Ceramic Materials and Engineering

Lon Hilton

First Edition, 2012

ISBN 978-81-323-2481-2

Published by:
Library Press
4735/22 Prakashdeep Bldg,
Ansari Road, Darya Ganj,
Delhi - 110002
Email: info@wtbooks.com

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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

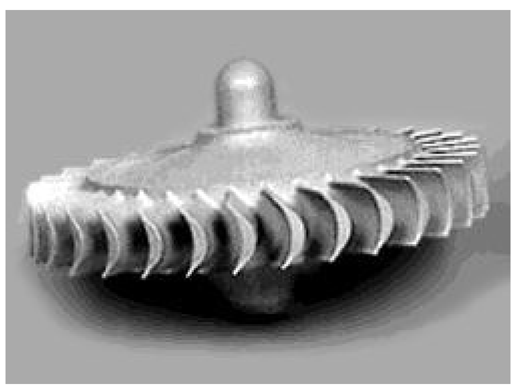
The physical properties of any ceramic substance are a direct result of its crystalline structure and chemical composition. Solid state chemistry reveals the fundamental connection between microstructure and properties such as localized density variations, grain size distribution, type of porosity and 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.

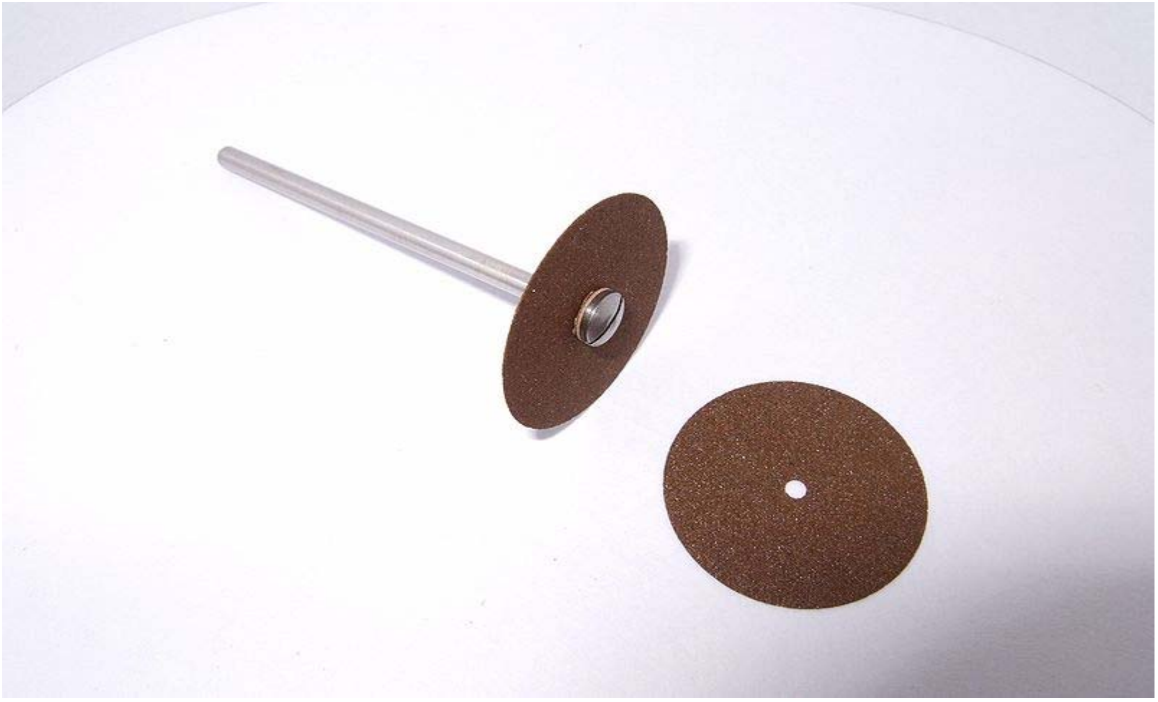
Ceramography is the art and science of preparation, examination and evaluation of ceramic microstructures. Evaluation and characterization of ceramic microstructures is often implemented on similar spatial scales to that used commonly in the emerging field of nanotechnology: from tens of angstroms (A) 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.

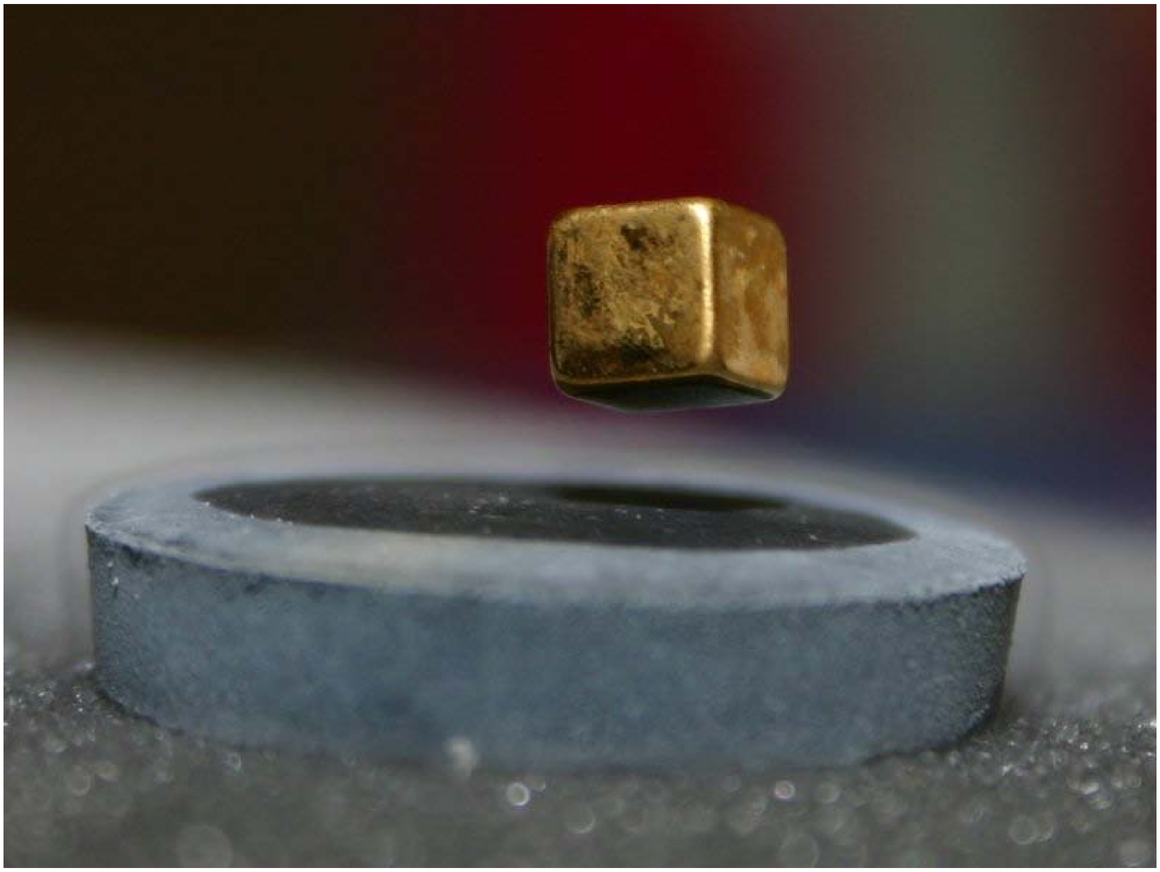
While there are prospects of mass producting blue LEDs from zinc oxide, ceramicists are most interested in the electrical properties that show grain boundary effects.

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

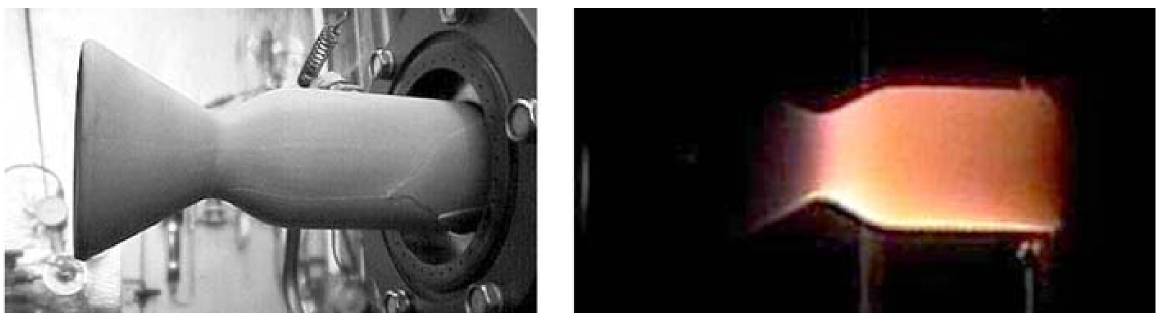
Piezoelectricity, a link between electrical and mechanical response, is exhibited by a large number of ceramic materials, including the quartz used to measure time in watches and other electronics. Such devices use both properties of piezoelectrics, using electricity to produce a mechanical motion (powering 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

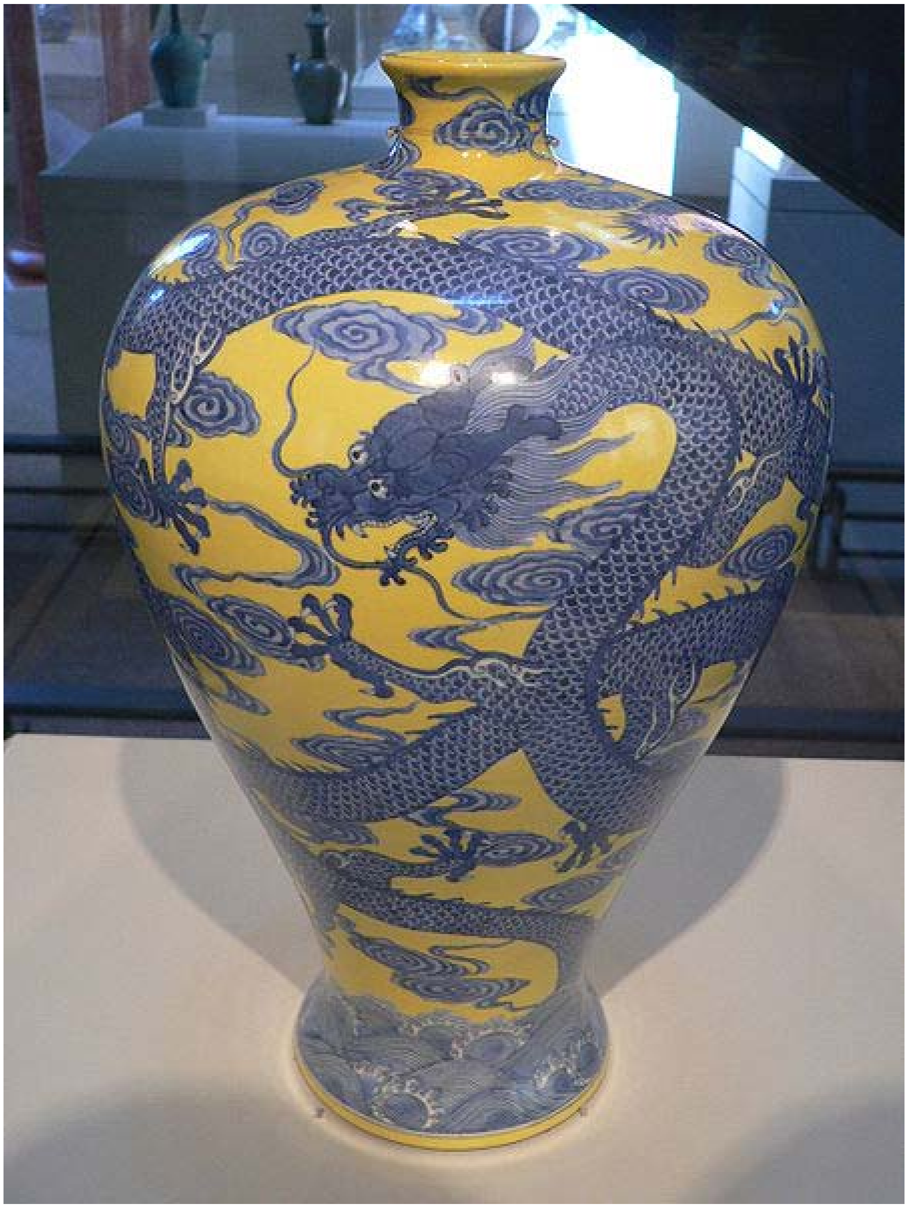
Ceramic BN crucible

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.

