The cover shows the structure of different phases of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ from the paper by C N R Rao
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Foreword

Stages in the progress of human civilization have often been characterized by the materials used, such as the Stone Age, Iron Age etc. Ceramics represent one of the oldest materials used by the human race, both as objects of utility and of beauty. Traditional ceramics have responded to basic human needs by providing building materials for shelter and pots for cooking and storage, besides refractories for high temperature furnaces, optical glass for spectacles, microscopes and telescopes, electrical and thermal insulation etc. Ceramics are made from inexpensive materials which occur abundantly in nature and hence are widely used.

As we approach the twenty-first century, three technologies – bio-technology, electronics and advanced materials – are becoming dominant. Among advanced materials, ceramics are moving to the centre of the stage. This is due to the steady progress in our scientific understanding of the structure-processing-property correlations in ceramics, often in quantitative terms. This special volume on advanced ceramics attempts to capture the breathtaking strides being made in this field.

The sharp distinction between traditional and advanced ceramics—in terms of starting materials, processing, properties and applications—is emphasized in an overview of the field in the first paper.

Many novel techniques have been developed for the synthesis of powders and the fabrication of ceramics. These techniques aim at atomic level mixing, fine particle size and high reactivity, enabling low temperature sintering in order to overcome the major disadvantages of traditional ceramic processing, namely compositional inhomogeneity and high temperature sintering. In his paper, Chakravorty examines organometallic routes for synthesis of ceramics.

The discovery in late 1986 of superconductivity in ceramics at unimaginably high temperatures (near 100 K) has been the most important achievement in decades in science as a whole and certainly in centuries in ceramics. Room-temperature superconducting ceramics appear to be around the corner. The fantastic range of applications, from loss-free power transmission, powerful magnets for medical use and nuclear fusion technology, to levitated trains, computers etc. has already electrified the science and technology community the world over like nothing else in recent history and is sure to change the way of human life. C N R Rao provides a crisp review of this fast changing field.

At the moment, the most important use of advanced ceramics in volume and value is in electronics. While alumina is by far the largest item for use as substrates, insulators etc., specialized ceramics—ferro-electric, piezoelectric, semiconducting and magnetic—play a critical role as projected by V C S Prasad in his paper.

Ceramics are best known as excellent electric insulators, but it is now possible to confer high electrical conductivity where the charge carriers can by choice be electrons or ions. “Super” ionic conductivity in ceramics is due to specific ions, for
example, oxygen in zirconia and sodium in beta-alumina. Maiti & Paria discuss the high temperature fuel cell which is based on oxygen ion conduction of doped zirconia.

In spite of their chemical inertness, high temperature stability and abundance, ceramics have always been disqualified for structural applications due to their poor tensile strength and the brittle fracture they are subject to. These handicaps are rapidly being overcome by several approaches. Ceramics composed of the first few elements in the periodic table—B, C, Al, N, O, Si—are proving to be excellent structural materials in auto and aerospace applications. The synthesis and fabrication of these unique light element ceramics require unconventional methods, which are reviewed by K J Rao and his associates.

Zirconia undergoes a martensitic phase transformation. A range of zirconia-based ceramics are now available which, through a process of transformation toughening, exhibit such high fracture toughness that these have been christened as ‘ceramic steel’. The science underlying these engineering ceramics is covered by Bhaduri in his paper.

An excellent example of increased productivity in manufacturing is illustrated by Komanduri in the use of ceramic tool materials, which increase the machining speeds markedly even though more stable machines are called for.

The best characteristics of metals and ceramics are exploited by coating metallic components by ceramics. The coated components have extended life under the severe environments encountered in a variety of industries. The materials, techniques and properties of such ceramic coatings are discussed by Karthikeyan & Mayuram.

Limitations of space prevented us from covering, in this volume, other equally exciting topics in advanced ceramics. It is however hoped that the present papers demonstrate that the subject of ceramics is undergoing a great renaissance and that we are on the threshold of an exciting Ceramic Age. Excellence in ceramic science leading to advanced engineering ceramics is a prerequisite for industrial progress and for the social well-being of nations in decades to come.

I am indebted to the authors for their excellent contributions to this volume and to the reviewers of Sādhanā for fearless criticism.

July 1988

E C SUBBARAO
Guest Editor
Advanced ceramics—an overview

E C SUBBARAO

Tata Research Development and Design Centre, 1, Mangaldas Road, Pune 411 001, India

Abstract. In sharp contrast to conventional ceramics, advanced ceramics use extensively processed starting materials of controlled purity and particle size, and novel fabrication techniques such as tape casting, chemical vapour deposition, in situ oxidation, injection moulding, followed by fast, often low temperature, sintering. Advanced ceramics exhibit unusual behaviour at times and quantum jumps in properties. Improved fracture toughness of structural ceramics makes them suitable candidates for stringent engineering applications. Composites involving special ceramics display some outstanding properties, e.g. piezoelectrics. Examples of dielectrics, super conductors, optical fibres and ionic conductors are cited.

Keywords. Materials preparation; processing; superconductors; optical fibres; toughened ceramics; composites.

1. Introduction

From the beginning of civilisation, ceramics provided objects of utility and beauty. Shelter for mankind is based on adobe, brick, tile, cement and window glass. Cooking and storing of food has always been done in ceramicware ranging from clay pots to modern glass-ceramics. The abundant and widespread availability of basic ceramic raw materials—clay, sand and other minerals—in nature enabled ceramics to meet basic human needs over the millennia. The growth in world population guaranteed the expansion of the traditional ceramic industry.

Superimposed on this steady, but slow, growth of ceramics, has been an important qualitative change in recent decades, based on a deeper scientific understanding of the composition-structure-processing-property correlations of ceramics. This arose in response to the stringent requirements of sophisticated applications in electronics, space, nucleonics and energy, among others. Ceramics to meet these newer, engineering applications are termed advanced ceramics (Subbarao 1987). Together with biotechnology and electronics, advanced ceramics has moved to the centre-stage of the second industrial revolution to propel mankind into the twenty-first century. The characteristics of these new-born industries are manifold increases in properties and performance, as well as typical annual growth rates of 50–100% (Kenney & Bowen 1983).

In this exciting area, a few pockets of excellence exist in India, which have made respectable contributions to the worldwide progress in advanced ceramics.
In this paper, the distinction between advanced and conventional ceramics is outlined, followed by an overview of the new material preparation techniques, their unusual processing methods, and the quantum jumps observed in their properties for meeting the stringent requirements of emerging engineering applications.

2. Characteristics

The important differences between conventional and advanced ceramics are summarised in table 1.

Modern applications call for enhanced, reliable properties, which can be met only when the starting materials have reproducible characteristics. This is not possible with naturally occurring minerals and ores, even after beneficiation. The higher cost of processed materials has to be justified by enhanced performance. Empiricism and experience which guided conventional ceramics are totally inadequate, and often inappropriate, for advanced ceramics, which can progress only through knowledge gained by multidisciplinary research and development.

3. Material preparation

The materials for advanced ceramics must possess:

(i) high purity—may be as high as 99-99%;
(ii) small and uniform particle size, which gives rise to large surface area and high reactivity;
(iii) reproducibility—homogeneous distribution of intentionally added impurities, called dopants, which may be present at ppm level.

Novel preparation techniques, such as sol-gel (Roy & Roy 1984; Lannutti & Clark 1985; Sen & Chakravorty 1986), precursors (Rao 1986; Mazdiyasni 1982), alkoxides (Mazdiyasni 1982), and topochemistry (Gopalakrishnan 1986), for this purpose arose from developments in solid state chemistry. These methods have made it possible to

<table>
<thead>
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<th>Table 1. Distinctions between conventional and advanced ceramics.</th>
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<tr>
<td><strong>Characteristic</strong></td>
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<td>Raw materials</td>
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<td>Processing</td>
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<td>Properties</td>
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<td>Applications</td>
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advanced ceramics—an overview

produce some materials which could not be produced otherwise. For example, utilising solid solution precursors of $\text{Ca}_1-x\text{Mn}_x\text{CO}_3$, a variety of oxides in the Ca-Mn-O system have been synthesised (Vidyasagar et al 1985). Some of the mixed carbonates which occur in nature could be made in the laboratory only by the precursor method. Similarly, dehydration as well as insertion and removal of protons, lithium ions etc. into compounds in a reversible way can be accomplished through topochemical reactions. Hydrolysis of zirconium tetrabutoxide in alcohol solution can be used to produce monodispersed $\text{ZrO}_2$ powders (Ogihara et al 1987).

Chemically prepared zirconia can be sintered to high density at 1400°C, several hundred degrees less than the usual temperatures (Gupta et al 1977). The incorporation of small quantities of La in $\text{BaTiO}_3$ to decrease its electrical resistivity by a factor of $10^{10}$ is best accomplished by a solution-decomposition route. These new methods enable mixing at an atomic scale, compared to the gross particle mixing by mechanical means, employed in conventional ceramic processing. The atomic level mixing means shorter diffusion distances for material transport (about 10 Å compared to about 10,000 Å in mixing of ceramic powders), leading to decreased temperatures and duration for sintering, besides greater compositional homogeneity. The disordered atomic arrangement in a gel is a better starting point for making glasses, which are amorphous in nature, compared to the use of well-crystallised oxides and other salts (Chakravorty 1988).

Alumina is by far the most important base material for advanced ceramics and accounts for over 80% of the raw materials employed in engineering ceramics. The other materials of importance are $\text{BaTiO}_3$, $\text{TiO}_2$, lead zirconate titanate (PZT), lead lanthanum zirconate titanate (PLZT), $\text{ZrO}_2$, $\text{SiC}$, $\text{Si}_3\text{N}_4$ and $\text{SiAlON}$.

4. Processing

While all the conventional ceramic processes such as pressing, slip casting, extrusion, drying, firing etc., are available for advanced ceramics, some newer fabrication technologies are developed to meet specific requirements. These include:

(i) Isostatic and hot isostatic pressing to achieve higher end point density and freedom from defects such as laminations, density gradients etc.
(ii) Tape casting to produce thin sheets of large area from a slurry of alumina, titanates etc., spread by a blade on a moving plastic sheet (Williams 1976; Prasad 1988). The surface of such substrates has a high degree of evenness (typically a few microns per linear meter). These sheets are often stacked in the green condition, with metal electrode paste applied over the entire area or as thin lines, and then the stack is fired to produce multilayer capacitors. Alumina sheets with a network of resistor and conductor paste, in the form of thin lines, are stacked (upto 150 layers) and fired to produce multilayer ceramic chips for modern computers. The manufacture of multilayer ceramics including metallic interconnections is often completed in a single firing operation (Dougherty & Greer 1983).
(iii) Injection moulding for small intricate shapes with projections and perforations.
(iv) Chemical vapour deposition of preforms from which optical fibres are drawn (MacChesney 1981, pp. 537–561).
(v) In situ oxidation. A component is cast from molten aluminium alloy and oxidation is allowed to take place at the moving liquid/solid interface to result in an
alumina component of the desired shape. The multitude of steps normally employed in the fabrication of alumina components is replaced by a single casting-oxidation step, which is completed at a much lower temperature and shorter time than those employed for sintering of alumina ceramics.

(vi) Electrophoretic deposition of beta-alumina electrode tubes for Na-S battery (Krishnarao et al 1986).

(vii) Sintering at a lower temperature and in shorter time. Ceramic dielectrics are now fired at temperatures below 1000°C compared to the usual 1300-1350°C employed for sintering titanate dielectrics. The entire sintering operation is completed in 1–2 h, much shorter than the traditional 20–24 h. The resulting energy saving is substantial. These improvements in sintering are due to:

(a) increased sinterability of the highly reactive, small particle size initial powders;
(b) sintering aids which provide transient liquid phase (Ramesh Choudhary & Subbarao 1981; Prasad 1988); and
(c) lower melting compositions such as niobates in place of titanates (Prasad 1988).

Since advanced ceramics are often used in engineering applications, often as components in a larger assembly, their dimensional tolerance, integrity and reproducibility are considerably more critical than those of conventional ceramics. Finishing operations, such as grinding, polishing etc., are expensive and may introduce defects and therefore should be employed sparingly. Hence, processing methods preferred for advanced ceramics are those which give the final net shape within required dimensional tolerance, with little or no subsequent finishing operations.

The high cost of starting materials, stringent specifications on properties and dimensions, and the need for reproducibility usually dictate the automation of the fabrication steps. The controls inherent in automation require a deeper knowledge of composition-structure-processing-property interdependence. The recent advances in ceramic science are making this possible.

5. Properties

The properties of advanced ceramics are both quantitively and, more importantly, qualitatively different from those of conventional ceramics. Following the successive replacement of vacuum tubes by transistors, integrated circuits and large scale integrated circuits (LSI), miniaturisation of other circuit elements such as ceramic capacitors has become necessary. This is achieved by gradual increase in the dielectric constant of capacitor materials by almost an order of magnitude every decade (figure 1). While TiO₂ and BaTiO₃ are new classes of dielectric materials, improvements in the last 30 years are due to modification of the basic titanate material. These innovations include fine grain size to inhibit domain reorientations (Buessem et al 1966), stacking of thin layers in a multilayer capacitor (Prasad 1988) or development of an insulating layer surrounding semiconducting titanate grain (Goodman 1981; Wernicke 1981).

While barium titanate is valued for its high electrical resistivity (> 10¹⁰ ohm cm) when it is used as a capacitor, it can be made semiconducting (resistivity ≈ 10² ohm cm) by doping it with a small amount of La or many other ions (analogous to semi-
conductor technology). The electrical resistivity of such a semiconducting barium titanate increases sharply (by about $10^4$) in the vicinity of its ferroelectric Curie temperature (Kulwicki 1981). This positive temperature coefficient of resistivity (PTCR) is made use of for motor protection, self-regulating heaters, etc.

Zirconia, doped with CaO, MgO, Y$_2$O$_3$ etc., exhibits a cubic, fluorite type structure. It has been established that the dopant cations (Ca$^{2+}$, Mg$^{2+}$, Y$^{3+}$ etc.) place the Zr$^{4+}$ ions and the charge balance is restored by the creation of an appropriate number of oxygen ion vacancies (Subbarao 1980). The existence of the oxygen ion vacancies, whose concentration is fixed by the amount of dopant and remains independent of temperature and oxygen partial pressure, leads to oxygen ion diffusion at rates a million-fold higher than that of cations (Subbarao 1981). Accompanying the mass transport of oxygen ions through the cubic zirconia lattice, there is a charge transport according to the Nernst–Einstein relationship

$$E = \frac{RT}{4F} \ln \left[ \frac{P_{O_2}}{P_{O_2}^{\text{ref}}} \right]$$

where $E$ is the EMF set up when a zirconia membrane separates gases with oxygen partial pressures of $P_{O_2}$ and $P_{O_2}^{\text{ref}}$ (reference, say air), $R$ is the gas constant, $T$ is absolute temperature and $F$ is the Faraday constant. Zirconia oxygen probes, using (1), measure oxygen contents in flue gases, heat treatment furnaces, molten steel etc. Application of a potential, dictated by (1), to a zirconia membrane can pump oxygen into or out of a gas stream to attain a desired oxygen content (down to a few parts per billion) (Subbarao & Maiti 1987). When the oxygen required for combustion in a fuel cell is transported across a zirconia membrane, the EMF developed becomes available to perform useful work. Such a zirconia-based high temperature fuel cell is an efficient power source without any moving parts (Maiti & Paria 1988).

In a beta-alumina lattice, Na$^+$ ions occupy some of the interstices between the spinel alumina blocks. The fact that only a few of the available sites are occupied by the Na$^+$ ions and the inter-ionic distances are larger than the size of the Na$^+$ ion enables easy sodium ion diffusion, making beta-alumina a suitable solid electrolyte separating two molten electrodes—sodium and sulphur—in a high energy density
battery, called the sodium-sulphur battery (Subbarao 1980). Since these batteries have a much higher energy density per unit weight or volume, compared to the conventional lead-acid battery, they are good candidates for load levelling and, possibly, automotive applications.

Since superconductivity was discovered in 1911 in solid mercury by Kammerlingh Onnes, only a few metals have exhibited this unique property. The transition from the normal to the super conducting state (which is signalled by a near total loss of electrical resistivity) arises a few degrees above absolute zero (less than 10 K) in these metals (table 2). After a gap of nearly 40 years during which the superconducting transition temperature nearly stagnated, a number of intermetallics in which the superconducting transition temperature was in the range of 10–20°K were found. Nb₃Ge exhibiting a record $T_c$ of 23 K (table 2) was discovered in 1973. After a gap of 13 years, Bednorz & Müller (1986) found that a rare earth–Ba–Cu oxide exhibits superconductivity at 36 K. This outstanding discovery started an intense scientific effort all over the world and a $T_c$ of 100 K, above the liquid nitrogen temperature (77 K), was achieved in a matter of weeks for a number of oxides. Originally thought of as La$_{2-x}$M$_x$CuO$_4$ where M = Ba, Sr, the superconducting oxide was reported as Y$_{1.2}$Ba$_{0.8}$CuO$_4$ (Wu et al 1987) with K$_2$NiF$_4$ structure type. Ganguly et al (1987a) reported a $T_c$ of 100–120 K for oxides in the system Y-Ba-Cu-O. The compound YBa$_2$Cu$_3$O$_7$±δ was found to have a perovskite-type (and not K$_2$NiF$_4$ type) structure (Ganguly et al 1987b). Other reports in this field, all in a space of three months, are by Uchida et al (1987), Chu et al (1987), Cava et al (1987) and Rao & Ganguly (1987). It may be noted from table 2 and figure 2 that metals exhibit superconducting transition temperatures ($T_c$) under 10 K, intermetallic compounds have $T_c$ up to 23 K and oxides, discovered in 1986–87, have $T_c$ between 36 and 120 K. There are claims of oxides with $T_c$ of 240 K, not much below the temperature of an ordinary refrigerator, if not of a room. The critical current density of these superconducting oxides is steadily increasing, so that device research has already begun. Superconductors are often used in the form of wires, made into coils, for producing intense magnetic fields. The production of flexible, long shapes from the conven-

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<tr>
<th>Metals</th>
<th>$T_c$ (K)</th>
<th>Intermetalllics</th>
<th>$T_c$ (K)</th>
<th>Oxides</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>0.53</td>
<td>Pb, Au</td>
<td>7.0</td>
<td>La$_{2-x}$M$_x$CuO$_4$</td>
<td>$\geq 36$</td>
</tr>
<tr>
<td>Zr</td>
<td>0.7</td>
<td>SnSb</td>
<td>3.9</td>
<td>M = Ba, Sr</td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td>0.35</td>
<td>Ti$_3$Bi$_3$</td>
<td>6.4</td>
<td>Y$<em>{1.2}$Ba$</em>{0.8}$CuO$_4$</td>
<td></td>
</tr>
<tr>
<td>Th</td>
<td>1.32</td>
<td>WC</td>
<td>2.5–4.2</td>
<td>YBa$_2$Cu$_3$O$_7$±δ</td>
<td>$\sim 100$</td>
</tr>
<tr>
<td>V</td>
<td>5.1</td>
<td>MoC</td>
<td>7.6–8.3</td>
<td>Bi-Sr-Ca-Cu-O</td>
<td>$\sim 105$</td>
</tr>
<tr>
<td>Nb</td>
<td>9.22</td>
<td>MoN</td>
<td>12.0</td>
<td>Ti-Ba-Ca-Cu-O</td>
<td>85–130</td>
</tr>
<tr>
<td>Ta</td>
<td>4.38</td>
<td>NbN</td>
<td>14.7</td>
<td></td>
<td></td>
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<tr>
<td>Zn</td>
<td>0.79</td>
<td>Nb$_3$Sn</td>
<td>18.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.54</td>
<td>Nb$_3$Al</td>
<td>18</td>
<td></td>
<td></td>
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<tr>
<td>Hg</td>
<td>4.12</td>
<td>V$_3$Si</td>
<td>16.8–17.1</td>
<td></td>
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<tr>
<td>Al</td>
<td>1.14</td>
<td>V$_3$Ga</td>
<td>16.8</td>
<td></td>
<td></td>
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<tr>
<td>Ga</td>
<td>1.07</td>
<td>Nb-25% Zr</td>
<td>10.8</td>
<td></td>
<td></td>
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<tr>
<td>In</td>
<td>3.37</td>
<td>Nb-60% Ti</td>
<td>8.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TI</td>
<td>2.38</td>
<td>Nb-Al-Ge</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>3.69</td>
<td>Nb$_3$Ge</td>
<td>23.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>7.26</td>
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tionally brittle ceramics is a challenging task. Novel fabrication techniques are being conceived, besides the established thin film methods.

This discovery of superconducting ceramics, when it is translated into commercial technology, is likely to have a major impact on electrical engineering practice including power transmission, energy storage, computer size, levitated transport (train and ship), nuclear fusion, medical diagnostics etc. (Rao 1988a).

Glass fibres have been used for decades for reinforcing plastics, as well as for thermal and sound insulation. The current interest in silica glass fibre stems from the discovery of its ability to transmit electrical signals over long distances with little attenuation (MacChesney 1981, pp. 537–561). Transmission losses are attributed to the presence of transition metal ions in starting materials which can be reduced through purification. For example, a single glass fibre can send $2 \times 10^{10}$ bits of information per second over a distance of 68 km length of fibre. This is equivalent to sending the data in 200 encyclopaedia volumes per second. The distance between repeaters in presently installed fibres is 30 km, which is expected to increase to
300 km. The repeaters, located between the light source and detectors in an optical fibre system, control the shape, time and strength of the weakening optical signals. The additional advantages of optical glass fibre over the conventional copper wire for transmission of information are its light weight, the abundance of raw materials, its lower cost, environmental stability, and insensitivity to electromagnetic interference. The material preparation and fibre production technologies, as well as the clean environment of the production facilities, are more akin to the semiconductor industry than to a ceramic factory. More recently, fluoride glasses \((\text{ZrF}_4-\text{ThF}_4-\text{BeF}_2)\) have shown lower transmission losses (0.01 to 0.001 dB/km) compared to about 0.2 dB/km for silica optical fibres. The decreasing trend of losses of transmission fibres is shown in figure 3 (Tummala & Shaw 1987). It shows that they have decreased from 10–200 dB/km for multicomponent glasses 20 years ago to 2–4 dB/km for present commercial silica fibres, and to 0.1 dB/km for laboratory fibres.

While ceramics are quite strong under compression, they are generally weak in tension and are rarely free from flaws which lead to brittle fracture, often catastrophically. This deficiency has been overcome in the case of glass by placing the surface under compression, either through a heat treatment operation, called tempering, or through ion exchange from molten salts. In crystalline ceramics, the presence of cracks and other flaws cannot be completely avoided. Therefore, recourse is taken to methods for inhibiting crack growth. One way to do so is by the incorporation of fibres. Another way is to utilise a phase transformation to absorb

![Figure 3. Trend of transmission losses of optical fibres.](image-url)
the energy associated with a stress concentration. In fact, both can be combined as was done by Claussen (1986) in the case of fibre-reinforced transformation-toughened zirconia. While fibre-reinforcement as a strengthening mechanism has been practised for quite sometime, strengthening and toughening of ceramics via a phase transformation was first demonstrated in zirconia by Garvie et al. (1975). Here the volume change accompanying the martensitic phase transition of zirconia (tetragonal to monoclinic) is exploited. The underlying mechanisms are reviewed by Bhaduri (1988). The transformation-toughened zirconia ceramics are used as dies for hot extrusion of ferrous and non-ferrous metals, engine and pump components, textile thread guides etc.

