The Materials Information Service helps those interested in improving their knowledge of engineering materials and highlights the national network of materials expertise.

This Profile is one of a series produced by the Materials Information Service.

For advice relating to your particular materials problem, you can contact the MIS at:

The Materials Information Service
The Institute of Materials, Minerals and Mining
Danum House, South Parade
Doncaster DN1 2DY

Tel: 01302 320 486
Fax: 01302 380 900
Introduction

Demand for engineering materials to withstand more and more hostile environments is increasing as pressure for greater efficiency continues. In this regard, ceramics are pre-eminent. Properties typical of engineering ceramics which make them ideal for use in such environments include: high compressive strength, high specific stiffness, retention of strength at elevated temperature, high hardness, wear resistance, corrosion resistance and good thermal insulation characteristics. It has been estimated that by the year 2000, ceramics in automobile engines alone could cut the world's annual energy bill by several £billions, as they allow hotter operating temperatures and the hotter an engine operates, the more efficiently it runs. Figure 1 illustrates some of the potential uses of ceramics in automobile engines. Hence, there is considerable current interest in engineering ceramics.

![Fig.1: Potential uses of advanced ceramic components in auto engines](image)

Production Techniques

Although the manufacture of ceramics is probably one of the oldest technologies known to mankind (ceramic utensils have been found in ruins dating back thousands of years), research and development in ceramics is very active at present. In contrast to "conventional" ceramics, e.g. crockery and sanitary ware, which are generally cast and kiln-fired, engineering ceramics are often produced at high temperatures and pressures in a process known as hot isostatic pressing (HIP or 'HIPping'). Alternatively, they may be plasma sprayed to form a coating, often on
metallic substrates. The resulting ceramics have an extremely fine grain size and can be virtually free of residual pores and defects. The attainment of high strength, high hardness, etc. is largely dependent on both starting powders and fabrication technique. A typical process flow diagram for the production of engineering ceramics is shown in Figure 2. Flaw elimination at all process stages is important for not only high strength but also high reliability. Clean-room processing can result in critical flaws of the order of 20 m, which has been shown to significantly enhance both mean strengths and the distribution of strengths as measured by the Weibull modulus, a statistical parameter often used for ceramics. In general, the critical flaw size for components is less than 50 m, but such defects cannot, as yet, be detected by non-destructive techniques such as ultrasonic testing or X-rays for sections thicker than about 1 mm. At present, the only suitable technique for obtaining verification of a ceramic component's mechanical reliability is by subjecting it to very short duration overload proof testing.

Raw material suppliers are now offering a range of starting powders which are highly sinter-active. The small particle sizes (typically 25 nm) and resultant high surface areas of these powders, together with high purity and chemical homogeneity, allow complete densification at temperatures as low as 1400°C. Powders with high green
density to prevent warpage are also now available. Keen competition has led to significant decreases in powder costs (>50% in some cases). However, in most instances the powder cost only constitutes about 10% of the component cost, with diamond grinding to precise tolerances often accounting for a large part of the manufacturing cost.

**Mechanical Properties**

The most notable advantage of ceramics over metals for engineering applications is their retention of high strength at elevated temperatures. However, the design concepts developed for metals cannot simply be transferred to the field of engineering ceramics. This is because of basic differences in the way metals and ceramics fail when put under a destructive load. The bonding in metals is by electrons that are only weakly bound to nuclei, allowing plastic deformation to occur upon loading by movement of dislocations. Dislocation movement during stressing is generally inhibited in ceramic materials at ambient temperature due to strong ionic or covalent bonding, and therefore very limited plastic deformation takes place. In the absence of extensive plastic deformation, stresses are concentrated around flaws such as cracks and pores within a ceramic body under load, since there is no mechanism by which the stresses may be reduced. Flaws at which the stress increases to a point where it exceeds the local fracture strength of the material will act as crack nucleation sites, and, in the absence of energy absorption processes, the crack will rapidly extend until catastrophic failure results.

Oxide ceramics have, in the main, ionic bonding, which results in strongly bound, closely packed atomic arrangements. This gives oxide ceramics relatively high densities, high strength and hardness and very high melting points (e.g. zirconia melts at 2770°C). Such materials are suitable for use in oxidizing, neutral or slightly reducing atmospheres at ambient to moderate temperatures under low or high stresses. On-oxide ceramics generally have covalent bonding, resulting in very strong directional bonds giving a more open atomic arrangement. Such materials are of lower density, good strength and very high hardness. Many non-oxides have high melting points or dissociation temperatures (e.g. Si₃N₄ dissociates at 1830°C). These materials are generally only suitable in reducing conditions at high temperatures, but can be used in most environments at ambient temperature. Of course, before such materials can be used in-service, perhaps under severe thermal and mechanical loading in large-scale commercial applications, their reliability and durability must be properly assessed.