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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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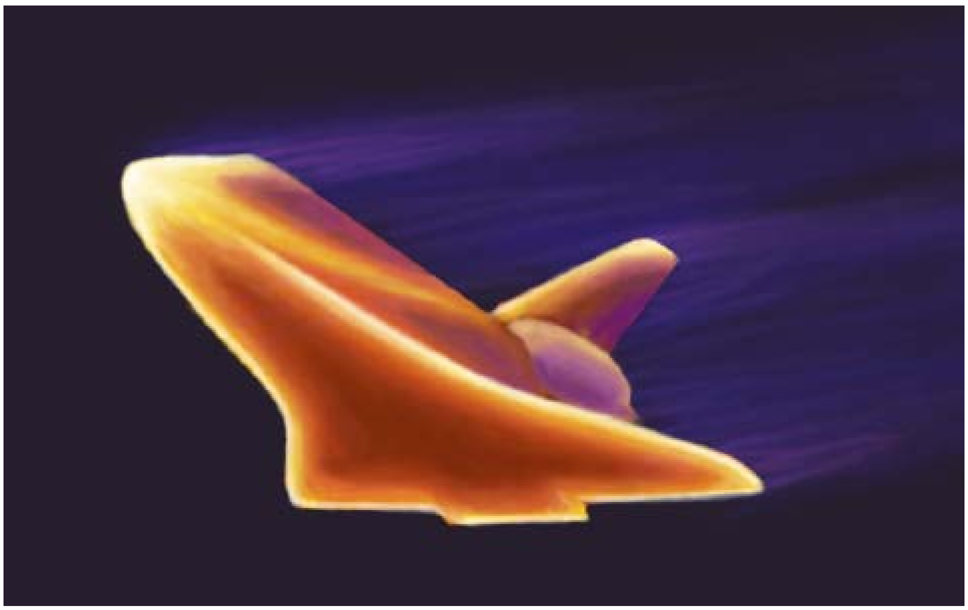
Chapter- 2

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 32^{nd}.

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.

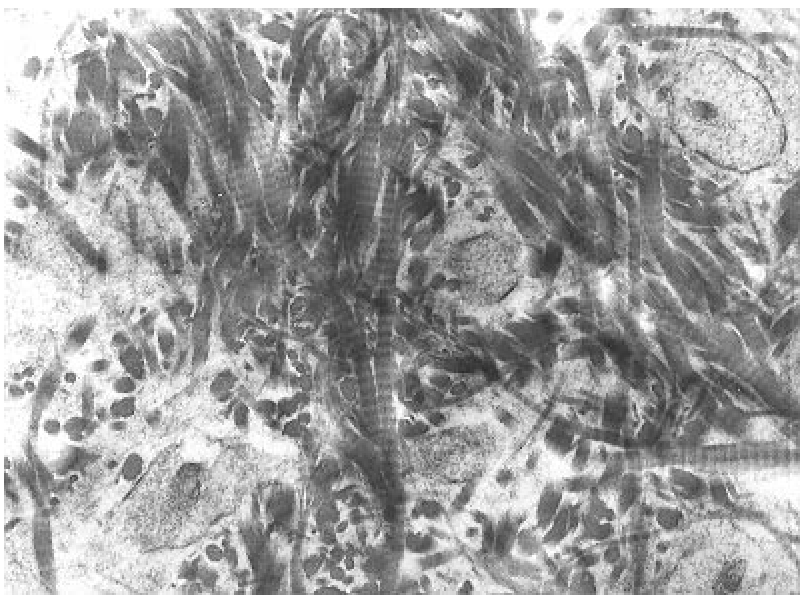
- Zirconium dioxide ceramics are used in the manufacture of knives. The blade of the ceramic knife will stay sharp for much longer than that of a steel knife, although it is more brittle and can be snapped by dropping it on a hard surface.

- 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.

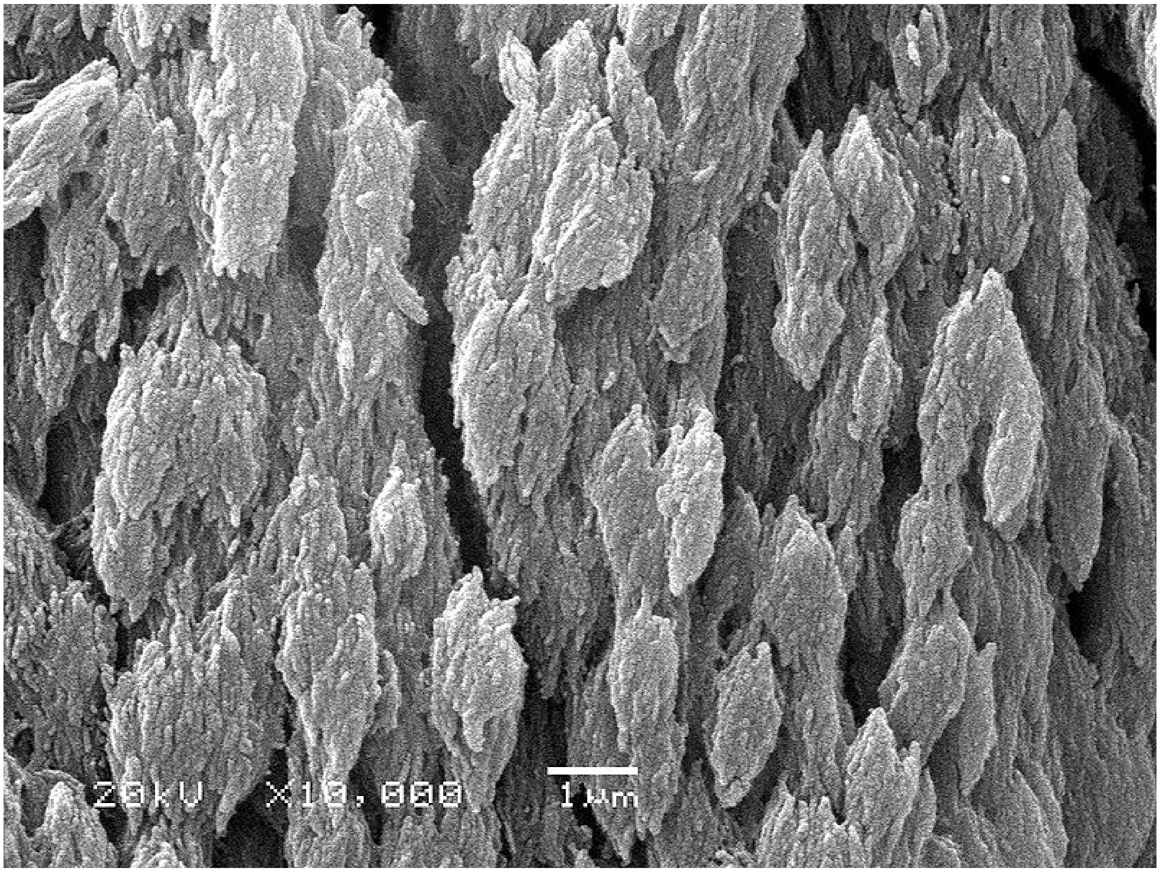
- Silicon nitride parts are used in ceramic ball bearings. Their higher hardness means that they are much less susceptible to wear and can offer more than triple lifetimes. They also deform less under load meaning they have less contact with the bearing retainer walls and can roll faster. In very high 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

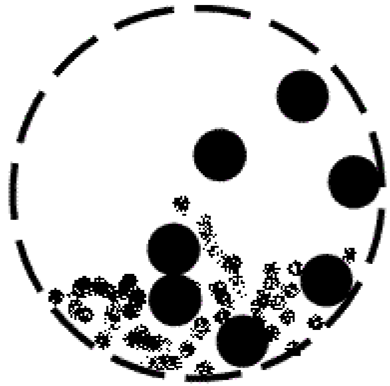
Glass-ceramic materials share many properties with both glasses and ceramics. Glass-ceramics have an amorphous phase and one or more crystalline phases and are produced by a so called "controlled crystallization", which is typically avoided in glass manufacturing. Glass-ceramics often contain a crystalline 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.

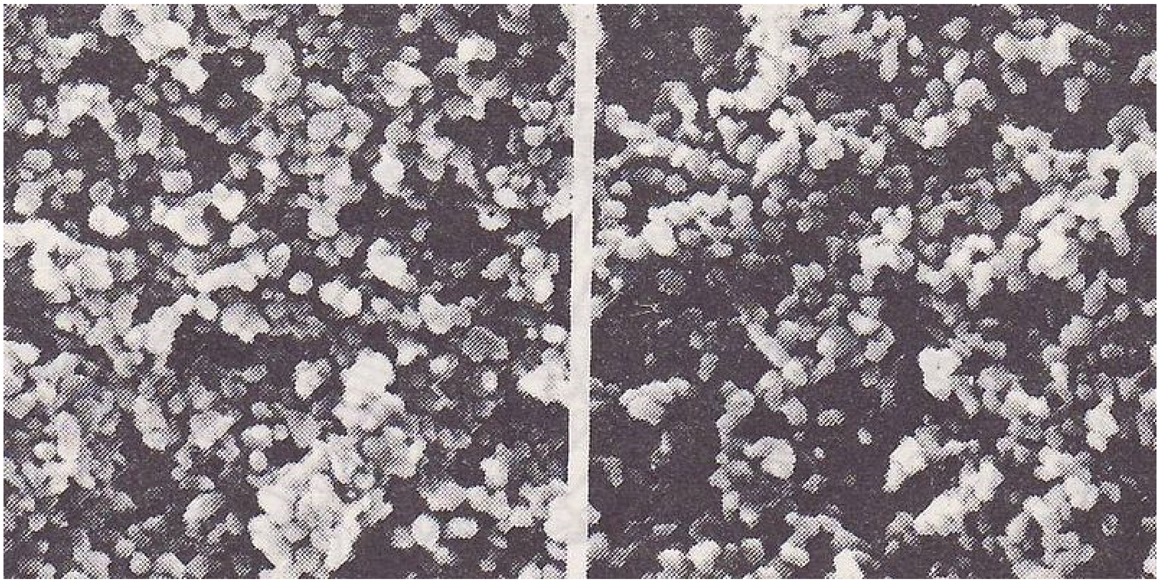
These forming techniques are well known for providing tools and other components with dimensional stability, surface quality, high (near theoretical) density and microstructural uniformity. The increasing use and diversity of specialty forms of ceramics adds to the diversity of process technologies to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