Silicon carbide, silicon nitride (Si$_3$N$_4$) and its derivative SiAlON are excellent structural ceramics, as discussed by Rao (1988b), and are good machining tool bits (Komanduri 1988).

Only a third of the fuel energy is utilised in the shaft power of an internal combustion or a diesel engine, with one-third wasted in the coolant and another third escaping with the exhaust (Horton & Compton 1984). Since metal components limit the temperature of operation of the engine, necessitating efficient cooling, advanced ceramic components are under examination for various parts of the engine. Significant improvement in engine efficiency is achieved because of the higher temperature at which the engine with ceramic components (as coatings, liners, or as such) can be operated, with consequent higher Carnot efficiency, and requiring less cooling. The higher operating temperatures also have a favourable effect on engine emissions. The ceramic coating technology is reviewed by Karthikeyan & Mayuram (1988).

One more point needs to be emphasized regarding structural ceramics. In order to achieve optimal benefit from structural ceramics, one should, instead of making a simple replacement of a metal part by a ceramic item, redesign the part taking into account the unique properties, including brittle fracture, of ceramics.

Only the unique, new or enhanced properties of advanced ceramics are discussed here. It must however be emphasized that all the other properties which have made conventional ceramics such useful materials are also exhibited by advanced ceramics. These include extreme inertness to environment and temperature, lightness, abundance of raw materials, a range of thermal expansion and thermal conductivity etc. If conventional ceramics responded to the basic needs of man, advanced ceramics answer the challenges posed by sophisticated industries.

6. Composites

A single-phase material with many excellent properties may still suffer from some deficiencies. This can be overcome by combining the desirable properties of two materials in the form of a composite. Fibre-reinforced materials, such as bamboo in adobe, steel rods in concrete, glass fibres in plastics, are well-established structural materials. Porous insulating materials are composites of solid and gas phases. Most ceramic products are composed of crystalline and glassy phases. Bone is a unique composite of a crystalline phosphate and a pore phase, with three dimensional connectivity for both phases. This has formed the basis for the development of
biocompatible ceramics, glasses and glass-ceramics for biomedical applications and as implants.

The chronological improvements in properties and the role of composites may be illustrated by the development of piezoelectric materials. In early 1940’s the ferroelectric behaviour of barium titanate was discovered. Since a ferroelectric is, by definition, a piezoelectric, barium titanate became an important piezoelectric material. In the late 1940’s, when it was demonstrated that ceramic barium titanate can be poled to confer non-isotropic domain orientation, ceramic barium titanate became the first piezoelectric, which is not a single crystal (unlike quartz, Rochelle’s salt, potassium dihydrogen phosphate etc.), and has all the unique properties of a ceramic—stability, ease of fabrication etc. Further, the piezoelectric properties of barium titanate were much higher than those of the single crystal piezoelectrics e.g. quartz. Soon after the discovery of ferroelectricity in BaTiO$_3$, a variety of ionic substitutions (for Ba and Ti) were attempted which resulted in a number of new ferroelectrics, such as PbTiO$_3$, which is isostructural (perovskite-type) with BaTiO$_3$. In 1950, PbZrO$_3$ was found to be isostructural with BaTiO$_3$ and also to possess spontaneous polarization. However, each crystallographic plane in it has its spontaneous polarization aligned in one direction but neighbouring planes have their polarization in opposite directions. Spontaneously polarized materials with antiparallel orientation of polarization in adjacent planes, leading to net zero polarization, are termed antiferroelectrics, in analogy with antiferromagnets. PbZrO$_3$, thus, became the first antiferroelectric. A study of the perovskite compositions in the binary system PbTiO$_3$-PbZrO$_3$ revealed a morphotropic phase boundary near the equimolar composition, which exhibits greatly enhanced piezoelectric modulus (Jona & Shirane 1962). Efforts over the next quarter century have not produced any piezoelectric material better than lead zirconate titanate (PZT). Newnham et al (1980) have produced PZT-polymer composites which have piezoelectric properties one to two orders of magnitude better than PZT itself. These composites contain only 10% of PZT mixed with 90% of inexpensive polymer. The size and distribution of the two phases are important parameters, but equally crucial is the connectivity of each phase. By assigning values of 0 (for unconnected), 1 (for rods), 2 (for sheets) and 3 (for three-dimensional continuity), one can make two-phase composites with connectivities ranging from 1-0 to 3-3. A variety of ingenious fabrication processes (some of which mimic natural products) are devised to make these composites. Some of these composites can be extruded as flexible cables.

7. Conclusions

Novel methods of preparing starting materials and new techniques of fabricating ceramic products have enhanced the properties of advanced ceramics in some cases and conferred unusual properties in others. As a result, ceramics have become very versatile. Thus, the electrical behaviour of ceramics ranges from being excellent insulators to electronic and ionic conductors and more recently to high temperature superconductors. While most ceramics are still mechanically weak and brittle, special ceramics are amongst the toughest, strongest and hardest materials available today. It looks as though civilisation has made a full circle, starting with clay-based ceramics at the beginning and having come to advanced ceramics at the present.
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Organometallic route to nanocomposite synthesis

D CHAKRAVORTY

Advanced Centre for Materials Science, Indian Institute of Technology, Kanpur 208 016, India

Present Address: Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India

Abstract. The nature and scope of different varieties of nanocomposite materials are described. The practical and basic aspects of the physical properties of nanocomposites are discussed. The principles underlying the preparation of diphasic materials involving either ceramic-metal or glass-metal combinations are delineated. The sol-gel technique involving suitable organometallic compounds has been shown to be a versatile method for making these materials. A brief survey is given about the different materials made to date following the organometallic route.

Keywords. Nanocomposite; organometallic compound; sol-gel; ceramic-metal composites; glass-metal composites; diphasic xerogel.

1. Introduction

Nanocomposites are materials containing one or more phases having dimensions of the order of a few nanometers dispersed in a suitable matrix (Roy & Roy 1984). Strictly speaking, the above definition should include solids containing defect clusters, e.g., the Willis (1964) clusters in $\text{UO}_2^{x+}$ and the Koch–Cohen (1969) clusters in $\text{Fe}^{x-8}\text{O}$ consisting of particular arrangements of vacancies and interstitials spread over several unit cells of the lattices concerned but coherently meshed in the host matrix. Solids exhibiting ordered or disordered intergrowth of two phases of similar structure but different compositions (Rao 1986, p. 10) could also fall under the same category. However, in the present discussion we restrict ourselves to systems which are diphasic (or multiphasic) in the phase rule sense.

There are a wide variety of nanocomposites which have been commercially exploited. Cermets consisting of fine metal grains dispersed in an oxide have been used as resistors in electronic circuits (Abeles et al 1975). Photosensitive, photochromic (Armistead & Stookey 1965), thermally darkenable photochromic (Seward 1975) and polychromatic glasses (Stookey et al 1978) depend for their respective properties on a microstructure consisting of nano-scale distribution of metal or halide particles within a glass matrix. The use of cobalt alumina cermets in solar photothermal conversion has been reported (Andersson et al 1980). Nano-size metal grains dispersed on a suitable substrate comprise an important group of catalysts for the chemical industry (Sinfelt 1977).
Glass-metal nanocomposites exhibit semiconduction due to electrons tunnelling from one metal grain to the next (Chakravorty et al 1977). In certain situations such composites have shown memory switching (Chakravorty & Murthy 1975). In some of the composites subjected to an ion-exchange treatment an enhanced ionic conductivity has been observed (Mozhi & Chakravorty 1982; Shrivastava & Chakravorty 1987). The latter phenomenon appears to have a correlation with the morphology of the glasses concerned at the nanolevel.

The physics of ultrafine particles has emerged as a rapidly growing field of research in recent years (Marlow 1982, p. 2). Most of the studies to date have been related to small metallic particles. Quantum-size effects have been investigated by measuring the specific heats of indium (Novotny & Meincke 1973) and palladium (Comsa et al 1977) nanoparticles. Analyses of electrical resistivity data for small particles of aluminium and silver show phonon softening (Ohshima et al 1977) as compared to that of the bulk material. Gorkov & Eliashberg (1965) theoretically predicted an anomalous enhancement of the static polarizability of fine metallic particles. Attempts at experimental verification of this phenomenon have, however, not proved successful so far (Meier & Wyder 1972; Dupree & Smithard 1972; Strassler & Rice 1972). Superconducting order as a function of particle size has been investigated theoretically (Schmidt 1967) and results predict a smooth temperature variation near the transition point. Such “rounded” phase transition in the so-called zero-dimensional superconductors has been studied by a variety of experimental techniques. Some of these are measurements of magnetic susceptibility on small aluminium particles (Buhrman & Halperin 1973), specific heat of granular aluminium films (Worthington et al 1978), ultrasonic attenuation in aluminium films (Tachiki et al 1975; Robinson et al 1974), nuclear magnetic resonance on fine aluminium and on tin particles (Kobayashi et al 1974). Thin films comprising small superconducting metallic grains have been reported to show a higher transition temperature as compared to bulk samples (Novotny & Meincke 1973). This phenomenon has been explained on the basis of surface phonon softening due to a high surface-to-volume ratio in these materials.

Apart from the effects of small size on the conventional properties of materials as explored by some of the investigations delineated above, studies on the electronic structure of ultra-fine metallic particles are expected to throw light on the understanding of the metallic and nonmetallic states of matter (Edwards 1986, p. 265). An interesting problem of fundamental importance in this regard is a possible metal-insulator transition at a critical diameter of the metallic particle (Wood & Ashcroft 1982).

It should be apparent from the above discussion that in order to investigate the effect of small size on the various physical properties of different materials one has to essentially prepare a nanocomposite comprising a distribution of small particles of the species in an inert matrix. Some of the conventional methods of preparing such composites have been discussed earlier (Chakravorty 1982). The sol-gel method has recently emerged as a versatile technique for preparing a wide variety of materials (Sen & Chakravorty 1986, p. 159). One of the most attractive features is that the processing can be carried out at fairly low temperatures. Glass-metal nanocomposites have recently been made by exploiting this method. The purpose of the present paper is to briefly review the present status of this technique.
2. Diphasic xerogels

Principles involved in the synthesis of di- or polyphasic xerogels with special reference to ceramic-metal composite systems have been discussed by Roy & Roy (1984). Two preparation routes have been proposed. In the first, a suitable solution containing all the components to be present in the ultimate product is prepared thereby forming a sol. The latter is then gelled, the process comprising the usual hydrolysis and polycondensation reactions (Yoldas 1982). After the desiccation step a xerogel is formed. Depending on the heat treatment given to the xerogel the product may lead to either a single-phase or a poly-phase material. In the second scheme the starting point is the preparation of a mixture of a sol comprising the oxide component and a solution containing the metallic salt, the latter acting as the metal phase precursor. After gelling this mixture it is dried to obtain the xerogel. This consists, in most of the cases studied by these workers, of two noncrystalline oxide phases, viz. the single component oxide and the heavy metal oxide phase, respectively. The two-phase solid prepared by either of the two processes described as above is then subjected to reduction treatment in a nitrogen and hydrogen gas mixture (95% N\textsubscript{2}, 5% H\textsubscript{2}) at temperatures ranging from 200° to 700°C. Some of the starting materials used in the preparation of the different ceramic-metal composites are aluminium-isopropoxide, zirconyl chloride and silicon-tetraethoxide for the matrix phases and metallic salts like copper nitrate, stannous chloride and nickel nitrate for the metal phase. The presence of metallic islands of different types having diameters ranging from 5 to 50 nm has been verified by detailed electron microscopic investigation. In table 1 some of the preparational features have been summarised.

3. Glass-metal composites

Gels prepared from metal alkoxide solutions are porous and have large surface areas (Brinker & Scherer 1985). They should therefore be ideal materials for use as catalyst carriers. In fact, it was observed by Karatani & Minakuchi (1983) that glucose oxidase on silica gel made by the hydrolysis-polycondensation reaction of tetraethyl ethoxysilane exhibited a much higher enzymatic activity than that immobilized on conventional porous glasses. This high activity has been ascribed to the high density of silanol groups on the alkoxy-derived gel. This principle has been extended to the preparation of the catalyst-carrier composite, viz., small metal particles in a silica glass. Ueno et al (1983) prepared a catalyst system of Ni/SiO\textsubscript{2} by hydrolysing a mixed solution of Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} and ethylene glycol solution of nickel hydroxide followed by drying, calcining and reduction treatment at 450°C. The metal particles were found to be highly dispersed, their sizes varying from 3 to 12 nm.

A variety of glass-metal nanocomposites have been investigated in the author's laboratory (Chakravorty 1984). Organometallic compounds have been used to prepare some composites of this type. Two approaches have been followed. In the first, a fairly low melting glass (essentially based on B\textsubscript{2}O\textsubscript{3} in our case) has been prepared with a suitable organometallic compound forming one constituent of the raw materials used during the melting operation. The product after quenching has a structure consisting of fine metal granules with diameters ranging from 5-50 nm.
Table 1. Summary of nanocomposites prepared by organometallic routes.

<table>
<thead>
<tr>
<th>System</th>
<th>Method</th>
<th>Microstructural features</th>
<th>Properties measured</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃; copper Platinum, Nickel</td>
<td>Gel</td>
<td>between 5-50 nm</td>
<td></td>
<td></td>
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<tr>
<td>Zirconia: Copper Nickel Silica: copper, Tin</td>
<td>Xerogel</td>
<td>Reduction treatment</td>
<td></td>
<td></td>
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<tr>
<td>2. Glass-metal composites</td>
<td>Hydrolysis of a mixed solution of Si(OC₂H₅)₄ and ethylene glycol solution of nickel hydroxide</td>
<td>Nickel particles of size between 3 and 12 nm</td>
<td>Catalytic activity</td>
<td>Ueno et al (1983)</td>
</tr>
<tr>
<td>(a) Ni/SiO₂</td>
<td>Gel</td>
<td>Reduction Glass-metal composite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) Ni/50BaO, 50B₂O₃ (wt%)</td>
<td>Melting of mixture of oxide components and Ni(C₆H₆ON)₂.2H₂O</td>
<td>Nickel particles of size between 5 and 8 nm</td>
<td>Optical absorption</td>
<td>Datta &amp; Chakravorty (1983)</td>
</tr>
<tr>
<td>Nickel content: varying between 0-1 and 0-3 wt%</td>
<td></td>
<td></td>
<td>Magnetic behaviour</td>
<td>Datta et al (1984)</td>
</tr>
<tr>
<td>(c) Ni/SiO₂</td>
<td>Sol of Si(OC₂H₅)₄ and Ni(C₆H₆ON)₂.2H₂O</td>
<td>Particle size between 5 and 30 nm</td>
<td>Magnetic behaviour</td>
<td>Datta et al (1986)</td>
</tr>
<tr>
<td>Nickel content: 0-8 wt%</td>
<td>Gel</td>
<td>Reduction Xerogel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d) Co/50BaO 50B₂O₃ (wt%)</td>
<td>Melting of oxide components with [Co(C₅H₅N)₄(SCN)]</td>
<td>Particle size between 5 and 35 nm</td>
<td></td>
<td>S S Mitra &amp; D Chakravorty (1986, unpublished)</td>
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<tr>
<td>Cobalt content 0-4 wt% (approximately)</td>
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<tr>
<td>(e) Pd/50BaO 50B₂O₃ (wt%)</td>
<td>Melting of oxide components with [Pd(C₅H₅N)₄(SCN)]</td>
<td>Particle size between 3 and 9 nm</td>
<td></td>
<td>S S Mitra &amp; D Chakravorty (1986, unpublished)</td>
</tr>
<tr>
<td>Palladium content: Varying between 0-1 and 0-3 wt% (approximately)</td>
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</table>

dispersed in the glass matrix. The choice of the organometallic species obviates the need for the reduction step as followed by previous workers. It is believed that
favourable oxygen fugacities are attained locally within the melt as a result of the breaking up of the compound which releases carbon, hydrogen and nitrogen atoms. The composites prepared so far consist of nickel, cobalt and palladium respectively in a barium borate glass. Nickel has been introduced in the form of oxinate Ni(C₉H₆ON)₂·2H₂O (Datta & Chakravorty 1983), cobalt and palladium as complexes formed between pyridine and the corresponding thiocyanates [Co(C₅H₅N)₄](SCN)₂ and [Pd(C₅H₅N)₄](SCN)₂, respectively. The amounts of metal content in the glasses range between 0·1 and 0·4 wt%.

In the second technique, a sol is first prepared containing both the glass and the metal precursors, viz. silicon tetraethoxide and nickel oxinate, in ethyl alcohol. The sol is then allowed to gel and subsequently dried, cooled and then heat-treated to a temperature of around 750°C for 2 h (Datta et al. 1986). The resultant product has a microstructure consisting of fine metallic nickel granules having diameters in the range 5 to 30 nm dispersed in the silica glass matrix. Table 1 gives a summary of the salient features of the preparational and characterization aspects of the above materials.

So far the physical properties investigated comprise only the optical absorption (Datta & Chakravorty 1983), magnetic susceptibility and EPR (Datta et al. 1984, 1986). The optical absorption has been explained satisfactorily on the basis of the usual effective medium theories (Granqvist & Hunderi 1977). Low temperature magnetic susceptibility of nickel nanogranules in borate glass shows a broad range of transition temperatures between 77 K and 300 K. A similar trend has also been shown by the EPR data. The results indicate a superparamagnetic behaviour. It is expected, however, that with narrow distribution of particle sizes of the metallic species effected by controlling the process parameters, it will be possible to undertake investigations on some of the fundamental aspects of fine particle physics.

4. Concluding remarks

Organometallic compounds have been used to make nanocomposite materials of the ceramic-metal and glass-metal varieties respectively. The processing parameters have been investigated by several workers. It now seems possible to combine a wide variety of metallic species with different oxide systems in a composite structure by suitable choice of starting materials. A more recent innovation has been to exploit the compositional heterogeneity on a "nano" scale to make densified products in several oxide systems (Komarneni et al. 1986). It is expected that the sol-gel technique of materials processing of the type discussed in this article will lead to preparation of materials exhibiting novel physical properties.

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High-temperature ceramic oxide superconductors

C N R RAO
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

Abstract. High-temperature superconductivity in oxides of the type La$_{2-x}$Ba$_x$(Sr$_x$)CuO$_4$, YBa$_2$Cu$_3$O$_{7-\delta}$, La$_{3-x}$Ba$_{3+x}$Cu$_6$O$_{14}$ and Bi(Tl)-Ca-Sr(Ba)-Cu-O systems is discussed, with special emphasis on the experimental findings from the author's laboratory. The importance of holes on oxygen and of the Cu$^{1+}$ ($d^{10}$) state is examined. A transition is shown to occur from chain- to sheet-superconductivity in YBa$_2$Cu$_3$O$_{7-\delta}$ accompanying a change in oxygen stoichiometry. Some of the important material parameters and technological applications are briefly presented. There is every hope that materials with $T_c$ close to room temperature will be discovered in the near future. All the high $T_c$ oxides found hitherto have perovskite-related structures with two-dimensional Cu-O sheets.

Keywords. High-temperature superconductivity; ceramic oxide superconductors; bismuth cuprates; thallium cuprates; LnBa$_2$Cu$_3$O$_7$; rare earth cuprates.

1. Introduction

The phenomenon of superconductivity has been an area of vital interest for the past several decades, ever since Kammerlingh Onnes discovered in 1911 that mercury becomes superconducting at 4.2 K. Many materials, mostly metals and alloys, and more recently, molecular systems including organic charge-transfer compounds, have been investigated for superconductivity, but the superconducting transition temperature did not cross 23 K till 1986. The average rate of increase in $T_c$ was about 3 degrees per decade and it appeared as though 23 K was the upper limit for the $T_c$. The highest $T_c$'s (in the 20 K region) were exhibited by the A15 compounds such as Nb$_3$Sn and Nb$_3$Ge. Some of the metal oxides also showed superconductivity, the highest $T_c$ amongst them being exhibited by Ba Pb$_{1-x}$Bi$_x$O$_3$ and LiTi$_2$O$_4$, both around 13 K.

Bednorz & Mueller (1986) showed the possibility of high-temperature superconductivity in oxides of the La-Ba-Cu-O system. It was established in January 1987 that these oxides had the general formula La$_{2-x}$Sr$_x$(Ba$_x$)CuO$_4$ and possessed the K$_2$NiF$_4$ structure; $T_c$ values in these oxides were in the 20–40 K region, the compositions corresponding to the maximum $T_c$ in the Sr and Ba systems being $x=0.2$ and 0.15, respectively (Cava et al 1987; Chu et al 1987; Ganguly et al 1987a;...
Uchida et al (1987). Following on the heels of this discovery, superconductivity above liquid nitrogen temperature was reported in March 1987 in the Y-Ba-Cu-O system (Wu et al 1987). It was soon found that the oxide responsible for superconductivity in this system did not possess the $K_2NiF_4$ structure, but instead had the defect perovskite structure with the composition $YBa_2Cu_3O_{7-\delta}$ (Ganguly et al 1987b; Rao et al 1987b; Siegrist et al 1987). In the last few weeks, the big news has been the discovery of superconductivity in Bi and Tl cuprates containing alkaline earth metals; these oxides show $T_c$'s in the 100–120 K range (Chu et al 1988; Ganguli et al 1988; Rao et al 1988; Subramanian et al 1988; Sheng & Hermann 1988).

The discovery of superconductivity above the liquid nitrogen temperature in oxide materials has raised much hope because of its important technological implications. Equally importantly, this has given a big boost to research in ceramic oxides. In what follows, some of the highlights of research on high $T_c$ oxide superconductors will be presented, with particular reference to the results obtained in the author's laboratory (Rao 1988). In addition, some of the special features of these ceramic oxides will be indicated along with their possible technological applications. It may be remarked here that research efforts in this laboratory related to the high-temperature superconducting oxides were initiated in the early part of January 1987, soon after information about the La$_{2-x}$Ba$_x$(Sr$_x$)CuO$_4$ system became available through the American participants in the International Conference on Valence Fluctuation held in Bangalore.