Although the wear resistance of engineering ceramics is advantageous in many applications, it does make them difficult to machine and prototype costs can be high. Their high hardness can, in certain circumstances, lead to an increase in wear, as any debris that is not removed from a wear surface can itself generate high point stresses, accelerating the wear process. The high stiffness and often low toughness of ceramics means that they do not usually display good impact resistance, although toughened ceramics are being developed.
**Toughened Ceramics**

Failure occurs from flaws within a ceramic (intrinsic flaws) at ambient temperature, and/or newly generated flaws at elevated temperature, and there are two basic methods for improving reliability: (i) reduce the size and/or number of flaws or (ii) increase the amount of energy absorbed by the ceramic whilst the crack is propagating, i.e. increase the fracture toughness. Point (i) can be achieved by refinement of the raw material and the fabrication process for the required ceramic, as discussed above. Point (ii) can be achieved by judicious microstructural design of monolithic ceramics or by using ceramic matrix composite (CMC) materials.

Microstructural design has led to transformation toughened ceramics. The key to transformation toughening in ceramics containing zirconia particles with tetragonal symmetry on an atomic scale is that the tetragonal to monoclinic symmetry transformation, which usually occurs in bulk ZrO₂ at approximately 1100°C, is suppressed except in the stress field of propagating cracks. Tetragonal zirconia transforms to monoclinic zirconia with a 3.5% volume increase, thus putting the material in compression (see Figure 3). This compressive force leads to a reduction in the tensile stress at the crack tip thus constituting an increase in toughness. Zirconia may be used in its own right as partially stabilised zirconia (PSZ) or as tetragonal zirconia polycrystals (TZP), or as a toughening agent in other ceramics such as zirconia toughened alumina (ZTA) and zirconia toughened mullite (ZTM).

![Fig.3: Schematic of the stress induced transformation toughening mechanism which operates in zirconia ceramics. Energy is expended by the advancing crack in transforming tetragonal particles to monoclinic and compressive strain within the process zone exerts back-stress on the crack.](image)

Production of CMCs involves the addition of a second reinforcing phase to the ceramic matrix, and leads to enhanced fracture toughness via additional energy
absorbing mechanisms, the nature of which is dependent on the type of reinforcing phase. Furthermore, due to the variety of reinforcements available, this gives the ceramicist the ability to tailor the composite material to the application by controlling the mechanical properties as well as properties such as the thermal expansion and thermal conductivity. The major difference between the characteristics of composite and monolithic ceramics during mechanical loading is that the former generally fails progressively with different damage modes at different stress states whereas the latter fails by initiation and propagation of discrete cracks, i.e. catastrophically. There are four main types of ceramic composites:

(i) Glass-Ceramics - ceramic matrix with glassy grain boundary; (ii) Particulate Reinforced Ceramics — high modulus particles in ceramic or glass matrix, e.g. Al₂O₃ or ZrO₂ particulate-toughened glass, Al₂O₃ particulate-toughened ZrO₂; (iii) Fibre/Whisker Reinforced Ceramics, which can be subdivided further into (a) Continuous fibres, e.g. Al₂O₃ fibres in ZrO₂; (b) Chopped fibres, e.g. SiC fibres in Si₃N₄ and (c) Whiskers, e.g. SiC whiskers in Al₂O₃ or ZrO₂; (iv) Ceramic-Metal (Cermet) Composites, e.g. WC in Co.

Of particular importance to the mechanical performance of the above are the microstructural property requirements of:

- the amount of reinforcement;
- reinforcement shape, size and distribution;
- the degree and type of interfacial bonding.

Particulate reinforcement increases the toughness of the material by crack bowing, crack deflection and crack branching and by the additional mechanisms of stress-induced microcracking and stress-induced transformation toughening in the presence of ZrO₂. Fibre- or whisker-reinforced materials have higher toughness by virtue of matrix-fibre debonding, fibre sliding, fibre fracture and finally fibre pull-out as shown in schematically in Figure 4.

![Fig.4: Schematic diagram of energy absorbing steps during loading of a fibre-reinforced ceramic resulting in fibre pull-out.](image-url)
**Ambient Temperature Mechanical Applications**

Mechanical applications at ambient temperature are largely a result of the combination of wear resistance, hardness and corrosion resistance exhibited by ceramics (see Table 1). Further applications using tough ceramics such as PSZ and TZP are evolving.