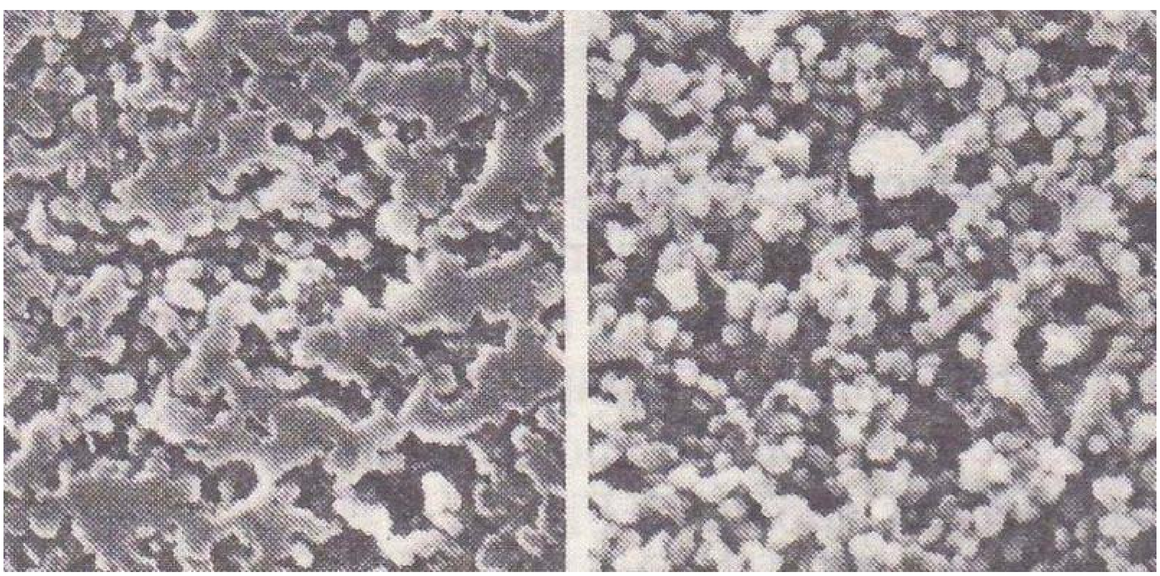
The other major layer structure is coating, where melt spraying is very important, but chemical and physical vapor deposition and chemical (e.g., sol-gel and polymer pyrolysis) methods are all seeing increased use. Besides open structures from formed tape, extruded structures, such as honeycomb catalyst 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.

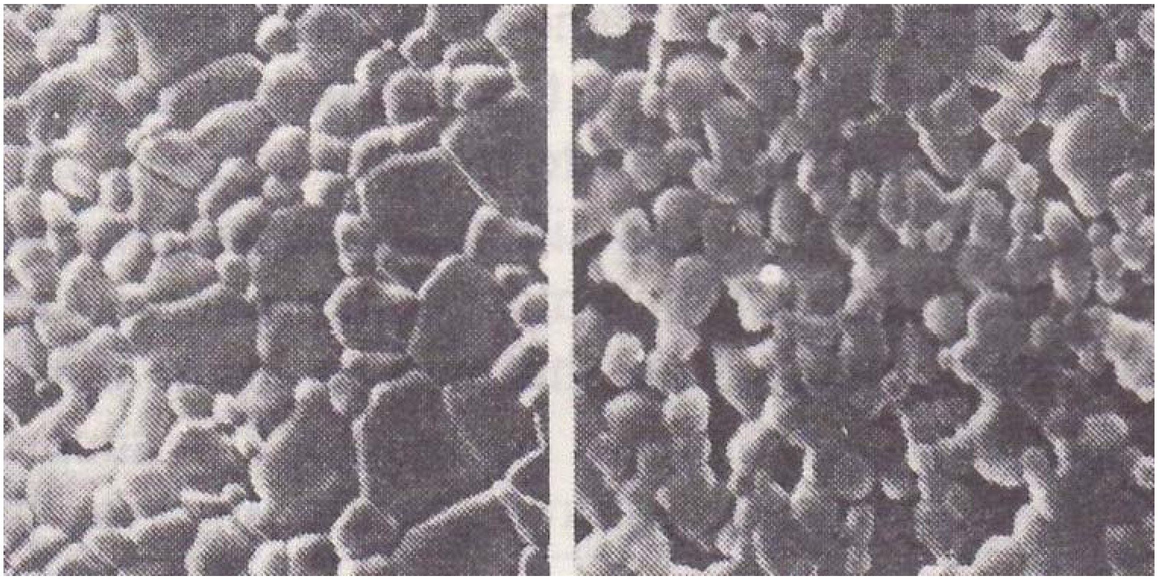
The sintering process



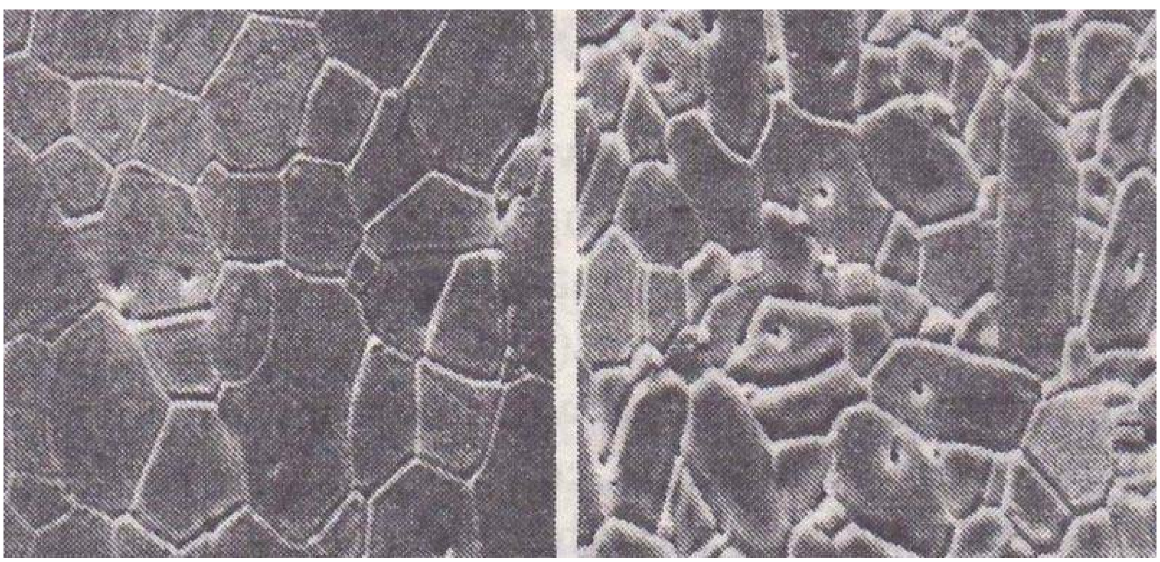
Scanning electron micrographs (SEM) of room temperature Al_2O_3 fine powder compact formed using a) colloidal processing and b) slip casting techniques. *Note: Mean particle diameter = 0.6 microns.



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

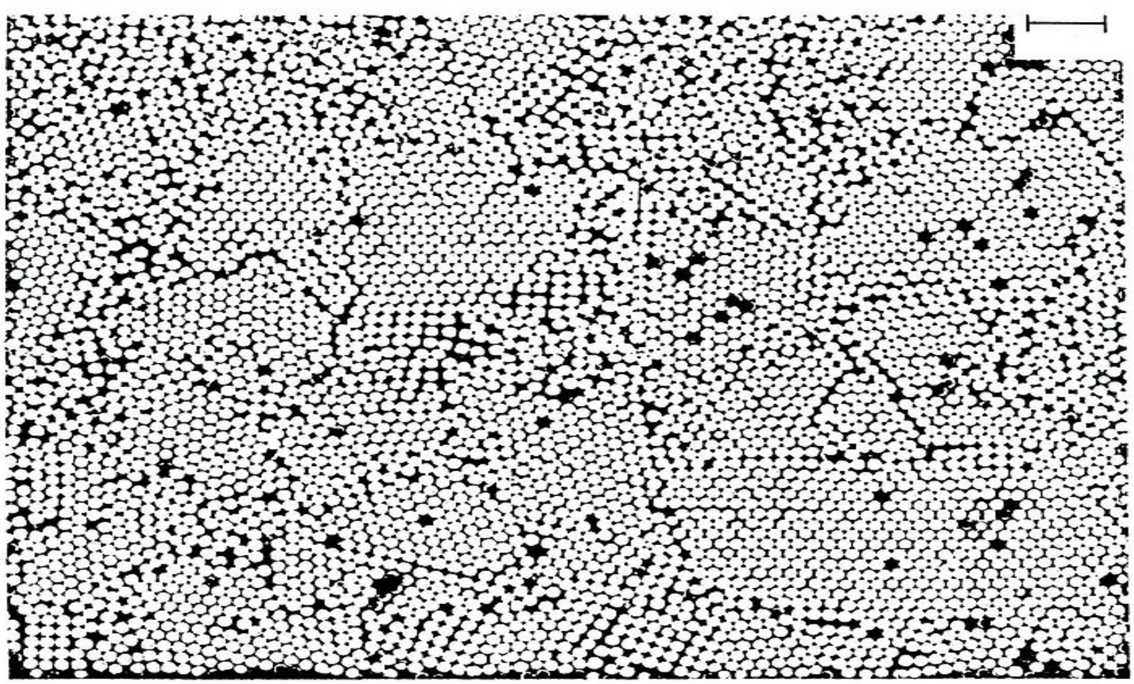
$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$$

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.

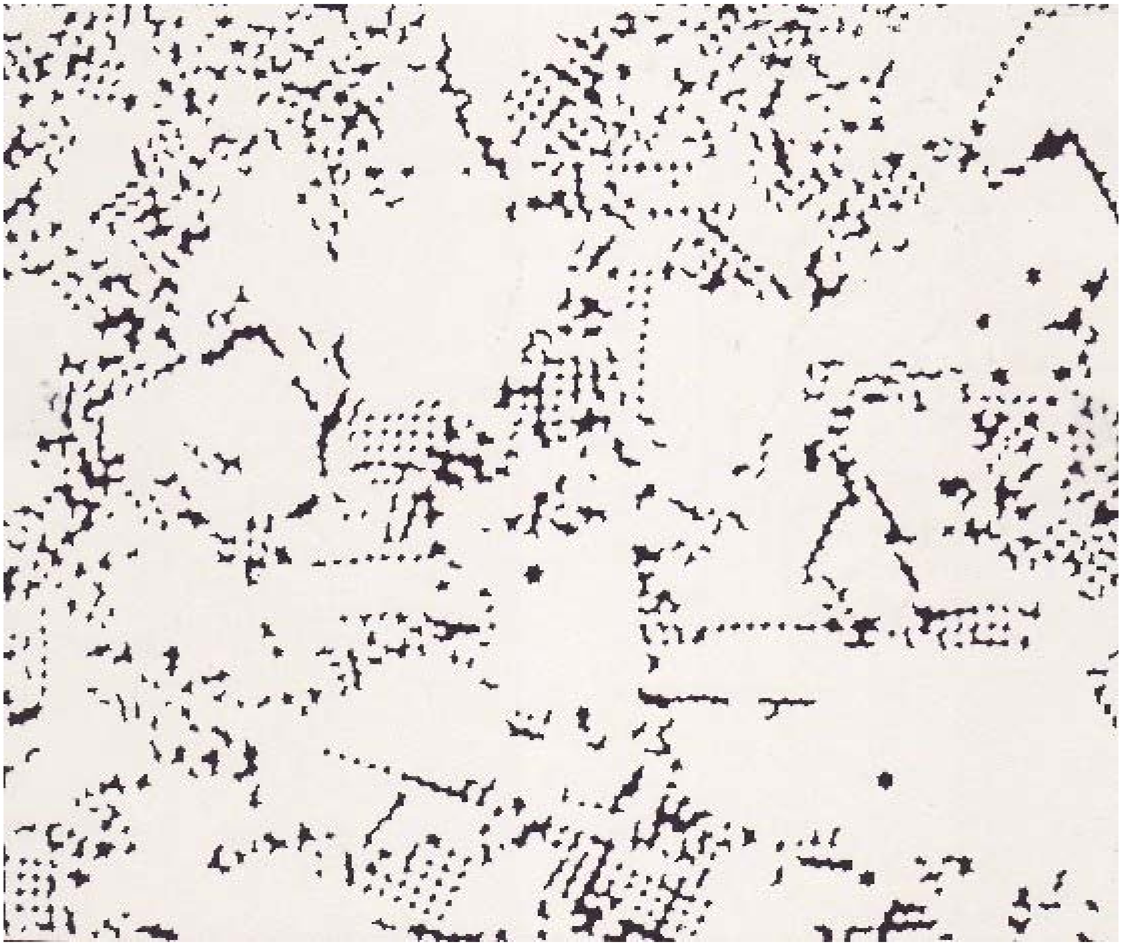
Theoretically, a material could be made infinitely strong if the grains are made infinitely small. This is, unfortunately, impossible because the lower limit of grain size is a single unit cell of the material. Even then, if the grains of a material are the size of a single unit cell, then the material 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.