2. La$_{2-x}$Ba$_x$(Sr$_x$)CuO$_4$

Oxides of the general formula $A_2BO_4$ possess the quasi two-dimensional $K_2NiF_4$ structure (figure 1) wherein the B ions interact only in the $ab$ plane. The structure and properties of the oxides of the $K_2NiF_4$ system have been examined in some detail recently by Ganguly & Rao (1984). It has been known for sometime that orthorhombic La$_2$CuO$_4$ is a relatively low-resistivity material ($\sim$ 1 ohm cm at 300 K, see figure 2) and becomes antiferromagnetic at low temperatures. Substitution of La by Ba or Sr in La$_{2-x}$Ba$_x$(Sr$_x$)CuO$_4$ ($x>0.05$) makes the structure tetragonal (at room temperature) and superconductivity manifests itself at low temperatures (Rao & Ganguly 1987a). Superconductivity is also found in the 15–40 K region in oxides of the type (La$_{1-x}$Ln$_x$)$_{2-x}$Ba$_x$(Sr$_x$)CuO$_4$ where Ln = Pr, Nd, Gd etc. (Ganguly et al 1987a; Mohan Ram et al 1987a). These oxides, containing planar CuO$_2$ units, show maximum $T_c$ around a specific value of $x$ (Sreethar et al 1987). Electrical resistivity values of these oxides in the normal state above $T_c$ are in the $10^{-2} - 10^{-3}$ ohm.cm range (figure 2) which correspond closely to Mott's minimum metallic conductivity (Rao & Ganguly 1985).

There have been several investigations of La$_2$CuO$_4$ and La$_{2-x}$Ba$_x$(Sr$_x$)CuO$_4$ in the last few months. Antiferromagnetism in La$_2$CuO$_4$ has been established by neutron scattering and diffraction studies, the $T_N$ being close to 290 K with a low-temperature Cu-moment of 0.43 $\mu_B$ (Mitsuda et al 1987). Besides establishing the magnetic structure, these studies have shown the occurrence of the orthorhombic-tetragonal distortion at 505 K. Muon spin rotation has also been employed to examine antiferromagnetism in La$_2$CuO$_4$ (Uemura et al 1987). The work of Shirane et al (1987) has shown that La$_2$CuO$_4$ is in a 2-dimensional $afm$ quantum fluid state wherein spins are ordered instantaneously over long distances, but there is no
measurable time-averaged moment. More interestingly, studies of oxygen-excess La$_2$CuO$_4$ has shown it to be superconducting with a $T_c$ of 40 K (Beille et al 1987); La-deficient samples also exhibit superconductivity in this temperature region.

Superconducting La$_{2-x}$Ba$_x$(Sr$_x$)CuO$_4$ undergoes a tetragonal-orthorhombic distortion around 180 K (Day et al 1987; Paul et al 1987). ESR studies have thrown light on microscopic magnetic interactions in these oxides (Thomann et al 1987). Static and dynamic aspects of the tetragonal-orthorhombic distortion in La$_{2-x}$Sr$_x$CuO$_4$ have been studied by neutron scattering and related studies and a classical soft phonon behaviour involving CuO$_6$ octahedra has been observed (Birgeneau et al 1987).

3. YBa$_2$Cu$_3$O$_{7-\delta}$ and related oxides

Wu et al (1987) reported superconductivity above liquid N$_2$ temperature in Y$_{1.2}$Ba$_{0.8}$CuO$_4$. This composition was actually biphasic, consisting of green Y$_2$BaCuO$_5$ and a black oxide. We had initiated studies (Ganguly et al 1987b) on the Y-Ba-Cu-O system with compositions of the type Y$_{3-x}$Ba$_{3+x}$Cu$_6$O$_{14-\delta}$ by analogy with La$_{3-x}$Ba$_{3+x}$Cu$_6$O$_{14-\delta}$ (Er-Rakho et al 1981). This was because Y$_2$CuO$_4$ (unlike La$_2$CuO$_4$) does not crystallize in the K$_2$NiF$_4$ structure. By comparing the X-ray diffraction patterns of Y$_{3-x}$Ba$_{3+x}$Cu$_6$O$_{14-\delta}$ and Y$_2$BaCuO$_5$, it was possible to identify the phase responsible for the high $T_c$ (90–95 K) superconductivity as
Figure 2. Electrical resistivity behaviour of La$_{2-x}$Sr$_x$CuO$_4$ and La$_2$CuO$_4$ (from Ganguly et al 1987a).

orthorhombic YBa$_2$Cu$_3$O$_{7-\delta}$ (Rao et al 1987b). AC susceptibility (Meissner effect) measurements showed the superconductivity to be a bulk property. Soon, many other related oxides such as Y$_{1-x}$Ln$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ (Ln = La, Lu etc) as well as LnBa$_2$Cu$_3$O$_{7-\delta}$ (Ln = Er, Dy, Gd etc.) were found to be high $T_c$ superconductors, all with $T_c \approx 90$ K (Mohan Ram et al 1987b; Raychaudhuri et al 1987; Tarascon et al 1987; Xiao et al 1987). Obviously Y and Ln ions play no role in the superconductivity; they only help to keep the structure together.

Superconductivity in YBa$_2$Cu$_3$O$_{7-\delta}$ is extremely sensitive to oxygen stoichiometry (Rao et al 1987a, 1988a; Rao & Ganguly 1987b). Thus, the $\delta \geq 0.6$ sample is non-superconducting and tetragonal. Oxygen is readily intercalated into the $\delta \geq 0.5$
samples and the stoichiometry reaches close to YBa$_2$Cu$_3$O$_{6.5}$ on intercalation (figure 3). Structures of the orthorhombic ($\delta = 0$) and the tetragonal ($\delta = 1$) phases differ in an interesting manner. Besides the CuO$_2$ sheets, the stoichiometric ($\delta = 0$) phase contains Cu-O-Cu chains (or corner-linked CuO$_4$) units which are absent in the non-superconducting ($\delta = 1$) sample (David et al 1987; Bordet et al 1987). In figure 4 we compare the orthorhombic and tetragonal structures of the $\delta = 0$ and the $\delta = 1$ samples. In the $\delta = 0.6 - 1$ range, it seems that the tetragonal phase has disordered oxygens giving rise to distorted CuO$_6$ octahedra as indicated in figure 4c (Jorgensen et al 1987). In general, oxygen non-stoichiometry in the YBa$_2$Cu$_3$O$_{7-\delta}$ system has to be understood in terms of both disorder and structural distortion.

The variation of the superconducting transition temperature of orthorhombic YBa$_2$Cu$_3$O$_{7-\delta}$ with $\delta$ (in the $\delta$-range 0.0-0.5) is most interesting. In figure 5, the resistivity data of a few members with different $\delta$ values is shown while in figure 6, the $T_c$ values from the resistivity data are plotted against $\delta$ (Rao et al 1988a). In figure 6, we also show results from the magnetic measurements of Johnston et al (1987). Although the actual $T_c$ values vary in the different sets of data (figure 6), we see that the $T_c$ is nearly constant around 90 K at low $\delta$ (0.0-0.2) and drops to a lower value (~60 K) above $\delta = 0.2$ showing a plateau-like behaviour. The $T_c$ in the plateau region is similar to that of La$_{2-x}$Ba$_x$(Sr$_x$)CuO$_4$ (of the K$_2$NiF$_4$ structure). Since in this composition range, the Cu-O-Cu chains of YBa$_2$Cu$_3$O$_7$ will be depleted, we believe that the ~60 K plateau is characteristic of superconductivity due to CuO$_2$.
sheets while the 90 K $T_c$ is characteristic of the sheets in the presence of Cu-O-Cu chains. Figure 6 may therefore be taken to represent a transition from chain-type to sheet-type superconductivity brought about by the change in oxygen stoichiometry.

Several workers have in recent months synthesised derivatives of YBa$_2$Cu$_3$O$_{7-\delta}$ where Cu is substituted by Zn, Ni, Co, Fe and such ions or Ba is substituted by La and other ions. Such substitution in general lowers $T_c$ or destroys the superconductivity, the oxide generally being tetragonal and oxygen-deficient. It should be noted that non-superconducting YBa$_2$Cu$_3$O$_{7-\delta}$ compositions also possess the tetragonal structure. Weakly orthorhombic or nearly tetragonal samples prepared by low-temperature methods are non-superconducting as well. Bulk superconductivity has, however, been recently reported in tetragonal YBa$_2$(Cu$_{0.96}$Co$_{0.04}$)$_3$O$_{7-\delta}$ (Langen et al 1988).

4. Other La-Ba-Cu-O and related systems

The La$_{3-x}$Ba$_{3+x}$Cu$_6$O$_{14+\delta}$ family of oxides were considered to be high $T_c$ superconductors (Mitzi et al 1988) even though they did not possess Cu-O chains (Er-Rakho et al 1981). It is now known that these oxides are related to the 123 oxides (Segre et al 1987), the relative occupation of the 01/05 sites determining the orthorhombicity. Truly high $T_c$ is found in this system only in the orthorhombic structure when $x=1$, $\delta \approx 0.0$ (Ganapathi et al 1988). All other compositions ($x \neq 1$, $\delta \neq 0.0$) are generally tetragonal. In figure 7, the various rare-earth-containing families of oxides investigated by us for superconductivity are shown.

5. Bismuth and thallium cuprates

Two new families of superconducting cuprates with structures related to the
Figure 5. Electrical resistivity behaviour of YBa$_2$Cu$_3$O$_{7-\delta}$ for different values of $\delta$ (unpublished results from this laboratory).

Figure 6. Variation of $T_c$ of YBa$_2$Cu$_3$O$_{7-\delta}$ with $\delta$. Magnetic measurements of Johnston et al (1987) are indicated by the cross-hatched region. Our resistivity data are shown by full dark circles (from Rao et al 1988a).
(21) La$_{2-x}$Ba$_x$(Sr$_x$)CuO$_4$ (SC)
(212) La$_2$SrCu$_2$O$_6$
(415)La$_4$BaCu$_5$O$_{13}$
(336) La$_{3-x}$Ba$_{3+x}$Cu$_6$O$_{14-6}$ (SC)
(123) Ln Ba$_2$Cu$_3$O$_{7-6}$ (SC)  
(Ln = La, Y, Eu, Gd, Ho, Er etc)
(Ln, Ba)$_{n+1}$Cu$_n$O$_{3n+1}$
(212) Ln$_2$BaCu$_2$O$_x$
Ln Ba$_2$Cu$_2$O$_x$
(223) Ln$_2$Ba$_2$Cu$_3$O$_x$

Aurivillius family of oxides with $T_c$'s in the 100 K region have been discovered. The initial discovery of superconducting bismuth cuprates was by Michel et al (1987) who found $T_c$ in the 7–22 K range in oxides of the type Bi$_2$Sr$_2$Cu$_2$O$_{7+\delta}$. Maeda et al (1988) then found high $T_c$ (~100 K) in a Bi-Ca-Sr-Cu-O system. High $T_c$ superconductivity (~110 K) is exhibited by bismuth cuprates of the type Bi$_2$(Ca,Sr)$_3$Cu$_2$O$_{8+\delta}$ (Chu et al 1988; Hazen et al 1988; Rao et al 1988; Subramanian et al 1988; Tarascon et al 1988). In figure 8, we compare the structures of Bi$_4$Ti$_3$O$_{12}$ with that of Bi$_2$CaSr$_7$Cu$_2$O$_9$. In figure 9, we show the variation of resistivity and AC susceptibility of a sample to indicate the high $T_c$ behaviour. The bismuth cuprates have less oxygen lability and seem to be more stable. The exact composition of the 110 K material is more complex than that indicated by the formula Bi$_2$(Ca,Sr)$_3$Cu$_2$O$_{8+\delta}$.

Thallium cuprates of the Tl-Ba-Cu-O and Tl-Ca-Ba-Cu-O systems show high $T_c$ superconductivity with onset in the 100–120 K range (Hazen et al 1988; Ganguli et al 1988; Sheng & Hermann 1988). In figures 10 and 11, we show the resistivity and susceptibility behaviour of typical members of the Tl-Ca-Ba-Cu-O system. The structure of the 2122 oxide is identical to that of the corresponding bismuth compound, Bi$_2$CaSr$_2$Cu$_2$O$_{8+\delta}$. All these oxides of Bi and Tl contain Cu-O sheets.

Electron microscopic studies of the Bi and Tl cuprates show the extensive presence of defects and dislocations just as in the Aurivillius family of oxides. Intergrowths are also present in these systems and they may be responsible for the high $T_c$'s (200–300 K) found in some of the samples in this laboratory.

6. Role of oxygen

Having established the crucial role of oxygen in the superconductivity of these ceramic oxides, we have further explored the mechanism of superconductivity by means of X-ray photoemission and related studies. Variable-temperature XPS studies
High-temperature ceramic oxide superconductors

7. Some unusual features of the ceramic oxide superconductors

The most unusual feature of the new sensational high-\(T_c\) oxides is that they are
ceramic materials (and not metals). As mentioned earlier, in the normal state, they are poor conductors. While $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ seems to exhibit measurable $^{18}\text{O}$ isotope effect, there appears to be essentially no isotope effect in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system (Batlogg et al 1987). This means that the traditional BCS* theory is not valid in these oxide superconductors. While electron-phonon interaction could still play an indirect role, the actual nature of the role is not clear at present. The optical gap in $\text{YBa}_2\text{Cu}_3\text{O}_7$ seems to be $\sim 200 \text{ cm}^{-1}$ (Cardona et al 1987; Genzel et al 1987). A high-energy excitonic band (0.5 eV) whose intensity varies with $T_c$ seems to be present in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and this may be of significance. Such bands need to be further explored. While a large number of papers on theoretical models have appeared in the

*BCS – Bardeen, Cooper, Schreiffer
High-temperature ceramic oxide superconductors

Figure 10. Resistivity behaviour of 2122, 2212, 2213 and 2223 members of the Tl-Ca-Ba-Cu-O system (from the author’s laboratory). Better samples of 2223 show a $T_c$ of 125 K.

In the recent literature, there is yet no simple model or theory to explain high $T_c$ in the oxide superconductors. It seems best to get good experimental data and look for models later. One of the noteworthy features is that $T_c$ seems to increase with the number of Cu-O layers in the unit cell. The oxygen hole concentration also seems to increase in the same direction as $T_c$.

Electron microscopic studies of YBa$_2$Cu$_3$O$_7$ show the presence of certain domains (see figure 14) and twin boundaries in addition to other defects (see for example, Rao et al 1987c, 1988a; Subbanna et al 1987). The nature of the domains is causing curiosity. Noting that the coherence length is only a few angstroms, people are wondering about the origin and implications of such domains. Are they due to the co-occurrence of metallic and insulating phases (with different stoichiometry)? If so, what does the observed structure mean? The broad bands or domains (figure 14) found by us sometime ago (Rao et al 1987c), seem to be due to different orientations...
of the \((\text{CuO}_2)_\infty\) units (Rao et al 1988a). Such macroscopic features may be responsible for the unstable very high \(T_c \sim 300\) K behaviour of some oxides.

An interesting property of \(\text{YBa}_2\text{Cu}_3\text{O}_7\) in the superconducting state is that it absorbs electromagnetic radiation over a wide range of frequencies from a few MHz to a few GHz (Bhat et al 1987). The absorption is extremely sensitive to temperature, particle size and the magnetic field and crucially depends on the presence of ambient oxygen. It is suggested that Josephson junctions formed by oxygen and the superconducting grains may be responsible for this effect.

8. Material parameters and applications

Since these new oxide superconductors are ceramic materials, there are inherent problems in obtaining them in the desired shape and form. However, there has already been considerable success in making wires, tapes and films. During the processing of these materials, there is a tendency to lose the labile oxygen which renders them non-superconducting; this can be solved by reheating the processed material in oxygen or by proper insulation in the initial stage itself. Another difficulty with these oxide ceramics is their chemical instability. Success in technological
applications will depend on several factors (material parameters, cost etc.) as shown below.

Since YBa$_2$Cu$_3$O$_7$ is superconducting well above the liquid nitrogen temperature, it holds much promise. We shall briefly examine the material parameters of this ceramic oxide. Electronic properties of this oxide are anistropic (just as the structure). Some of its important properties are as follows (Malozemoff et al 1987):

1. It is a Type II superconductor.
2. Hall carrier density: $4 \times 10^{21}$ cm$^{-3}$ (for a material of resistivity $\sim 400 \mu\Omega$ cm just above the $T_c$).
Figure 13. Cu(L₃VV) Auger spectrum of YBa₂Cu₃O₇ at different temperatures. In the inset, the temperature variation of the intensity of the 942 eV feature relative to that of the 933 eV feature in the Cu(2p₃/₂) spectrum is shown. 1 and 2 refer to independent sets of measurements (from Sarma & Rao 1987).

3. \( \frac{dH_{c2}}{dT} = 2T/K \),
   BCS coherence length \( \approx 1.4 \text{ nm} \),
   London penetration depth \( \approx 200 \text{ nm} \),
   Mean free path \( \approx 1.2 \text{ nm} \).

4. \( H_c(0) \approx 1T \).

5. \( H_{c2}(0) \approx 120T \).
Critical current density: in ceramic samples $\sim 10^3$ A/cm$^2$ at 77 K, in films (on SrTiO$_3$) $\sim 10^5$ A/cm$^2$ at 77 K, in crystals and films $\sim 10^6$ A/cm$^2$ at 4.2 K.

Depairing current density: $10^7 - 10^8$ A/cm$^2$ (estimated).

The big market for superconducting materials is in magnetic resonance imaging for medical applications. The other magnetic applications with commercial implications are in high energy physics, high field magnets for scientific investigations and magnetic separation. Magnetic confinement of plasma (fusion), levitating transportation vehicles and magnetohydrodynamics are some of the applications where commercialization will not be in the near future. In all these applications the factors that will determine the use of the new ceramics are cost advantages and material performance characteristics. The most crucial material parameter is the critical current density; it is necessary to obtain high values in large scale production of the ceramic material. Even if this becomes possible, the material cost per ampere metre will be crucial. The biggest factor is the refrigeration cost. At present, the cost of YBa$_2$Cu$_3$O$_7$ (for use at 77 K) seems to be much higher than traditional superconductors. It is however hopeful that the usable current density of YBa$_2$Cu$_3$O$_7$ will soon be higher than Nb$_3$Sn for high-field applications. In the mean time, problems of fabrication and chemical stability have to be sorted out.

Use of these superconducting oxides for power transmission lines is a possibility. While the cost factor (of the material and for refrigeration) has to be carefully examined, there is every hope that YBa$_2$Cu$_3$O$_7$ at 77 K can be used profitably in the long run at least for underground lines.

The most immediate application that seems realistic is the use of YBa$_2$Cu$_3$O$_7$ as interconnects in computers. Other electronic applications are in mm-wave detection, high-speed digital and analog signal processing and digital Josephson technology. Electronic instruments utilizing superconductivity such as sensitive SQUID magneto-
meters, high speed samplers and voltage standards based on Josephson effects as well as non-Josephson devices such as superconducting bolometers and SIS mixers are areas where success is likely. Transistor-like devices compatible with oxide superconductors need to be explored vigorously.

The new bismuth cuprates are promising since they are more stable chemically and with respect to oxygen stoichiometry; good films have already been made. Thallium cuprates may not be used as they are poisonous.

9. Concluding remarks

The tremendous possibilities for wide application of YBa$_2$Cu$_3$O$_7$ and other high $T_c$ ceramic oxides make this area of research most exciting. Clearly, the high-temperature ceramic oxide superconductors constitute the most sensational discovery since the transistor; it has given a great boost to research in solid state science and engineering. There is no doubt that within a short time frame, some commercial applications will become a reality even with existing materials. The future offers unlimited vistas and opportunities in electromagnetic technology as well as in oxide ceramics research. Synthesis of materials with $T_c$'s close to room temperature or higher is no longer a remote possibility.

The author thanks the Department of Science and Technology, Government of India, and the University Grants Commission for support of this research. He also expresses his deep sense of gratitude to his collaborators for their enthusiastic participation in the research activities related to oxide superconductors.

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Electronic ceramics

V C S PRASAD
Materials Development Department, Bharat Electronics Ltd, Bangalore 560 013, India

Abstract. Electronic ceramics represent an important segment of advanced ceramics and will probably constitute a major share of the advanced ceramic markets at least till 2000 AD. Yet, other than ferrites, this area has not been sufficiently examined in this country. Therefore, this review covers briefly the science and technology status, the markets and the possible future projections of these ceramics the world over vis a vis the Indian situation and indicates the scope for indigenous effort in this vital area of electronic components.

Keywords. Multilayer ceramics; grain boundary devices; PZT ceramics; dielectric resonators; barium titanate; tape casting.

1. Introduction

Since electronic ceramics are expected to constitute a major share of the advanced ceramic markets at least till 2000 AD (Rah 1986), it is important to examine this topic in the Indian context vis a vis the world situation. Included in this review are multilayer ceramics, the newer ceramics and very briefly the sensors and the microwave dielectrics. Typical useful features of these devices and their availability status in India are given in table 1. The literature review is by no means exhaustive but serves to highlight the important aspects. Dielectric and optical materials were recently reviewed by Subbarao et al (1981, pp. 217-245) and ferrites by Das (1981, pp. 75-100), Alam & Nair (1981) and Jain & Sarnot (1982).

2. Multilayer ceramics

Multilayer ceramics are evolved mainly to increase the volumetric efficiency of the components thereby achieving circuit miniaturization. In the case of multilayer capacitors, high capacitance density can be achieved (Goodman 1981) by connecting a number of dielectric layers in parallel using internal metal electrodes. In the case of multilayer packages used for packaging of integrated circuits, the third dimension is used to increase the number of metal conductors for increasing the I/O counts. In the case of more complex packages called modules, the third dimension is used to accommodate a number of functions (Schwartz 1984) including that of substrate, interconnections, cooling, environmental protection etc. In the case of multilayer
<table>
<thead>
<tr>
<th>Item</th>
<th>Useful features</th>
<th>Availability from indigenous sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multilayer capacitors</td>
<td>High volumetric efficiency and wide capacitance range, possibility of replacing the Ta capacitors reducing the dependence on the scarce Ta metal. Suitability for surface mount assembly</td>
<td>NA*</td>
</tr>
<tr>
<td>Multilayer packages and substrates</td>
<td>Packaging of high reliability IC, scope for manufacture of high component density custom made substrates for miniaturisation and cost reduction. Indispensable as a hybrid substrate</td>
<td>NA</td>
</tr>
<tr>
<td>IBL capacitors</td>
<td>High volumetric efficiency, better temperature and loss characteristics compared to the conventional barrier layer capacitors</td>
<td>NA</td>
</tr>
<tr>
<td>PTC resistors</td>
<td>Semiconductivity at room temperature and insulating characteristics above the Curie point. Useful for a number of devices based on current limiting, and temperature sensing characteristics. Typical applications are in industrial and consumer electronics, telecommunications and power engineering</td>
<td>Scantily available but likely to be available soon in larger quantities</td>
</tr>
<tr>
<td>Varistors</td>
<td>High nonlinear current voltage characteristics with much greater current and energy handling capacity than the Zener diodes. Useful for transient surge suppression. Typical applications are in industrial and consumer electronics, telecommunications and power engineering</td>
<td>NA</td>
</tr>
<tr>
<td>PZT ceramics</td>
<td>Large electromechanical coupling coefficient resulting in a number of devices in the sonic and ultrasonic frequency range and also for use as resonators and filters with better volumetric efficiency, temperature characteristics and large band width when compared to their conventional counterparts</td>
<td>Scantily available but likely to be available soon in larger quantities</td>
</tr>
<tr>
<td>PZT ceramics a) Homogenous</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>b) Composites</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>Dielectric resonators</td>
<td>Improved volumetric efficiency and better temperature stability and ease of manufacture when compared with their conventional counterparts</td>
<td>NA</td>
</tr>
</tbody>
</table>

*NA - not available
Development to suit the surface mount assembly is being done wherever possible

multicomponent substrates (MMC), the third dimension is used to increase the number of components embedded in a single monolithic substrate (Utsumi et al 1985).