<table>
<thead>
<tr>
<th>Application</th>
<th>Property requirement</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump seals</td>
<td>High strength; high hardness; excellent surface finish; wear and corrosion resistance</td>
<td>ZrO$_2$, Al$_2$O$_3$, SiC</td>
</tr>
<tr>
<td>Bearings and guides for dot-matrix printers</td>
<td>Excellent surface finish, long-life at low stresses, wear resistance</td>
<td>Al$_2$O$_3$, ZrO$_2$</td>
</tr>
<tr>
<td>Cutting blades</td>
<td>Excellent surface finish, high strength</td>
<td>Sialon, ZrO$_2$, ZTA</td>
</tr>
<tr>
<td>Abrasive wheels, cutting tools</td>
<td>High strength, wear resistance, good toughness</td>
<td>ZTA, Sialon, Al$_2$O$_3$/SiC</td>
</tr>
<tr>
<td>Protheses</td>
<td>High strength, wear resistance, excellent surface finish, toughness, biocompatibility</td>
<td>Al$_2$O$_3$, ZrO$_2$</td>
</tr>
</tbody>
</table>

Table 1: Ambient temperature mechanical applications

**Elevated Temperature Mechanical Applications**

The main attraction of engineering ceramics in this area is their retention of high strength at elevated temperatures coupled with high hardness, wear and corrosion resistance. The main problem restricting the wider utilisation of this class of materials is the relative brittleness of these ceramics, scarcity of high temperature test data (especially wear and fatigue) and the difficulty of design, i.e. the prediction of performance at elevated temperature under cyclic stresses and thermal loading. Ceramics can be susceptible to thermal shock, as a result of their low thermal conductivity and high stiffness, which can limit their use under thermal cycling conditions. However, thermal shock resistance can be improved by the introduction of stress relieving slots or discontinuities in critical areas within the component. Some of the more notable high temperature applications are given in Table 2.

Ceramic coatings, in the form of plasma sprayed PSZ, have been used on a number of diesel engine parts including combustion chamber walls, cylinder liners and heads, piston crowns and intake/exhaust parts. Such coatings provide heat, wear and corrosion resistance, allowing the engine to run hotter and reducing the
requirement for cooling systems. Also, PSZ has a very similar thermal expansion coefficient to that of cast iron, so that thermal mismatch is not a problem.

<table>
<thead>
<tr>
<th>Application</th>
<th>Property requirement</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extrusion and wire</td>
<td>High wear resistance, excellent surface finish, good</td>
<td>ZrO₂</td>
</tr>
<tr>
<td>drawing dies</td>
<td>dimensional stability</td>
<td></td>
</tr>
<tr>
<td>Cutting tools</td>
<td>High strength and toughness, wear resistance, corrosion</td>
<td>ZTA/Sialon</td>
</tr>
<tr>
<td>Gas turbine blades</td>
<td>High temperature strength, creep resistance, thermal</td>
<td>Si₃N₄</td>
</tr>
<tr>
<td>Engine components</td>
<td>Thermal insulation, wear resistance</td>
<td>ZrO₂, Si₃N₄, SiC,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al₂O₃-TiO₂</td>
</tr>
</tbody>
</table>

Table 2: Elevated temperature mechanical applications

**Bioceramic Properties**

Bioceramic materials are employed in the field of bioengineering for the production of temporary or permanent implant devices, used to aid or restore the function of a diseased or weakened skeletal part or tissue. Ceramics are particularly suitable as prosthetics as they display superior wear and erosion characteristics compared with other materials, and generally exhibit biocompatibility in the corrosive environment of the human body. Their high specific stiffness is also an obvious advantage.

Of the "bioinert" ceramic materials, alumina is the only one to be employed clinically to date, with other non-toxic oxides, nitrides and carbides still undergoing biocompatibility testing. Alumina is used mainly for load bearing bone replacement devices; the femoral head of hip joint implants and dental implants, for example. Its application as a bioceramic is limited by its relative brittleness, low tensile strength and the fact that without the use of special cements, notably polymethylmethacrylate (PMMA), only mechanical bonding via bone ingrowth into a porous structure is possible. Bioactive materials, on the other hand, exhibit some solubility which facilitates bonding with the surrounding tissue.

Essentially, a calcium phosphate layer is formed on the implant which allows the bone to bond chemically to the implant, which is much preferred to an adhesively bonded implant which tends to loosen with time. At present, however, bioactive materials, which include glasses, glass-ceramics and dense calcium phosphate-based materials, can only be used for low load devices due to their low tensile strength and fracture toughness.