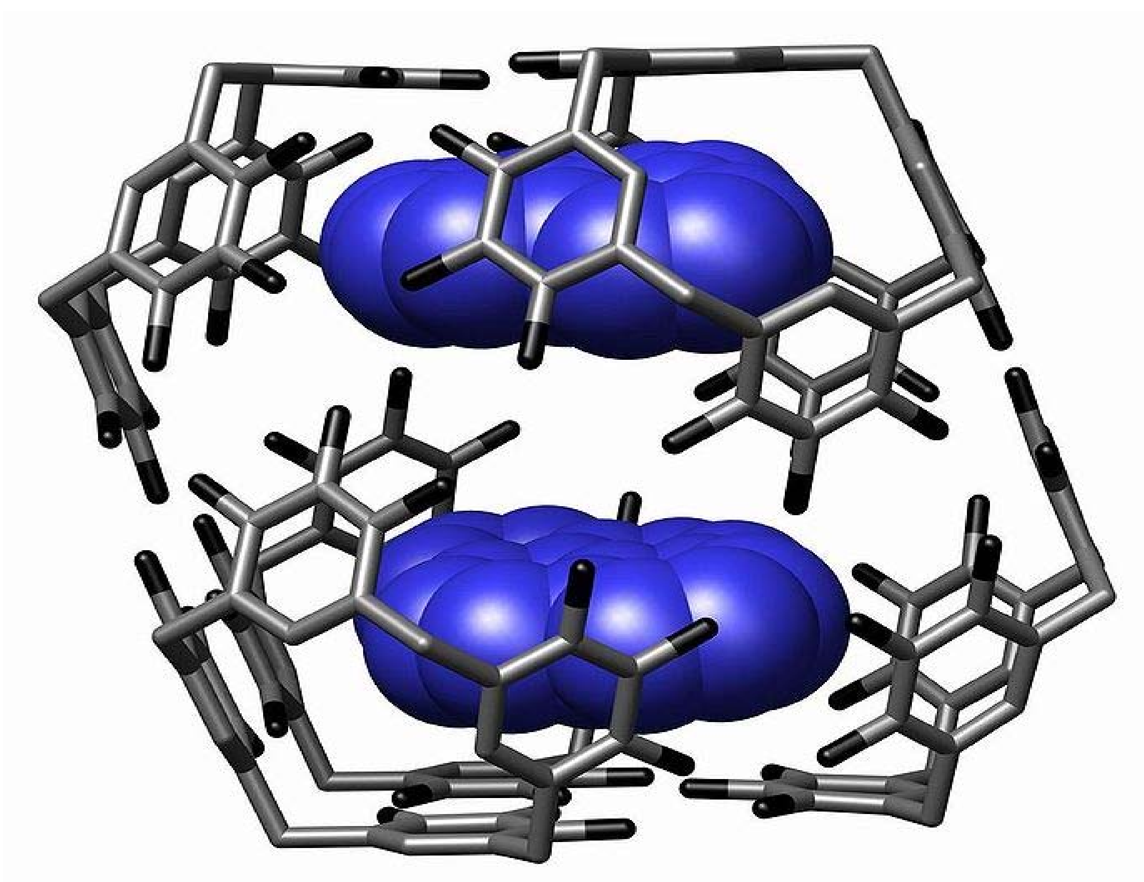
In addition, any fluctuations in packing density in the compact as it is prepared for the kiln are often amplified during the sintering process, yielding inhomogeneous densification. Some pores and other structural defects associated with density variations have been shown to play a detrimental role 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.

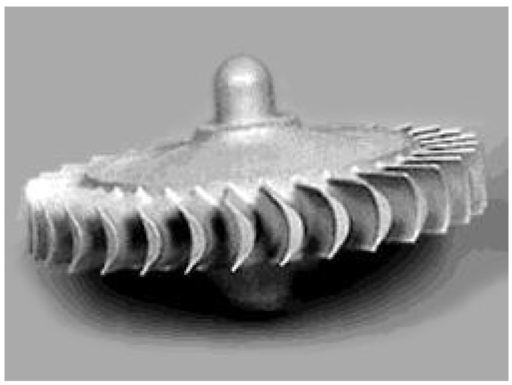
From the technological standpoint, a particularly desirable approach to fabricating particulate composites is to coat the matrix or its precursor onto fine particles of the dispersed phase with good control of the starting dispersed particle size and the resultant matrix coating thickness. One should 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.

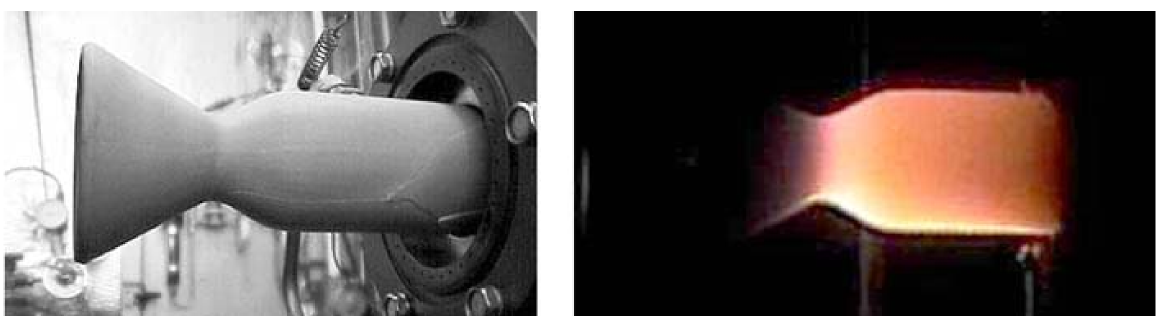
Clearly, there are possibilities of using melt casting for many of these approaches. Potentially even more desirable is using melt-derived particles. In this method, quenching is done in a solid solution or in a fine eutectic structure, in which the particles are then processed by more typical ceramic 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

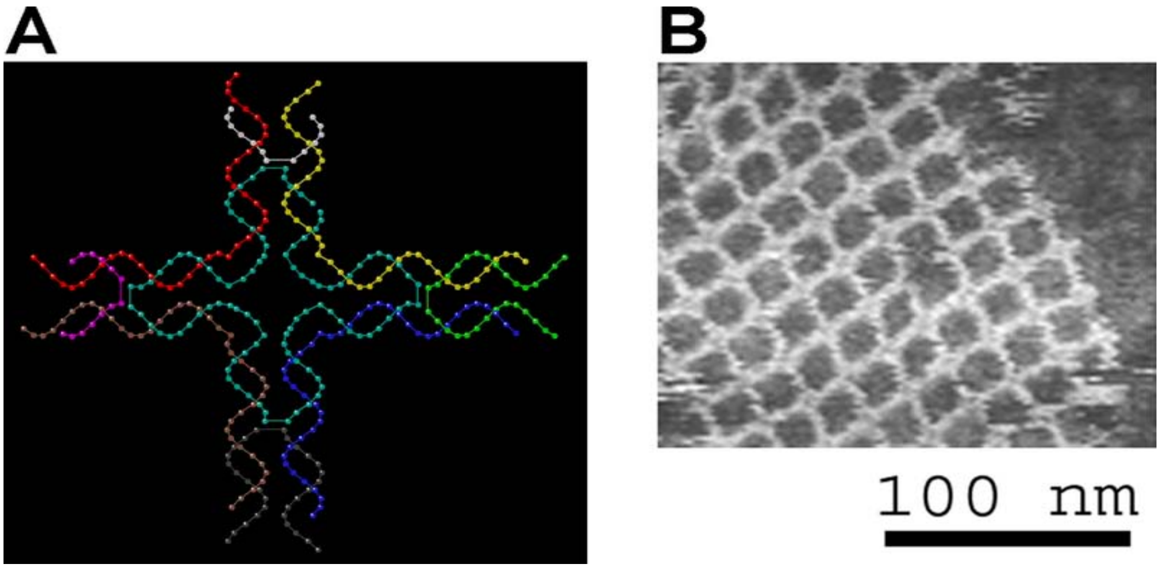
Optical

- 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.

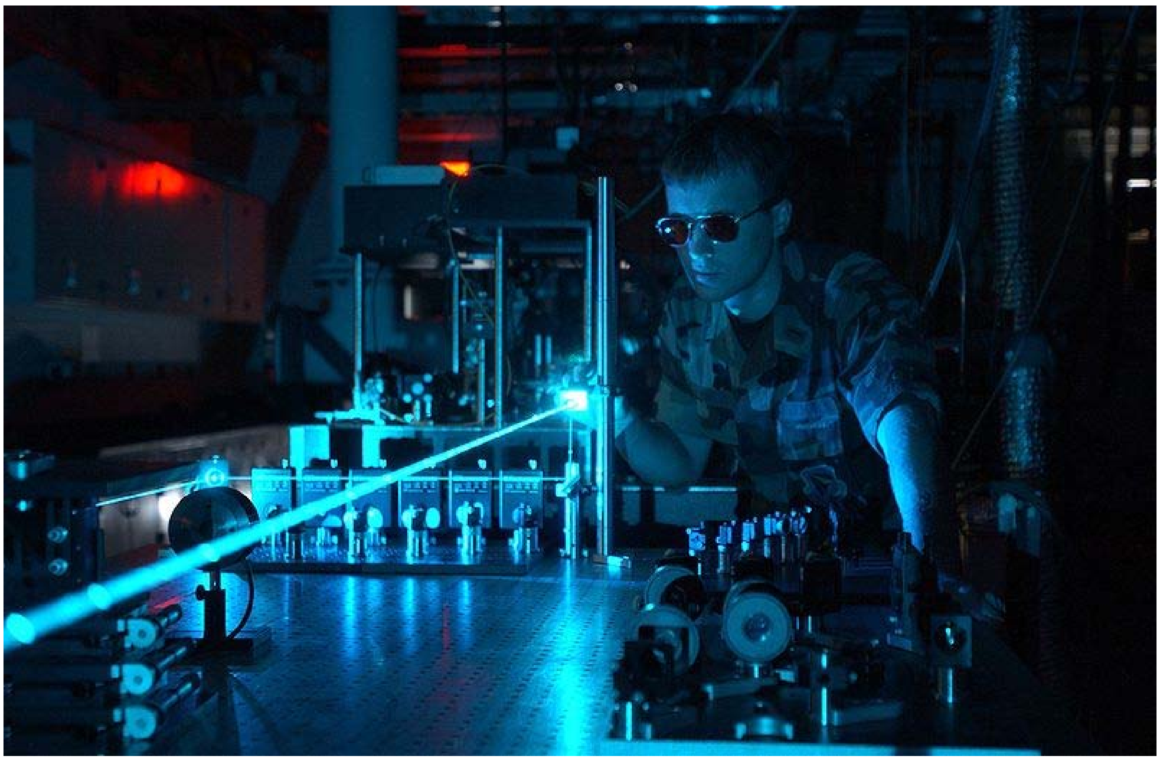
The iridescent nacre inside a Nautilus shell

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.

