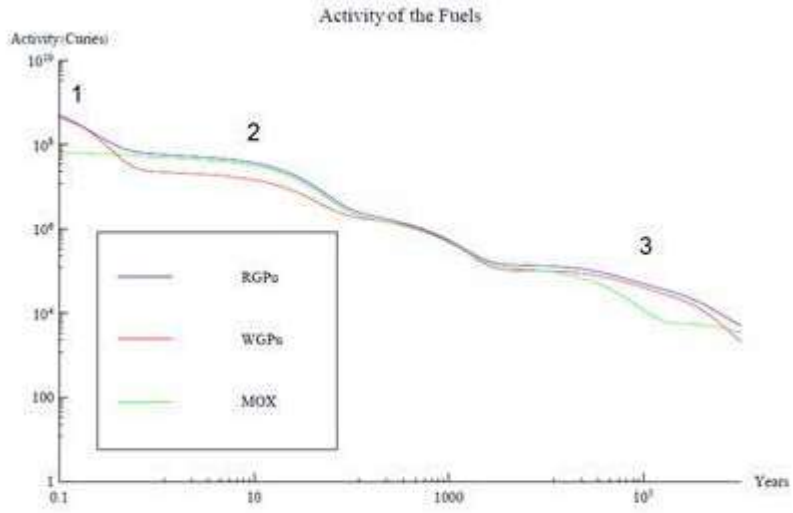
It is important to distinguish the processing of uranium to make fuel from the reprocessing of used fuel. Used fuel contains the highly radioactive products of fission. Many of these are neutron absorbers, called neutron poisons in this context. These eventually build up to a level where they absorb so many neutrons that the chain reaction stops, even with the control rods completely removed. At that point the fuel has to be replaced in the reactor with fresh fuel, even though there is still a substantial quantity of

uranium-235 and plutonium present. In the United States, this used fuel is stored, while in countries such as Russia, the United Kingdom, France, Japan and India, the fuel is reprocessed to remove the fission products, and the fuel can then be re-used. This reprocessing involves handling highly radioactive materials, and the fission products removed from the fuel are a concentrated form of high-level waste as are the chemicals used in the process. While these countries reprocess the fuel carrying out single plutonium cycles, India is the only country known to be planning multiple plutonium recycling schemes.

Fuel composition and long term radioactivity



Activity of U-233 for three fuel types



Total activity for three fuel types

Long-lived radioactive waste from the back end of the fuel cycle is especially relevant when designing a complete waste management plan for spent nuclear fuel (SNF). When looking at long term radioactive decay, the actinides in the SNF have a significant influence due to their characteristically long half-lives. Depending on what a nuclear reactor is fueled with, the actinide composition in the SNF will be different.

An example of this effect is the use of nuclear fuels with thorium. Th-232 is a fertile material that can undergo a neutron capture reaction and two beta minus decays, resulting in the production of fissile U-233. The SNF of a cycle with thorium will contain U-233, an isotope with a half-life of maximum 20 years. Its radioactive decay will strongly influence the long-term activity curve of the SNF around 1 million years. A comparison of the activity associated to U-233 for three different SNF types can be seen in the figure on the top right.

The burnt fuels are thorium with reactor-grade plutonium (RGPu), thorium with weapons-grade plutonium (WGPu) and Mixed Oxide fuel (MOX). For RGPu and WGPu, the initial amount of U-233 and its decay around 1 million years can be seen. This has an effect in the total activity curve of the three fuel types. The absence of U-233 and its daughter products in the MOX fuel results in a lower activity in region 3 of the figure on the bottom right, whereas for RGPu and WGPu the curve is maintained higher due to the presence of U-233 that has not fully decayed.

The use of different fuels in nuclear reactors results in different SNF composition, with varying activity curves.

Proliferation concerns

Since uranium and plutonium are nuclear weapons materials, there have been proliferations concerns. Ordinarily (in spent nuclear fuel), plutonium is reactor-grade

plutonium. In addition to plutonium-239, which is highly suitable for building nuclear weapons, it contains large amounts of undesirable contaminants: plutonium-240, plutonium-241, and plutonium-238. These isotopes are difficult to separate, and more cost-effective ways of obtaining fissile material exist (e.g. uranium enrichment or dedicated plutonium production reactors).

High-level waste is full of highly radioactive fission products, most of which are relatively short-lived. This is a concern since if the waste is stored, perhaps in deep geological storage, over many years the fission products decay, decreasing the radioactivity of the waste and making the plutonium easier to access. The undesirable contaminant Pu-240 decays faster than the Pu-239, and thus the quality of the bomb material increases with time (although its quantity decreases during that time as well). Thus, some have argued, as time passes, these deep storage areas have the potential to become "plutonium mines", from which material for nuclear weapons can be acquired with relatively little difficulty. Critics of the latter idea point out that the half-life of Pu-240 is 6,560 years and Pu-239 is 24,110 years, and thus the relative enrichment of one isotope to the other with time occurs with a half-life of 9,000 years (that is, it takes 9000 years for the *fraction* of Pu-240 in a sample of mixed plutonium isotopes, to spontaneously decrease by half—a typical enrichment needed to turn reactor-grade into weapons-grade Pu). Thus "weapons grade plutonium mines" would be a problem for the very far future (>9,000 years from now), so that there remains a great deal of time for technology to advance to solve it.

Pu-239 decays to U-235 which is suitable for weapons and which has a very long half life (roughly 10^9 years). Thus plutonium may decay and leave uranium-235. However, modern reactors are only moderately enriched with U-235 relative to U-238, so the U-238 continues to serve as a denaturation agent for any U-235 produced by plutonium decay.

One solution to this problem is to recycle the plutonium and use it as a fuel e.g. in fast reactors. But in the minds of some, the very existence of the nuclear fuel reprocessing plant needed to separate the plutonium from the other elements represents a proliferation concern. In pyrometallurgical fast reactors, the separated plutonium and uranium are contaminated by actinides and cannot be used for nuclear weapons.

Nuclear weapons decommissioning

Waste from nuclear weapons decommissioning is unlikely to contain much beta or gamma activity other than tritium and americium. It is more likely to contain alpha-emitting actinides such as Pu-239 which is a fissile material used in bombs, plus some material with much higher specific activities, such as Pu-238 or Po.

In the past the neutron trigger for an atomic bomb tended to be beryllium and a high activity alpha emitter such as polonium; an alternative to polonium is Pu-238. For reasons of national security, details of the design of modern bombs are normally not released to the open literature.

Some designs might contain a radioisotope thermoelectric generator using Pu-238 to provide a long lasting source of electrical power for the electronics in the device.

It is likely that the fissile material of an old bomb which is due for refitting will contain decay products of the plutonium isotopes used in it, these are likely to include U-236 from Pu-240 impurities, plus some U-235 from decay of the Pu-239; due to the relatively long half-life of these Pu isotopes, these wastes from radioactive decay of bomb core material would be very small, and in any case, far less dangerous (even in terms of simple radioactivity) than the Pu-239 itself.

The beta decay of Pu-241 forms Am-241; the in-growth of americium is likely to be a greater problem than the decay of Pu-239 and Pu-240 as the americium is a gamma emitter (increasing external-exposure to workers) and is an alpha emitter which can cause the generation of heat. The plutonium could be separated from the americium by several different processes; these would include pyrochemical processes and aqueous/organic solvent extraction. A truncated PUREX type extraction process would be one possible method of making the separation.

Legacy waste

Due to historic activities typically related to radium industry, uranium mining, and military programs, there are numerous sites that contain or are contaminated with radioactivity. In the United States alone, the Department of Energy states there are "millions of gallons of radioactive waste" as well as "thousands of tons of spent nuclear fuel and material" and also "huge quantities of contaminated soil and water." Despite copious quantities of waste, the DOE has stated a goal of cleaning all presently contaminated sites successfully by 2025. The Fernald, Ohio site for example had "31 million pounds of uranium product", "2.5 billion pounds of waste", "2.75 million cubic yards of contaminated soil and debris", and a "223 acre portion of the underlying Great Miami Aquifer had uranium levels above drinking standards." The United States has at least 108 sites designated as areas that are contaminated and unusable, sometimes many thousands of acres. DOE wishes to clean or mitigate many or all by 2025, however the task can be difficult and it acknowledges that some may never be completely remediated. In just one of these 108 larger designations, Oak Ridge National Laboratory, there were for example at least "167 known contaminant release sites" in one of the three subdivisions of the 37,000-acre (150 km^2) site. Some of the U.S. sites were smaller in nature, however, cleanup issues were simpler to address, and DOE has successfully completed cleanup, or at least closure, of several sites.

It is a common misconception that nuclear waste has to be stored in a cave after its 20-year decommissioning process.

Medical

Radioactive medical waste tends to contain beta particle and gamma ray emitters. It can be divided into two main classes. In diagnostic nuclear medicine a number of short-lived

gamma emitters such as technetium-99m are used. Many of these can be disposed of by leaving it to decay for a short time before disposal as normal waste. Other isotopes used in medicine, with half-lives in parentheses, include:

- Y-90, used for treating lymphoma (2.7 days)
- I-131, used for thyroid function tests and for treating thyroid cancer (8.0 days)
- Sr-89, used for treating bone cancer, intravenous injection (52 days)
- Ir-192, used for brachytherapy (74 days)
- Co-60, used for brachytherapy and external radiotherapy (5.3 years)
- Cs-137, used for brachytherapy, external radiotherapy (30 years)

Industrial

Industrial source waste can contain alpha, beta, neutron or gamma emitters. Gamma emitters are used in radiography while neutron emitting sources are used in a range of applications, such as oil well logging.