Much work is currently focused on the use of hydroxyapatite (the primary mineral content of bone) as a bioactive material. Calcium phosphate-based ceramic
prosthetics can also be designed to degrade in-situ with the possibility of total conversion to living bone. Their potential is at present limited by their low tensile strength, although they are used as bone augmentation materials and as dental implants.

It is estimated that by the end of the century, the value of the bioceramic market world-wide will be £6billion.

**Chemical Properties**

The general inertness of ceramics towards chemical reactions over a range of temperatures often makes them ideal candidates for containment of reactive materials. This is particularly true in the petrochemical industry, where ceramics are often used as linings for reactive and containment vessels. The combination of wear resistance and chemical resistance has led to the use of ceramics in hostile environments such as deep drilling operations for oil and natural gas and their transports, i.e. valve and pipe linings.

Increasing operation temperatures in engines such as gas turbines, driven by the need for increased efficiency, continue to impose demands on the chemical stability of the materials of construction. Oxide ceramics currently find use as coatings for superalloys when they combine the functions of thermal insulation and chemical resistance. Non-oxides (particularly CMCs) are also under consideration for structural components.

Continuing pressures for increased efficiency and throughput will increase the future demands made on the chemical stability of materials; in this respect the application of ceramic materials due to their chemical inertness is likely to increase dramatically. It should be noted at this point, however, that in non-oxidising atmospheres or in contact with reducing species, oxide ceramics may be susceptible to corrosion as a result of partial reduction of the oxide or reaction of the oxide which can result in low melting point reactive phases. Oxidation of nitrides and carbides may produce a surface scale which is protective towards further oxidation. However, thermal cycling can disrupt the formation of this protective scale.

**Electrical and Magnetic Properties**

The attributes of electroceramics include: good insulation, conductivity and voltage control. Some ceramics, including SiC, can serve as resistors and heating elements for furnaces. Other ceramics have semiconducting behaviour and are used for thermistors and rectifiers. For example, yttria-stabilised zirconia is used extensively as an oxygen sensor in petrol engine exhaust streams.

Another group of ceramics display excellent dielectric, piezoelectric and ferroelectric behaviour. Piezoelectric applications include gas ignitors, impact fuses, ultrasonic generators, loudspeakers, sensors and resonators. The piezoelectric properties of barium titanate make it an attractive material for capacitors and transducers.
Most ceramic insulators consist of glasses, glass ceramics, porcelains or dense single-phase or mixed-oxide materials. Generally, electrical insulators should have a very low amount of porosity, hence clays that have completely vitrified, such as porcelain and glass, are used for electrical insulators at high temperature. When high temperature resistance at high frequencies is required, as in automotive spark plugs, crystalline alumina performs better.

Ferrites are the predominant magnetic ceramic materials. They are basically oxides with Fe₂O₃ as the major compositional component. Soft ferrites are used in the manufacture of inductor cores for telecommunications and low power transformers. Hard ferrites are used to make permanent magnets for loudspeakers, D.C. motors, door catches etc. Single crystal ferroelectric materials possess high optical transparency and useful electro-optic properties. Thin polished plates of PLZT (PbZrO₃-PbTiO₃-La₂O₃), when used in conjunction with polarized light, make excellent wide aperture shutters. They are used in devices such as anti-flash goggles, electronic welding helmets and optical data recording.

There is currently much interest in superconducting ceramics. Based on Yb₂Cu₃O₇ and similar materials, superconductivity has been obtained at temperatures above liquid nitrogen temperature (-196°C). The potential applications of such materials are enormous: superfast computers, loss-free power transmission, compact electric motors etc. However, further research into the manufacture of superconductors is required before such applications can be realised.

**Design Considerations**

Don’t use sharp corners or notches which can act as stress raisers.

Do make sure of a good surface finish.

Do utilise compressive joints and connections rather than threads and flanges.

Do use soft gaskets at assembly faces to avoid high spot loadings.

Do allow for thermal expansion mismatch, as metals can have expansion coefficients up to 10 times those of ceramics.

Do make use of proof-testing procedures if possible

Do note the batch-to-batch variability of ceramics

Do specify dimensions carefully as ceramics are very difficult to machine compared to metals.