Chapter- 3

Transparent Ceramics



Large laser elements made from transparent ceramics can be produced at a relatively low cost. These components are free of internal stress or intrinsic birefringence, and allow relatively large doping levels or optimized custom-designed doping profiles. This makes ceramic laser elements particularly important for high-energy lasers.

Many ceramic materials, both glassy and crystalline, have found use as optically transparent materials in various forms from bulk solid-state components to high surface area forms such as thin films, coatings and fibers. Such devices 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.

While single-crystalline ceramics may be largely defect-free (particularly within the spatial scale of the incident light wave) optical transparency in polycrystalline materials is limited by the amount of light which is scattered by their microstructural features. The amount of light scattering therefore depends on the wavelength of the incident radiation, or light.

For example, since visible light has a wavelength scale on the order of a micrometer, or 'micron' (one millionth of a meter), scattering centers will have dimensions on a similar spatial scale. Most ceramic materials, such as alumina and its compounds, are formed from fine powders, yielding a fine grained polycrystalline microstructure which is filled with scattering centers comparable to the wavelength of visible light. Thus, they are generally opaque as opposed to transparent materials. Recent nanoscale technology has, however, made possible the production of (poly) crystalline **transparent ceramics** such as alumina Al_2O_3, yttria alumina garnet (YAG), and neodymium-doped Nd:YAG.

The "Arrow" anti-ballistic IR heat-seeking missile in launch mode

Introduction

Transparent ceramics have recently acquired a high degree of interest and notoriety. Basic applications include lasers and cutting tools, transparent armor windows, night vision devices (NVD) and nose cones for heat seeking missiles. Currently available infrared (IR) transparent materials typically exhibit a trade-off between optical performance and mechanical strength. For example, sapphire (crystalline alumina) is very strong, but lacks full transparency throughout the 3-5 micrometer mid-IR range. Yttria is fully transparent from 3-5 micrometers, but lacks sufficient strength, hardness, and thermal shock resistance for high-performance aerospace applications. Not surprisingly, a combination of these two materials in the form of the yttria-alumina garnet (YAG) has proven to be one of the top performers in the field.

In 1961, GE began selling transparent alumina Lucalox bulbs. In 2004, Anatoly Rosenflanz and colleagues at 3M used a "flame-spray" technique to alloy aluminium oxide (or alumina) with rare-earth metal oxides in order to produce high strength glass-ceramics with good optical properties. The method avoids many of the problems encountered in conventional glass forming and may be extensible to other oxides. This goal has been readily accomplished and amply demonstrated in laboratories and research facilities worldwide using the emerging chemical processing methods encompassed by the methods of sol-gel chemistry and nanotechnology.

Many ceramic materials, both glassy and crystalline, have found use as hosts for solid-state lasers and as optical window materials for gas lasers. The first working laser was made by Theodore H. Maiman in 1960 at Hughes Research Laboratories in Malibu, who had the edge on other research teams led by Charles H. Townes at Columbia University, Arthur Schawlow at Bell Labs, and Gould at TRG (Technical Research Group). Maiman used a solid-state light-pumped synthetic ruby to produce red laser light at a wavelength of 694 nanometers (nm). Synthethic ruby lasers are still in use.

Crystals

Ruby lasers consist of single-crystal sapphire alumina (Al_2O_3) rods doped with a small concentration of chromium Cr, typically in the range of 0.05%. The end faces are highly polished with a planar and parallel configuration. Neodymium-doped YAG (Nd:YAG) has proven to be one of the best solid-state laser materials. Its indisputable dominance in a broad variety of laser applications is determined by a combination of high emission cross section with long spontaneous emission lifetime, high damage threshold, mechanical strength, thermal conductivity, and low thermal beam distortion. The fact that the Czochralski crystal growth of Nd:YAG is a matured, highly reproducible and relatively simple technological procedure adds significantly to the value of the material.

Nd:YAG lasers are used in manufacturing for engraving, etching, or marking a variety of metals and plastics. They are extensively used in manufacturing for cutting and welding steel and various alloys. For automotive applications (cutting and welding steel) the power levels are typically 1-5 kW. In addition, Nd:YAG lasers are used in ophthalmology to correct posterior capsular opacification, a condition that may occur after cataract surgery, and for peripheral iridotomy in patients with acute angle-closure glaucoma, where it has superseded surgical iridectomy. Frequency-doubled Nd:YAG lasers (wavelength 532 nm) are used for pan-retinal photocoagulation in patients with diabetic retinopathy. In oncology, Nd:YAG lasers can be used to remove skin cancers. These lasers are also used extensively in the field of cosmetic medicine for laser hair removal and the treatment of minor vascular defects such as spider veins on the face and legs. Recently used for dissecting cellulitis, a rare skin disease usually occurring on the scalp. Using hysteroscopy in the field of gynecology, the Nd:YAG laser has been used for removal of uterine septa within the inside of the uterus. In dentistry, Nd:YAG lasers are used for soft tissue surgeries in the oral cavity.

High powered Nd:YAG lasers as large as a football field are currently used used for inertial confinement fusion, nuclear weapons research and other high energy density physics experiments.

Glasses

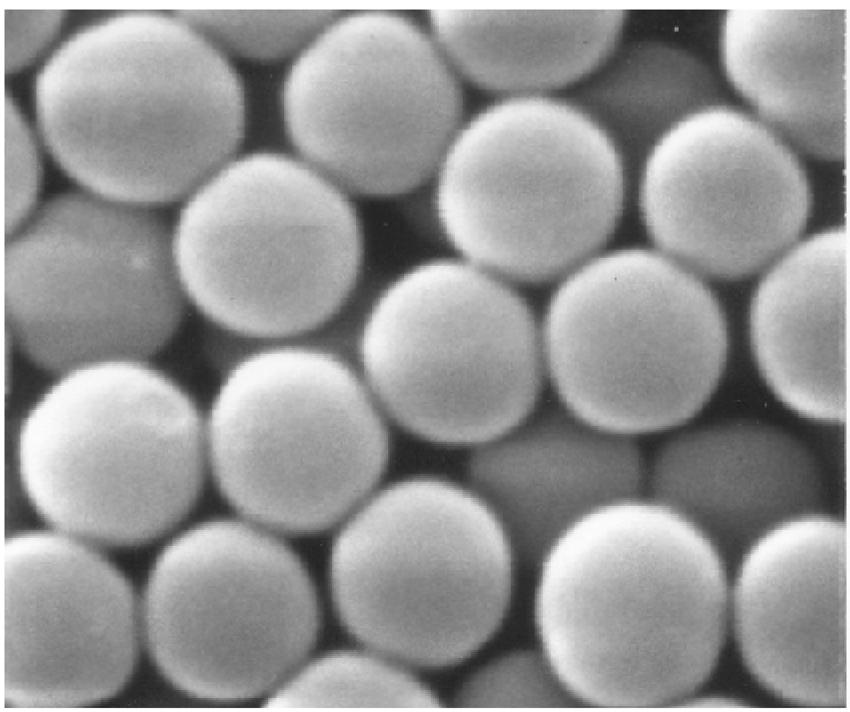
Glasses (non-crystalline ceramics) are also widely used as host materials for lasers. Relative to crystalline lasers, they offer improved flexibility in size and shape and may be readily manufactured as large, homogeneous, isotropic solids with excellent optical properties. The indices of refraction of glass laser hosts can be varied between about 1.5 and 2.0, and both the temperature coefficient of n and hte the strain-optical coefficient can be tailored by altering the chemical composition. Glasses have lower thermal conductivities than the alumina or YAG, however, which imposes limitations on their use in continuous and high repitition-rate applications.

The principal differences between the behavior of glass and crystalline ceramic laser host materials are associated with the greater variation in the local environment of lasing ions in amorphous solids. This leads to a broadening of the fluorescent levels in glasses. For example, the width of the Nd^{3+} emission in YAG is ~ 10 angstroms as compared to ~ 300 angstroms in typical oxide glasses. The broadened fluorescent lines in glasses make it more difficult to obtain continuous wave laser operation (CW), relative to the same lasing ions in crystalline solid laser hosts.

Several glasses are used in transparent armor, such as normal plate glass (soda-lime-silica), borosilicate glass, and fused silica. Plate glass has been the most common glass used due to its low cost. But greater requirements for the optical properties and ballistic performance have necessitated the development of new materials. E.G. Chemical or thermal treatmtents can increase the strength of glasses, and the controlled crystallization of certain glass compositions can produce optical quality glass-ceramics. AREVA, Ltd.,currently produces a lithium disilicate based glass-ceramic known as TransArm™, for use in transparent armor systems. It has all the workability of an amorphous glass, but upon recrystallization it demonstrates properties similar to a crystalline ceramic. Vycor™ is 96% fused silica glass, which is crystal clear, lightweight and high strength. One advantage of these type of materials is that they can be produced in large sheets and other curved shapes..

Nanomaterials

It has been shown fairly recently that laser elements (amplifiers, switches, ion hosts, etc.) made from fine-grained ceramic nanomaterials—produced by the low temperature sintering of high purity nanoparticles and powders—can be produced at a relatively low cost. These components are free of internal stress or intrinsic birefringence, and allow relatively large doping levels or optimized custom-designed doping profiles. This highlights the use of ceramic nanomaterials as being particularly important for high-energy laser elements and applications.



SEM of hydrated colloidal silica particles with an average particle diameter = 600 nm.

Primary scattering centers in polycrystalline nanomaterials—made from the sintering of high purity nanoparticles and powders—include microstructural defects such as residual porosity and grain boundaries. Thus, opacity partly results from the incoherent scattering of light at internal surfaces and interfaces. In addition to porosity, most of the interfaces or internal surfaces in ceramic nanomaterials are in the form of grain boundaries which separate nanoscale regions of crystalline order. Moreover, when the size of the scattering center (or grain boundary) is reduced well below the size of the wavelength of the light being scattered, the light scattering no longer occurs to any significant extent.

In the processing of high performance ceramic nanomaterials with superior opto-mechanical properties under adverse conditions, the size of the crystalline grains is determined largely by the size of the crystalline particles present in the raw material during the synthesis or formation of the object. Thus a reduction of the original particle size well below the wavelength of visible light (~ 0.5 μm or 500 nm) eliminates much of the light scattering, resulting in a translucent or even transparent material.

Furthermore, results indicate that microscopic pores in sintered ceramic nanomaterials, mainly trapped at the junctions of microcrystalline grains, cause light to scatter and prevented true transparency. it has been observed that the total volume fraction of these nanoscale pores (both intergranular and intragranular porosity) must be less than 1% for high-quality optical transmission. I.E. The density has to be 99.99% of the theoretical crystalline density.

One example of such a material is that which has ben developed by researchers at the Fraunhofer Institute for Ceramic Technologies and Sintered Materials. This sintered alumina nanomaterial is very hard and virtually transparent over a range of wavelengths. Yet like other sintered materials using larger particles of larger diameter and less sophisticated processing methodologies, it can be produced at temperatures (1000-1200 °C) much lower than its melting point (2070 °C).

Advantages

Tests have clearly shown that the transparent nanomaterials have exceeded all expectations. For example, the amount of scattered light in the nanomaterials is similar to that measured from single crystalline Nd:YAG components. This is due primarily to the fact that grain boundaries, which act as the primary scattering centers in this theoretically dense material, measure something less than 1 nm in average width. In addition, the nanomaterials have exhibited no more wavefront distortion than that expected from surface polishing.

One research team has found that laser amplifier slabs made from nanomaterials offer several advantages over those made from single crystals. Perhaps most basic is that these slabs can be obtained in a regular, timely fashion without unexpected additional costs. Nanomaterials are more easily fabricated into larger sizes for greater power and they can also be made any size and shape—limited only by the size of the sintering furnace. The time required to produce such slabs of optically transparent nanomaterials is much shorter than the time to grow crystal boules of the same chemical composition. E.G.