Naturally occurring radioactive material (NORM)

Processing of substances containing "natural" radioactivity is often known as NORM. A lot of this waste is alpha particle-emitting matter from the decay chains of uranium and thorium. The main source of radiation in the human body is potassium-40 (^{40}K). Most rocks, due to their components, have a certain, but low, level of radioactivity.

Coal

Coal contains a small amount of radioactive uranium, barium, thorium and potassium, but, in the case of pure coal, this is significantly less than the average concentration of those elements in the Earth's crust. The surrounding strata, if shale or mudstone, often contain slightly more than average and this may also be reflected in the ash content of 'dirty' coals. The more active ash minerals become concentrated in the fly ash precisely because they do not burn well. The radioactivity of fly ash is about the same as black shale and is less than phosphate rocks, but is more of a concern because a small amount of the fly ash ends up in the atmosphere where it can be inhaled.

Oil and gas

Residues from the oil and gas industry often contain radium and its daughters. The sulfate scale from an oil well can be very radium rich, while the water, oil and gas from a well often contain radon. The radon decays to form solid radioisotopes which form coatings on the inside of pipework. In an oil processing plant the area of the plant where propane is processed is often one of the more contaminated areas of the plant as radon has a similar boiling point to propane.

Types of radioactive waste

Removal of very low-level waste

Although not significantly radioactive, *uranium mill tailings* are waste. They are byproduct material from the rough processing of uranium-bearing ore. They are sometimes referred to as 11(e)2 wastes, from the section of the U.S. Atomic Energy Act that defines them. Uranium mill tailings typically also contain chemically hazardous heavy metals such as lead and arsenic. Vast mounds of uranium mill tailings are left at many old mining sites, especially in Colorado, New Mexico, and Utah.

Low level waste (LLW) is generated from hospitals and industry, as well as the nuclear fuel cycle. It comprises paper, rags, tools, clothing, filters, etc., which contain small amounts of mostly short-lived radioactivity. Commonly, LLW is designated as such as a precautionary measure if it originated from any region of an 'Active Area', which frequently includes offices with only a remote possibility of being contaminated with radioactive materials. Such LLW typically exhibits no higher radioactivity than one would expect from the same material disposed of in a non-active area, such as a normal office block. Some high activity LLW requires shielding during handling and transport but most LLW is suitable for shallow land burial. To reduce its volume, it is often compacted or incinerated before disposal. Low level waste is divided into four classes, class A, B, C and GTCC, which means "Greater Than Class C".

Intermediate level waste (ILW) contains higher amounts of radioactivity and in some cases requires shielding. ILW includes resins, chemical sludge and metal reactor fuel cladding, as well as contaminated materials from reactor decommissioning. It may be solidified in concrete or bitumen for disposal. As a general rule, short-lived waste (mainly non-fuel materials from reactors) is buried in shallow repositories, while long-lived waste (from fuel and fuel-reprocessing) is deposited in deep underground facilities. U.S. regulations do not define this category of waste; the term is used in Europe and elsewhere.

Spent Fuel Flasks are transported by railway in the United Kingdom. Each flask is constructed of 14 in (360 mm) thick solid steel and weighs in excess of 50 tons

High level waste (HLW) is produced by nuclear reactors. It contains fission products and transuranic elements generated in the reactor core. It is highly radioactive and often thermally hot. HLW accounts for over 95% of the total radioactivity produced in the process of nuclear electricity generation. The amount of HLW worldwide is currently increasing by about 12,000 metric tons every year, which is the equivalent to about 100 double-decker buses or a two-story structure with a footprint the size of a basketball court. A 1000-MWe nuclear power plant produces about 27 tonnes of spent nuclear fuel (unreprocessed) every year.

Transuranic waste (TRUW) as defined by U.S. regulations is, without regard to form or origin, waste that is contaminated with alpha-emitting transuranic radionuclides with half-lives greater than 20 years, and concentrations greater than 100 nCi/g (3.7 MBq/kg), excluding High Level Waste. Elements that have an atomic number greater than uranium are called transuranic ("beyond uranium"). Because of their long half-lives, TRUW is disposed more cautiously than either low level or intermediate level waste. In the US it arises mainly from weapons production, and consists of clothing, tools, rags, residues, debris and other items contaminated with small amounts of radioactive elements (mainly plutonium).

Under US law, transuranic waste is further categorized into "contact-handled" (CH) and "remote-handled" (RH) on the basis of radiation dose measured at the surface of the waste container. CH TRUW has a surface dose rate not greater than 200 mrem per hour (2 mSv/h), whereas RH TRUW has a surface dose rate of 200 mrem per hour (2 mSv/h) or greater. CH TRUW does not have the very high radioactivity of high level waste, nor its high heat generation, but RH TRUW can be highly radioactive, with surface dose rates up to 1000000 mrem per hour (10000 mSv/h). The US currently permanently disposes of defense-related TRUW at the Waste Isolation Pilot Plant.

Management of waste

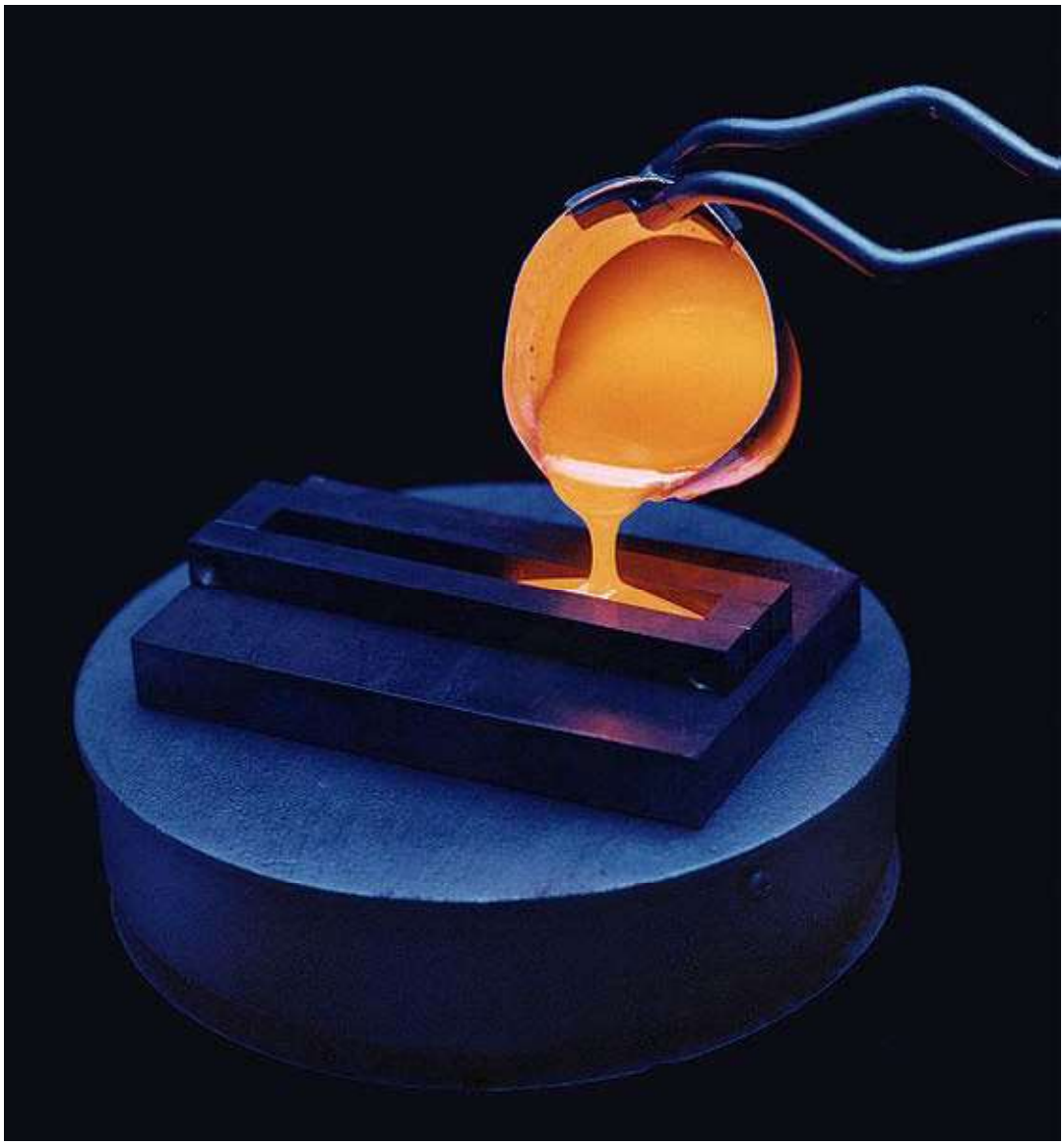
Modern medium to high level transport container for nuclear waste.

Of particular concern in nuclear waste management are two long-lived fission products, Tc-99 (half-life 220,000 years) and I-129 (half-life 17 million years), which dominate

spent fuel radioactivity after a few thousand years. The most troublesome transuranic elements in spent fuel are Np-237 (half-life two million years) and Pu-239 (half life 24,000 years). Nuclear waste requires sophisticated treatment and management to successfully isolate it from interacting with the biosphere. This usually necessitates treatment, followed by a long-term management strategy involving storage, disposal or transformation of the waste into a non-toxic form. Governments around the world are considering a range of waste management and disposal options, though there has been limited progress toward long-term waste management solutions.