Joining techniques between ceramic and ceramic or metal and ceramic are limited. However, electric discharge welding, brazing and diffusion bonding of ceramics to metal are all receiving attention. Vapour deposition has been used to modify the wetting behaviour of the ceramics and to deposit reactive materials which are needed for bonding. Cutting, slicing, polishing, etc. are also problematic, as they tend to produce small surface flaws which reduce the strength and fracture toughness of the component. Surface treatment may be beneficial for some applications. Ion implantation with nickel, for example, has been found to improve
the fracture toughness of alumina as it puts the surface into compression and closes surface flaws. In the laser glazing process the surface of the ceramic is locally melted and can flow to fill pores or cracks. This process can seal porous materials for use in vacuum equipment as well as improve the toughness of the ceramic. Ceramic on ceramic friction can be very high, and this in turn can lead to high wear. In order to reduce this friction, a thin lubricating coating such as molybdenum disilicide can be applied to the ceramic surface by physical vapour deposition (PVD) techniques.

**Short Glossary of Materials**

*Alumina* (A12O3) is polymorphic and is used in its various forms for a range of applications including seal rings in pumps used to convey corrosive liquids, stirrers, grinding balls, as crucibles in analytical chemistry because of its low contamination characteristics, insulators in spark plugs and for muffles in furnaces where purity and gas-tightness is important, a-alumina is widely used in metallurgy in the form of bricks and crucibles because of its low reactivity with molten metals and good resistance to slag-attack. But applications involving alkaline melts or alkali metal oxide fume, e.g. from glaze firing, need to be approached with caution, because alkalis react with α-alumina to form β-alumina which is very different in its physical properties from α-alumina.

*Zirconia* (ZrO2) in its pure form is useless as an engineering ceramic because it undergoes a phase change as it passes through temperatures around 1000°C. The resulting change in volume can lead to cracking of the part. However, by adding MgO, CaO, Y2O3 or CeO2 the phase change can be modified or suppressed. Magnesia-stabilised zirconia is relatively inexpensive and is used extensively for crucibles for melting and for casting superalloys in gas turbine rotor blades, but the stabilisation is less permanent than that provided by CaO or Y2O3. Yttria-stabilised zirconia materials are extremely tough at low temperatures. However, the structure can be degraded by water vapour at temperatures as low as 200°C. The yttria tends to migrate out of the crystals and accumulate in the grain boundaries, facilitating attack by acidic corrosive agents. Yttria substitution by ceria wholly or in part, is intended to retain the advantages of yttria stabilisation whilst resisting attack by moisture.

*Magnesia* (MgO) is used extensively as a refractory for steel-making. It resists corrosion by slag and helps remove acidic oxide impurities like SiO2 or P2O5. It is not as strong as alumina, so finds little application as an engineering ceramic but has some specialised applications, e.g. in high energy-density batteries and for containing clay-ware which evolves Na2O vapour during firing.

*Silicon carbide* (SiC) is resistant to oxidation at temperatures above the melting point of steel, and is used as a coating for metals, carbon-carbon composites and other ceramics to provide protection at these extreme temperatures. SiC is also used in particulate, fibre and whisker forms as reinforcement in metal and ceramic matrix composites.
Silicon nitride (Si₃N₄) has similar properties to SiC, although its oxidation resistance and high-temperature strength are somewhat lower. Both SiC and Si₃N₄ are likely candidates for components for automotive and gas turbine engines.

Sialon (Si₃A1₃O₃N₅) is a relatively new advanced ceramic material in which aluminium and oxygen are partially substituted for silicon and nitrogen in silicon nitride. Typically, sialon crystals are embedded in a matrix of Y₂O₃, resulting in a ceramic with good specific stiffness, low thermal expansion coefficient and good fracture toughness. Sialon may find applications in engine components and other uses involving both high temperatures and wear conditions.

The Technical Ceramics Handbook (ISBN 0 948593 547) written by Ceram Research and published by Wade Advanced Ceramics Ltd (1992) was used as the basis for this Profile.

Where to Get Advice

Ceram Research
Queens Road
Penkhull
Stoke-on-Trent ST4 7LQ
Telephone: 01782 45431
Fax: 01782 412331
Contact: Ann Pace

National Physical Laboratory
Teddington
Middlesex TW11 OLW
Telephone: 0181-977 3222
Fax: 0181-943 2155
Contact: Dr Roger Morrell

Sources of Further Information

Handbook of Properties of Technical & Engineering Ceramics. Part 1: An Introduction for the Engineer & Designer,

Handbook of Properties of Technical & Engineering Ceramics. Part 2: Data Reviews Section 1: High Alumina Ceramics,

Corrosion Resistance of Technical Ceramics,

ISBN 0 901716 405. (Details of other titles in the series available from The Institute of Materials.)

*Advanced Ceramics Report*, Elsevier
Advanced Technology. ISSN 0268-9847

*British Ceramic Transactions*, Institute of Materials. ISSN 0307-7357

*High Tech Ceramics News*, Business Communications Co. Inc., USA., ISSN 1045-2397