2.1 Multilayer capacitors

Because of the scope for circuit miniaturization and the possibility of using the components (as chips) in surface mount assembly applications, the usage of multilayer capacitors (MLC) is growing rapidly the world over. For example, in the
US, in the last decade, the annual growth rate (Blum et al 1985) averaged between 25% to 35% and the growth has followed closely that of the integrated circuits. There are many excellent articles (e.g., Capozzi 1975) on the science and technology of the manufacture of MLC capacitors. The main R & D thrust areas are the following:

a) Improving the capacitance density as much as possible by the development of ultrathin high density tapes (Tormey et al 1984, pp. 140–149) and also higher dielectric constant compositions.

b) Developing suitable dielectric compositions which can cofire with less noble metal electrodes to reduce the costs and also to reduce the dependence on the precious and scarce noble metals (e.g. Burn & Secaur 1986, unpublished).

c) Developing suitable dielectric compositions to have improved dielectric saturation characteristics to extend the range for higher voltage applications (e.g., Subbarao et al 1981, pp. 217–245).

d) Improving the lot to lot variations through the complete characterization of the initial raw materials and instituting process controls (e.g. Stynes 1981, unpublished).

e) Working for process innovations to minimize some of the inherent problems associated with the MLC capacitor manufacture such as the delamination problems etc, e.g. the Corning ACE process or the fugitive electrode process (Newnham & Hiremath 1985).

The typical dielectric materials of promise are still the BaTiO₃ based compositions (such as the Z5U and X7R. Figure 1 shows the improvements in the latter over the years, Cantagrel 1986). However, lead based perovskite relaxor materials (such as lead magnesium niobate, PMN) which sinter at temperatures as low as 900°C for use with near hundred percent silver electrodes (≥85% Ag) are some of the latest compositions being tried by the industry (Takamizawa et al 1981; Yonezewa 1983). The processing and powder purity strongly influence the dielectric behaviour of these materials (Swartz et al 1984 and Chen et al 1986).

Achieving high yield and reliability are some of the technological problems receiving considerable attention in the MLC capacitor manufacture. The reasons for the poor yield and reliability are gross defects and processing accidents which are often
aggravated by complex interactions between ceramic dielectric, flux and electrode materials (R E Newnham 1984, unpublished). In addition, other interactions arise from the organic binders and vehicles used in tape casting, from the solder and other materials used in terminations, encapsulation and from the environment etc.,

2.2 IC packages

The standard ceramic IC packages are three-layered structures (Reiss & Glicksmann 1981) the top layer containing the seal ring, the middle one the bonding pads, and the bottom one the die pad (figure 2). Appropriate conductor patterns (with refractory metal conductors such as Mo or W) are printed on green alumina ceramics, laminated and cofired to give rise to monolithic ceramic packages. The chip carriers are the space saving, cheaper versions of the standard dual in-line packages (DIP). For housing complicated ICs with high I/O count, (say > 8, 4 and sometimes even 64) the pin grid array (Ohr 1983) was introduced by IBM. IBM makes some highly complex custom-made ceramic packages for housing ICs used in high speed computers. For example, some of the IBM arrays have 23 layers and 261 pins housing multiple IC chips (Schwartz 1984). However, for most of the applications, the DIP and the chip carriers are used and the latter is going to replace the DIP particularly in the 40-84 pin count range where the DIP's size and the cost are too high to be competitive.

The main R&D areas of interest for packaging (Schwartz 1984) are the

Figure 2. Exploded view of a DIP and a chip carrier (Reiss & Glicksman 1981).
Electronic ceramics

Table 2. Ceramic materials currently used in substrates and packages.

<table>
<thead>
<tr>
<th>Material</th>
<th>Dielectric constant</th>
<th>Thermal expansion ((10^{-6}/°C))</th>
<th>Thermal conductivity ((W/mK))</th>
<th>Strength ((MPa))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina 96%</td>
<td>10</td>
<td>7-1</td>
<td>21</td>
<td>280</td>
</tr>
<tr>
<td>Alumina 92%</td>
<td>9-5</td>
<td>6-9</td>
<td>17</td>
<td>320</td>
</tr>
<tr>
<td>Alumina 90%</td>
<td>8-5</td>
<td>7-0</td>
<td>17</td>
<td>280</td>
</tr>
<tr>
<td>Alumina 55% + glass 45%</td>
<td>7-5</td>
<td>4-2</td>
<td>4-2</td>
<td>300</td>
</tr>
<tr>
<td>SiC</td>
<td>40</td>
<td>3-4</td>
<td>33</td>
<td>280</td>
</tr>
<tr>
<td>BeO</td>
<td>7-0</td>
<td>8-0</td>
<td>25</td>
<td>170</td>
</tr>
</tbody>
</table>

Reference: Schwartz (1986)

development of low dielectric constant ceramics of matching thermal expansion to that of silicon and processes capable of finer resolutions for printing the conductor patterns. New methods of synthesizing the starting powders, improved precursor materials, clean room operations, and optical processing will be the additional future R & D thrust areas in ceramic packaging. Schwartz (1986) gives the list of ceramic packaging materials that are currently used (table 2) and those under consideration for the future (table 3).

2.3 Multilayer multicomponent substrates

The demand for greater circuit miniaturization and consequent cost reduction resulted in innovative packaging techniques using the multilayer ceramic technology in which the passive components such as capacitors, resistors and wiring conductors are integrated into the package (Utsumi et al 1985). Such a package is called the monolithic multicomponent ceramic package (MMC). In this package, in addition to the insulator layers printed with conductors and resistors, dielectric layers prepared with materials of suitable dielectric properties are cofired. An exploded vertical section of the MMC substrate for a voltage controlled crystal oscillator is shown in figure 3. The total substrate size is 17 mm \(\times\) 10 mm \(\times\) 1 mm, involving 8 capacitor elements and 10 resistor elements as shown within the dotted lines of the circuit. The typical flow sheet for the fabrication of such a package is shown in figure 4. This process is more or less a combination of the multilayer capacitors and multilayer packaging processes. It is different from the more commonly used multilayer hybrid technology in that the insulation layers are made of ceramic tape instead of being printed with insulating glass paste. The use of conventional capacitors instead of printed capacitors in the package would result in an extremely complex type of

Table 3. Ceramics for future use in substrates and packages.

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Dielectric constant</th>
<th>Thermal expansion ((10^{-6}/°C))</th>
<th>Thermal conductivity ((W/mK))</th>
<th>Strength ((MPa))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum nitride</td>
<td>8-8</td>
<td>4-6</td>
<td>84-250</td>
<td>360</td>
</tr>
<tr>
<td>Silicon nitride</td>
<td>6-0</td>
<td>3-2</td>
<td>33</td>
<td>590</td>
</tr>
<tr>
<td>Glass-ceramics</td>
<td>4-5-6-5</td>
<td>2-5-6-5</td>
<td>0-84-2-1</td>
<td>241</td>
</tr>
<tr>
<td>Mullite</td>
<td>6-1</td>
<td>4-5</td>
<td>2-1</td>
<td>210</td>
</tr>
</tbody>
</table>

Reference: Schwartz (1986)
wiring network resulting in high values of lead inductances consuming the real estate space. The integration of capacitor elements into the package minimizes this problem.

The necessity of cofiring the insulators, dielectrics, conductors, and resistors imposes considerable restriction on the choice of materials to be used in this type of package. For example, the Japanese (Utsumi et al. 1985) have used a mixture of alumina and lead borosilicate (55% and 45% respectively) for the insulator layers, low firing lead based compositions such as $\text{Pb(Fe}_{2/3}\text{·W}_{1/3})\text{O}_3\cdot\text{Pb(Fe}_{1/2}\text{·Nb}_{1/2})\text{O}_3$ binary systems for the dielectric layers, Ag-Pd, Pd and Au for internal conductors,
Au and Au-Pt for external terminations and RuO$_2$ based pastes for the resistor materials. The composite substrate can be fired at 900°C. These composite substrates were used in the development of voltage controlled crystal oscillator circuits (VCXO) and RC active filters. The VCXO are used in digital communication equipment as clock generators and as timing signal generators. A size reduction to 1/10th and a weight reduction to 1/3rd is claimed to have been achieved by integrating the different passive components in the substrate.
In addition to the above devices using the multilayer technology, a number of electronic ceramic devices are being contemplated in multilayer configurations such as multilayer barrier layer capacitors, multilayer PTC thermistors, multilayer piezoelectric transducers and resonators, multilayer fuel cells, composite multilayer devices etc. particularly using the fugitive electrode process (Newnham & Hiremath 1985). Many advantages in addition to volumetric efficiency are foreseen in most of these devices. For example, a multilayer sonar transducer can be driven with much lower voltages involving the use of smaller size transformers than when using thick solid transducers, a multilayer PTC device can have a much lower room temperature resistance than a solid PTC etc.

3. Devices based on grain boundary phenomenon

The properties of polycrystalline electrical ceramics are greatly influenced by the electrical and mechanical boundary conditions existing at grain and phase boundaries. Properties may be engineered into polycrystalline systems which never could be obtained in single crystals alone. Notable examples are internal boundary layer (IBL) capacitors, positive temperature coefficient of resistance (PTCR) devices and varistors exhibiting highly nonlinear current-voltage characteristics.

3.1 IBL capacitors

In the IBL capacitors, anomalously high dielectric constants are obtained in materials with semiconducting grains surrounded by insulating boundaries (Waku 1969). The value is directly proportional to the diameter of the grains and inversely proportional to the thickness of the boundary. Goodman (1981, pp. 215–231) has presented an excellent review on this topic.

Although ferroelectric BaTiO₃ ceramics were originally used for this application, SrTiO₃ ceramics have become more popular because of their better temperature characteristics (these have almost flat temperature capacitance curves, figure 5a), higher stability with respect to capacitance change under d.c. biasing field and lower loss over a wide frequency range. Typical dielectric properties of a material developed with regard to high dielectric constant are given in figure 5b.

Usually the insulating second phase layers around the semiconducting grains are formed by painting on the ceramic a paste consisting of low melting glasses such as PbO-Bi₂O₃-B₂O₃. When this coated ceramic is refired, the low melting glass penetrates the grain boundaries and dissolves in the excess TiO₂ phase of the ceramic giving rise to insulating boundary layers (Wernicke 1981, pp. 261–271). The structure (schematic) and equivalent circuit of a grain boundary are shown in figure 6 (Wernicke 1981, pp. 272–281). Work on single fire processes to achieve the insulating boundaries through solute segregation is also being attempted (Yan & Rhodes 1983).

The capacitance density of an SrTiO₃ boundary layer dielectric is generally higher than that of the electrode barrier layer (table 4) although for the packaged capacitor, this difference is less and even insignificant for some types. These capacitors are increasingly used in the field of TV, VCR, radio etc. They are also being tried as replacements of organic film capacitors because of their markedly increased capacitance range.
Electronic ceramics

Composition: $\text{Sr}_{100} (\text{Ti}_{100} \text{Nb}_{1.5}) \text{O}_{300+\delta}$ $k_{\text{eff}} = 9400$ at $25^\circ\text{C}$
Additions: 0-1 wt% $\text{Al}_2\text{O}_3$ 0-2 wt% $\text{SiO}_2$ $\tan \delta = 0.6\%$
Sintering: 1450°C in $\text{H}_2/\text{N}_2$ $\Delta C/C_{25} < \pm 1\%$ ($-55$ to $125^\circ\text{C}$)
Second firing: 1100°C $\rho_{\text{eff}} > 10^{11} \Omega \text{cm at 1 kV/cm}$

Composition: $\text{Sr}_{100} (\text{Ti}_{100} \text{Nb}_{1.0}) \text{O}_{300+\delta}$ $k_{\text{eff}} = 65,000$ at $25^\circ\text{C}$
Addition: 0-05 wt% $\text{SiO}_2$ $G/A = 110 \text{nF/cm}^2$
Sintering: 1470°C in $\text{H}_2/\text{N}_2$ $\tan \delta = 0.7\%$
Second firing: 1150°C $\Delta C/C_{25} < \pm 22\%$ ($-55$ to $125^\circ\text{C}$)
$\rho_{\text{eff}} > 10^{10} \Omega \text{cm at 1 kV/cm}$

Figure 5. Dielectric properties of a boundary layer capacitor material developed with regard to (a) a low temperature coefficient (b) a high dielectric constant (Wernicke 1981, pp. 272-281).

3.2 PTC resistors

These devices also have a semiconductive grain structure interleaved with a very narrow barrier layer system at the boundary just as in the case of the IBL capacitors. However, the barrier layer here is the intrinsic boundary layer due to the barium vacancy diffusion (Daniels et al 1979) whose thickness can be controlled by the cooling rates.

In $\text{BaTiO}_3$, which is a component of all PTC resistors, the resistivity change occurs near the Curie temperature at around $130^\circ\text{C}$ and may encompass 8 orders (Daniels & Wernicke 1976). The PTC mechanism was first explained by Heywang (1961) by means of a grain boundary barrier model (figure 7) according to which the Schottky-type grain boundary barriers originate from two-dimensional layers of negative
grain boundary

semicond. Sr TiO₃ \(d_g \sigma_0\)

insulating Sr TiO₃ \(d_1/2, k_1, \sigma_1\)

second phase \(d_2, k_2, \sigma_2\)

equivalent circuit

\[
C_1 = \varepsilon_0 k_1 \frac{A}{d_1}, \quad R_1 = \frac{1}{\sigma_1 A}, \\
C_2 = \varepsilon_0 k_2 \frac{A}{d_2}, \quad R_2 = \frac{1}{\sigma_2 A}, \quad \text{(second phase layers)}
\]

\[
R_g = \frac{1}{\sigma_0 A}, \quad \text{(grain resistance)}
\]

\[
\frac{1}{k_{eff}} = \frac{1}{\varepsilon_0 k_1} \left( \frac{d_1 + d_2}{k_1 + k_2} \right), \quad \frac{1}{\sigma_{eff}} = \frac{1}{\varepsilon_0 \sigma_1} \left( \frac{d_1 + d_2}{\sigma_1 + \sigma_2} \right) + \frac{1}{\varepsilon_0},
\]

where \(k\) represents the dielectric constant, \(d\) the thickness, \(\sigma\) the conductivity, \(A\) the area of cross-section, \(R\) the resistance, \(C\) the capacitance, \(\varepsilon_0\) the permittivity of vacuum.

Figure 6. Structure and equivalent circuit of a grain boundary (Wernicke 1981, pp. 272–281).

charge caused by acceptor states at the boundary. The acceptor character could arise due to the oxygen adsorption. These surface states take up conduction electrons from the immediate vicinity, thus giving rise to a negatively charged boundary layer

<table>
<thead>
<tr>
<th>Type</th>
<th>Packaged capacitor</th>
<th>Dielectric only (mfd/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrode barrier layer</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Disk, 0.1 mfd, Y5U, 75V</td>
<td>0.1</td>
<td>0.76</td>
</tr>
<tr>
<td>Disk, 0.1 mfd, Y5U</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>BaTiO₃ GBBL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tube 0.1 mfd, Y5 (?) 63V</td>
<td>0.65</td>
<td>3.22</td>
</tr>
<tr>
<td>Disk 0.022 mfd, Y5T</td>
<td>0.085</td>
<td></td>
</tr>
<tr>
<td>SrTiO₃ GBBL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tube, 0.01 mfd, Y5U</td>
<td>0.27</td>
<td>2.27</td>
</tr>
<tr>
<td>Disk, 0.1 mfd, Y5U</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>Disk, 0.1 mfd, Y5R, 25V</td>
<td>0.25</td>
<td>2.53</td>
</tr>
<tr>
<td><strong>Monolithic, conventional</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 mfd, Z5U</td>
<td>4.03</td>
<td>13.5</td>
</tr>
<tr>
<td>0.1 mfd, Z5U</td>
<td>2.69</td>
<td>7.93</td>
</tr>
</tbody>
</table>

*50 V rated, unless otherwise indicated
with, on both sides, a positive space charge that forms a symmetrical potential barrier for the remaining conduction electrons. The resistivity is proportional to \( \exp(e\phi/KT) \) where \( \phi \) is the height of the potential barrier. According to the theory \( \phi \propto N_s^2/en \) where \( N_s \) is the density of surface states, \( e \) the dielectric constant and \( n \) the concentration of the conduction electrons. Since \( \phi \) is inversely proportional to the dielectric constant, the height of the potential barrier rapidly increases at a temperature above the Curie point where the dielectric constant sharply decreases (figure 8). This would explain the steep rise in the electrical resistivity above the Curie point. Below the Curie point, the surface states are wholly or partly compensated by the proper alignment of the spontaneous polarization (figure 9) that is associated with the ferroelectric state. Therefore, the resistivity is low.

Ihrig (1983) attempted a modification of this model by assuming a constant density dispersion of the grain surface acceptor energies and studied the PTC effect as a function of different technological parameters. Daniels et al (1979) have improved the

**Figure 7.** A potential barrier caused by surface states S at a grain boundary B of donor-doped BaTiO\(_3\) (schematic), \( \phi \) is the height of the potential barrier, C conduction band (Daniels et al 1979).

**Figure 8.** (a) Variation of resistivity with temperature of a BaTiO\(_3\) PTC thermistor. (b) Variation of the permittivity with temperature of ceramic BaTiO\(_3\) (Jonker 1981).
understanding of the PTC mechanism by using the defect chemistry of doped BaTiO$_3$. An exhaustive review on PTC materials technology was made by Kulwicki (1981). Ryan & Subbarao (1962) showed that the charge carriers in semiconducting BaTiO$_3$ are of the $n$-type using the Hall effect measurement.

Considerable effort in PTC materials technology has been made to lower the cold resistivity without losing the PTC jump. The cold resistivity is not only influenced by the charge carrier density and the intrinsic mobility of the material but also by the presence of the residual grain boundary barriers or charge. A homogenous grain structure is expected to minimise the grain boundary barrier (Ihrig 1983) through the formation of a homogenous domain structure. Therefore, a homogenous micro-structure is required to get a high performance PTC device.

The PTC phenomenon has been utilized to produce a number of commercial devices such as degausser elements for colour TV, motor starters and crankcase heaters for refrigeration and air conditioning compressors, time delay relays, air heaters for hair dryers, hair curlers, food warmers and a wide range of thermistors and current limiters for electronic applications.

3.3 Varistors

Varistors based on ZnO are novel ceramic semiconductor devices with highly nonlinear current-voltage characteristics (figure 10) similar to back-to-back Zener diodes but with much greater current and energy handling capabilities. The varistors are

---

**Figure 9.** Ferroelectric domains at a boundary between two crystallites of different orientations, with compensating surface charges (Jonker 1981).

**Figure 10.** Current-voltage characteristics of a varistor (Matsuoka 1981).
produced by a ceramic sintering process that gives rise to a structure composed of conductive ZnO grains surrounded by electrically insulating barriers. These barriers are derived from trap states at the grain boundaries induced by additive elements such as Si, Co, Pr, Mn etc. A typical composition given by Matsuoka (1971) contains 97 mol% ZnO, 1 mol% Sb$_2$O$_3$ and ½ mol% each of Bi$_2$O$_3$, CaO, MnO and Cr$_2$O$_3$. Excellent reviews (Matsuoka 1981; Levinson & Philipp 1986) on this topic exist in the literature. Varistors based on semiconducting silicon carbide were the earlier versions but they have a lower surge current capacity than the ZnO varistors.

The nonlinear current properties of the ZnO varistors were explained (Mahan 1982, p. 333) in terms of the formation of a Schottky barrier adjacent to the interface of each ZnO grain. The nonlinear electrical behaviour is caused by electrons trying to get past this barrier. Electron transport through the interface is believed to be a two-step process, whereby first the electron goes from a ZnO grain to the interface and secondly on to the next ZnO grain.

The application of ZnO varistors is predominantly in the field of circuit over-voltage protection, although it is used sometimes as a circuit element. These components have come into prominence with the advent of the solid state circuitry because the solid state components cannot in general withstand the amount of overvoltage imposed upon the circuitry by typical power system transients. On the application of an external field, the device is insulating up to a certain level, the breakdown field, above which it becomes highly conducting (figure 10).

4. Piezoelectrics

A number of piezoelectric compositions, most of them proprietary, are developed in the lead zirconate titanate system more commonly known commercially as PZT-4, PZT-5A and 5H, PZT-6A and 6B, PZT-7A etc. These still form the basis for most ceramic piezoelectric transducers (Jaffe et al 1971). A great amount of effort has been concentrated, particularly in Japan, upon modifications to the PZT compositions to trim properties and facilitate fabrication for specific device structures and a wide range of options are now available, from very low coercivity (ultra-soft) high sensitivity compositions to heavily self-biased high coercivity hard compositions (Takahashi & Takahashi 1972). Some are based on ternary and quaternary systems such as Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-Pb(Sn$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$-PbZrO$_3$ suitable for high power applications (Nishida et al 1980). Development work on relaxor compositions with larger strain, lower hysteresis and ageing effects than for normal varieties of PZT is an interesting area of activity (Uchino et al 1980) with application in precise position control etc. These compositions are generally in the family Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (0-9 PMN-0-1 PT). Typical electromechanical and thermo-mechanical data for these ceramics are given in figure 11. These ceramics reveal huge strains up to 0.1% (i.e. a 1 cm sample can elongate by 10 μm) without hysteresis, eminently suitable as electrostrictive actuators (Uchino 1986).

A very important new direction of work in the PZT ceramics is the synthesis of composite PZT consisting of ceramic powders and polymers with controlled connectivity (Skinner et al 1978) of the phases to expand the range of properties substantially when compared with the conventional PZT ceramics. For example, in one such 3-3 composite of PZT and rubber, the longitudinal voltage coefficient $g_{33}$ is
Figure 11. (a) Transverse strain of a ceramic specimen of 0.9 PMN:0.1 PT in a typical hard PZT8 piezoelectric ceramic under slowly varying electric fields. Strain levels are comparable in the two materials but the relaxor is more reproducible because of the field induced deaging in the PZT. (b) Thermal strain in ceramic 0.9 PMN:0.1 PT. Linear expansion is about $10^{-5}$/°C at 400°C and less than $10^{-6}$/°C at room temperature (Cross 1984).