Initial treatment of waste

Vitrification



A vitrification experiment for the study of nuclear waste disposal

Long-term storage of radioactive waste requires the stabilization of the waste into a form which will neither react nor degrade for extended periods of time. One way to do this is through vitrification. Currently at Sellafield the high-level waste (PUREX first cycle raffinate) is mixed with sugar and then calcined. Calcination involves passing the waste through a heated, rotating tube. The purposes of calcination are to evaporate the water from the waste, and de-nitrate the fission products to assist the stability of the glass produced.

The 'calcine' generated is fed continuously into an induction heated furnace with fragmented glass. The resulting glass is a new substance in which the waste products are bonded into the glass matrix when it solidifies. This product, as a melt, is poured into stainless steel cylindrical containers ("cylinders") in a batch process. When cooled, the fluid solidifies ("vitrifies") into the glass. Such glass, after being formed, is highly resistant to water.

After filling a cylinder, a seal is welded onto the cylinder. The cylinder is then washed. After being inspected for external contamination, the steel cylinder is stored, usually in an underground repository. In this form, the waste products are expected to be immobilized for a long period of time (many thousands of years).

The glass inside a cylinder is usually a black glossy substance. All this work (in the United Kingdom) is done using hot cell systems. The sugar is added to control the ruthenium chemistry and to stop the formation of the volatile RuO_4 containing radio ruthenium. In the west, the glass is normally a borosilicate glass (similar to Pyrex), while in the former Soviet bloc it is normal to use a phosphate glass. The amount of fission products in the glass must be limited because some (palladium, the other Pt group metals, and tellurium) tend to form metallic phases which separate from the glass. Bulk vitrification uses electrodes to melt soil and wastes, which are then buried underground. In Germany a vitrification plant is in use; this is treating the waste from a small demonstration reprocessing plant which has since been closed down.

Ion exchange

It is common for medium active wastes in the nuclear industry to be treated with ion exchange or other means to concentrate the radioactivity into a small volume. The much less radioactive bulk (after treatment) is often then discharged. For instance, it is possible to use a ferric hydroxide floc to remove radioactive metals from aqueous mixtures. After the radioisotopes are absorbed onto the ferric hydroxide, the resulting sludge can be placed in a metal drum before being mixed with cement to form a solid waste form. In order to get better long-term performance (mechanical stability) from such forms, they may be made from a mixture of fly ash, or blast furnace slag, and Portland cement, instead of normal concrete (made with Portland cement, gravel and sand).

Synroc

The Australian Synroc (synthetic rock) is a more sophisticated way to immobilize such waste, and this process may eventually come into commercial use for civil wastes (it is currently being developed for US military wastes). Synroc was invented by the late Prof Ted Ringwood (a geochemist) at the Australian National University. The Synroc contains pyrochlore and cryptomelane type minerals. The original form of Synroc (Synroc C) was designed for the liquid high level waste (PUREX raffinate) from a light water reactor. The main minerals in this Synroc are hollandite ($BaAl_2Ti_6O_{16}$), zirconolite ($CaZrTi_2O_7$) and perovskite ($CaTiO_3$). The zirconolite and perovskite are hosts for the actinides. The strontium and barium will be fixed in the perovskite. The caesium will be fixed in the hollandite.

Long term management of waste

The time frame in question when dealing with radioactive waste ranges from 10,000 to 1,000,000 years, according to studies based on the effect of estimated radiation doses. Researchers suggest that forecasts of health detriment for such periods should be examined critically. Practical studies only consider up to 100 years as far as effective planning and cost evaluations are concerned. Long term behavior of radioactive wastes remains a subject for ongoing research projects.

Geologic disposal

The process of selecting appropriate deep final repositories for high level waste and spent fuel is now under way in several countries (Schacht Asse II and the Waste Isolation Pilot Plant) with the first expected to be commissioned some time after 2010. The basic concept is to locate a large, stable geologic formation and use mining technology to excavate a tunnel, or large-bore tunnel boring machines (similar to those used to drill the Channel Tunnel from England to France) to drill a shaft 500–1,000 meters below the surface where rooms or vaults can be excavated for disposal of high-level radioactive waste. The goal is to permanently isolate nuclear waste from the human environment. Many people remain uncomfortable with the immediate stewardship cessation of this disposal system, suggesting perpetual management and monitoring would be more prudent.

Because some radioactive species have half-lives longer than one million years, even very low container leakage and radionuclide migration rates must be taken into account. Moreover, it may require more than one half-life until some nuclear materials lose enough radioactivity to cease being lethal to living things. A 1983 review of the Swedish radioactive waste disposal program by the National Academy of Sciences found that country's estimate of several hundred thousand years—perhaps up to one million years—being necessary for waste isolation "fully justified."

Storing high level nuclear waste above ground for a century or so is considered appropriate by many scientists. This allows the material to be more easily observed and

any problems detected and managed, while decay of radionuclides over this time period significantly reduces the level of radioactivity and associated harmful effects to the container material. It is also considered likely that over the next century newer materials will be developed which will not break down as quickly when exposed to a high neutron flux, thus increasing the longevity of the container once it is permanently buried.

Sea-based options for disposal of radioactive waste include burial beneath a stable abyssal plain, burial in a subduction zone that would slowly carry the waste downward into the Earth's mantle, and burial beneath a remote natural or human-made island. While these approaches all have merit and would facilitate an international solution to the problem of disposal of radioactive waste, they would require an amendment of the Law of the Sea.

Article 1 (Definitions), 7., of the 1996 Protocol to the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, (the London Dumping Convention) states:

> "Sea" means all marine waters other than the internal waters of States, as well as the seabed and the subsoil thereof; it does not include sub-seabed repositories accessed only from land."

The proposed land-based subductive waste disposal method disposes of nuclear waste in a subduction zone accessed from land, and therefore is not prohibited by international agreement. This method has been described as the most viable means of disposing of radioactive waste, and as the state-of-the-art in nuclear waste disposal technology. Another approach termed Remix & Return would blend high-level waste with uranium mine and mill tailings down to the level of the original radioactivity of the uranium ore, then replace it in inactive uranium mines. This approach has the merits of providing jobs for miners who would double as disposal staff, and of facilitating a cradle-to-grave cycle for radioactive materials, but would be inappropriate for spent reactor fuel in the absence of reprocessing, due to the presence in it of highly toxic radioactive elements such as plutonium.

Deep borehole disposal is the concept of disposing of high-level radioactive waste from nuclear reactors in extremely deep boreholes. Deep borehole disposal seeks to place the waste as much as five kilometers beneath the surface of the Earth and relies primarily on the immense natural geological barrier to confine the waste safely and permanently so that it should never pose a threat to the environment.

Transmutation

There have been proposals for reactors that consume nuclear waste and transmute it to other, less-harmful nuclear waste. In particular, the Integral Fast Reactor was a proposed nuclear reactor with a nuclear fuel cycle that produced no transuranic waste and in fact, could consume transuranic waste. It proceeded as far as large-scale tests, but was then canceled by the US Government. Another approach, considered safer but requiring more

development, is to dedicate subcritical reactors to the transmutation of the left-over transuranic elements.

An isotope that is found in nuclear waste and that represents a concern in terms of proliferation is Pu-239. The estimated world total of plutonium in the year 2000 was of 1,645 MT, of which 210 MT had been separated by reprocessing. The large stock of plutonium is a result of its production inside uranium-fueled reactors and of the reprocessing of weapons-grade plutonium during the weapons program. An option for getting rid of this plutonium is to use it as a fuel in a traditional Light Water Reactor (LWR). Several fuel types with differing plutonium destruction efficiencies are under study.

Transmutation was banned in the US in April 1977 by President Carter due to the danger of plutonium proliferation, but President Reagan rescinded the ban in 1981. Due to the economic losses and risks, construction of reprocessing plants during this time did not resume. Due to high energy demand, work on the method has continued in the EU. This has resulted in a practical nuclear research reactor called Myrrha in which transmutation is possible. Additionally, a new research program called ACTINET has been started in the EU to make transmutation possible on a large, industrial scale. According to President Bush's Global Nuclear Energy Partnership (GNEP) of 2007, the US is now actively promoting research on transmutation technologies needed to markedly reduce the problem of nuclear waste treatment.

There have also been theoretical studies involving the use of fusion reactors as so called "actinide burners" where a fusion reactor plasma such as in a tokamak, could be "doped" with a small amount of the "minor" transuranic atoms which would be transmuted (meaning fissioned in the actinide case) to lighter elements upon their successive bombardment by the very high energy neutrons produced by the fusion of deuterium and tritium in the reactor. A study at MIT found that only 2 or 3 fusion reactors with parameters similar to that of the International Thermonuclear Experimental Reactor (ITER) could transmute the entire annual minor actinide production from all of the light water reactors presently operating in the United States fleet while simultaneously generating approximately 1 gigawatt of power from each reactor.

Re-use of waste

Another option is to find applications for the isotopes in nuclear waste so as to re-use them. Already, caesium-137, strontium-90 and a few other isotopes are extracted for certain industrial applications such as food irradiation and radioisotope thermoelectric generators. While re-use does not eliminate the need to manage radioisotopes, it reduces the quantity of waste produced.