Nanomaterials may be fabricated in several days, whereas it would take several weeks to grow single crystals of similar chemical composition.

Slabs made form nanomaterials are exhibit a higher value of fracture toughness (and stress intensity factor, K_{Ic}) than single-seed crystal slabs and much less prone to undergo a catastrophic failure or fracture. i.e. When a crystalline slab fractures, the propagation of primary crack is virtually unimpeded, yielding a large (and fairly linear) path of least resistance. Thus, the crack can easily "run", extending some distance from the original crack site and often branching or making a random turn towards the center of the crystal in order to relieve internal stress. In fine-grained nanomaterials, because crack propagation is impeded by grain boundaries, resistance to fracture is significant. Nanomaterials also exhibit lower residual stress, as evidenced by the increased distortion of the laser beam in crystalline materials, which can be a contributing factor to failure of the materials.

Nanomaoterials can accommodate higher concentrations of dopants (rare earth ions such as neodymium Nd^{3+} or yterbium Yb^{3+}) which could permit pumping at wavelengths that might otherwise be impractical. Dopant concentrations are quite homogeneous in nanomaterials and be precisely controlled. In crystals, dopants tend to segregate preferentially towards the bottom of the growing boule.

Nanomaterials also provide the possibility of novel composite structures. The different materials would be co-sintered in order to produce a single (monolithic) integral structure. Another possible approach is to embed different powders with the same host before sintering the slab in order to create a progressive and continuous concentration gradient of the dopant ions—a molecular configuration evidenced in some phase transformations in solids which proceed by the mechanism of spinodal decomposition.

Powder Prep

Nd:YAG

Initially, Akin prepared YAG powder by Self-Propagating Combustion synthesis. Then Chung used citrate gel methods for YAG powder synthesis. Also Graskite reported that the single-phase Ln:YAG (Ln = Ce, Nd, Ho, Er)is formed after heating of resulting powder by Sol-gel methods at 1000 C.

One group in Iran used Sol-gel methods for synthesizing Nd:YAG powder which can be sintered to transparency for laser applications. High purity Nd_2O_3, Y_2O_3 and $Al(NO_3)_3 \cdot 9 H_2O$ were used with stoichiometric amounts as the starting materials, including 4 atomic percent of Nd dopant. Initially, the neodymia and yttria powders were dissolved separately in acetic acid at 75 degrees C. This was then combined in solution with the aluminum nitrate and some distilled water, followed by stirring for 3 hours at about 65 degrees C. Then 1,2-ethanediol was added and stirred in thoroughly for about 3 hours at 65 C. The transparent gel formed after a final evaporation of fluid components at 65 C. The gel was then dried at 110 C, then grounded nad pre-heated at 800 C for 2 hours in air. The resulting white powder was ground finely and heated to 900 C for 2 hours in air. Microstructure and morphology of the powders were studied by EXDX analysis and Scanning Electron Microscopy.

Another group in India synthesized nanopowders of YAG which can be prepared by solution/ sol-gel methods. This method yields a precursor powder that forms a phase-pure YAG powder at a lower temperature due to better compositional homogeneity than can be achieved in the solution-based processing. A homogeneous co-precipitation technique is a process in which the particle size distribution and morphology can be tailored by appropriately choosing the precursors salt and modifying their concentrations and reaction temperature appropriately. Due to the molecular evolution of one of the reactants (e.g. ammonia from hydrolysis of urea) a minimum degree of local fluctuation of reactant concentration occurs, leading to the formation of a large number of nuclei, followed by orderly growth into compact particles. However, it would result in sequential precipitation in the case of a two component system due to he difference in the chemistry of different metals, but still results in the mixing of components in the nano- dimension, if not in the molecular level. If the precipitate is already gelled upon filtering and drying, then the particles get strongly agglomerated and require extensive grinding in order to form a powder. One way of getting rid of the problem is to form granular precursor powder directly in the desired particle size range by proper calcining at a higher temperature. In this study, the granular precursor powder was prepared by the homogeneous co-precipitation reaction of aqueous aluminum nitrate - yttrium nitrate-urea in the presence of ammonium sulfate was studied at 95 C.

$$Al(NO_3)_3 + Y(NO_3)_3 + (NH_4)_2SO_4 + CO(NH_2)_2$$

The chemistry of the Al^{3+} and the Y^{3+} are such that precipitation begins at a ph ~ 4.5 and ends at a pH ~ 6.5.

Using the yttria powder produced from the method described here and a commercial ultrafine Al_2O_3 powder, fully transparent YAG nanomaterials were fabricated by vacuum sintering at 1700 °C for 4 h through a solid-state reaction method. It was found that the addition of 0.5 wt.% tetraethyl orthosilicate (TEOS) is suitable for successful processing and fabrication. If the amount of TEOS is less than 0.05 wt.%, abnormal grain growth occurs, and intergranular pores become entrapped. If the amount of TEOS is more than 3 wt.%, a large amount of liquid phase is yielded, leaving some residual inclusions at grain boundaries which cause some light scattering and attenuation.

Yttria, Y_2O_3

One group in China describes a precipitation process for synthesizing nanocrystalline yttria powder and sintering transparent yttria ceramics. In this work, a hydroxide precursor of Y_2O_3 with an approximate composition of [$Y_2OH \cdot 5\ NO_3 \cdot H2O$] was synthesized by using ammonia water as precipitant (and morphological catalyst) and yttrium nitrate as the starting salt. Employing appropriate striking method and optimum synthetic conditions, yttrium hydroxide with a card-house or spherical structure can be formed. The addition of a small amount of ammonia sulfate in the yttrium nitrate solution reduces the agglomeration and particle size of the produced yttria powders. Yttria nanoparticels of 60 nm diameter were obtained by calcining the precursor at 1100 °C for 4 hours. Transparent yttria nanomaterials were fabricated from the nanopowders by vacuum sintering at 1700 °C for 4 hours.

Huang emphasized that pH value at the end of the precipitation process has a significant effect on the size and morphology of the precursor and the yttria powders. Under the same calcination condition, the yttria powders made from the precursor obtained at a pH of 8 are smaller in mean particle size and narrower in size distribution than those made from the precursor obtained at a pH of 10. It was found that the optimum calcination temperature is 1000 °C, and the yttria powder obtained is fine (30 nm) and well dispersed. Using the yttria powder, transparent yttria nanomaterials were produced by vacuum sintering at 1700 °C for 4 hours without any additives.

In Jeong's synthesis by precipitation, three different precipitants such as NH_4OH, mixture of NH_4OH and NH_4HCO_3 and NH_4HCO_3 were used. It was observed that the size of yttria powder is significantly affected by type of precipitant depending on the rate of formation of precipitate. It is seen that NH_4HCO_3 shows the most significant pH decrease during the formation of Y_2CO_3, thus leading to the formation of large crystalline nanoparticles. The result also shows that the crystal size depends on calcinations temperature, and that the degree of agglomeration is more significant beyond 800 °C where the morphology has changed from flake to spherical shapes which are connected to each other. Finally, the nano-sized yttria powder of on the average 114 nm shows excellent uniform coating, sufficient transmittance and excellent brightness for lamp.

Dupont utilized a sol–gel method which they adopted to synthesize a precursor gel which, after being heated, leads to high purity Y_2O_3 nanopowders. In these studies, two main parameters are taken into account: the nature of the chelating agent and the relative concentrations of yttrium to the chelating agent. The influence of these parameters on the composition and crystallization state of the precursor gel has been studied in the first part and on the grain morphologies of the resulting yttria powder in the second part. It has been shown that, depending on the chelating agent, nanometric powders presenting either needles, platelets or spherical shapes can actually be obtained at 800°C or 1100°C.

Comparison has been made of the achievable purity levels and agglomeration characteristics of zirconia powders obtained via six different wet chemical routes where the starting material was an impure Zr-oxychloride solution obtained from Indian zircon sand. For the highest purity (2–15 ppm of other oxides except Hf), two routes were found to be effective: crystallization of the oxychloride via the basic sulphate, or double crystallization of the oxychloride, followed by dissolution and hydroxide precipitation. The average agglomerate size was the largest (10–15 µm) for the powders obtained by direct decomposition of the basic sulphate at 1000°C, though the size distribution was narrow and distinctly monomodal. For smaller agglomerates (1.5 – 2.5 µm), on the other hand, the size distribution was very wide. Calcination at 800°C of powders obtained via hydroxide precipitation from a solution always yielded only tetragonal zirconia as the crystalline phase. Roles of calcination and sintering schedules on the final sintered density and microstructure of yttria powder compacts and nanomaterials were studied by Rasmussen. The studies of his group showed clearly that the optimum calcination procedure appeared to be at 1000°C and for one hour in air atmosphere. Final sintered density of 95% theoretical was achieved around 1450° and nearly pore free (>99% theoretical) pellets were obtained at 1650°C for one hour sintering in vacuum. High heating/cooling rates when coupled with high sintering temperature caused discontinuous grain growth and large internal cracks in the final stages of densification.

La-doped yttria powder was synthesized by a co-precipitation method using ammonia for pH control. After calcinations, finer particles with narrow distribution and large surface area were obtained. After dry pressing, samples were sintered at 1500–1700° for 4 h in vacuum to produce transparent nanomaterials with uniform grain size. Samples with 9 mol% lanthanum were transparent in visible light after being sintered at 1500° for 4 h. The grain sizes increased with lanthanum doping levels, in comparison to those of pure yttria under the same conditions. The relative density of the transparent ceramic was 99.7%. The in-line transmittance was 73% at 580 nm wavelength after milling and polishing.

Lasers

Nd:YAG

For example, a 1.46 kW Nd:YAG laser has been demonstrated by Konoshima Chemical Co. in Japan. In addition, Livermore researchers realized that these fine-grained ceramic nanomaterials 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 nanomaterials 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.

Assisted by several workers from the NIF, the Livermore team has produced 15 mm diameter samples of transparent Nd:YAG from nanoscale particles and powders, and determined the most important parameters affecting their quality. In the these objects, the team largely followed the Japanese production and processing methodologies, and used an in house furnace to vacuum sinter the nanopowders. All specimens were then sent out for hot isostatic pressing (HIP). Finally, the components were returned to Livermore for coating and testing, with results indicating exceptional optical quality and properties.

One Japanese/East Indian consortium has focused specifcially on the spectroscopic and stimulated emission characteristics of Nd^{3+} in transparent YAG nanomaterials for laser applications. Their materials were synthesized using vacuum sintering techniques. The spectroscopic studies suggest overall improvement in absorption and emission and reduction in scattering loss. SEM and TEM observations revealed an excellent optical quality with low pore volume and narrow grain boundary width. Fluorescence and

Raman measurements reveal that the Nd^{3+} doped YAG nanomaterial is comparable in quality to its single-crystal counterpart in both its radiative and non-radiative properties. Individual Stark levels are obtained from the absorption and fluorescence spectra and are analyzed in oredr to identify the stimulated emission channels possible in the material. Laser performance studies favor the use of high dpoant concentration in the design of an efficient microchip laser. With 4 at% dopant, the group obtained a slope efficiency of 40%. High-power laser experiments yield an optical-to-optical conversion efficiency of 30% for Nd (0.6 at%) YAG nanomaterial as compared to 34% for an Nd (0.6 at%) YAG single crystal. Optical gain measurements conducted in these materials also show values comparable to single crystal, supporting the contention that these materials could be suitable substitutes to single crystals in solid-state laser applications.

Yttria, Y_2O_3

The initial work in developing transparent yttrium oxide nanomaterials was carried out by General Electric in the 1970s, motivated by lighting and ceramic laser applications. Greskovich and Woods fabricated transparent yttrium oxide Y_20_3 containing ~ 10% thorium oxide (ThO_2) which they called Yttralox™. The additive served to control grain growth during densificaiotn, so that porosity remained on grian boundaries and not trapped inside grains where it would be quite difficult to eliminate during the initial stages of sintering. Typically, as polycrystalline ceramics densify during heat treatment, grains grow in size while the remaining porosity decreases both in volume fraction and in size. Optically transparent ceramics must be virtually pore-free.