Piezoelectric ceramics are not only used as transducers but also as resonators and filters (Schuessler 1974; Onoe 1979). Ceramic filters are piezoelectric ceramic substrates with electrodes (interdigital patterns) designed to convert electric signals to mechanical vibrations to obtain filter characteristics by utilizing the mechanical resonance of the substrates. Suitable vibration modes are selected depending upon the filter frequencies needed. Ceramic filters are characterized by small size, high selectivity and high stability as compared to the conventional LC filters and do not
require adjustment (e.g. Cross 1984). They play an important role in radio circuits, determining their selective performance and in video circuit separating audio from video signals. The FM single chip IC radio uses PZT ceramics as discriminators. Typical transmission characteristics of a monolithic filter element are shown in figure 12.

The PZT ceramics in their shear mode are also used in delay lines for colour TV sets and also in high frequency military communication and detection. These ceramics are also one of the candidate materials for use as substrate for surface acoustic wave (SAW) devices. High frequency filters can be easily fabricated by merely varying the interdigital transducer (IDT) pitch. This can be accomplished by utilizing IC manufacturing techniques. However, LiNbO3 single crystal substrates are more popular for this application in spite of their somewhat higher cost.

5. Sensors

The various special properties of ceramics such as the grain boundary phenomenon (e.g. positive temperature coefficient of resistivity, voltage dependent resistivity etc.), the piezoelectric effects, oxygen ion conductivity, or controlled pore structure (water vapour condensation) etc. are going to be utilized increasingly for the next generation of sensors for various applications (e.g. Fisher 1986; Murata & Itoh 1985). Ceramic sensors can be optimized and tailored to specific applications. Given the extremely diverse and specialised nature of the market, interest by the process

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Table 5. Comparison of several transducer materials.

<table>
<thead>
<tr>
<th>Property</th>
<th>PVF2</th>
<th>Homogenous PZT-501A</th>
<th>Flexible 3-3 composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>$1.8 \times 10^3$ kg/m$^3$</td>
<td>$7.9 \times 10^3$ kg/m$^3$</td>
<td>$3.3 \times 10^3$ kg/m$^3$</td>
</tr>
<tr>
<td>Compliance</td>
<td>High</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>$d_{33} \times 10^{-12}$ c/N</td>
<td>14</td>
<td>400</td>
<td>100</td>
</tr>
<tr>
<td>$e_{R}$</td>
<td>10</td>
<td>2000</td>
<td>40</td>
</tr>
<tr>
<td>$\theta_{33} \times 10^3$ Vm/N</td>
<td>140</td>
<td>20</td>
<td>300</td>
</tr>
</tbody>
</table>

Reference: Skinner et al 1978

---

Figure 12. Transmission characteristic of monolithic filter element (coupling coefficient 1.65%, matching resistors 125Ω, transmission loss $\alpha_d = 2.4$ dB (Schuessler 1974)
industry could have a strong guiding effect on ceramic sensor development (Wachtman J B Jr, unpublished).

An interesting and very important line of development is the integration of sensing elements on to the same silicon chip as microcircuitry (Allen 1984). Force, proximity, heat, motion and chemical analysis sensors are being developed very actively.

6. Dielectric resonators

These ceramics work on the principle that dielectric samples exhibit electromagnetic resonance as soon as the wavelength gets shorter than the sample size. If the resonant frequency versus time, temperature etc., is stable, such devices are very useful for making microwave filters and oscillators allowing size reduction and easier manufacturing (Plourde 1981). The applications are in military communication equipment, TV satellite reception etc.

A number of materials have been studied for these applications which include the zirconate systems, barium nanotitanate \( (\text{Ba}_2 \text{Ti}_9 \text{O}_{20}) \), \( (\text{Zr, Sn}) \text{TiO}_4 \), \( \text{BaO-Nd}_2 \text{O}_3-\text{TiO}_2 \), \( \text{Ba(Zn, Ta) O}_3 \), etc. An excellent review on high frequency dielectrics was recently presented by Wakino & Tamura (1986-unpublished). Two of the above compositions, the nanotitanate and the \( (\text{Zr, Sn}) \text{TiO}_4 \) seem to have been in commercial production. Since the damping constant, or the quality factor, depends on lattice imperfections and impurities, minimization of various defects in the grains is very essential for successful manufacture.

7. Processing and fabrication

A good deal of work is going on particularly in Japan and USA on the development of novel processing routes for the synthesis of high quality powders (high purity and controlled particle size) (e.g. Mazdiyasni 1984) for use as starting materials. However, the bulk of the commercial production still appears to be done using the powders prepared from the conventional solid state route because of the high cost of the former. Nevertheless, high quality powders will be increasingly used for the newer sophisticated applications (e.g. figure 1). Considerable control of the microstructure is being done through careful selection of the initial raw materials and careful processing for the majority of the items discussed and invariably for the devices based on grain boundary phenomenon.

A ceramic fabrication process that was exclusively developed for the fabrication of thin ceramics and multilayers is the tape casting process. In this process, ceramic powder in the form of a slurry (consisting also of binders, plasticizers, surfactants and solvents) is cast on to a moving carrier belt or tape, using a doctor blade to control the thickness. There are many excellent articles (Shanefield & Mistler 1971; Williams 1976) on the details of this process and a good deal of development effort is going on to minimise the extent of polymer and the total organic content in the ceramic slurries and also to remove the polymer phase through reactive chemical processing instead of burning (Tormey \textit{et al} 1984). Cosintering of metals and ceramics in the multilayer ceramics is a careful operation necessitating close control.
In the case of PZT ceramics, fine powders prepared by the special processing routes are used in some applications such as substrates for SAW filters etc. Hot pressing techniques are being tried for the production of very high density material and also for translucent ceramics. Innovative processing techniques are being developed to fabricate composite PZT. One such is the lost wax technique to replicate skeletal structures described in detail by Skinner et al (1978). Semiconductor processing techniques such as photolithography and thin film technology are widely used for printing fine line conductor patterns on PZT ceramics used for filter applications. The other supporting technologies that are often used are screen printing, electroplating, brazing etc. In addition to materials processing technologies, special encapsulation and packaging techniques are to be evolved for some of the devices (e.g., ceramic filters for TV SIF stage) for successful production.

8. Status in India

A summary of R & D activities on different electronic ceramic materials in India is given in table 6. It is clear from the table that R & D work of fairly high quality has been done in most of the areas of electronic ceramics reviewed. However, total production technologies leading to a competitive position in the market place are yet to be significantly evolved by indigenous efforts. Bharat Electronics Ltd., Bangalore, and Central Electronics Ltd., Sahibabad, are engaged in such activity to some extent. In some areas such as PZT ceramics, although considerable amount of R & D work has been done by a number of institutions in the country, the extent of commercialization is not proportional. This is to some extent due to the small quantity demands for many of the items. On the other hand, in areas such as multilayer ceramics and related materials (including substrates) the effort is not significant, although these products are likely to command considerable markets including defence requirements in the future.

The availability status of the basic raw materials required for electronic ceramics is given in table 7. It can be seen that India has almost all the basic raw materials that are generally used in the production of electronic ceramics. However, the purity levels and the powder characteristics need to be further tailored to meet the exact requirements of many of the sophisticated applications.

9. Markets

In the field of advanced ceramics, electronic ceramics are expected to constitute a major share of the market at least till 2000 AD. The industry analysis division of the US Department of Commerce (Rah 1986) indicates markets worth $1825 million for advanced ceramics in the year 1985 out of which about $1700 million is for electronic ceramics. The predicted figure in 2000 AD is $3485 million for electronic ceramics out of a total of $5895 million for advanced ceramics. The markets in Japan are slightly higher, $1800 million in 1985 and $2200 million by 1990. These two countries together share more than 80% of the world market and this trend is expected to continue in the future also. The market figures indicated above are only approximate and are meant to convey general trends. The figures vary from source to source. A
Table 6. Summary of R&D activities on various electronic ceramic materials in India.

<table>
<thead>
<tr>
<th>Nature of work</th>
<th>Centre/or centres where carried out*</th>
<th>Nearest application area</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Mn-doped BaTiO$_3$ and study of the saturation characteristics of PLZT composition with different dopants</td>
<td>IIT, Kanpur (Desu &amp; Subbarao 1981; Gururaja &amp; Subbarao 1980)</td>
<td>Multilayer ceramic capacitors</td>
</tr>
<tr>
<td>b) Low temperature firable dielectric compositions</td>
<td>IIT, Kanpur (Ramesh Choudhary &amp; Subbarao 1981) BEL, Bangalore (Mukherjee &amp; Ravishankar 1978)</td>
<td>Multilayer ceramic capacitors</td>
</tr>
<tr>
<td>Low temperature firable glass ceramic compositions</td>
<td>BEL, Bangalore</td>
<td>Multilayer substrates</td>
</tr>
<tr>
<td>Tape casting process technology</td>
<td>BEL, Bangalore (Prasad &amp; Kannan 1982)</td>
<td>Multilayer ceramics, alumina substrates and some PZT transducer devices</td>
</tr>
<tr>
<td>Effect of process variables, EPR studies for characterizing the internal boundary layers, micro-structural studies etc.</td>
<td>IISc, Bangalore (Kutty et al 1984; Murugaraj &amp; Kutty 1985). IIT, Kharagpur</td>
<td>IBL capacitors</td>
</tr>
<tr>
<td>a) Investigations on the PTC effect in BaTiO$_3$, effect of different dopants, process variables, study of the interfacial resistance and EPR studies.</td>
<td>IISc, Bangalore (Gajbhiye 1981) IIT, Kharagpur (Maiti et al 1986) IIT Madras</td>
<td>Devices based on PTC phenomenon</td>
</tr>
<tr>
<td>b) Process technology</td>
<td>BEL, Bangalore</td>
<td>Devices based on PTC phenomenon</td>
</tr>
<tr>
<td>Grain growth kinetics in ZnO varistors</td>
<td>NPL, Delhi (Kalsi &amp; Das 1983)</td>
<td>ZnO varistors</td>
</tr>
<tr>
<td>Device development activity</td>
<td>BHEL, Hyderabad and W.S. Insulators Madras</td>
<td>ZnO varistors</td>
</tr>
<tr>
<td>a) Development of different PZT compositions, effect of process variables, different dopants etc.</td>
<td>NPL, Delhi, NCL, Poona (Deshpande &amp; Roy Choudhary 1982) NCML, Bombay (Ramjilal &amp; Ramakrishnan 1984) ARDE, Poona (Dhami et al 1986) BEL, Bangalore</td>
<td>Different PZT applications</td>
</tr>
<tr>
<td>b) Establishment of standards, biomedical applications etc.</td>
<td>NPL, Delhi (e.g. Bindal &amp; Kumar 1985)</td>
<td>Highly demanding PZT applications</td>
</tr>
<tr>
<td>c) Novel processing routes for powders</td>
<td>TIFR, Bombay (Palkar &amp; Multani 1979) IISc, Bangalore (Kutty &amp; Balachandran 1984) NCML, Bombay BEL, Bangalore, CEL, Sahibabad, NPL, New Delhi, ARDE, Poona</td>
<td>Highly demanding PZT applications</td>
</tr>
<tr>
<td>d) Devices</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Abbreviations used: ARDE—Armanents Research & Development Establishment; BEL—Bharat Electronics Ltd.; BHEL—Bharat Heavy Electricals Ltd.; CEL—Central Electronics Ltd.; IISc—Indian Institute of Science; IIT—Indian Institute of Technology; NCL—National Chemical Laboratory; NCML—Naval Chemical & Metallurgical Laboratory; NPL—National Physical Laboratory; TIFR—Tata Institute of Fundamental Research.

Recent revised projection of the Japan Fine Ceramic Research Association (Ceram. Ind. (Chicago) 1986a) indicates a value of $18.8 billion for electronic and magnetic ceramics out of a total of $30.6 billion by the year 2000.
Table 7. Availability status in India of the major raw materials for electronic ceramics.

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Purity of the powder available in India</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bauxite (oxide of aluminium)</td>
<td>Al₂O₃ - 99.5%</td>
<td>Suitable for technical and electronic ceramics yet to be established. India has one fifth of the total world resources of bauxite</td>
</tr>
<tr>
<td>Barytes (sulphate of barium)</td>
<td>BaCO₃ - 98.7%</td>
<td>Further improvements are required to make it suitable for many of the electronic ceramic applications</td>
</tr>
<tr>
<td>Galena (sulphide of Pb)</td>
<td>PbO - 99.5% (?</td>
<td>Suitable for many of the PZT ceramic applications</td>
</tr>
<tr>
<td>Ilemenite (iron titanate)</td>
<td>TiO₂ - 98%</td>
<td>Although of pigment grade, fairly suitable for use in ceramic capacitor and PZT production particularly for commercial applications. Much purer powders are required for PTC applications</td>
</tr>
<tr>
<td>Rare earths (monazite beach sands)</td>
<td>La₂O₃</td>
<td>Suitable for electronic ceramic applications</td>
</tr>
<tr>
<td>Zircon (silicate of zirconium)</td>
<td>ZrO₂, 96-97.5%</td>
<td>Suitable for use in dielectric and PZT production for commercial applications</td>
</tr>
<tr>
<td>Zinc blend (ZnS)</td>
<td>ZnO - 99.5%</td>
<td>Purer powders were tried for the laboratory investigations (Kalsi &amp; Das 1983). But, considering the extremely competitive nature of the product, the cheapest raw materials which can give the required properties should be chosen</td>
</tr>
</tbody>
</table>

The current demand for electronic ceramics in India (author's own estimate) is about Rs. 240 million (approximately $20 million) which is expected to grow to about Rs. 1700 million (approximately $140 million) by the end of the century (a three-fold increase* during the 7th plan, and about 10% annual increase thereafter is assumed). Right now about 40 to 50% of the requirement seems to be met by indigenous production consisting mainly of ferrites and ceramic capacitors. However, most of this production is for commercial markets and not significantly for professional markets. Very few of the products that are under discussion in this review (table 1) are being manufactured in India right now. The approximate break up of the current demand position of different categories is given in table 8 which also includes the world sales for 1985 and the expected growth (%) during 1985–1990 for each of the categories. According to the table, ferrites constitute the major share of the markets in India (nearly 42%) whereas the world trend is different. In the latter case, packages and substrates constitute the major share (41%) followed by ceramic capacitors (24%). The same trend is likely to appear in India with the increasing use of integrated circuits and the general growth of the electronics industry. Japan dominates (Kenney & Bowen 1983) at least two areas of electronic ceramics, viz., the ceramic packages (at least 70-80% of the world market) and PZT ceramics (about

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*A five-fold increase in electronic systems is predicted during the 7th plan.*
Table 8. Estimated demand of different electronic ceramics in India as compared to world figures

| Item                                                                 | Estimated Indian market | World market sales in 1985* |
|                                                                     |                      |                           |
|                                                                     | Millions of rupees in | Millions of dollars       |
|                                                                     | 1986                  |                             |
|                                                                     | Millions of dollars   |                             |
|                                                                     | Predicted growth      | till 1990 (%)             |
| a) Substrates and packages                                          | 10                    | 0·77                       |
| b) Other alumina ceramics for electron tubes, headers etc.          | 6                     | 0·46                       |
| Capacitors                                                          |                       |                             |
| a) Discs                                                            | 40                    | 3·8                        |
| b) Multilayers                                                      | 40                    | 3·8                        |
| Ferrites*                                                           | 100                   | 7·7                        |
| Piezoelectric ceramics (including telephones elements)              | 35                    | 2·7                        |
| Thermistors and varistors                                          | 10                    | 0·76                       |
|                                                                     | 241                   | ≈ 20·00                    |

References: *Jain & Sarnot (1982); +Ceram. Ind. (Chicago) (1986b)

90% of the world market). The Indian market right now is about 0·5% of the world market.

10. Summary and concluding remarks

Circuit miniaturization and cost reduction are the two aspects at which most of the developments in electronic ceramics are aimed. This is particularly so for components like multilayer ceramics, the IBL capacitors, the dielectric resonators and many of the filters (table 1). Based on the unique grain boundary phenomenon in some of the electronic ceramics which is still to be adequately understood (particularly the structure and chemistry of the boundaries) a number of useful devices have been evolved such as the PTC thermistors, the IBL capacitors and the varistors etc. Efforts will continue to improve the characteristics of these devices for more demanding applications and some of them will find increasing use as sensors in different applications. The use of PZT ceramics is on the increase in the areas of communication and biomedical applications and newer composites are expected to diversify their scope still further. Many advantages are foreseen by the use of the majority of the electronic ceramic devices in multilayer configurations and therefore a good amount of work is expected in this direction. Development of newer innovative processing techniques to improve the device performance and reduce the costs are expected to continue.

Although there is a fair amount of R & D activity in many of the areas of electronic ceramics in the country, cost effective production techniques leading to a competitive position in the market place are yet to be significantly evolved. More emphasis therefore has to be placed on the technology development aspects in order to fill this gap. Perhaps the suggestion (Am. Ceram. Soc. Bull. 1986) by the Federation of the Materials Societies of US, viz., fostering the attitude that involvement in processing science and manufacturing technology is not a ‘lower calling’ than more traditional research and development, has to be followed vigorously in India. In
addition, the natural advantages of the raw materials have to be utilized better. The report (IPAG 1976) of the panel on interministerial coordination for indigenous development of electronic materials recommends electronic ceramics as one of the priority materials for indigenous development because it meets at least three of the five criteria laid down for selecting the projects for indigenization, viz., good development and production infrastructure, availability of raw materials and strategic importance. This recommendation holds good even today (nearly a decade after the recommendation), particularly in view of the important role electronic ceramics play in computers, communications, process control instrumentation and in a host of other commercial and military applications.

The author acknowledges the encouragement he received from the management of the Bharat Electronics Ltd. during the preparation of this review.

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High temperature fuel cells

H S MAITI* and M K PARIA

1Electroceramics Section, Central Glass & Ceramic Research Institute, Calcutta 700 032, India
2Refractories Division, National Metallurgical Laboratory, Jamshedpur 831 007, India

Abstract. A high temperature fuel cell using a solid oxide electrolyte, and operated at temperatures above 700°C, is a highly efficient energy conversion device utilizing primarily gaseous fuels like H$_2$ and CO. It can also be operated in the reverse manner as a high temperature steam electrolyser to produce hydrogen. The operating principle and the construction details of different design concepts have been discussed. Nonavailability of suitable electrode and interconnection materials has hampered commercial exploitation. Recent trends in the development of these materials have been focussed upon, both in the national and the international context.

Keywords. Fuel cell; steam electrolysis; solid electrolyte; battery design; thin film.

1. Introduction

A fuel cell is an electrochemical device which directly converts the chemical energy of a fuel into electrical energy. In a fuel cell, the fuel and the oxidant, which is usually oxygen or air, are supplied continuously from an external source and power is also drawn continuously. In a conventional battery, on the other hand, the fuel and the oxidant are contained within and when these reactants are consumed the battery must be replaced or recharged.

Since a fuel cell produces power by electrochemical reactions, unlike thermal machines, its efficiency is not limited by the Carnot cycle. Thus it has the potential for highly efficient conversion of chemical to electrical energy. Furthermore, its efficiency is essentially independent of size; small power plants operate nearly as efficiently as the large ones. As the by-products are water, carbon dioxide and nitrogen, fuel cell power plants are clean and quiet. They have considerable flexibility and can be designed to use either liquid or gaseous fuels (e.g., hydrogen, hydrazine, hydrocarbon, methanol, coal gas etc.) and produce a wide range of DC or AC power outputs. Like batteries, they are modular in construction and can be configured in

*On leave from Indian Institute of Technology, Kharagpur
any capacity from milliwatts to megawatts. Above all their attraction lies in their flexibility and the many diverse applications they can be used in.

2. Classification of fuel cells

Fuel cells are classified into direct and indirect-fuelled systems based on the type of fuel used. In the direct-fuelled system, the fuel is readily oxidised electrochemically and is fed directly. In the other kind, the fuel is first converted in a fuel-processing subsystem to an easily oxidisable hydrogen-rich gas, which is then fed into the fuel cell. They can also be classified, based on the temperature of operation. The low temperature system operates below 260°C and the electrolytes are normally acids (H₂SO₄, H₃PO₄), solid polymer electrolytes or aqueous alkalies (KOH). The intermediate temperature systems (260–750°C) use molten carbonates (Li₂CO₃, Na₂CO₃) or molten alkalies (KOH). High temperature systems (>750°C) use solid oxide electrolytes (ZrO₂) which have sufficient thermal and structural stability above 750°C.

The low temperature fuel cells which consist of liquid electrolytes (acid or alkali) suffer from the problem of corrosion of container or carbonation of the electrolyte. Low temperature operation favours electrode polarisation and poisoning of the electrodes by impurities. Besides these problems, the difficulty of maintaining a stable 3-phase contact (liquid-solid-gas) creates design problems at the electrodes. The molten alkaline system is not attractive because of the complexity. The high temperature fuel cell (HTFC) based on solid oxide electrolyte has a favourable effect on the reaction kinetics and mass transfer at the electrodes due to high operating temperature (~1000°C). High current and power densities are obtained without much polarisation loss and without application of a noble metal catalyst.

The high temperature solid electrolyte fuel cell can also be used as a high temperature steam electrolyser (HTSE) by allowing the electrochemical reaction to take place in the reverse direction so that water vapour can be electrolysed at high temperature into hydrogen and oxygen by supplying electrical energy and heat to the same cell. The efficiency of HTSE is considerably higher than that of conventional low temperature water electrolysis (Spacil & Tedmon 1969). Overall plant efficiency of 40–50% has been predicted compared to below 30% for conventional electrolysis (Doenitz et al 1980).

3. Principles of HTFC and HTSE

Although the principle of HTFC was first conceived by Baur & Preis (1937) a laboratory model was developed only in the early sixties (Weissbart & Ruka 1962; Archer & Sverdup 1962; Carter et al 1963; Archer et al 1964). Extensive developmental programmes have been undertaken in the latter part of the seventies and the early eighties by three main research groups, namely, Westinghouse Electric Corporation, USA (Isenberg 1978, 1981; Feduska & Isenberg 1983), Brown Boveri, West Germany (Rohr 1968, 1978, pp. 431–462) and AERE, Harwell, UK (Markin 1972; Markin et al 1976, pp. 15–35). Presently, the principles of operations of HTFC and HTSE are well-understood and are shown schematically in figure 1 which
includes the use of both oxide ion and proton ion conductors. The cell is usually made of thin-walled solid electrolyte tube. The inner and outer surfaces of the tube are coated with electronically conducting electrodes. A gaseous fuel like hydrogen or a mixture of H₂ and CO is led to the inner electrode, and oxygen or air is led to the outer electrode. Due to the difference in oxygen activity at the electrodes, an electrical potential is developed, the magnitude of which depends on the temperature and oxygen partial pressures at the electrodes. The theoretical EMF \( E_0 \) of the cell is given by the equation

\[
E_0 = \frac{RT}{4F} \ln \left[ \frac{p_{O_2} (c)}{p_{O_2} (a)} \right],
\]

where \( p_{O_2} (c) \) and \( p_{O_2} (a) \) are the oxygen partial pressures at the cathode and the anode, respectively.