The Nuclear Assisted Hydrocarbon Production Method, Canadian patent application 2,659,302, is a method for the temporary or permanent storage of nuclear waste materials comprising the placing of waste materials into one or more repositories or boreholes constructed into an unconventional oil formation. The thermal flux of the waste materials

fracture the formation, alters the chemical and/or physical properties of hydrocarbon material within the subterranean formation to allow removal of the altered material. A mixture of hydrocarbons, hydrogen, and/or other formation fluids are produced from the formation. The radioactivity of high-level radioactive waste affords proliferation resistance to plutonium placed in the periphery of the repository or the deepest portion of a borehole.

A 1990 proposed type of breeder reactor called a traveling wave reactor is claimed, if it were to be built, to be able to be fueled by depleted uranium, which is currently considered nuclear waste.

Space disposal

Space disposal is an attractive notion because it permanently removes nuclear waste from the environment. It has significant disadvantages, not least of which is the potential for catastrophic failure of a launch vehicle which would spread radioactive material into the atmosphere and around the world. The high number of launches that would be required — because no individual rocket would be able to carry very much of the material relative to the material needed to be disposed of—makes the proposal impractical (for both economic and risk-based reasons). To further complicate matters, international agreements on the regulation of such a program would need to be established.

In the future, alternative, non-rocket spacelaunch technologies may provide a solution. It has been suggested that through the use of a stationary launch system many of the risks of catastrophic launch failure could be avoided. A promising concept is the use of high power lasers to launch "indestructible" containers from the ground into space. Such a system would require no rocket propellant, with the launch vehicle's payload making up a near entirety of the vehicle's mass. Without the use of rocket fuel on board there would be little chance of the vehicle exploding.

National management plans

Most countries are considerably ahead of the United States in developing plans for high-level radioactive waste disposal. Sweden and Finland are furthest along in committing to a particular disposal technology, while many others reprocess spent fuel or contract with France or Great Britain to do it, taking back the resulting plutonium and high-level waste. “An increasing backlog of plutonium from reprocessing is developing in many countries... It is doubtful that reprocessing makes economic sense in the present environment of cheap uranium.”

In many European countries (e.g., Britain, Finland, the Netherlands, Sweden and Switzerland) the risk or dose limit for a member of the public exposed to radiation from a future high-level nuclear waste facility is considerably more stringent than that suggested by the International Commission on Radiation Protection or proposed in the United States. European limits are often more stringent than the standard suggested in 1990 by the International Commission on Radiation Protection by a factor of 20, and more

stringent by a factor of ten than the standard proposed by the US Environmental Protection Agency (EPA) for Yucca Mountain nuclear waste repository for the first 10,000 years after closure. Moreover, the U.S. EPA's proposed standard for greater than 10,000 years is 250 times more permissive than the European limit.

Illegal dumping

Authorities in Italy are investigating a 'Ndrangheta mafia clan accused of trafficking and illegally dumping nuclear waste. According to a turncoat, a manager of the Italy's state energy research agency Enea paid the clan to get rid of 600 drums of toxic and radioactive waste from Italy, Switzerland, France, Germany, and the US, with Somalia as the destination, where the waste was buried after buying off local politicians. Former employees of Enea are suspected of paying the criminals to take waste off their hands in the 1980s and 1990s. Shipments to Somalia continued into the 1990s, while the 'Ndrangheta clan also blew up shiploads of waste, including radioactive hospital waste, and sending them to the sea bed off the Calabrian coast. According to the environmental group Legambiente, former members of the 'Ndrangheta have said that they were paid to sink ships with radioactive material for the last 20 years.

Accidents involving radioactive waste

A number of incidents have occurred when radioactive material was disposed of improperly, shielding during transport was defective, or when it was simply abandoned or even stolen from a waste store. In the Soviet Union, waste stored in Lake Karachay was blown over the area during a dust storm after the lake had partly dried out. At Maxey Flat, a low-level radioactive waste facility located in Kentucky, containment trenches covered with dirt, instead of steel or cement, collapsed under heavy rainfall into the trenches and filled with water. The water that invaded the trenches became radioactive and had to be disposed of at the Maxey Flat facility itself. In other cases of radioactive waste accidents, lakes or ponds with radioactive waste accidentally overflowed into the rivers during exceptional storms. In Italy, several radioactive waste deposits let material flow into river water, thus contaminating water for domestic use. In France, in the summer of 2008 numerous incidents happened; in one, at the Areva plant in Tricastin, it was reported that during a draining operation, liquid containing untreated uranium overflowed out of a faulty tank and about 75 kg of the radioactive material seeped into the ground and, from there, into two rivers nearby; in another case, over 100 staff were contaminated with low doses of radiation.

Scavenging of abandoned radioactive material has been the cause of several other cases of radiation exposure, mostly in developing nations, which may have less regulation of dangerous substances (and sometimes less general education about radioactivity and its hazards) and a market for scavenged goods and scrap metal. The scavengers and those who buy the material are almost always unaware that the material is radioactive and it is selected for its aesthetics or scrap value. Irresponsibility on the part of the radioactive material's owners, usually a hospital, university or military, and the absence of regulation concerning radioactive waste, or a lack of enforcement of such regulations, have been

significant factors in radiation exposures. For an example of an accident involving radioactive scrap originating from a hospital see the Goiânia accident.

Transportation accidents involving spent nuclear fuel from power plants are unlikely to have serious consequences due to the strength of the spent nuclear fuel shipping casks.

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Chapter 6

Warm Glass

Higgins Glass, fused and slumped ashtray and bowl

Fused glass piece with dichroic glass highlights

Warm glass or **kiln-formed glass** is the working of glass, usually for artistic purposes, by heating it in a kiln. The processes used depend on the temperature reached and range from fusing and slumping to casting.

'Warm' glass is in contrast to the many cold-working glass processes, such as leaded glass. 'Hot' glass, glass blowing or lampworking is the working of glass in a direct flame, such as for laboratory glassware and beadmaking.

Processes

Warm glass working uses a variety of processes, according to the working temperature and the time the glass spends at this temperature. The glass becomes progressively softer, less rigid and less viscous with temperature. Kiln-worked glass (unlike lamp working) responds slowly though, and so the amount by which this affects the glass depends on the time it spends at working temperature.

There are three main processes, with variations within them. The broad process depends on the temperature, the variation within it depends on the time and also on slight variations of temperature. These processes are:

- Fusing

  The glass retains its shape, but becomes sticky and adjacent glass pieces join together.

- Slumping

  The glass deforms in shape, becoming flexible but still retaining its approximate solid form.

- Casting

  The glass melts, becoming a viscous liquid that takes its shape from that of its containing mould.

It is common for one piece to use several of these processes in turn. Coloured glass may be fused together to make a composite multi-coloured sheet. This glass is then cut cold and re-assembled in pieces, which are then fused back together. The piece is finally slumped into a mould to shape it.

Glass is usually worked for only one process in a heating cycle. Where a piece requires multiple cycles, it is returned to a lower temperature between them.

Fusing

Fused glass platter

Fusing is the use of heat to join the glass by fusion welding, either with or without an associated change in shape, depending on the temperature.

Tack fusing

Tack fusing is the joining together of glass, with as little change to the shape of the pieces as possible. Tack fusing may be used either decoratively, or to assemble a large piece of glass from laminations.

Where tack fusing is used to apply small decorative details to a larger piece, it is often desired to partially melt the small pieces so that they change shape (usually becoming more spherical, under the influence of surface tension), but without changing the shape of the carrier piece. This can be done by using an increased temperature, but only briefly. The large piece, of large thermal mass, heats up more slowly than the small decorations.

Full fusing

Full fusing is like tack fusing, but the temperature is higher so that the fused pieces begin to coalesce. In the complete case, decorative additions to a surface are absorbed entirely into it and the surface becomes flat again. It is usually done for decorative effect.

Slumping

Platter, slumped into a shallow mould

Slumped glass is heated to the temperature at which the glass softens and begins to deform. It may either bend along a single curvature or, if heated sufficiently, may become elastic enough to stretch and curve to follow a compound curvature, such as a bowl.

Mould slumping

Mould slumping begins with a sheet of flat glass placed above a ceramic mould. When heated, the glass slumps into the mould under its own weight.

These moulds are usually commercially made and are offered in a range of standard shapes and sizes: bowls, trays etc. For custom pieces, a glass worker may also make a specialised or temporaty mould as a one-off.

To avoid trapped air, the mould is perforated with a small vent hole. The hot glass otherwise forms a good seal with the lip of the mould and an air bubble is trapped. Such a trapped bubble often causes problems - when cooling this air may contract to form a partial vacuum that is enough to break the glass. As the glass is not heated enough to become liquid, this air cannot escape as bubbles and so venting is required.

Kiln wash is used beforehand to prevent the glass sticking to the mould.

Free fall slumping

A mould for free-fall slumping is in the form of a ring with a central opening. When heated, the glass falls through this opening and forms a bowl. Depending on the temperature and time, this bowl may be shallow or deep. If a kiln shelf is placed beneath the ring mould, this catches the falling glass and gives a vessel with a flat base.