GE's transparent Yttralox™ was folllowed by GTE's lanthana-doped yttria with similar level of additive. Both of these materials required extended firing times at temperatures above 2000 C. La_20_3 - doped Y_20_3 is of interest for infrared (IR) applications because it is one of the longest wavelength transmitting oxides. It is refractory with a melting point of 2430 deg C and has a moderate coefficient of thermal expansion coefficient. The thermal shock and erosion resistance is considered to be intermediate among the oxides, but outstanding compared to non-oxide IR transmitting materials. A major consideration is the low emissivity of yttria, which limits background radiation upon heating. It is also known that the phonon edge gradually moves to shorter wavelengths as a material is heated.

In addition, ytrria itself, Y_2O_3 has been clearly identified as a prospective solid-state laser material. In particular, lasers with ytterbium as dopant allow the efficient operation both in cw operation and in pulsed regimes. At high concentration of excitations (of order of 1%) and poor cooling, the quenching of emission at laser frequency and avalanche broadband emission takes place.

Future

The Livermore team is also exploring new ways to chemically synthesize the initial nanopowders. Borrowing on expertise developed in CMS over the past 5 years, the team is synthesizing nanopowders based on sol-gel processing, and then sintering them accordingly in order to obtain the solid-state laser components. Another technique being tested utilizes a combustion process in order to generate the powders by burning an organic solid containing yttrium, aluminum, and neodymium. The smoke is then collected, which consists of spherical nanoparticles.

The Livermore team is also exploring new forming techniques (e.g. extrusion molding) which have the capacity to create more diverse, and possibly more complicated, shapes. These include shells and tubes for improved coupling to the pump light and for more efficient heat transfer. In addition, different materials can be co-extruded and then sintered into a monolithic transparent solid. E.G. An amplifier slab can formed so that part of the structure acts in guided lightwave transmission in order to focus pump light from laser diodes into regions with a high concentration of dopant ions near the slab center.

In general, nanomaterials promise to greatly expand the availability of low-cost, high-end laser components in much larger sizes than would be possible with traditional single crystalline ceramics. E.G. Many classes of laser designs could benefit from nanomaterial-based laser structures such as amplifies with built-in edge claddings. Nanomaterials could also provide more robust and compact designs for high-peak power, fusion-class lasers for stockpile stewardship, as well as high-average-power lasers for global theater ICBM missile defense systems (e.g. Strategic Defense Initiative SDI, or more recently the Missile Defense Agency.

Night vision

Panoramic Night Vision Goggles in testing

A night vision device (NVD) is an optical instrument that allows images to be produced in levels of light approaching total darkness. They are most often used by the military and law enforcement agencies, but are available to civilian users. Night vision devices were first used in World War II and came into wide use during the Vietnam War. The technology has evolved greatly since their introduction, leading to several "generations" of night vision equipment with performance increasing and price decreasing. The United States Air Force is experimenting with Panoramic Night Vision Goggles (PNVGs) which double the user's field of view to around 95 degrees by using four 16 mm image intensifiers tubes, rather than the more standard two 18 mm tubes.

Thermal images are actually visual displays of the amount of infrared (IR) energy emitted, transmitted, and reflected by an object. Because there are multiple sources of the infrared energy, it is difficult to get an accurate temperature of an object using this method. A thermal imaging camera is capable of performing algorithms to interpret that data and build an image. Although the image shows the viewer an approximation of the temperature at which the object is operating, the camera is actually using multiple sources of data based on the areas surrounding the object to determine that value rather than detecting the actual temperature.

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

Night vision infrared devices image in the near-infrared, just beyond the visual spectrum, and can see emitted or reflected near-infrared in complete visual darkness. All objects above the absolute zero temperature (0 K) emit infrared radiation. Hence, an excellent way to measure thermal variations is to use an infrared vision device, usually a focal plane array (FPA) infrared camera capable of detecting radiation in the mid (3 to 5 μm) and long (7 to 14 μm) wave infrared bands, denoted as MWIR and LWIR, corresponding to two of the high transmittance infrared windows. Abnormal temperature profiles at the surface of an object are an indication of a potential problem. Infrared thermography, thermal imaging, and thermal video, are examples of infrared imaging science. Thermal imaging cameras detect radiation in the infrared range of the electromagnetic spectrum (roughly 900–14,000 nanometers or 0.9–14 µm) and produce images of that radiation, called *thermograms*.

Since infrared radiation is emitted by all objects near room temperature, according to the black body radiation law, thermography makes it possible to see one's environment with or without visible illumination. The amount of radiation emitted by an object increases with temperature. Therefore, thermography allows one to see variations in temperature. When viewed through a thermal imaging camera, warm objects stand out well against cooler backgrounds; humans and other warm-blooded animals become easily visible against the environment, day or night. As a result, thermography is particularly useful to the military and to security services.

Thermogram of a lion

Thermography

Thermography has a long history, although its use has increased dramatically with the commercial and industrial applications of the past fifty years. Firefighters use thermography to see through smoke, to find persons, and to localize the base of a fire. Maintenance technicians use thermography to locate overheating joints and sections of power lines, which are a tell-tale sign of impending failure. Building construction technicians can see thermal signatures that indicate heat leaks in faulty thermal insulation and can use the results to improve the efficiency of heating and air-conditioning units. Some physiological changes in human beings and other warm-blooded animals can also be monitored with thermal imaging during clinical diagnostics.

In thermographic imaging, infrared radiation with wavelengths between 8-13 microns strikes the detector material, heating it and thus changing its electrical resistance. This resistance change is measured and processed into temperatures which can be used to create an image. Unlike other types of infrared detecting equipment, microbolometers utilizing a transparent ceramic detector do not require cooling. Thus, a microbolometer is essentially an uncooled thermal sensor.

Seen through a Night Vision Device (NVD), paratroopers conduct a raid on a suspected terrorist's home in Fallujah, Iraq. The soldiers are assigned to the: *82nd Airborne Division's Company B, 1st Battalion, 505th Parachute Infantry Regiment, U.S. Army.*

The material used in the detector must demonstrate large changes in resistance as a result of minute changes in temperature. As the material is heated, due to the incoming infrared radiation, the resistance of the material decreases. This is related to the material's temperature coefficient of resistance (TCR) specifically its negative temperature coefficient. Industry currently manufactures microbolometers that contain materials with TCRs near -2%.

VO_2 and V_2O_5

The most commonly used ceramic material in IR radiation microbolometers is vanadium oxide. The various crystalline forms of vanadium oxide include both VO_2 and V_2O_5. Deposition at high temperatures and performing post-annealing allows for the production of thin films of these crystlalline compounds with superior properties, which may be easily integrated into the fabrication process. VO_2 has low resistance but undergoes a metal-insulator phase change near $67^{o}C$ and also has a lower TCR value. On the other hand, V_2O_5 exhibits high resistance and also high TCR.

Other IR transparent ceramic materials that have been investigated include doped forms of CuO, MnO and SiO.

Missiles

AIM-9 Sidewinder

Place of origin	United States

Many ceramic nanomaterials of interest for transparent armor solutions are also used for electromagnetic (EM) windows. These applications include radomes, IR domes, sensor protection, and multi-spectral windows. Optical properties of the materials used for these applications are critical, as the transmission window and related cut-offs (UV - IR)control the spectral bandwidth over which the window is operational. Not only must these materials possess abrasion resistance and strength properties common of most armor applications, but due to the extreme temperatures associated with the environment of military aircraft and missiles, the must also possess excellent thermal stability.

Thermal radiation is electromagnetic radiation emitted from the surface of an object which is due to the object's temperature. Infrared homing refers to a passive missile guidance system which uses the emission from a target of electromagnetic radiation in the infrared part of the spectrum to track it. Missiles that use infrared seeking are often referred to as "heat-seekers", since infrared is just below the visible spectrum of light in frequency and is radiated strongly by hot bodies. Many objects such as people, vehicle engines and aircraft generate and retain heat, and as such, are especially visible in the infrared wavelengths of light compared to objects in the background.

Sapphire

The current material of choice for high-speed infrared-guided missile domes is single-crystal sapphire. The optical transmission of sapphire does not actually extend to cover the entire mid-infrared range (3–5 μm), but starts to drop off at wavelengths greater than approximately 4.5 μm at room temperature. While the strength of sapphire is better than that of other available mid-range infrared dome materials at room temperature, it weakens above ~600 °C.

Limitations to larger area sapphires are often business related, in that larger induction furnaces and costly tooling dies are necessary in order to exceed current fabrication limits. However, as an industry, sapphire producers have remained competitive in the face of coating-hardened glass and new ceramic nanomaterials, and still managed to offer high performance and an expanded market.

Yttria, Y_2O_3

Alternative materials, such as yttrium oxide, offer better optical performance, but inferior mechanical durability. Future high-speed infrared-guided missiles will require new domes that are substantially more durable than those in use today, while still retaining maximum transparency across a wide wavelength range. A long standing trade-off exists between optical bandpass and mechanical durability within the current collection of single-phase infrared transmitting materials, forcing missile designers to compromise on system performance. Optical nanocomposites may present the opportunity to engineer new materials that overcome this traditional compromise.

The first full scale missile domes of transparent yttria manufactured from nanoscale ceramic powders were developed in the 1980s under Navy funding. Raytheon perfected and characterized its undoped polycrystalline yttria, while lanthana-doped yttria was similarly developed by GTE Labs. The two versions had comparable IR transmittance, fracture toughness, and thermal expansion, while the undoped version exhibited twice the value of thermal conductivity.

Renewed interest in yttria windows and domes has prompted efforts to enhance mechanical properties by using nanoscale materials with submicron or nanosized grains. In one study, three vendors were selected to provide nanoscale powders for testing and evaluation, and they were compared to a conventioanl (5 μm) yttria powder previously used to prepare transparent yttria. While all of the nanopowders evaluated had impurity levels that were too high to allow processing to full transparency, 2 of them were processed to theoretical density and moderate transparency. Samples were sintered to a closed pore state at temperatures as low as 1400 C.

After the relatively short sintering period, the component is placed in a hot isostatic press (HIP) and processed for 3 – 10 hours at ~ 30 kpsi(~200 MPa) at a temperature similar to that of the initial sintering. The applied isostatic pressure provides additional driving force for densification by substantially increasing the atomic diffusion coefficients, which promotes additional viscous flow at or near grain boundaries and intergranular pores. Using this method, transparent yttria nanomaterials were produced at lower temperatures, shorter total firing times, and without extra additives which tend to reduce the thermal conductivity.

Recently, a newer method has been devleoped by Mouzon, which relies on the methods of glass-encapsulation, combined with vacuum sintering at 1600 °C followed by hot isostatic pressing (HIP) at 1500 °C of a highly agglomerated commercial powder. The use of evacuated glass capsules to perform HIP treatment allowed samples that showed open porosity after vacuum sintering to be sintered to transparency. The sintering response of the investigated powder was studied by careful microstructural observations using scanning electron microscopy and optical microscopy both in reflection and transmission. The key to this method is to keep porosity intergranular during pre-sintering, so that it can be removed subsequently by HIP treatment. It was found that agglomerates of closely packed particles are helpful to reach that purpose, since they densify fully and leave only intergranular porosity.

Composites

Prior to the work done at Raytheon, optical properties in nanocomposite ceramic materials had received little attention. Thier studies clearly demonstrated near theoretical transmission in nanocomposite optical ceramics for the first time. The yttria/magnesia binary system is an ideal model system for nanocomposite formation. There is limited solid solubility in either one of the constituent phases, permitting a wide range of compositions to be investigated and compared to each other. According to the phase diagram, bi-phase mixtures are stable for all temperatures below ~ 2100 degrees C. In addition, neither yttria nor magnesia shows any absorption in the 3 - 5 μm mid-range IR portion of the EM spectrum.