During power generation, oxygen at the cathode picks up an electron forming an oxygen ion. This oxygen ion passes through the oxide solid electrolyte and reacts with H₂ or CO at the anode to form H₂O or CO₂. The electrons released at the anode by this electrochemical process flow back to the cathode through the external circuit. In this way, electrical energy is available in the external circuit. The theoretical EMF of the H₂/O₂ fuel cell \( (E_0^{FC}) \) is given by the equation

\[
E_0^{FC} = \frac{RT}{2F} \ln \left[ K_{H_2} p_{O_2}^{1/2}/p_{H_2O} (a) \right],
\]
where \( K \) = equilibrium constant of the reaction

\[
H_2 (g) + \frac{1}{2} O_2 (g) \rightleftharpoons H_2 O (g), \tag{3}
\]

\( p_{H_2} \) and \( p_{H_2O} \) are the partial pressures of \( H_2 \) and \( H_2O \) respectively. Similarly for the proton ion conductor fuel cell, the EMF \( (E_{HFC}) \) is given by the following equation.

\[
E_{HFC} = \left( \frac{RT}{2F} \right) \ln \left[ K_{pH_2} p_{O_2}^{1/2} / p_{H_2O} (c) \right] \tag{4}
\]

In case of the high temperature steam electrolysis, steam, electrical energy and heat are led to the same type of cell. All the reactions at the electrodes, the flow of ions within the electrolyte, and the flow of electrons in the external circuit, take the reverse direction. In case of an oxygen ion conductor, hydrogen is produced at the inner electrode and in case of a proton conductor, hydrogen is produced at the outer electrode and oxygen at the inner electrode (figure 1).

Hydrogen may be used as a fuel in the cell using either an oxide ion conductor or a proton conductor. But carbon monoxide can be used as a fuel only if an oxide ion conductor is used as the electrolyte and the cell reaction is

\[
2CO + O_2 \rightleftharpoons 2CO_2. \tag{5}
\]

When the fuel cell delivers a current \( I \), the voltage \( E \) decreases below the theoretical value \( E_0 \), due to ohmic losses \( IR_i \) (\( R_i \) = internal resistance of the cell) and polarisation losses \( V_p \) at the electrodes. As an approximation

\[
E = E_0 - IR_i - V_p. \tag{6}
\]

The ratio

\[
\eta_E = (E/E_0) = 1 - [(IR_i + V_p)/E_0], \tag{7}
\]

is considered the voltage efficiency of the cell. The most important factor in the development of the fuel cell is the optimisation of efficiency in respect of ohmic loss and polarisation loss, taking into account other factors like life-time, material and manufacturing cost.

4. Materials for cell construction

4.1 Solid electrolyte

a) Oxide ion conductor: The oxide solid electrolyte to be used for construction of a fuel cell and a steam electrolyser should have the following characteristics at the operating temperature of about 1000°C: (1) high oxygen ion conductivity with negligible electronic conductivity, (2) phase stability, (3) mechanical strength, (4) gas tightness, (5) thermal shock resistance, (6) chemical resistance to the reacting gases, and (7) compatibility with the electrodes and interconnection materials. Most of these requirements are met satisfactorily by ceramic solid electrolyte of doped zirconia (Archer et al 1964). Attempts have been made to replace \( \text{ZrO}_2 \) by \( \text{CeO}_2 \) solid electrolyte. But \( \text{CeO}_2 \)-based solid electrolytes suffer from the disadvantages that, due to the higher electronic conductivity in a reducing atmosphere, the cell voltage and efficiency are reduced (Kudo & Obayashi 1976; Ross & Benjamin 1977).

Doped \( \text{ZrO}_2 \) with lower valent metal oxides results in a higher oxygen ion
conduction and stabilisation of the cubic crystal structure over a very broad
temperature range (Etsel & Flengas 1970). ZrO₂ is usually doped with 15 mol\% calcium oxide or 10 mol\% yttrium oxide (Archer et al 1964) or 4 mol\% yttrium oxide and 4 mol\% ytterbium oxide (Eysel & Rohr 1967). The specific electrical resistivities ($\rho_E$) at 800°C and 1000°C are given in table 1. The table also gives the allowed maximum wall thickness $d_E$ of the solid electrolyte for power densities up to 0.25 W/cm², in the case that no other electrical losses would exist. Long term behaviour and life tests of cells with Y₂O₃/Yb₂O₃-doped ZrO₂ electrolyte at 1000°C showed that during a working period of more than three years, the required properties of the electrolyte were not affected (Rohr 1975; Brown Boveri 1975).

b) Proton conductor: The protonic solid electrolyte to be used for construction of HTFC/HTSE should have properties similar to oxide solid electrolytes. Proton conduction has been observed in a number of materials like $\beta/\beta''$-Al₂O₃ (Frase & Farrington 1984) doped SrCeO₃, stabilised ZrO₂, ThO₂, Cu₂O, CuO, NiO and SiO₂ etc. (Iwahara et al 1982, 1983). Among these materials only $\beta/\beta''$-Al₂O₃ and SrCeO₃ are potential materials so far as electrical conductivity is concerned. Even then their electrical conductivity has to be improved to reduce the operating temperature of the cell. SrCeO₃ doped with rare earths like Y₂O₃, Yb₂O₃ and Sc₂O₃ has been studied for fabrication of steam concentration cells and HTSE (Iwahara et al 1983a). The performance of the cell has been quite satisfactory as far as stability of the material is concerned. But no HTFC has so far been fabricated out of these materials even on a laboratory scale.

### 4.2 Electrodes

The performance of the HTFC depends not only on the quality of the solid electrolyte but also on the properties of the electrode material and the method of deposition. The electrical properties of the electrode materials are characterised by the ratio of resistivity ($\rho_e$) to thickness ($d_e$) and also by the polarisation voltage losses ($V_p$).

Due to the reducing atmosphere of the fuel electrode (anode) normal metals like cobalt and nickel may be used up to an operating temperature of 1000°C. Cermets of zirconia with nickel and cobalt are used for better thermal expansion matching (Markin et al 1976, pp. 15–35; Isenberg 1977). Polarisation losses of these electrodes are shown in table 2.

As an oxidising atmosphere prevails around the air electrode (cathode), only noble metals and oxides with appropriate thermal and chemical stability along with high electronic conductivity at the operating temperature, are suitable as cathode material. The use of a noble metal like platinum is ruled out because of its cost and insufficient

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$\rho_E$ (Ohm cm)</th>
<th>$d_E$ (mm)</th>
<th>$\rho_E$ (Ohm cm)</th>
<th>$d_E$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂-15 mol% CaO</td>
<td>250</td>
<td>0.04</td>
<td>50</td>
<td>0.2</td>
</tr>
<tr>
<td>ZrO₂-10 mol% Y₂O₅</td>
<td>45</td>
<td>0.22</td>
<td>10</td>
<td>1.0</td>
</tr>
<tr>
<td>ZrO₂-4 mol% Y₂O₅</td>
<td>20</td>
<td>0.50</td>
<td>5</td>
<td>2.0</td>
</tr>
<tr>
<td>-4 mol% Yb₂O₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
long-term stability. A number of simple and mixed oxides like indium oxide-doped tin oxide (In$_2$O$_3$/SnO$_2$) (Sverdup et al 1969; Markin et al 1976, pp. 15–35) Sr-doped LaMnO$_3$ (Rohr 1975), perovskite type oxides like Bi-doped LaNiO$_3$ (Steiner et al 1972. p. 113) and Ca-doped LaCoO$_3$ (Ochno et al 1981; Nagata et al 1980, pp. 193–195) have been studied as cathode material. The electrode characteristics of some of the well-tested oxides are given in table 2. It may be noted that the ohmic loss ($I_{R_i}$) at 0.5 A/cm$^2$ due to electrode resistance and polarisation losses ($V_p$) are more or less same.

4.3 Interconnection material

For making an HTFC battery, individual cells are connected in series by interconnection material (ICM) which joins the air electrode of one cell to the fuel electrode of the next cell. The interconnection material should have the following characteristics at the operating temperature of 1000°C: (1) high electronic conductivity and negligible ionic conductivity in both oxidising and reducing atmospheres; (2) good chemical and structural stability; (3) gas tightness and mechanical strength; and (4) good adherence and compatibility with ZrO$_2$ electrolyte and the electrodes. Several mixed oxides like CoCr$_2$O$_4$ with 2% Mn (Sun et al 1972), LaCrO$_3$ doped with Sr and Ni (Baukal et al 1976), LaMnO$_3$ doped with Nb$_2$O$_5$, Ta$_2$O$_5$ or WO$_3$ (Markin et al 1976) and LaCrO$_3$ doped with Mg and Al (Ruka 1978) have been studied but only CoCr$_2$O$_4$ and LaCrO$_3$ have shown satisfactory performance.

5. Cell characteristics and its stability

The voltage-current characteristics of an HTFC depend on the cell parameters and working condition, specially on the electrical properties and the dimensions of both electrolyte and electrodes as well as on the operating temperature and partial pressures of the reacting gases. For voltage-current and long term behaviour of the cells with conical or tubular shapes having diameters of $D_E \leq 25$ mm, heights of $h_E \leq 12$ mm and wall thicknesses of $d_E \geq 0.4$ mm have been studied (Rohr 1978). The height of the cell is limited by the ratio $p_e/d_e$ of the oxide cathode and the operating temperature ranges from 800°C to 1000°C. The reactants are either oxygen or air at the cathode and hydrogen or gas mixtures of hydrogen, carbon monoxide, water and carbon dioxide at the anode.
Typical voltage-current characteristics of an HTFC when operated with H₂ and O₂ or an H₂/CO mixture and air are shown in figure 2. At an operating temperature of 1000°C and thickness of the electrolyte, \( d_E = 0.5 \text{ mm} \), maximum power densities of 0.3 W/cm² (H₂/O₂) or 0.2 W/cm² (3H₂ + CO/air) have been achieved. The experimental open circuit voltage varies from 0.9 to 1.1 V depending on the fuel gas and corresponds well with the theoretical value.

For making the HTFC economically viable, the life of the cell should be five to ten years. With an experimental unit cell at a operating temperature of 1000°C, the cell voltage and power density remained practically constant for more than three years (28,000 operation hours) (Rohr 1975). The test cell was of tubular solid electrolyte of 1.2 mm thickness, having plasma-sprayed electrodes of nickel (anode) and doped LaNiO₃ (cathode). With a constant load of 120 mA/cm² over a period of 28,000 h, practically constant values of open cell voltage (approximately 1 V) were obtained after some start-up effects during the first 1000 h of operation.

6. Design and fabrication of battery

For making a series connection of the cells in a battery, two basic concepts have been developed: (1) the self-sustaining module using ZrO₂ solid electrolyte tube segments with a minimum wall-thickness of 0.4 to 0.5 mm, sufficient to provide the necessary mechanical strength to the battery, and (2) the thin film design comprising a porous ceramic support coated with the electrolyte and electrode films of 30 to 100 μm thickness.

6.1 Self-sustaining module concept

The module is constructed in the form of a long tube from conical or cylindrical tubular segments, each forming a unit cell, by simply fitting one cell into the other. Only ZrO₂ electrolytes have so far been fabricated for this purpose. A number of techniques have been successfully employed to fabricate nonporous tubes. These techniques are conventional ceramic sintering followed by machining (Archer et al...
1965, p. 51), isostatic pressing and sintering (Steiner 1972; Fischer et al. 1971), electrophoresis (UK Patent 1972) and plasma spraying (Markin et al. 1976, pp. 15–35). The application of cathode and anode materials have been tried by different techniques like plasma spraying, chemical vapour deposition, painting and screen printing followed by firing. Satisfactory porous electrode films have been obtained by painting or screen-printing techniques. The series connection of the electrode tubes is obtained by connecting the anode of one cell to the cathode of the next cell by a gas-tight and electron-conducting interconnection material (figure 3) which is usually applied by plasma spraying (Markin et al. 1976, pp. 15–35). In this way 100 to 120 cells are connected in series; the performance of the battery is presented in figure 4. For a battery of 120 cells, total voltage 110–115 V and a maximum power output of 115 W corresponding to 0.22 W/cm² have been obtained at 1000°C with H₂/air as the reaction gases. The voltage losses in a 10-cell battery module under load at 1000°C, resulting from the ohmic resistances of the solid electrolyte (Rₑ), oxide cathode (Rₑ), nickel anode (Rₐ) and inter-connection material (RₑM), as well as from the polarisation at the cathode and the anode (Vₑ + Vₐ) are

![Figure 3. Schematic cross-section of a self-sustaining cell assembly.](image)

![Figure 4. Current vs. voltage and power characteristics of a 120-cell assembly (after Rohr 1978).](image)
Improvement of battery performance has been obtained by reducing these polarisation losses in the thin film module concept.

6.2 **Thin film module concept**

Better design and reduction of battery manufacturing costs have been achieved in this module. The nonporous electrolyte, the interconnection film and the porous electrode films (both anode and cathode) are deposited on a porous support tube one after another as shown in figure 6. The technique employed for deposition of the films are either CVD, EVD (electrochemical vapour deposition), plasma spraying or combined spraying and sintering (Rohr 1978). The thicknesses of the different films are 30–100 μm. Using these techniques, multicell modules with tubular support (Isenberg...
et al 1969) or plate-type support (Brown Boveri 1975) can be constructed. Consequently, besides the saving in materials and the simplification of the manufacturing process, the operating temperature may be brought down to 700–800°C as well, which reduces technological problems arising at high operating temperature.

7. **HTFC integrated plant**

For achieving maximum efficiency of the large scale HTFC power plant, some auxiliary equipment like heat exchangers, equipment for dressing of fuels and exhaust gases, combustion control etc. are necessary. A schematic flow diagram of one such integrated HTFC power plant of 220 MW capacity is shown in figure 7, which produces only DC power, and all the waste heat is utilised to generate process steam (Summers & Vidt 1981). This system was designed for an integrated aluminium production plant to study its economic and technical viability.

8. **Technical status**

The HTFC technology is still in the developmental stage. So far, neither an integrated power plant nor a prototype battery has been constructed for commercial power generation. However, extensive research and developmental programmes have been undertaken by a number of countries like USA, UK, West Germany and Japan. A few laboratory-scale battery modules have been fabricated both in USA and West Germany and they have been successfully operated for considerable lengths of time. The design of the battery module and the fabrication techniques have been found satisfactory on the laboratory scale, but further development is necessary before commercial exploitation becomes feasible. The cost of power generation has to be reduced mainly by increasing the life of the cell. It has been conceived that if the life of the cell is increased from 5 to 10 years the HTFC, with performance so far achieved, will be commercially viable (Rohr 1978). Test modules upto 5 KW output power have been fabricated by Westinghouse Electric Corporation, USA, and they are presently engaged in designing a 50 KW module.

In India, no attempt has so far been made to develop any HTFC module even on a laboratory scale. However, there have been some isolated activities on the material development, particularly on studies of the electrical and electrochemical properties of possible electrolyte and electrode materials. Subbarao at the Indian Institute of Technology (IIT), Kanpur, initiated the main activity in this direction within the country (Maiti 1975; Choudhary 1975). Later, the present authors continued and extended this activity at IIT, Kharagpur. They have designed, fabricated and tested a number of electrochemical cells (oxygen sensors and oxygen pumps which operate on the same principle as fuel cells) using imported electrolyte tubes (Paria 1982). A laboratory scale steam electrolyzer has also been fabricated and its performance studied (Maiti et al 1985). Moorthy and colleagues at BARC, Bombay studied the sintering characteristics of stabilized zirconia but have not made any serious attempt to prepare impervious electrolyte shapes required for fuel cell application. Karthikeyan and others of the Plasma Physics division of BARC have extensive experi-
Figure 7. Flow diagram of HTFC aggregate plant (220 MW) utilising all waste heat as process steam (after Feduska & Isenberg 1983).
ence in plasma spraying of ceramic oxides in connection with their MHD project. It is possible to use this expertise to initiate any HTFC programme in this country.

9. Areas of application

The most important advantages of the HTFC power plants are
a) very high efficiency (overall plant efficiency is expected to be 45–55% for plant capacities of the order of megawatts);
b) very low level of pollution;
c) possibility of using the same plant either as a generator or for storage of electricity.

Hence, HTFC power plants are most suitable in remote areas like in space and under the sea where system weight and volume are the most important parameters. These can be used as captive power plants in small and medium scale industries in isolated places. HTFC is best suited for load levelling due to its dual mode of operation. It is very useful in congested areas particularly for avoiding environmental pollution.

10. Summary and conclusions

a) A high temperature fuel cell using a solid oxide electrolyte is one of the most efficient energy conversion devices without the limitations of the Carnot cycle. Expected plant efficiency is 45–55%.
b) It can be operated with fuels like pure hydrogen, gasified coal, natural gas etc.
c) It can be operated either in the fuel cell mode for power generation or in the reverse mode as a steam electrolyzer for generation of hydrogen.
d) Prototype batteries have been developed in some of the advanced countries and have been found satisfactory. Nevertheless some material problems still exist. Thin-film design is likely to be more successful than the self-supported concept. Selection of electrode and inter-connection materials and their fabrication techniques appear to play a key role in the ultimate commercialization of the technology.
e) Great potentiality also exists in India for this technology as an alternative power source, particularly in remote and isolated areas.

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Light element ceramics

K J RAO*, K B R VARMA and A R RAJU

Materials Research Laboratory, Indian Institute of Science, Bangalore 560 012, India

Abstract. An overview of a few structurally important light element ceramics is presented. Included in the overview are silicon nitride, sialon, aluminium nitride, boron nitride, boron carbide and silicon carbide. Methods of preparation, characterization and industrial applications of these ceramics are summarized. Mechanical properties, industrial production techniques and principal uses of these ceramics are emphasized.

Keywords. Silicon nitride; sialon; aluminium nitride; boron nitride; boron carbide; silicon carbide.

1. Introduction

Some of the best known natural ceramics like silica, alumina, and carbon (in its various allotropic forms) are composed of only the light elements of the short periods in the periodic table. The best man-made ceramics such as borides, carbides, nitrides and oxides are also largely made up of light elements. The abundance of these light elements in nature and the extraordinary properties exhibited by a variety of ceramics resulting from their combination provides great attraction for research and development of light element ceramics.

Light element ceramics considered in this review are the stable binary, ternary and polynary ceramic phases obtained by chemical combination of the elements boron, carbon, nitrogen, oxygen, aluminium and silicon. Though alumina is a light element ceramic of great importance, it is not discussed here. Upon considering the volume of work reported in the literature and the proven importance of various light element ceramics, they are discussed in this report in the following order; silicon nitride, sialon, aluminium nitride, boron nitride, boron carbide and silicon carbide. Some of the ternaries and quaternaries related to these binaries are also discussed at appropriate places. Known methods of preparation of each material, particularly as relevant to large-scale manufacture, are first reviewed and then a brief presentation of their significant properties is given. Emphasis is placed on putting together well-documented data related to mechanical properties since light element ceramics are projected the world over as the advanced structural ceramics of the future.

*Contribution No. 76 from the Materials Research Laboratory
*For correspondence
2. Silicon nitride

2.1 Methods of preparation

There are several methods in vogue for the preparation of silicon nitride. They include (a) direct nitridation, (b) carbothermal reduction, (c) gas-phase reaction, (d) silicon-sulphur-nitrogen reaction and (e) liquid phase reaction.

2.1a Direct nitridation: A commercially-known nitridation process involves heating of pure Si powder (particle dia < 10 \( \mu m \)) in the temperature range of 1200–1450°C in an atmosphere of \( NH_3/H_2 \) or \( N_2 \):

\[
3 \text{Si} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4.
\]

The above reaction is exothermic and the process yields \( \text{Si}_3\text{N}_4 \) lumps which are later crushed and milled to fine size particles. Hirao et al (1986) have adopted a method called self-propagating high temperature synthesis (SHS) to prepare fine \( \text{Si}_3\text{N}_4 \). In this process Si powder compacts are burnt in nitrogen at 10 MPa pressure. The method is suitable for obtaining homogeneous \( \text{Si}_3\text{N}_4 \) submicron particles with a uniform size distribution.

2.1b Carbothermal reduction: When a mixture of fine powders of carbon and silica is subjected to carbothermal reduction, followed by nitridation, \( \text{Si}_3\text{N}_4 \) lumps are obtained.

\[
3\text{SiO}_2 + 6\text{C} + 2\text{N}_2 \xrightarrow{1200–1450°C} \text{Si}_3\text{N}_4 + 6\text{CO}
\]

The advantage of this method over direct nitridation is that both \( \text{SiO}_2 \) and \( \text{C} \) are more readily available than pure Si. It is always better to obtain the precursor in a finely divided form in order to prepare a final product with tailored properties. A sol-gel process has certain advantages in this context over conventional techniques using powder mixtures. In the sol-gel process, aqueous suspensions of oxides and hydrous oxides are mixed to give a composition corresponding to the required multicomponent ceramic. Szweda et al (1981) have examined the nitridation of gel powders in an \( \text{N}_2/H_2 \) atmosphere. A \( \text{SiO}_2 \) sol derived from a flame-hydrolyzed material was mixed with C powder (C/\( \text{SiO}_2 \) = 2:1) and nitrided between 1400 and 1600°C. The product was found to be either \( \alpha-\text{Si}_3\text{N}_4 \) or \( \beta-\text{Si}_3\text{N}_4 \) depending on the drying process adopted. The final powder has been heated to 600–650°C in air to burn out excess carbon. The sol-gel preparative route uses organic compounds of silicon such as tetraethoxysilane \( \text{Si}(\text{OC}_2\text{H}_5)_4 \) which undergoes hydrolysis giving rise to \( \text{SiO}_2 \).

\[
\text{Si}(\text{OC}_2\text{H}_5)_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{C}_2\text{H}_5\text{OH}, \quad \text{Si(OH)}_4 \rightarrow \text{SiO}_2 + 2\text{H}_2\text{O}.
\]

Hydrolysis leads to substitution of alkoxy groups by hydroxyl groups which further condense into polymerized hydrous oxides. Silica gel thus derived from \( \text{Si}(\text{OC}_2\text{H}_5)_4 \) has been nitrided by Hoch and co-workers (Hoch et al 1977; Hoch & Nair 1979). Submicron \( \alpha-\text{Si}_3\text{N}_4 \) was obtained by nitriding at 1350°C in \( \text{NH}_3 \) gas. Preparation of high purity \( \text{Si}_3\text{N}_4 \) from a disilane compound with the general formula \( R_n \text{X}_{6-n} \text{Si}_2 \) (\( R = \text{H}, \text{alkyl}, \text{alkenyl}, \text{aryl}; \text{X} = \text{halogen atom}, n = 1–5 \)) by hydrolyzing it in the presence of C powder and nitriding the product at 1350–1550°C has been reported.
The product was a pale green powder containing approximately 93% α-Si₃N₄. Sharma et al (1984) and Hanna et al (1985) obtained Si₃N₄ by firing rice husk at 1200–1500°C for about 0.5–2 h in an ammonia atmosphere. The silicon nitride produced was in the form of α-Si₃N₄ with minor amounts of the β-form.