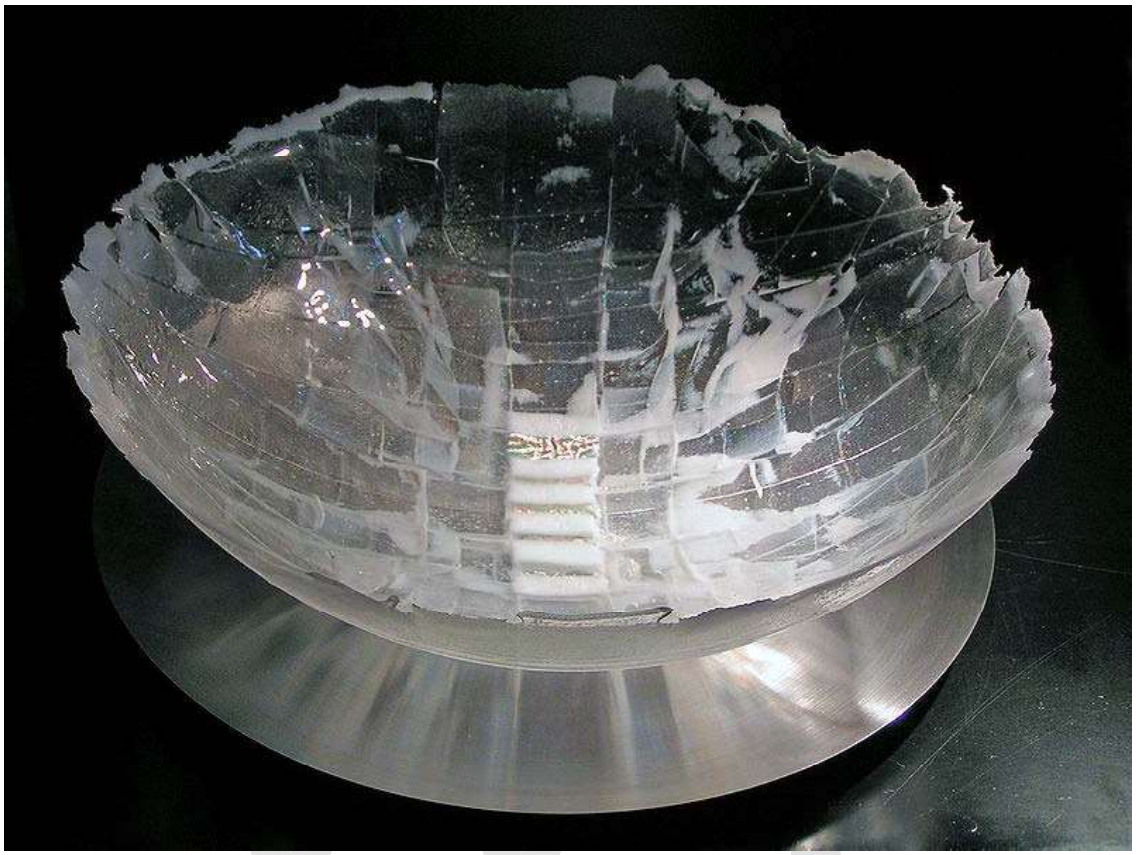
Free fall slumping is used to make taller vessels with steeper sides, such as vases.

Draping

Draping is a variety of free-fall slumping, where the mould former is placed in the centre of the piece and the outer edge falls under the heat. As this outer edge is unconstrained, it tends to fall in large folds. The edge is thus highly uneven, although a carefully draped piece may still retain perfect symmetry. For this reason draped pieces are often used as vases or wavey-edged bowls, but are difficult to use as a more functional vessel.

Draped pieces are sometimes sawn down and smoothed when cold, so as to reduce the unevenness of their edge.

Casting



Cast bowl

Casting is the process where the glass begins to melt and behave as a liquid. Its shape is now constrained entirely by the mould and the previous shape is lost. Glass is vicous though and unlike metal casting, the soft glass does not flow through the mould. Variations in the glass are thus preserved in the final piece, so colours and inclusions present beforehand may still remain in the cast item.

Glass may be cast from either billets (solid ingots), sheet, loosely stacked pieces of glass (these are usually used with a low-temperature casting, so that their boundaries remain deliberately visible afterwards) or frit, ground or powdered glass.

Moulds for casting may be either re-usable ceramic moulds, or else a one-use investment mould of plaster. This mould may in turn have been formed by the lost wax process.

Pâte de Verre

Three pâte de verre vessels.

Pâte de verre (literally *glass paste*) is cast from powdered frit, mixed with a glue binder. This allows the paste to be applied to the sides of a large mould in a thin layer. When fired, a thin-walled vessel is formed. The transparency of the finished casting depends on the size of the frit used: fine powder produces an opaque cast, medium or coarse frit may be used to cast a transparent piece.

Other processes

Fire polishing

Heating the edges to smooth and round them.

Combing

This is one of the few processes that involves manual work on the hot glass while still in the kiln. In a similar manner to slip trailing in ceramics, a pattern is formed on the surface, then trailed into feathers with a pointed metal rake.

Firing

Warm glass working is similar to that for ceramics, in that a piece is assembled, placed into a cold kiln and then heated through a pre-defined cycle, including a slow cooling phase afterwards. Unlike hot glass, warm glass is rarely worked manually whilst hot.

Kilns

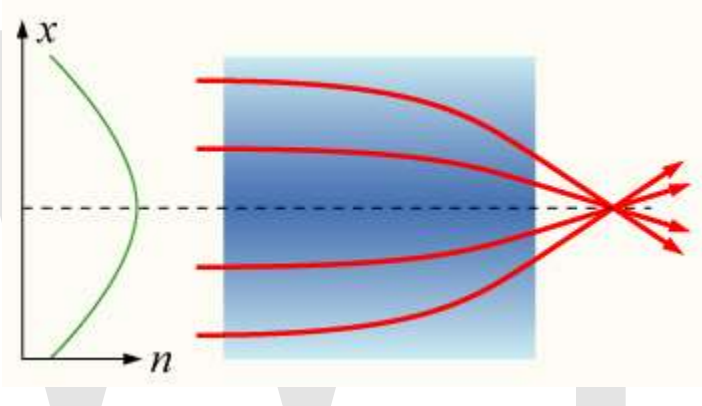
Contemporary warm glass work is almost universally done in an electrically-heated kiln, although some gas or oil-fired kilns are still used. The reason for this is the extra control accuracy and programmability available with electric heating, as well as their lower capital cost and convenient installation.

All kilns for glass work require a pyrometer, usually based on a thermocouple, as knowledge of the kiln temperature is essential for controlling the process.

Electric kilns have controllers with a variety of sophistication: the simplest is the "Infinity Control", a simple open-loop power regulator. As this only controls power, rather than temperature, such a kiln must be manually controlled throughout the cycle. As firing cycles extend over several hours, potentially days for large architectural pieces, automatic unattended control is obviously important. Automatic temperature control uses a PID controller that maintains a constant set temperature. More sophisticated controllers allow the ramp heating and cooling rates to be controlled too, an important factor in glass heating. Controllers dedicated for glass kiln use have their entire heating cycles defined before use with multiple set temperatures, hold times and ramps between them. The most sophisiticated controllers of all are dedicated to glass use and allow pre-defined cycles such as "Fuse" or "Slump" to be selected from a simple menu, without their operator needing to be aware of the precise temperatures required.

Chapter 7

Gradient-Index Optics



A gradient-index lens with a parabolic variation of refractive index (n) with radial distance (x). The lens focuses light in the same way as a conventional lens.

Gradient-index optics is the branch of materials science dealing with the production and characterization of gradually changing refractive index lenses. These lenses are able to eliminate the aberrations caused by traditional spherical lenses without requiring variation to the shape of the lens. Gradient index lenses may have a refraction gradient that is spherical, axial, or radial.

Gradient-Index Lenses in Nature

A variety of inhomogeneous lenses exists in nature that allow for different functions. The most obvious lens in nature is the lens present in the eye. Nature progressively varies the refractive index of the lens in order to optimise the optics required for survival. Eagles have the ability to maintain focus and high resolution at large distances. The eyes of an antelope have a broad field of view, which allows them to detect predators. In humans, the lens is able to highly resolve and reduce aberration for both short and long distances (Shirk et al, 2006). The quality of the lens does, however, deteriorate with age with

noticeable effects usually occurring after the age of 40 in humans. Another phenomenon related to the varying refractive indexes of materials in nature is the Mirage. Since refractive index generally increases with density of the material, it is seen that cool air has a higher refractive index than hot air. Therefore, in a desert, light passes from the cool air to the warm air causing the path of the light ray reaching an observer to bend, thus giving them a misconception of the object's spatial displacement, i.e. The object may appear closer to the observer than it actually is.

History

In 1854, J C Maxwell suggested a lens whose refractive index distribution would allow for every region of space to be sharply imaged. Known as the Maxwell Fisheye Lens, it involves a spherical index function and would be expected to be spherical in shape as well (Maxwell, 1854). This lens, however, is impractical to make and has little usefulness since, only points on the surface and within the lens are sharply imaged and extended objects suffer from extreme aberrations. In 1905, R W Wood used a dipping technique creating a gelatin cylinder with a refractive index gradient that varied symmetrically with the radial distance from the axis. Disk shaped slices of the cylinder were later shown to have plane faces with radial index distribution. He showed that even though the faces of the lens were flat, they acted like converging and diverging lens depending on whether the index was a decreasing or increasing relative to the radial distance (Wood, 1905). In 1964, was published a posthumous book of R. K. Luneburg where he discovered a lens that converge all rays of light onto a point which is located on the opposite surface of the lens (Luneburg, 1964). This also limits the applications of the lens, in that it is difficult to be used to focus visual light, however, it was thought to have had some usefulness in microwave applications.