In optical nanocomposites, two or more interpenetrating phases are mixed in a sub-micrometer grain sized, fully dense body. Infrared light scattering can be minimized (or even eliminated) in the material as long as the grain size of the individual phases is significantly smaller than infrared wavelengths. Experimental data suggests that limiting the grain size of the nanocomposite to approximately 1/15th of the wavelength of light is sufficient to limit scattering.

Nanocomposites of yttria and magnesia have been produced with a grain size of approximately 200 nm. These materials have yielded good transmission in the 3-5 μm range and strengths higher than that for single-phase individual constituents. Enhancement of mechanical properties in nanocomposite ceramic materials has been extensively studied. Significant increases in strength (2–5 times), toughness (1–4 times), and creep resistance have been observed in systems including SiC/Al_2O_3, SiC/Si_3N_4, SiC/MgO, and Al_2O_3/ZrO_2.

The strengthening mechanisms observed vary depending on the material system, and there does not appear to be any general consensus regarding strengthening mechanisms, even within a given system. In the SiC/Al_2O_3 system, for example, it is widely known and accepted that the addition of SiC particles to the Al_2O_3 matrix results in a change of failure mechanism from intergranular (between grains) to intragranular (within grains) fracture. The explanations for improved strength include:

- A simple reduction of processing flaw concentration during nanocomposite fabrication.
- Reduction of the critical flaw size in the material—resulting in increased strength as predicted by the Hall-Petch relation)
- Crack deflection at nanophase particels due to residual thermal stresses introduced upon cooling form processing temperatures.
- Microcracking along stress-induced dislocations in the matrix material.

Armor

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.

Existing transparent armor systems typically have many layers, separated by polymer (e.g. polycarbonate) interlayers. The polymer interlayer is used to mitigate the stresses from thermal expansion mismatches, as well as to stop crack propagation from ceramic to polymer. The polycarbonate is also currently used in applications such as visors, face shields and laser protection goggles. The search for lighter materials has also led to investigations into other polymeric materials such as transparent nylons, polyurethane, and acrylics. The optical properties and durability of transparent plastics limit their use in armor applications. Investigations carried out in the 1970s had shown promise for the use of polyurethane as armor material, but the optical properties were not adequate for transparent armor applications.

Several glasses are utilized in transparent armor, such as normal plate glass (soda-lime-silica), borosilicate glasses, and fused silica. Plate glass has been the most common glass used due to its low cost, but greater requirements for the optical properties and ballistic performance have generated the need for new materials. Chemical or thermal treatments can increase the strength of glasses, and the controlled crystallization of certain glass systems can produce transparent glass-ceramics. The AREVA T&D Technology Centre (Stafford, UK), currently produces a lithium disilicate based glass-ceramic known as TransArm, for use in transparent armor systems. The inherent advantages of glasses and glass-ceramics include having lower cost than most other ceramic materials, the ability to be produced in curved shapes, and the ability to be formed into large sheets.

Transparent crystalline ceramics are used to defeat advanced threats. Three major transparent candidates currently exist: aluminum oxynitride (AlON), magnesium aluminate spinel (spinel), and single crystal aluminum oxide (sapphire). Aluminum oxynitride spinel ($Al_{23}O_{27}N_5$), one of the leading candidates for transparent armor, is produced by Raytheon Corporation as AlON and marketed under the trade name Raytran. The incorporation of nitrogen into an aluminum oxide stabilizes a spinel phase, which due to its cubic crystal structure, is an isotropic material that can be produced as a transparent polycrystalline material. Polycrystalline materials can be produced in complex geometries using conventional ceramic forming techniques such as pressing, (hot) isostatic pressing, and slip casting.

AlON^R

Aluminum oxynitride spinel ($Al_{23}O_{27}N_5$), one of the leading candidates for tranparent armor, is produced by the Raytheon Corporation as AlON^TM and marketed under the trade name Raytran^TM. The incorporation of nitrogen into aluminum oxide stbailizes a crystalline spinel phase, which due to its cubic crystal structure and unit cell, is an isotropic material which can be produced as transparent ceramic nanomaterial. Thus, fine-grained polycrystalline nanomaterials can be produced and formed into complex geometries using conventional ceramic forming techniques such as hot pressing and slip casting.

The Surmet Corporation has acquired Raytheon's ALON^R business and is currently building a market for this technology in the area of point-of-sale scanner windows and as an alternative to quartz and sapphire in the semiconductor market. The high hardness of AlON^TM provides a scratch resistance which exceeds even the most durable coatings for glass scanner windows, such as those used in supermarkets. Surmet has successfully produced a 15" by 18" curved ALON^R window and is currently attempting to scale up the technology and reduce the cost. In addition, the U.S. Army and U.S. Air Force are both pushing the envleope for development into next generation applications.

Spinel

Magnesium aluminate spinel ($MgAl_2O_4$) is a transparent ceramic with a cubic crystal structure with an excellent optical transmission from 0.2 to 5.5 microns in its polycrystlalline form. Optical quality transparent spinel has been produced by sinter/HIP, hot pressing, and hot press/HIP operaiotns, and it has been shown that the use of a hot isostatic press can improve its optical and physical properties.

As shown clearly in the field demonstration in this Online video clip a Spinel ceramic plate can survive a direct hit from a .50 BMG round fired at close range. By all indications, this is an important new technology that should find its way into military vehicles in the near future. ArmorLine's manufacturing facility, scheduled to come on-line in the first quarter of 2011, will supply transparent spinel ceramic plates to window, lens, and optical system suppliers and end-users.

Spinel offers some processing advantages over AlON^{TM}, such as the fact that spinel powder is available from commercial manufacturers while AlON powders are proprietary to Raytheon. It is also capable of being processed at much lower temperatures than AlON^{TM}, and has been shown to possess superior optical properties within the infrared (IR) region. The improved optical characteristics make spinel attractive in sensor applications where effective communication is impacted by the protective missile dome's absorption characteristics.

Spinel shows promise for many applications, but is currently not available in bulk form from any manufacturer, although efforts to commercialize spinel are underway. The spinel products business is being pursued by two key U.S. manufacturers: "Technology Assessment and Transfer" and the "Surmet Corporation".

An extensive NRL review of the literature has indicated clearly that attempts to make high-quality spinel have failed to date because the densification dynamics of spinel are poorly understood. They have conducted extensive research into the dynamics involved during the densification of spinel. Their research has shown that LiF, although necessary, also has extremely adverse effects during the final stages of densification. Additionally, its distribution in the presursor spinel powders is of critical importance.

Traditional bulk mixing processes used to mix LiF sintering aid into a powder leave failry inhomogeneous distribution of Lif that must be homogenized by extended heat treatment times at elevated temperatures. The homogenizing temperature for Lif/Spinel occurs at he temperatureof fast reaction between the LiF and the Al_2O_3. In order to avoid this detrimental reaction, they have developed a new process that uniformly coats the spinel particles with the sintering aid. This allows them to reduce the amount of Lif necessary for densificaiotn and to rapdily heat through the temperature of maximum reactivity. These developments have allowed NRL to fabricate $MgAl_2O_4$ spinel to high transparency with extremely high reproducibility that should enable military as well as commercial use of spinel.

Sapphire

Synthetic sapphire

Single-crystal aluminum oxide (sapphire – Al_2O_3) is a transparent ceramic. Sapphire's crystal structure is rhombohedral and thus its properties are anisotropic vary with crystallographic orientation. Transparent alumina is currently one of the most mature transparent ceramics from a production and application perspective, and is available from several manufacturers. But the cost is high due to the processing temperature involved, as well as machining costs to cut parts out of single crystal boules. It also has a very high mechanical strength – but that is dependent on the surface finish.

The high level of maturity of sapphire from a production and application standpoint can be atrributed to two areas of business: EM windows for missiles and domes, and electronic/semiconductor industries and applications.

There are current programs to scale-up sapphire grown by the heat exchanger method or edge defined film-fed growth (EFG) processes. Its maturity stems from its use as windows and in semiconductor industry. Crystal Systems Inc. which uses single crystal growth techniques, is currently scaling their sapphire boules to 13-inch (330 mm) diameter and larger. Another producer, the Saint-Gobain Group produces transparent sapphire using an edge, defined growth technique. Sapphire grown by this technique produces an optically inferior material to that which is grown via single crystal techniques, but is much less expensive, and retains much of the hardness, transmission, and scratch-resistant characteristics. Saint-Gobain is currently capable of producing 0.43" thick (as grown)sapphire, in 12" × 18.5" sheets, as well as thick, single-curved sheets.ARL is currently investigating use of this material in a laminate design for transparent armor systems. The Saint Gobain Group have commercialized the capability to meet flight requirements on the F-35 Joint Strike Fighter and F-22 Raptor next generation fighter aircraft.

Composites

Future high-speed infrared-guided missiles willl require new dome materials that are substantially more durable than those inuse today, while retinaing maximum transparency across the entire operational spectrum or bandwidth. A long-standing compromise exists between optical bandpass and mechanical durability within the current group of single-phase (crystalline or glassy) IR transmitting ceramic materials, forcing missile designers to accept substandard overall system performance. Optical nanocomposites may provide the opportunity to engineer new materials that may overcome these traditional limitations.

For example, transparent ceramic armor consisting of a light weight composite has been formed by tilizing a face plate of transparent alumina Al_2O_3 (or magnesia MgO) with a back-up plate of transparent plastic. The two plates (bonded together with a transparent adhesive) afford complete ballistic protection against 0.30 AP M2 projectiles at 0° obliquity with a muzzle velocity of 2770 ft. per second. Another transparent composite armor provided complete protection for small arms projectiles up to and including caliber .50 AP M2 projectiles consisting of two or more layers of transparent ceramic material.

Nanocomposites of yttria and magnesia have been produced with an average grain size of ~ 200 nm. These materials have exhibited near theoretical transmission in the 3 - 5 μm IR band. Additionally, such composites have yielded higher strengths than those observed for single phase solid-state components. Despite a lack of agreement regarding mechanism of failure, it is widely accepted that nanocomposite ceramic materials can and do offer improved mechanical properties over those of single phase materials or nanomaterials of uniform chemical composition.

It should also be noted here that nanocomposite ceramic materials also offer interesting mechanical properties not achievable in other materials, such as superplastic flow and metal-like machinability. It is anticipated that further development will result in high strength, high transparency nanomaterials which are suitable for application as next generation armor..

Future

With regard to future developments, a European consortium of companies and institutions has been working to develop a transparent alumina Al_2O_3. The main objective is the development of significantly improved alumina ceramic nanomaterials with an extremly reduced grain size. These components must exhibit the following physical properties: exceptional mechanical strength ~700 MPa; high optical transparency; improved corrosion resistance (e.g. against metal halides); and a complex hollow shape (vs. cylindrical). The improved material should solve problems in existing applications (e.g. metal halide lamps) and may lead to new applications such as scratch-resistant windows for bar-code scanners (now sapphire). Improvements in metal halide lamps could lead to substantial energy savings up to 7 billion kWh in Europe, which corresponds to one big power station or 4.5 million tons of CO_2 production.

Researchers at OSU have made significant advances in the emerging science of transparent electronics, creating transparent copper oxide (CuO) based semiconductors which exhibit more than 200 times the conductivity of previously competitive materials. This basic research is opening the door to new types of electronic circuits which, when deposited onto glass, are literally invisible. The studies are so cutting edge that the products which could emerge from them have not yet been invented—although they may find applications ranging everywhere from flat-panel displays (e.g. automobile dashboard displays) to invisible circuits on screens and visors.