2.1c Gas phase reaction: Prochazka & Greskovitch (1978) have prepared Si₃N₄ powder with particle diameter in the range of 300–2000 Å by allowing SiH₄ to react with NH₃ at 500–900°C at atmospheric pressure. SiCl₄ and SiH₄ react with NH₃,

$$3\text{SiCl}_4(g) + 4 \text{NH}_3(g) \rightarrow \text{Si}_3\text{N}_4(s) + 12\text{HCl}(g),$$
$$3\text{SiH}_4(g) + 4 \text{NH}_3(g) \rightarrow \text{Si}_3\text{N}_4(s) + 12\text{H}_2(g).$$

The use of SiCl₄ leads to corrosive by-products while SiH₄ is even more hazardous due to its spontaneous flammability in air. Several workers (Cannon et al 1982; Danforth & Haggerty 1983) have employed a CO₂ laser (150 W power, 10-6 μm wavelength) as the heat source with both unfocussed and focussed geometries to prepare Si₃N₄ powder. Here SiH₄ is preferred over SiCl₄ since SiH₄ has an absorption band at 10-6 μm. When SiH₄ was heated with CO₂ laser in the presence of NH₃, it yielded monodisperse, pure, loosely agglomerated Si₃N₄ powders with a production rate of up to 10 g h⁻¹. Seiji et al (1986) have reported the preparation of Si₃N₄ layers at low pressures and temperatures of 800–1300°C using the (CVD) technique. Sugawara et al (1986) have employed the ion vapour deposition method (IVD) to prepare Si₃N₄ films. This method involves electron beam evaporation of Si and simultaneous nitrogen ion implantation which gives rise to Si₃N₄ films.

The plasma-activated vapour deposition method (Goodwin 1982) has been used for depositing Si₃N₄ films on substrates. This technique is particularly recommended for use in the electronic industry. Fletcher et al (1971, p. 145) achieved 7% conversion of Si powder into Si₃N₄ using 14% N₂ in Ar plasma. 15% conversion to a mixture of α and β-Si₃N₄ was reported by Canteloup & Mocellin (1975). Formation of ultrafine Si₃N₄ powder has been reported in an arc plasma (Segal 1986). Conditions favourable for deposition of Si₃N₄ on steel substrates by the CVD technique have been reported by Fumiyoshi & Hiroyuki (1986).

2.1d Silicon-sulphur-nitrogen reaction: Morgan (1984) has reported that ultrapure Si₃N₄ can be obtained from Cl-free reactants. Si powder was reacted at 900°C in a stream of 10% H₂S/Ar to form SiS₂. SiS₂ was then reacted with NH₃ at 1200–1450°C to give α-Si₃N₄. The synthesis of Si-S compounds specifically silane thiols, sithians and mercaptosilanes has been described by Eaborn (1960, p. 333). Recently, the preparation of Si₃N₄ by the SiS₂ precursor route was reported by Morgan & Pugar (1985). The important role of nitrogen in the preparation of Si₃N₄ and related ceramics has been discussed by Morgan (1986).

2.1e Liquid phase reaction: Mazdiyasni et al (1978) have prepared α-Si₃N₄ in the form of fibre bundles (1.3 μm dia) by pyrolysis of hexaphenyl cyclotrisilazane in nitrogen at 1400°C, while Seyferth et al (1983) have shown that the polysilazane oil (H₂SiNH)x derived from reaction of dichloro-silane and ammonia in dichloromethane could be pyrolyzed in N₂ at 1150°C to get α-Si₃N₄ fragments.

It is of historical interest to note that Persoz as early as 1830 had obtained a white precipitate from the interaction of SiCl₄ and NH₃ (g) in an inert solvent (benzene) at 0°C. This precipitate was then considered to be silicon tetramide Si(NH₂)₄ and subsequently confirmed by Lengfeld (1899). Nevertheless the precipitate was unstable.
and decomposed at ambient temperatures to give silicon diamide $\text{Si(NH}_2\text{)}_2$ and ammonium chloride. Glemser & Newmann (1903) and Billy (1959) also obtained similar products on carrying out the reactions in liquid ammonia. Recently Segal (1985) has given a series of possible intermediates which are formed during the preparation of $\alpha$-silicon nitride from silicon tetrachloride and ammonia.

$$\text{SiCl}_4(\text{l})/\text{NH}_3(\text{g}) \xrightarrow{0^\circ \text{C}} \text{silicon diamide} + \text{NH}_4\text{Cl}$$

\[ \begin{align*}
6[\text{Si(NH}_2\text{)}_2]_n & \quad \text{Loss of } \text{NH}_4\text{Cl} \text{ and polymerisation up to } 360^\circ \text{C} \\
2[\text{Si(NH}_3\text{)}_2\text{N}_2]_n + 2n\text{NH}_3 & \quad 400^\circ \text{C} \\
3[\text{Si}_2(\text{NH})\text{N}_2]_n + n\text{NH}_3 & \quad 650^\circ \text{C} \\
\alpha\text{-Si}_3\text{N}_4 & \quad 1200-1400^\circ \text{C}
\end{align*} \]

Mazdiyasni & Cooke (1973) have shown that powder produced from pyrolysis is initially X-ray amorphous and that it is transformed into the $\beta$-phase on heating between 1200 and 1400°C for about 8 hours.

### 2.2 Characterization

The Si$_3$N$_4$ powders prepared by various methods have been characterized using high resolution electron microscopy, IR, Raman and X-ray photoelectron spectroscopies. These techniques also yield information about the quality of the preparation and the nature of impurities present in the powders.

Mehmet et al (1985) have discussed the usefulness of high resolution electron microscopy in analysing microstructural characteristics of light element ceramics in general. They have also presented evidence of the presence of amorphous phases of Si$_3$N$_4$ (also mullite and AlN ceramics) in the grain boundaries. The glassy phase was absent at some grain boundaries in Si$_3$N$_4$ and instead a second phase was noticed. The nature and composition of the surface of Si$_3$N$_4$ powder were investigated using high voltage – high resolution TEM, XPS and SIMS* by Rahaman et al (1986). Both XPS and SIMS studies indicate that oxygen is present as a major impurity. Minor impurities such as Cl, F, C, Fe and Na are also present in the sample. IR absorption and Raman spectroscopic studies (Takase & Tani 1986) have been carried out on sintered Si$_3$N$_4$ containing additions of Al$_2$O$_3$ and rare earth oxides (Y$_2$O$_3$, CeO$_2$, La$_2$O$_3$). It is noticed that there is an increase in the widths of the Raman bands in the spectral range of 400–1100 cm$^{-1}$ as the Al$_2$O$_3$ content in Si$_3$N$_4$ is increased. It is attributed to the increasing degree of structural disorder in $\alpha$-Si$_3$N$_4$ network caused by the replacement of Si and N by Al and O respectively. Toshio et al (1985) have employed inductively coupled plasma emission spectrometry to determine the impurities present in Si$_3$N$_4$. Nobuo et al (1985) have reviewed the possible use of

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*Secondary ion mass spectroscopy.
Light element ceramics

thermal and analytical methods such as DTA, DSC and thermogravimetry in the characterization of ceramics. Use of TEM and electron diffraction for analysing fine ceramics in general has been reviewed by Yoshio (1985).

2.3 Industrial production techniques, properties and uses

Most high performance Si$_3$N$_4$ ceramic products rely on the quality of the starting elements, Si and N$_2$. However, it is necessary to sinter the products using sintering aids in order to ensure better performance of products. Negita (1985) has discussed the role of sintering aids on the basis of chemical bonding. His studies indicated that electronegativities and ionic radii of the cations in the additives are important parameters which affect the densification of Si$_3$N$_4$ ceramics. In general, the majority of Si$_3$N$_4$ products are produced either as hot-pressed silicon nitride (HPSN) or as reaction-bonded silicon nitride (RBSN). Hot-pressed Si$_3$N$_4$ can be produced by either uniaxial (Vasilos 1977, pp. 367–382) or hot isostatic pressing (Larker et al 1975). One generally starts with α-Si$_3$N$_4$ powder along with densification aids such as MgO or ZrO$_2$. Depending upon the purity of the starting Si$_3$N$_4$ powder, and the type of additives, milling procedures and hot pressing parameters used, one can obtain a very wide range of strength, creep, fracture toughness or oxidation behaviour. Hot-pressed silicon nitride (HPSN) obtained with Y$_2$O$_3$ additive possesses typically higher strengths at both room and elevated temperatures. It also possesses better oxidation resistance, fracture toughness and slower crack growth features as compared to MgO-containing HPSN (Gazza et al 1978). Si$_3$N$_4$ of very high strength has been obtained by Komeya et al (1977) with Y$_2$O$_3$ and Al$_2$O$_3$ as additives and by using the grain boundary crystallization approach.

The fabrication of RBSN components begins with a silicon metal powder preform which is made by slip casting, dry pressing, flame spraying, injection moulding or other techniques. The preform is then nitrided in an atmosphere of pure H$_2$ or N$_2$ + H$_2$ with either a preselected temperature schedule (Messier & Wong 1974, p. 181) or by using a nitrogen demand cycle (Wong & Messier 1978). This process of nitriding of a Si preform is remarkable for its simplicity but is still imperfectly understood. While the reaction 3 Si + 2N$_2$ → Si$_3$N$_4$ is associated with a 23% increase in the solid volume compared to Si when this reaction is carried out on a preform, there is essentially no change in dimensions (0-1%). The reason for this appears to be that Si$_3$N$_4$ is formed in the voids in Si-preforms via a vapour phase or surface diffusion reaction. This procedure is therefore of great importance and can be used in mass production of products to tight dimensional tolerances.

Reaction-bonded silicon nitride can exhibit creep rates significantly lower than those of HPSN (Larsen et al 1978). It has also been reported that as a consequence of the reaction bonding process, RBSN is of necessity at least 10% porous which makes it less oxidation resistant than HPSN at intermediate temperatures (McLean 1978) but limits its strength to less than 415 MPa. The quality of products obtained from reaction-bonded silicon nitride has been improved considerably over the past few years. However, when high strength and greater oxidation resistance is required, it would be desirable to have readily sinterable fully dense silicon nitride. This has been the impetus for the development of sintered silicon nitride (SSN).

Sintered Si$_3$N$_4$ of at least 95% density has been prepared successfully and it is reported that densities greater than even 99% have been achieved. Gazza et al (1978) have recently reviewed the status of SSN. SSN components which are formed by
injection moulding require little machining. It is also possible that sintered Si$_3$N$_4$ bodies of over 95% theoretical density may be used as preforms for cladless hot isostatic pressing. Materials like SSN and HPSN are only in the initial stages of development. Sinter densities of $\geq$ 95% could be obtained by adding only 2 wt% MgO. Products should be targeted to possess a low concentration of sintering aids at high temperatures. HPSN with Y$_2$O$_3$ as sintering aid is quite oxidation resistant. A HPSN product prepared from quartz sand and air has been found to be highly resistant to wear and thermal shock even at high temperatures. These are comparable to the Lulea hard metal oxide ceramics, cubic boron nitride and industrial diamonds.

Mechanical properties of both hot-pressed and reaction-bonded Si$_3$N$_4$ ceramics have been investigated in detail. Friction and wear properties of hot-pressed Si$_3$N$_4$ were studied by Ishigaki et al. (1986). The friction coefficient was correlated with the fracture toughness of Si$_3$N$_4$. Frictional anisotropy was also observed in hot-pressed Si$_3$N$_4$. Kim et al. (1986) have carried out wear tests on Si$_3$N$_4$ in dry rolling contact at room temperature. The wear rate of Si$_3$N$_4$ was found to be less than that of any other ceramic material. Observations of worn out surfaces and wear debris revealed that ceramic materials have two types of wear, one related to real contact area and the other related to Hertzian contact area. Brittle fracture dominates the wear process of ceramic materials in dry rolling contact. Nancy (1986) has recently reported that the microstructural changes associated with creep in Si$_3$N$_4$ are due to the operation of both cavitation and crack propagation mechanisms within the bonding phase below plastic deformation temperature of the matrix grains. Bandyopadhyay & French (1986) have reviewed the preparation of Si$_3$N$_4$ jet engine components by injection molding. Steinmann (1986) has reviewed crack-formation and propagation in hot-pressed Si$_3$N$_4$ during creep and on the durability of Si$_3$N$_4$ product as a function of temperature and load. These products have high corrosion resistance, good electrical insulation and are non-magnetic. Kaji & Mamoru (1986) have carried out systematic studies on microstructure and room temperature strength of Si$_3$N$_4$-Y$_2$O$_3$-Al$_2$O$_3$ pressureless sintered compacts. Thermal conductivity and microhardness of Si$_3$N$_4$ with and without additives have been studied by Tsukuma et al. (1981). High pressure hot-pressing of Si$_3$N$_4$ without additives was performed by Shimada (1986) using a mixture of a-Si$_3$N$_4$, amorphous Si$_3$N$_4$ and $\beta$-Si$_3$N$_4$ in the ratio 4:1:2 as starting material. Figure 1 shows the variation of microhardness of Si$_3$N$_4$ with temperature in these studies.

3. Sialons

3.1 Methods of preparation

The term 'sialon' was chosen to particularize any composition containing elements Si, Al, O and N as major constituents (Oyama & Kamigaito 1971; Jack & Wilson 1972; Oyama 1972; Jack 1976). Sialons can be made by high temperature reaction between silicon nitride or oxynitride and alumina. During the reaction silicon and nitrogen are replaced partially and simultaneously by aluminium and oxygen atoms, respectively. The $\alpha'$-structure results in M-Si-Al-O-N systems and is derived from the Si$_{12}$N$_{16}$ unit cell by partial replacement of Si$^{4+}$ by Al$^{3+}$ (M is Li, Mg, Ca or Y). All the sialons have the compositions represented by $M_x$(Si, Al)$_{12}$ (O, N)$_{16}$ where...
x > 2 and are structurally related to α- and β-silicon nitrides (Hampshire et al. 1978). Detailed compatibility and phase equilibria studies of sialons have been reported by a number of workers (Jack 1976; Hampshire et al. 1978; Gauckler et al. 1975). Jack has included the data obtained from specimens hot-pressed at temperatures ranging from 1550–2000°C in the phase diagram. According to Jack, the β'-sialon region extends from Si$_3$N$_4$ to Si$_{6-x}$Al$_x$O$_x$N$_{8-x}$ with x = 4–2. β'-sialon forming regions are reported in other systems such as Si$_3$N$_4$–Al$_2$O$_3$–Be$_2$SiO$_4$, Si$_3$N$_4$–Al$_2$O$_3$–Li$_2$O and Si$_3$N$_4$–Al$_2$O$_3$–MgO etc by Jack (1973), Oyama (1973) & Husbey et al. (1975). The possible reactions of Si$_3$N$_4$ and Al$_2$O$_3$ which produce β'-sialon with x = 4 are

\[
\begin{align*}
4\text{Si}_3\text{N}_4 + 6\text{Al}_2\text{O}_3 & \rightarrow \text{Si}_2\text{Al}_4\text{O}_4\text{N}_4 + 6\text{SiO} + 2\text{N}_2, \\
\text{Si}_3\text{N}_4 + 2\text{Al}_2\text{O}_3 + \text{C} & \rightarrow \text{Si}_2\text{Al}_4\text{O}_4\text{N}_4 + \text{SiO} + \text{CO}, \\
\text{Si}_3\text{N}_4 + 2\text{Al}_2\text{O}_3 & \rightarrow \text{Si}_2\text{Al}_4\text{O}_4\text{N}_4 + \text{SiO}_2.
\end{align*}
\]

Similar β'-sialon phases were obtained by reacting Si$_3$N$_4$ with lithium-aluminium spinel (LiAl$_5$O$_8$) and also with magnesium aluminium spinel (MgAl$_2$O$_4$). In addition to the sialon phases α', β', o' and x which were originally reported by Jack (1973, 1976), six unidentified phases nearer to the AlN corner of the Si$_3$N$_4$–AlN–Al$_2$O$_3$–SiO$_2$ system have been prepared by Gauckler et al. (1975). The complex phase diagram reported by Jack (1976) is shown in figure 2. Aluminosilicate minerals provide a convenient source of β'-sialon phases through the carbothermal reaction. β'-sialon powders prepared by this method have been characterized by Mostaghaci et al. (1986). The effect of agglomeration in the sialon powder on densification and microstructure development during hot pressing has been examined. Baldo et al. (1983, p. 437) have reported the preparation of sinterable sialon powders from hydrated silicates of aluminium with carbon and nitrogen. This route is considered to be more economical for preparing sialons. A variety of β'-sialon powders based on natural raw materials such as kaolin, clay, pyrophyllite, sillimanite and kyanite have been reported by Baldo et al. (1983, p. 437). Table 1 indicates compositions of several natural silicates used as reacting materials.

Figure 1. Variation of microhardness of silicon nitride with temperature (adapted from Shimada 1986).
Approximate compositions of $\beta'$-sialons ($\text{Si}_6-x\text{Al}_x\text{O}_x\text{N}_8-x$) obtained with the above materials are listed below.

$$\frac{\text{Al}}{\text{Si}} \quad x \quad \text{Sialon composition}$$

<table>
<thead>
<tr>
<th>$\frac{\text{Al}}{\text{Si}}$</th>
<th>$x$</th>
<th>Sialon composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>$\text{Si}_3\text{N}_4$</td>
</tr>
<tr>
<td>$\frac{1}{2}$</td>
<td>2</td>
<td>$\text{Si}_4\text{Al}_2\text{O}_3\text{N}_6$</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>$\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>$\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$</td>
</tr>
</tbody>
</table>

A typical carbothermal reaction resulting in the formation of a sialon may be represented as follows.

$$3(\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}) + 27\text{C} + \text{N}_2 \rightarrow 4[\text{Si}_3\text{N}_4 \cdot 1/2(\text{Al}_2\text{O}_3\text{N})] + 27\text{CO} + 6\text{H}_2\text{O} + \text{N}_2.$$ 

The preparation of $\beta'$-sialon from china clay and coal is described by Higgins & Hendry (1986). It is a chemical reaction in which the important stages are (i) dissociation of kaolinite to mullite and silica, (ii) formation of silicon carbide, and 

<table>
<thead>
<tr>
<th>Silicate</th>
<th>Formula</th>
<th>Ratio (Al/Si)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>$\text{SiO}_2$</td>
<td>0</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>$\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$</td>
<td>1/2</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$</td>
<td>1</td>
</tr>
<tr>
<td>Kyanite</td>
<td>$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$</td>
<td>2</td>
</tr>
</tbody>
</table>
(iii) simultaneous reduction and nitridation of mullite by carbon and silicon carbide in the presence of nitrogen gas. The reaction rate is controlled by the nitrogen flow rate because of its effect on the removal of carbon monoxide formed by reduction of the oxides. The reaction corresponding to the formation of $\beta''$ phase is reversible through the control of the carbon monoxide partial pressure. Hanna & Ghoneim (1986) have employed pure kaolin and coked rice hulls ($\text{SiO}_2 : \text{C} = 47:52$) for the preparation of sialon. The formation of $\beta''$-sialon powder was investigated by firing kaolin and coked rice hulls containing 20, 30, 40 and 50 wt% at 1300–1500°C under NH$_3$.

Translucent sialon ceramics have been prepared (Nobuyuki 1985) from Si$_3$N$_4$, Al$_2$O$_3$ and AlN. The resulting $\beta''$-sialon has the formula Si$_2$Al$_4$O$_4$N$_4$ and light transmissions of 43 and 70% at wavelength 0.4 and 4 $\mu$m, respectively. These translucent materials are useful in making container tubes for high voltage sodium lamps, windows for high temperature vessels and integrated circuit substrates.

3.2 Characterization

Sialons have been characterized using X-ray diffraction analysis (Jack & Wilson 1972; Izumi 1983; Thommy & Bertil 1986; Thompson et al 1983, p. 61) and analytical electron microscopy (Thompson et al 1983; Izumi et al 1984; Bonnel et al 1986; Johnson & Hendry 1979). Investigations have been carried out on materials of different compositions prepared under different processing conditions. Greil & Weiss (1983, pp. 359–374) have used TEM to characterize a hot-pressed solid solution material with 11 wt% Al$_3^+$ and varying oxygen content. With increasing amounts of oxygen, it is found that prismatic grains containing increasing amounts of amorphous phase are formed. Raman studies have been used to determine the changes in force constants which occur when interatomic distances and bonding characteristics are altered (Jack 1976). Magic angle spinning high resolution solid state NMR (MASNMR) has been used to monitor the quantity and co-ordination of aluminium in sialon and other ceramic materials (Fyfe & Gobbi 1983). Aluminium and silicon are found to be present as AlO$_4$ and SiO$_4$ tetrahedra and as AlO$_6$ octahedra. It was noted that in addition to SiO$_4$ tetrahedra, SiO$_3$N, SiO$_2$N$_2$, SiON$_3$ and SiN$_4$ tetrahedra can also be present because each type of tetrahedra can be linked to neighbouring tetrahedra in five possible ways. Sanyal & Mukerji (1986) have used Mössbauer spectroscopic techniques to study the effect of iron on the conversion of clay into $\beta''$-sialon. These studies indicate that no Fe is present in the metallic state in sialon.

3.3 Industrial production techniques, properties and uses

Hot-pressing has been widely used in the fabrication of sialon products. Various material combinations listed in table 2 have been pressed at temperatures where simultaneous chemical reaction and densification were found to take place. MgO has been commonly used as an additive to promote densification. The most effective hot-pressing temperature and time appear to be 1650–1750°C and 30 minutes to 2 hours, respectively. The experimental studies indicated in table 2 illustrate the varied nature of investigations in hot-pressed $\beta''$-sialons.

Pressureless-sintering studies have been conducted with various material combinations with and without additives. Sintering was conducted at about one
Table 2. Fabrication of sialon by hot-pressing.