Theory

Yet to upload images and equations.

When considering aberrations, it is necessary to interpret the projections of light in terms of Gaussian Principles. If a ray is emitted from point P, and passes near point P', and Δx and Δy are the deviations from P', then Δx and Δy are measures of the aberration for the rays perceived (Figure 1) (Marchand, 1976). Inhomogeneous GRIN lenses attempt to reduce the aberrations Δx and Δy to zero.

Figure 1: Cartesian Interpretation of Aberrations. Rays of light leaving point P are refracted at the lens plane, and pass through point A. Point P' is the point at which the light rays would ideally converge if an aberration free lens was used. Point A and point P' differ by the values Δx and Δy.

Figure 2: How a Two Dimensional Gradient Index Lens Works. Gradient index lens converge all light rays onto a common point, by refracting light through a changing refractive index (many different refractive indices).

An inhomogeneous gradient-index lens possesses a refractive index whose change follows the function: n=f(x,y,z) of the coordinates of the region of interest in the medium. According to Fermat's principle, the light path integral (L), taken along a ray of light joining any two points of a medium, is stationary relative to its value for any nearby curve joining the two points. The light path integral is given by the equation:

$$\int_{S_o}^{S} n\, dS$$

Where n is the refractive index and S is the arc length of the curve. If Cartesian coordinates are used, this equation is modified to incorporate the change in arc length for a spherical gradient, to each physical dimension:

$$\int_{S_o}^{S} n(x,y,z)\sqrt{x'^2 + y'^2 + z'^2}\, dS$$

where prime corresponds to d/ds (Marchand, 1978). The light path integral is able to characterize the path of light through the lens in a qualitative manner, such that the lens may be easily reproduced in the future.

The refractive index gradient of GRIN lenses can be mathematically modelled according to its method of production. For example, GRIN lenses made from a radial gradient index material, such as SELFOC® (Flores-Arias et al, 2006), express a refractive index that varies according to:

$$n_r = n_o\left(1 - \frac{A_r^2}{2}\right)$$

Where, n_r the refractive index at a distance, r, from the optical axis; is the design index on the optical axis and A is a positive constant.

Design and Manufacture of GRIN Lenses

The GRIN lens is designed in two separate phases. In the first phase, the lens is evaluated by analytical techniques. The second phase involves the design of the lens. When considering the manufacturing of GRIN lenses, there are two important features of any technique: the depth of the gradient; and the magnitude of the change in index-of-refraction, Δn, throughout the lens (Moore, 1980). Production techniques involve: • Neutron Irradiation (Sinai, 1971) – Boron-rich glass is bombarded with neutrons in order to cause a change in the boron concentration, and thus the refractive index of the lens. • Chemical Vapour Deposition (Keck et al, 1975) – Involving the deposition of different glass with varying refractive indexes, onto a surface to produce a cumulative refractive change. • Partial Polymerisation (Moore, 1973) – Organic monomer is partially polymerised using UV light at varying intensities in order to give a refractive gradient. •

Ion Exchange (Hensler, 1975) – Ions, such as lithium replace sodium ions already present in a glass substrate. When this technique is modulated spatially, a gradient index lens is formed. • Ion Stuffing (Mohr, 1979) – Phase separation of a specific glass causes pores to form, which can later be filled using a variety of salts or concentration of salts to give a varying gradient.

Applications

The main uses of GRIN lenses involve applications in telecommunications and optical imaging. In telecommunications, a long fibre many kilometres in length but only a 20-100μm diameter have refractive gradients engineered to vary radially from the centre, with refractive index decreasing as distance from the centre increases. This allows for a sinusoidal height distribution of the ray within the fibre, preventing the ray from touching the walls. This differs from the traditional optical fibres which rely on total internal reflection, in that all modes of the GRIN fibres propagate at the same velocity, thus allowing for a higher temporal bandwidth for the fibre (Moore, 1980). Imaging using GRIN lenses is used to mainly reduce the aberrations and increase focus. This involves detailed calculations of aberrations as well as the efficient manufacture of the lenses. Recently, a number of different methods of gradient production have been implemented, such as, optical glasses; plastics; germanium; zinc selenide; and sodium chloride.

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Chapter 8

Glass Transition

The **liquid-glass transition** (or **glass transition** for short) is the reversible transition in amorphous materials (or in amorphous regions within semicrystalline materials) from a hard and relatively brittle state into a molten or rubber-like state. An amorphous solid that exhibits a glass transition is called a glass. Supercooling a viscous liquid into the glass state is called vitrification.

Despite the massive change in the physical properties of a material through its glass transition, the transition is not itself a phase transition of any kind; rather it is a laboratory phenomenon extending over a range of temperature and defined by one of several conventions. Such conventions include a constant cooling rate (20 K/min) and a viscosity threshold of 10^{12} Pa·s, among others. Upon cooling or heating through this glass transition range, the material also exhibits a smooth step in the thermal expansion coefficient and in the specific heat, with the location of these effects again being dependent on the history of the material. However, the question of whether some phase transition *underlies* the glass transition is a matter of continuing research.

T_g is always lower than the melting temperature, T_m, of the crystalline state of the material, if one exists.

Introduction

The glass transition of a liquid to a solid like state may occur with either cooling or compression. The transition comprises a smooth increase in the viscosity of a material by as much as 17 orders of magnitude without any pronounced change in material structure. The consequence of this dramatic increase is a glass exhibiting solid-like mechanical properties on the timescale of practical observation. This transition is in contrast to the freezing or crystallization transition, which is a first-order phase transition in the Ehrenfest classification and involves discontinuities in thermodynamic and dynamic properties such as volume, energy, and viscosity. In many materials that normally

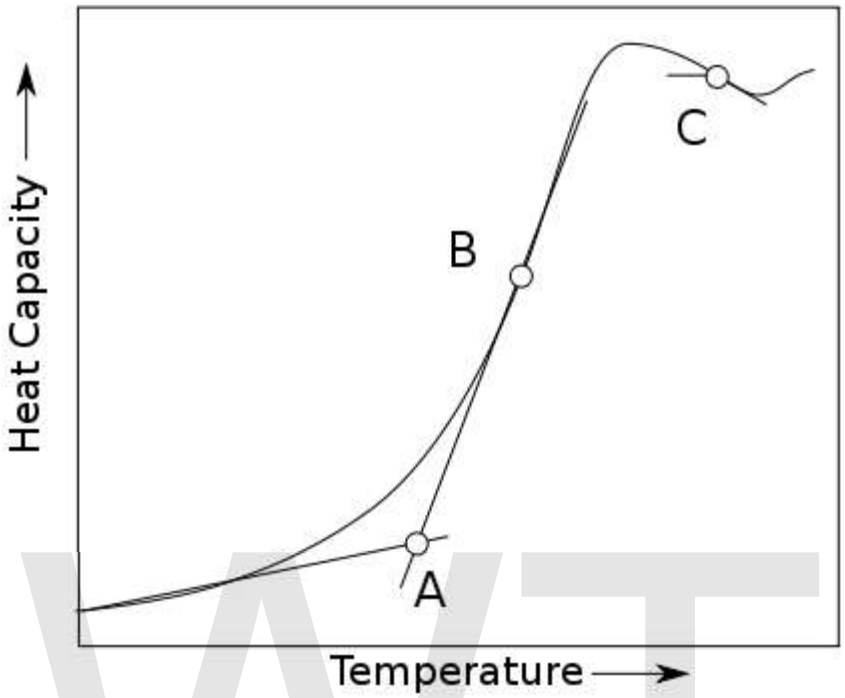
undergo a freezing transition, rapid cooling will avoid this phase transition and instead result in a glass transition at some lower temperature. Other materials, such as many polymers, lack a well defined crystalline state and easily form glasses, even upon very slow cooling or compression.

Below the transition temperature range, the glassy structure does not relax in accordance with the cooling rate used. The expansion coefficient for the glassy state is roughly equivalent to that of the crystalline solid. If slower cooling rates are used, the increased time for structural relaxation (or intermolecular rearrangement) to occur may result in a higher density glass product. Similarly, by annealing (and thus allowing for slow structural relaxation) the glass structure in time approaches an equilibrium density corresponding to the supercooled liquid at this same temperature. T_g is located at the intersection between the cooling curve (volume versus temperature) for the glassy state and the supercooled liquid.

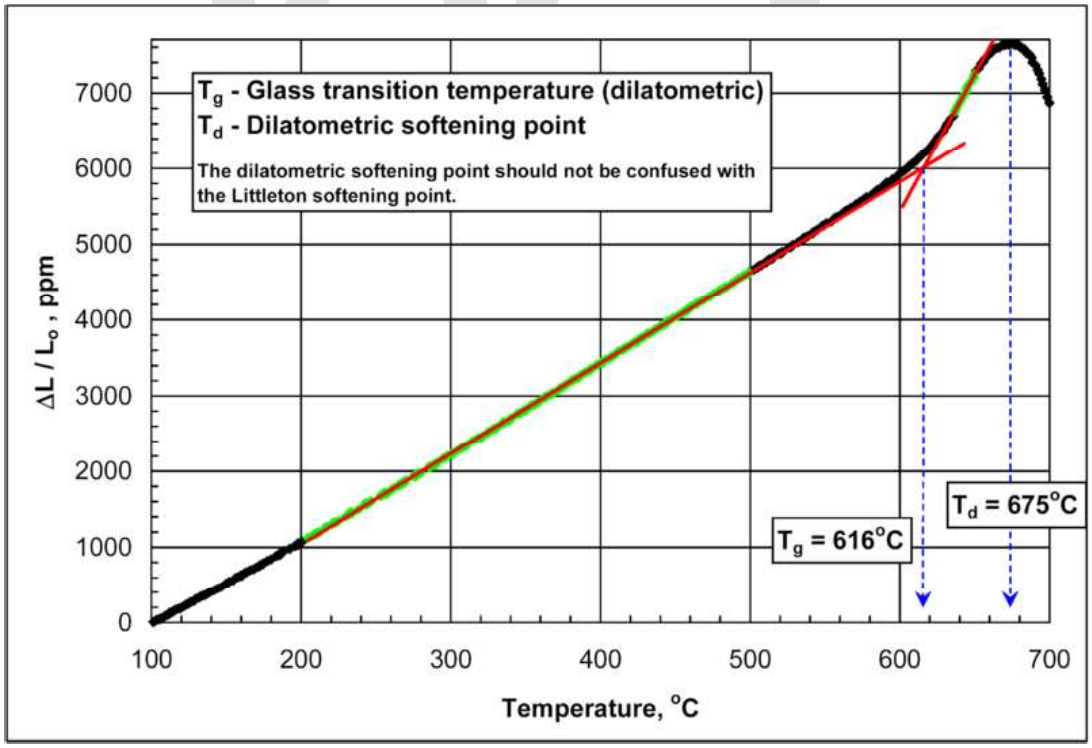
The configuration of the glass in this temperature range changes slowly with time towards the equilibrium structure. The principle of the minimization of the Gibbs free energy provides the thermodynamic driving force necessary for the eventual change. It should be noted here that at somewhat higher temperatures than T_g, the structure corresponding to equilibrium at any temperature is achieved quite rapidly. In contrast, at considerably lower temperatures, the configuration of the glass remains sensibly stable over increasingly extended periods of time.

Thus, the liquid-glass transition is not a transition between states of thermodynamic equilibrium. It is widely believed that the true equilibrium state is always crystalline. Glass is believed to exist in a kinetically locked state, and its entropy, density, and so on, depend on the thermal history. Therefore, the glass transition is primarily a dynamic phenomenon. Time and temperature are interchangeable quantities (to some extent) when dealing with glasses, a fact often expressed in the time-temperature superposition principle. On cooling a liquid, *internal degrees of freedom successively fall out of equilibrium*. However, there is a longstanding debate whether there is an underlying second-order phase transition in the hypothetical limit of infinitely long relaxation times.

Transition temperature T_g



Measurement of T_g by differential scanning calorimetry



Determination of T_g by dilatometry.

Refer to the figure on the right plotting the heat capacity as a function of temperature. In this context, T_g is the temperature corresponding to point A on the curve. The linear sections below and above T_g are colored green. T_g is the temperature at the intersection of the red regression lines.

Different operational definitions of the glass transition temperature T_g are in use, and several of them are endorsed as accepted scientific standards. Nevertheless, all definitions are arbitrary, and all yield different numeric results: at best, values of T_g for a given substance agree within a few kelvins. One definition refers to the viscosity, fixing T_g at a value of 10^{13} poise (or 10^{12} Pa·s). As evidenced experimentally, this value is close to the annealing point of many glasses.

In contrast to viscosity, the thermal expansion, heat capacity, and many other properties of inorganic glasses show a relatively sudden change at the glass transition temperature. Any such step or kink can be used to define T_g. To make this definition reproducible, the cooling or heating rate must be specified.

The most frequently used definition of T_g uses the energy release on heating in differential scanning calorimetry. Typically, the sample is first cooled with 10 K/min and then heated with that same speed.

Yet another definition of T_g uses the kink in dilatometry. Here, heating rates of 3-5 K/min are common. Summarized below are T_g values characteristic of certain classes of materials.

Polymers

Material	T_g (°C)
Tyre rubber	−70
Polypropylene (atactic)	−20
Polypropylene (isotactic)	0
Poly-3-hydroxybutyrate (PHB)	15
Poly(vinyl acetate) (PVAc)	30
Polyethylene terephthalate (PET)	70
Poly(vinyl chloride) (PVC)	80
Poly(vinyl alcohol) (PVA)	85
Polystyrene	95
Poly(methylmethacrylate) (atactic)	105
Poly(carbonate)	145
Polynorbornene	215

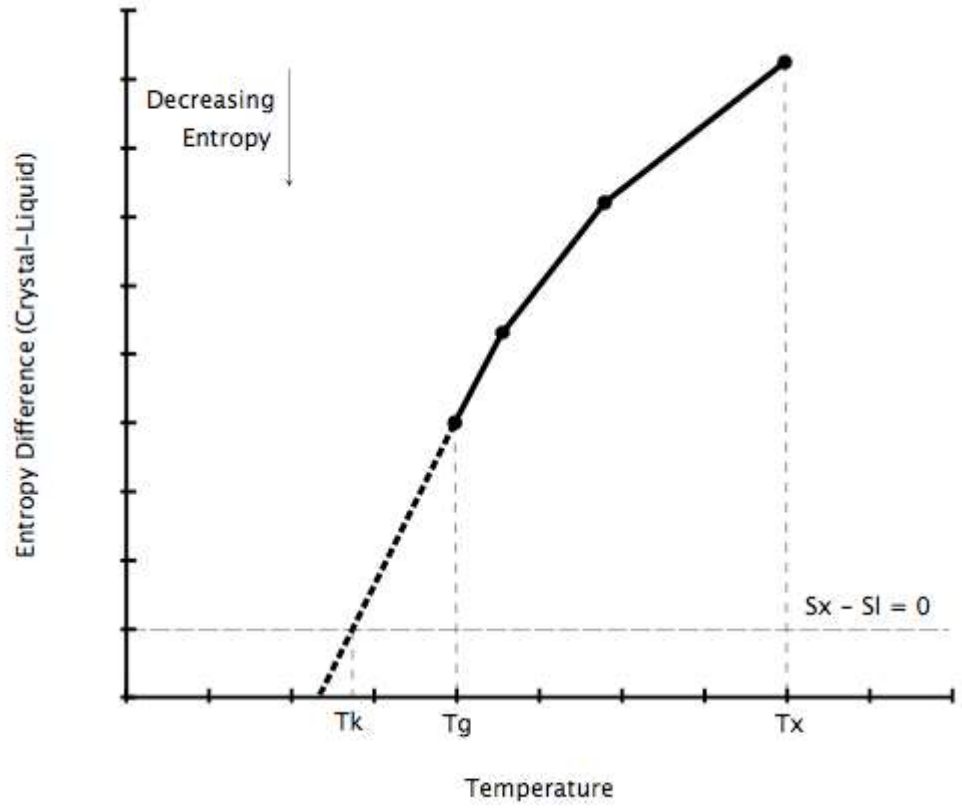
These are only mean values, as the glass transition temperature depends on the cooling rate, molecular weight distribution and could be influenced by additives. Note also that for a semi-crystalline material, such as polyethylene that is 60-80% crystalline at room

temperature, the quoted glass transition refers to what happens to the amorphous part of the material upon cooling.

Silicates and other covalent network glasses

Material	T_g (°C)
Chalcogenide GeSbTe	150
Chalcogenide AsGeSeTe	245
ZBLAN fluoride glass	235
Tellurium dioxide	280
Fluoroaluminate	400
Soda-lime glass	520-600
Fused quartz	~1200

Kauzmann's paradox



Entropy difference between crystal and undercooled melt

As a liquid is supercooled, the difference in entropy between the liquid and solid phase decreases. By extrapolating the heat capacity of the supercooled liquid below its glass

transition temperature, it is possible to calculate the temperature at which the difference in entropies becomes zero. This temperature has been named the **Kauzmann temperature**.

If a liquid could be supercooled below its Kauzmann temperature, and it did indeed display a lower entropy than the crystal phase, the consequences would be paradoxical. This **Kauzmann paradox** has been the subject of much debate and many publications since it was first put forward by Walter Kauzmann in 1948.

One resolution of the Kauzmann paradox is to say that there must be a phase change before the entropy of the liquid decreases. In this scenario, the transition temperature is known as the *calorimetric ideal glass transition temperature* T_{0c}. In this view, the glass transition is not merely a kinetic effect, i.e. merely the result of fast cooling of a melt, but there is an underlying thermodynamic basis for glass formation. The glass transition temperature:

$$T_g \rightarrow T_{0c} \text{ as } {}^{dT}/_{dt} \rightarrow 0.$$

There are at least three other possible resolutions to the Kauzmann paradox. It could be that the heat capacity of the supercooled liquid near the Kauzmann temperature smoothly decreases to a smaller value. It could also be that a first order phase transition to another liquid state occurs before the Kauzmann temperature with the heat capacity of this new state being less than that obtained by extrapolation from higher temperature. Finally, Kauzmann himself resolved the entropy paradox by postulating that all supercooled liquids must crystallize before the Kauzmann temperature is reached.

The glass transition in specific materials

Silica, SiO_2

Silica (the chemical compound SiO_2) has a number of distinct crystalline forms in addition to the quartz structure. Nearly all of the crystalline forms involve tetrahedral SiO_4 units linked together by *shared vertices* in different arrangements. Si-O bond lengths vary between the different crystal forms. For example, in α-quartz the bond length is 161 pm, whereas in α-tridymite it ranges from 154-171 pm. The Si-O-Si bond angle also varies from 140° in α-tridymite to 144° in α-quartz to 180° in β-tridymite. Any deviations from these standard parameters constitute microstructural differences or variations which represent an approach to an amorphous, vitreous or glassy solid.

The transition temperature T_g in silicates is related to the energy required to break and re-form covalent bonds in an amorphous (or random network) lattice of covalent bonds. The T_g is clearly influenced by the chemistry of the glass. For example, addition of elements such as B, Na, K or Ca to a silica glass, which have a valency less than 4, helps in breaking up the network structure, thus reducing the T_g. Alternatively, P which has a valency of 5, helps to reinforce an ordered lattice, and thus increases the T_g.

T_g is directly proportional to bond strength, e.g. it depends on quasi-equilibrium thermodynamic parameters of the bonds e.g. on the enthalpy H_d and entropy S_d of configurons – broken bonds: $T_g = H_d / [S_d + R\ln[(1-f_c)/ f_c]$ where R is the gas constant and f_c is the percolation threshold. For strong melts such as SiO_2 the percolation threshold in the above equation is the universal Scher-Zallen critical density in the 3-D space e.g. $f_c = 0.15$, however for fragile materials the percolation thresholds are material-dependent and $f_c << 1$. The enthalpy H_d and the entropy S_d of configurons – broken bonds can be found from available experimental data on viscosity.

Polymers

In polymers the glass transition temperature, T_g, is often expressed as the temperature at which the Gibbs free energy is such that the activation energy for the cooperative movement of 50 or so elements of the polymer is exceeded. This allows molecular chains to slide past each other when a force is applied. From this definition, we can see that the introduction of relatively stiff chemical groups (such as benzene rings) will interfere with the flowing process and hence increase T_g.

The stiffness of thermoplastics decreases due to this effect. When the glass temperature has been reached, the stiffness stays the same for a while, i.e., at or near E_2, until the temperature exceeds T_m, and the material melts. This region is called the rubber plateau.

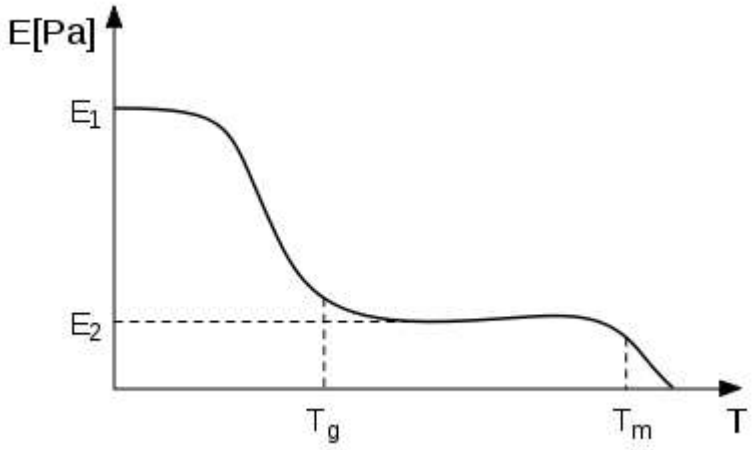
WT

In ironing, a fabric is heated through the glass-rubber transition.

In ironing, a fabric is heated through this transition so that the polymer chains become mobile. The weight of the iron then imposes a preferred orientation. T_g can be significantly decreased by addition of plasticizers into the polymer matrix. Smaller molecules of plasticizer embed themselves between the polymer chains, increasing the spacing and free volume, and allowing them to move past one another even at lower temperatures. The "new-car smell" is due to the initial outgassing of volatile small-molecule plasticizers used to modify interior plastics (e.g., dashboards) to keep them from cracking in the cold of winter weather. The addition of nonreactive side groups to a polymer can also make the chains stand off from one another, reducing T_g. If a plastic with some desirable properties has a T_g which is too high, it can sometimes be combined with another in a copolymer or composite material with a T_g below the temperature of intended use. Note that some plastics are used at high temperatures, e.g., in automobile engines, and others at low temperatures.

In viscoelastic materials, the presence of liquid-like behavior depends on the properties of and so varies with rate of applied load, i.e., how quickly a force is applied. The silicone toy 'Silly Putty' behaves quite differently depending on the time rate of applying a force:

pull slowly and it flows, acting as a heavily viscous liquid; hit it with a hammer and it shatters, acting as a glass.



Stiffness versus temperature

On cooling, rubber undergoes a *liquid-glass transition*, which has also been called a *rubber-glass transition*. For example, the Space Shuttle Challenger disaster was caused by rubber O-rings that were being used well below their glass transition temperature on an unusually cold Florida morning, and thus could not flex adequately to form proper seals between sections of the two solid-fuel rocket boosters.

Mechanics of vitrification

Molecular motion in condensed matter can be represented by a Fourier series whose physical interpretation consists of a superposition of longitudinal and transverse waves of atomic displacement with varying directions and wavelengths. In monatomic systems, we call these waves: *density fluctuations*. (In polyatomic systems, they may also include compositional fluctuations.)

Thus, thermal motion in liquids can be decomposed into elementary longitudinal vibrations (or acoustic phonons) while transverse vibrations (or shear waves) were originally described only in elastic solids exhibiting the highly ordered crystalline state of matter. In other words, simple liquids cannot support an applied force in the form of a shearing stress, and will yield mechanically via macroscopic plastic deformation (or viscous flow). Furthermore, the fact that a solid deforms locally while retaining its rigidity -- while a liquid yields to macroscopic viscous flow in response to the application of an applied shearing force -- is accepted by many as the mechanical distinction between the two.

The inadequacies of this conclusion, however, were pointed out by Frenkel in his revision of the kinetic theory of solids and the theory of elasticity in liquids. This revision follows

directly from the continuous characteristic of the structural transition from the liquid state into the solid one when this transition is not accompanied by crystallization—ergo the supercooled viscous liquid. Thus we see the intimate correlation between transverse acoustic phonons (or shear waves) and the onset of rigidity upon vitrification, as described by Bartenev in his mechanical description of the vitrification process.

The velocities of longitudinal acoustic phonons in condensed matter are directly responsible for the thermal conductivity which levels out temperature differentials between compressed and expanded volume elements. Kittel proposed that the behavior of glasses is interpreted in terms of an approximately constant "mean free path" for lattice phonons, and that the value of the mean free path is of the order of magnitude of the scale of disorder in the molecular structure of a liquid or solid. The thermal phonon mean free paths or relaxation lengths of a number of glass formers have been plotted versus the glass transition temperature, indicating a linear relationship between the two. This has suggested a new criterion for glass formation based on the value of the phonon mean free path.

It has often been suggested that heat transport in dielectric solids occurs through elastic vibrations of the lattice, and that this transport is limited by elastic scattering of acoustic phonons by lattice defects (e.g. randomly spaced vacancies). These predictions were confirmed by experiments on commercial glasses and glass ceramics, where mean free paths were apparently limited by "internal boundary scattering" to length scales of 10 - 100 micrometers. The relationship between these transverse waves and the mechanism of vitrification has been described by several authors who proposed that the onset of correlations between such phonons results in an orientational ordering or "freezing" of local shear stresses in glass-forming liquids, thus yielding the glass transition.

Electronic structure

The influence of thermal phonons and their interaction with electronic structure is a topic which was appropriately introduced in a discussion of the resistance of liquid metals. Lindemann's theory of melting is referenced, and it is suggested that the drop in conductivity in going from the crystalline to the liquid state is due to the increased scattering of conduction electrons as a result of the increased amplitude of atomic vibration. Such theories of localization have been applied to transport in metallic glasses, where the mean free path of the electrons is very small (on the order of the interatomic spacing).

The formation of a non-crystalline form of a gold-silicon alloy by the method of splat quenching from the melt led to further considerations of the influence of electronic structure on glass forming ability, based on the properties of the metallic bond.

Other work indicates that the mobility of localized electrons is enhanced by the presence of dynamic phonon modes. One claim against such a model is that if chemical bonds are important, the nearly free electron models should not be applicable. However, if the model includes the buildup of a charge distribution between all pairs of atoms just like a

chemical bond (e.g., silicon, when a band is just filled with electrons) then it should apply to solids.

Thus, if the electrical conductivity is low, the mean free path of the electrons is very short. The electrons will only be sensitive to the short-range order in the glass since they do not get a chance to scatter from atoms spaced at large distances. Since the short-range order is similar in glasses and crystals, the electronic energies should be similar in these two states. For alloys with lower resistivity and longer electronic mean free paths, the electrons could begin to sense that there is disorder in the glass, and this would raise their energies and destabilize the glass with respect to crystallization. Thus, the glass formation tendencies of certain alloys may therefore be due in part to the fact that the electron mean free paths are very short, so that only the short-range order is ever important for the energy of the electrons.

It has also been argued that glass formation in metallic systems is related to the "softness" of the interaction potential between unlike atoms. Some authors, emphasizing the strong similarities between the local structure of the glass and the corresponding crystal, suggest that chemical bonding helps to stabilize the amorphous structure.

Other authors have suggested that the electronic structure yields its influence on glass formation through the directional properties of bonds. Non-crystallinity is thus favored in elements with a large number of polymorphic forms and a high degree of bonding anisotropy. Crystallization becomes more unlikely as bonding anisotropy is increased from isotropic metallic to anisotropic metallic to covalent bonding, thus suggesting a relationship between the group number in the periodic table and the glass forming ability in elemental solids.