<table>
<thead>
<tr>
<th>Starting materials</th>
<th>Additives</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Pressure (MN/m²)</th>
<th>Nature of investigation (Reference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Si}_3\text{N}_4, \text{Al}_2\text{O}_3, \text{Li}_2\text{CO}_3)</td>
<td>—</td>
<td>1750</td>
<td>20</td>
<td>29</td>
<td>Solid solubility (Oyama &amp; Kamigaito 1971)</td>
</tr>
<tr>
<td>(\text{Si}_3\text{N}_4, \text{Al}_2\text{O}_3)</td>
<td>—</td>
<td>1700</td>
<td>60</td>
<td>—</td>
<td>Formation, structure and thermal expansion (Jack &amp; Wilson 1972)</td>
</tr>
<tr>
<td>(\text{Si}_3\text{N}_4, \text{AlN}, \text{Al}_2\text{O}_3)</td>
<td>—</td>
<td>1730</td>
<td>30</td>
<td>25</td>
<td>Solid solubility (Oyama 1972)</td>
</tr>
<tr>
<td>(\text{Si}_3\text{N}_4, \text{Ga}_2\text{O}_3, \text{Al}_2\text{O}_3)</td>
<td>—</td>
<td>1730–1800</td>
<td>20–180</td>
<td>25</td>
<td>Solid solubility and thermal expansion (Jack 1973)</td>
</tr>
<tr>
<td>(\text{Si}_3\text{N}_4, \text{Al}_2\text{O}_3, \text{AlN}, \text{SiO}_2)</td>
<td>—</td>
<td>1760</td>
<td>60–300</td>
<td>30</td>
<td>Phase equilibria and compatibility relation (Arrol 1974, p. 729)</td>
</tr>
<tr>
<td>(\text{Si}_3\text{N}_4, \text{AlN}, \text{Al}_2\text{O}_3, \text{SiO}_2, \text{Si}_2\text{N}_2\text{O})</td>
<td>—</td>
<td>1500–2000</td>
<td>—</td>
<td>—</td>
<td>Phase equilibria, compatibility and structure (Gauckler et al 1975)</td>
</tr>
<tr>
<td>(\text{Si}_3\text{N}_4, \text{Al}_2\text{O}_3)</td>
<td>—</td>
<td>1700</td>
<td>60</td>
<td>15</td>
<td>Microstructure &amp; phase analysis (Drew &amp; Lewis 1974)</td>
</tr>
<tr>
<td>(\text{Si}_3\text{N}_4, \text{Al}_2\text{O}_3)</td>
<td>—</td>
<td>1700</td>
<td>30</td>
<td>—</td>
<td>Phase analysis (Gugel et al 1975)</td>
</tr>
<tr>
<td>(\text{Si}_3\text{N}_4, \text{Be}_3\text{N}_2, \text{BeO}, \text{SiO}_2)</td>
<td>—</td>
<td>1765–1880</td>
<td>60–120</td>
<td>28</td>
<td>Phase equilibria (Husby et al 1975)</td>
</tr>
<tr>
<td>(\text{Si}_3\text{N}_4, \text{Al}_2\text{O}_3)</td>
<td>—</td>
<td>1650–1850</td>
<td>6–60</td>
<td>25</td>
<td>Sintering, grain growth and phase equilibria (Oyama &amp; Kamigaito 1971)</td>
</tr>
<tr>
<td>(\text{Si}_3\text{N}_4, \text{AlN}, \text{SiO}_2)</td>
<td>\text{MgO}</td>
<td>1750</td>
<td>60</td>
<td>20</td>
<td>Fabrication, chemistry and creep (Lumby et al 1975, p. 283)</td>
</tr>
<tr>
<td>(\text{Si}_3\text{N}_4, \text{Al}_2\text{O}_3, \text{AlN}, \text{SiO}_2)</td>
<td>\text{MgO}</td>
<td>1760</td>
<td>—</td>
<td>—</td>
<td>Physical, mechanical and thermal properties (Gauckler et al 1977)</td>
</tr>
<tr>
<td>(\text{Si}_3\text{N}_4, \text{AlN}, \text{SiO}_2)</td>
<td>\text{MgO}</td>
<td>1800</td>
<td>60</td>
<td>15</td>
<td>Formation, microstructure characterization (Lewis et al 1977)</td>
</tr>
<tr>
<td>(\text{Si}_3\text{N}_4, \text{Al}_2\text{O}_3)</td>
<td>—</td>
<td>1500–1700</td>
<td>120</td>
<td>5.5–27.5</td>
<td>Effects of pressure and temperature on sintering (Yeh &amp; Watters 1977)</td>
</tr>
</tbody>
</table>

*dash indicates not reported.*

atmosphere of nitrogen to produce bodies with as high as 98% theoretical densities. Various aspects of sintering of sialons have been discussed by Jack and others (Jack 1973; Gugel et al 1975; Gauckler et al 1978, p. 559; Drew & Lewis 1974). In a special sintering procedure known as ‘transient liquid phase sintering’ (TLP), sialon of composition \(\text{Si}_{1.4}\text{Al}_{1.6}\text{O}_{1.6}\text{N}_{2.4}\) was obtained from two pre-reacted compositions, one of which was the \(X\)-phase which melts near 1700°C (Baldo et al 1983, p. 437). The microstructures of both hot-pressed and sintered-materials consist of \(\beta\)-sialons as the predominant phase with some isolated porosity and metallic looking phase in a uniform \(\beta\)-matrix. In some cases isolated grains of the \(X\)-phase and a 15R polytype phase were found with sizes varying between 0.2–2 μm (Greil & Weiss 1983, pp. 359–374; Takase & Tani 1984). The grain morphology in both sintered- and hot-pressed
materials was characteristic of the presence of a liquid phase during densification. This liquid phase was retained in intercrystalline spaces during cooling from hot-pressing (Evans & Moulson 1983, pp. 237–243) or sintering temperature (Takase & Tani 1984) and formed a glassy phase at the grain boundaries. Density values of hot pressed β'-sialons vary from 3.09 to 3.16 g/cm³ while the densities of other phases (X and 15 R) have been found to be between 3.05 g/cm³ and 3.08 g/cm³ (Gauckler et al. 1977).

Most of the mechanical properties reported in the literature refer to β'-sialon in (Si, Al, O, N) systems. Other systems such as (Si, Be, N, O), (Si, Al, Be, N, O) etc, have been examined primarily with respect to solid solubility, phase relationships and structure. The room temperature strength of sintered β'-sialon compares favourably with room temperature strength of sintered Si₃N₄. On the other hand, the room temperature strength of sintered β'-sialon is considerably lower than that of hot-pressed Si₃N₄. At high temperature (1370°C) the strength of sintered β'-sialon is equivalent to or higher than the strength of sintered Si₃N₄ but lower than that of hot-pressed Si₃N₄ (figure 3). Creep behaviour of several hot-pressed sialons have been measured and compared (Baldo et al. 1983, p. 437) with available data on hot-pressed Si₃N₄, hot-pressed SiC and reaction-bonded Si₃N₄. The sintered sialon has a creep rate lower than that of hot-pressed or reaction-bonded Si₃N₄. Lumby et al (1975, p. 283) have noted a strong dependence of creep behaviour on AlN concentration.

Fracture toughness (KIC) values have been reported in the literature for various compositions. Generally, the values are lower than those of hot-pressed Si₃N₄. Wills et al (1977) have suggested that the presence of X-phase should be kept at very low levels and preferably be eliminated completely to improve the fracture toughness of sialons. Lumby et al (1978, p. 893) have however observed a high fracture toughness

![Figure 3. Comparison of strength of silicon nitride and sialon at various temperatures (adapted from Lumby et al. 1978, p. 893).](image-url)
value for a pressureless sintered sialon which is similar to that of hot-pressed Si$_3$N$_4$. It has also been suggested that the increase in $K_{IC}$ values at high temperatures is associated with viscous deformation of the grain boundary phase. The variation in $K_{IC}$ values could probably be attributed to variation in sialon composition as well as fabrication and measuring techniques. The oxidation resistance of $\beta'$-sialon is better than that of hot-pressed Si$_3$N$_4$ (Arrol 1974, p. 729). It has also been observed that the oxidation rate of TLP sintered Si$_{1.4}$Al$_{1.6}$O$_{1.6}$N$_{2.4}$ is an order of magnitude less than that of hot-pressed Si$_3$N$_4$ at 1400°C.

The coefficient of linear thermal expansion of $\beta'$-sialon is $2.7 \times 10^{-6} \text{K}^{-1}$ and is less than that of $\beta$-Si$_3$N$_4$ ($3.5 \times 10^{-6} \text{K}^{-1}$). Gauckler et al (1977) have reported an average value of $3.4 \times 10^{-6} \text{K}^{-1}$ which compares with the value for pure $\beta$-Si$_3$N$_4$. It has been observed that essentially linear decrease (Gauckler et al 1977; Wills et al 1977) of the thermal expansion coefficient occurs with increasing Al concentration in sialons. Several investigators (Gauckler et al 1977; Lumby et al 1978, p. 893) have reported the value of water-quenched thermal shock resistance ($\Delta T_c$) of several sialons. While $\Delta T_c$ values for $\beta'$-sialons are comparable to those of various silicon carbide ceramics and RBSN, they are considerably lower than that of hot-pressed Si$_3$N$_4$.

Aliprandi (1986) has reviewed sialon ceramics with regard to their suitability in extrusion and drawing of metals. Recently high temperature properties of ceramics in the (Si, Al, O, N) system were studied by Bonnel et al (1986). The fracture toughness generally decreases with temperature. Short time annealing raises the toughness at lower temperatures whereas further annealing brings it back to the value characteristic of hot-pressed material. The problems associated with mass transport processes in the oxidation of calcium doped $\beta'$-sialon were studied by Chukukere & Riley (1986). The effects of creep on anelastic strain recovery, bulk and surface morphologies of sialon ceramics were examined using 3-point bending creep tests in air at 1200°C and 240 MPa by Besson et al (1986). TEM examination showed a marked decrease in the amount of glassy phase in the bulk of the samples after creep. No cavitation was however detected.

4. Aluminium nitride

Aluminium nitride is another useful nitride ceramic which exhibits a number of interesting properties. These include excellent high temperature strength, oxidation and thermal shock resistance and resistance against the attack of liquid metals. It is a good thermal conductor while it is electrically insulating.

4.1 Preparation and characterization

AlN powder is usually synthesized by two methods. The first one which has been widely adopted is direct nitridation of aluminium powder (or Al$_2$O$_3$ with C-black or graphite) by heating in a nitrogen or NH$_3$ atmosphere (Pierre et al 1985; Liping et al 1986). In the second method a high purity free-flowing AlN powder with low oxygen content is prepared by treating Al$_2$S$_3$ with NH$_3$ or N$_2$ at $>1100^\circ$C (Ibrahim 1986).

Fumino et al (1986) have reported the deposition of amorphous AlN films by a plasma CVD method using a metal organic aluminium source and NH$_3$ as the starting materials. The powder samples of AlN were characterized using X-ray diffraction and ESCA (Ibrahim 1986). It is found that the particles are associated with high surface concentration of O and grain sizes are of the order of 2000 Å.
4.2 Industrial production techniques, properties and uses

Polycrystalline compacts of AlN have been prepared by several methods such as sintering of pressed powder (Matsue et al 1965), reaction sintering of Al-AlN mixture (Taylor & Lenie 1960) and hot-pressing (Komeya & Inoue 1969). Although AlN is difficult to sinter without any flux, Komeya & Inoue (1969) found that very fine powders can be easily sintered though the extent of oxygen impurity in such powders is not known. Sakai & Iwata (1977) used hot-pressing techniques and studied the sintering behaviour and strength of sintered samples with various oxygen contents. Densification has been carried out by hot-pressing (Weston & Carruthers 1973) in an inductively heated graphite die. To avoid reaction between AlN and graphite die at high temperatures, graphite was coated with high purity boron nitride suspended in an aqueous solution of methyl cellulose. Methods of preparing AlN multilayer ceramic substrates for hybrid integrated circuits have been described which are suitable for mass production (Nobuo et al 1984; Komeya & Inoue 1974; Billy & Mexmain 1985).

Fully densified AlN has a microhardness value of 150 on the Vicker’s scale which is comparable to those of silicon oxynitride and Si₃N₄. The strength of AlN at room temperature is greater than that of RBSN but decreases when temperature increases and reaches a stable value between 800-1400°C. At 1400°C the strength is of the same order as that of other nitrides (Lecompte et al 1983, pp. 293–298). Trontelj & Kolar (1975, p. 39) have shown that with 99 AlN-1 Ni (wt%) powders, dense compounds could be sintered having a bend strength of 300 MN/m². Komeya & Inoue (1971) have studied the properties of AlN containing Y₂O₃ prepared by pressureless sintering. The highest value of the strength (328 MN/m²) could be obtained with a composition of 75 AlN-25 Y₂O₃. AlN with single oxide additives such as Li₂O, CaO, MgO, SiO₂, B₂O₃, NiO, Cr₂O₃ (1 wt%) has been used to study the sintering effect. Complete densification has been achieved through sintering under nitrogen at comparatively low firing temperatures (Schwetz et al 1983, pp. 245–252). McCauley & Corbin (1979) have shown that it is possible to reactively sinter Al₂O₃ with 27-40 mol % AlN to form a single phase cubic oxynitride spinel. The resultant material has a unique combination of properties and possesses mechanical properties very similar to Al₂O₃ of similar grain size. The final product, AlON, is optically isotropic.

Kazuo et al (1986) have reported that AlN mixed with 3 wt% strontium oxalate hot-pressed at 1800°C under a pressure of 300 kg/cm² has a thermal conductivity of 58 W/mK. The effect of sintering parameters such as pressure, particle size and temperature of AlN powders (coated with a thin film of Al₂O₃) on the densification rate was investigated in order to determine the sintering mechanism of AlN (Gossain et al 1985). Effect of CaO additives on electrical conductivity of hot-pressed AlN ceramic was studied by Zulfequar & Kumar (1986). A review on heat conducting aluminium nitride boards have been presented by Nobuo & Kazuo (1986).

5. Boron nitride

Lately, boron nitride has been recognized as a potential material for use at high temperatures. There is a marked similarity between BN and carbon, as they are isoelectronic. Boron nitride is known to exhibit three polymorphic modifications;
hexagonal graphite type (h-BN), cubic zinc blende type (c-BN) and wurtzite type (w-BN).

5.1 Methods of preparation

Various methods of preparation of BN have been described in the literature (Giardini 1953). Sorrel & McCartney (1986) have reviewed the history of development, method of manufacture, properties and application of c-BN ceramics. Fujio & Kozo (1986) have reported the preparation of hexagonal BN. In this process borax and melamine are heated at 150°C in an N₂ atmosphere for about 1 h and cooled in the same atmosphere overnight. The powder is washed with HCl and water and dried at 100°C for 2 h when white BN powder with 90-6% yield is obtained. A summary of known methods of preparation of hexagonal boron nitride is given by Ingles & Popper (1960, pp. 144–167) and the preparation of powder by the reaction of a mixture of boric oxide and calcium orthophosphate with ammonia at 900°C is discussed in detail. A flow sheet for the preparation of boron nitride powder from boric oxide and ammonia (Ingles & Popper 1960, pp. 144–167) is given below.
Cubic BN in general is synthesized from h-BN under high pressure–high temperature conditions, typically 65 kbar and 1700°C. The General Electric Company of America has succeeded in the preparation of c-BN from h-BN by applying very high pressure (60,000 atm) at a high temperature (1600°C) (Wentorf 1957). w-BN is also synthesized from h-BN employing even higher pressure, mostly by a shock process which involves a shear mechanism. The conversion of h-BN to c-BN is kinetically a difficult process, even in the thermodynamically stable regime of c-BN. This is due to the high activation barrier involved. Therefore the transformation is usually carried out in the presence of some catalyst material which lowers the activation barrier. c-BN compacts are synthesized at high temperature and pressure with suitable binders (Hibbs & Wentorf 1974; Fukunaga et al 1978, p. 328; Rapoport & Nadiv 1985).

5.2 Industrial production techniques, properties and uses

c-BN is an industrially important hard material, useful in abrasive and cutting tool applications. New methods for easier and more economical production are therefore constantly sought. Rapoport & Nadiv (1985) have examined mechano-chemical processing which can provide some extra activation to h-BN powder and assist in its conversion to c-BN. AIN was chosen as an additive to h-BN in view of its reported role as a catalyst in the conversion of h-BN to c-BN. Akashi & Sawaoka (1986) have prepared compacts of cubic boron nitride with 94% theoretical density and a Vickers microhardness value of 30.3 GPa from coarse c-BN powder by a shock compaction technique. According to them the mechanical and chemical properties of cubic boron nitride are very similar to those of diamond except for reduced reactivity with ferrous materials at high temperatures. Sintered w-BN compacts were characterized (Singh 1987) with regard to their different crystalline phases, which are formed at high temperatures and pressures, composition and particle size distribution. The cubic BN consists of particles with sharp blade edges and well-developed (111) faces and it is useful as a cutting and grinding material. Lavrenko & Alekseev (1986) have studied the oxidation resistance of BN samples obtained by various methods using thermogravimetric analysis, DTA and IR spectroscopy.

Composite materials were prepared using sialon and 5–20 vol % BN fibres by hot-pressing. The products had high thermal shock resistance and were used for the manufacture of special rings for horizontal continuous casting of steel (Peizhi et al 1986). The DC conductivities of hexagonal boron nitride and BN-containing composites were measured as a function of temperature up to 2400°C. The results confirm that at high temperatures BN is an intrinsic semiconductor with an energy gap of 6.2±0.4 eV (Frederikse et al 1985).

The mechanical and chemical stability and the high electrical resistivity of hexagonal boron nitride at high temperatures (2500°C) makes this compound a principal candidate for use as microwave windows in re-entry vehicle communication systems. However hexagonal boron nitride sublimes at 2500°C (Ingles & Popper 1960, pp. 144–167).

6. Boron carbide

Boron carbide which has a high melting point is among the refractory carbides. The
commercial importance of refractory carbides is mainly due to their extreme hardness.

6.1 Preparation

Boron carbide was initially produced in an electric furnace by Joly (1883) and Moissan (1894). For the production of pure boron carbide on an industrial scale, boric acid, which is available in high purity and in adequate amounts, is generally used. The formation of boron carbide from $\text{B}_2\text{O}_3$ is represented by the equation

$$2\text{B}_2\text{O}_3 + 7\text{C} \rightarrow \text{B}_4\text{C} + 6\text{CO}.$$  

Recently boron carbide has been prepared by high temperature reaction involving boric oxide and carbon (Ramamurthy 1985; Seiji 1986).

6.2 Characterization

Boron carbide has already been known for 50 years, since its crystal structure was elucidated by Laves (1934–35). The elementary cell was described by Silver & Bray (1959) on the basis of NMR investigations. The B-C phase diagram has been described in detail by Samsonov (1958 a, b, c). X-ray data were used by Samsonov and coworkers for generating the phase diagrams. Metallographic investigations were also carried out along with measurements of density, hardness and electrical resistance.

6.3 Properties, industrial production techniques and uses

The most important property of boron carbide is its extraordinary hardness. After diamond and cubic boron nitride (the so-called Borazon), boron carbide is the hardest industrial material known. However, hardness values of boron carbide are reported in different ways in the literature (Knoop 1939). Figure 4 shows the

![Figure 4](image)

Figure 4. Vicker's hardness as a function of B/C ratio for boron carbide (adapted from Niihara et al 1984).
Vicker’s hardness as a function of the B/C ratio for boron carbide. It appears that the hardness values range from 20–80 kN/mm² and lie between the hardness values of corundum and diamond. Lipp (1965) has presented an interesting review on the physico-chemical properties and reactivity of boron carbide.

7. Silicon carbide

Silicon carbide was first artificially produced and later discovered in the natural state. The mineralogical name of silicon carbide is moissanite. Moissan (1905) discovered hexagonal silicon carbide interlaced with diamond in the meteoric iron found in the Diablo Canyon (Arizona). Several authors (Kaypov & Baymuratov 1970) have reported the occurrence of Moissanite since 1950 in various volcanic rocks in the Soviet Union. About a decade ago, it was reported that silicon carbide along with some other compounds was detected in the gaseous phase of certain stars (Friedmann 1969; Gilman 1969; Lefevre 1970). SiC occurs most probably in the circumstellar space of cool stars that contain carbon and oxygen in almost equal proportions (Gilman 1969), the presence of silicon carbide was detected by absorption spectral analysis (Lefevre 1970). Acheson developed a process for the manufacture of silicon carbide on an industrial scale in 1891. The process is frequently mentioned in the literature as the Acheson process. Silicon carbide is produced batchwise in an electric furnace by high temperature solid phase reaction of coal and quartz sand. The production of silicon carbide even today is carried out exclusively by this process. Efforts (Lanyi 1955, p. 284) have been made over the past eight decades to produce silicon carbide on an industrial scale by improved methods. It is rather difficult to evaluate either the present situation or the current trends of development precisely because of the nonavailability of complete research literature on SiC production. However, a few standard methods of producing SiC are discussed below.

7.1 Methods of preparation

For the production of industrial SiC, silica and carbon are used as basic materials along with various additives: saw dust, sodium chloride and also other modifying components. The correct proportion of raw materials, their pretreatment, optimum grain size, applied additives and modifying components etc. are discussed in the literature (Acheson 1896, 1912; Dadape et al 1947; Tomonari 1956). The formation of silicon carbide can be summarized (Ruff 1935) in the following two steps,

\[
\begin{align*}
\text{SiO}_2 + 2C & \rightarrow \text{Si} + 2\text{CO} \quad \text{(first step)} \\
\text{Si} + \text{C} & \rightarrow \text{SiC} \quad \text{(second step)}
\end{align*}
\]

Production of silicon carbide starting from silicon and coal, silicon tetrachloride, trichloro silane, alkyl silanes and aluminium silicates etc. have been described in the early literature. Silicon carbide has been prepared from carbon tetrachloride and alkyl silanes in a hydrogen atmosphere on a glowing carbon rod at a temperature above 1700° C (Pring & Fielding 1909). It is also possible to obtain silicon carbide from a mixture of silicon tetrachloride and toluene using hydrogen as a carrier gas.
on fibres of carbon using thallium carbide or zirconium carbide as crystal growth promoting agents (Agte & Moers 1931). Aluminium silicates have been used as starting materials instead of silica (Hayakawa 1949).

Hoch & Nair (1978, pp. 33-40) have reported the preparation of ultrafine powders of SiC from organometallic complexes. The process can be represented by the following equation,

$$\text{Si(OH)}_4 + \text{CH}_4 \rightarrow \text{SiC} + 4\text{H}_2\text{O}$$

Fine powders of $\beta$-SiC were obtained by the vapour phase reaction of a SiH$_4$-CH$_4$ system at about 1400°C and by the thermal decomposition of (CH$_3$)$_4$Si in hydrogen atmosphere above 1000°C (Okabe et al 1979). The formation processes of SiC particles in these reaction systems are summarized as follows:

(a) \[\text{SiH}_4(g) + \text{CH}_4(g) \rightarrow \text{SiC}(s) + 4\text{H}_2(g),\]

$$\text{[SiH}_4(g) \xrightarrow{500-700^\circ C} \text{Si \ (particles)}]\]

$$\text{Si \ (particles)} + \text{CH}_4(g) \xrightarrow{1000^\circ C} \text{SiC \ (particles)};$$

(b) \[(\text{CH}_3)_4\text{Si}(g) \rightarrow \text{SiC}(s) + 3\text{CH}_4(g),\]

$$\text{[(CH}_3)_4\text{Si \ (g)} \xrightarrow{700^\circ C} \text{polymer \ particles},$$

$$\text{polymer \ particles} \xrightarrow{900^\circ C} \text{SiC \ (particles)}].$$

Silicon carbide whiskers can be made by a variety of methods. The most economical one is the carbothermic reaction of SiO$_2$ and carbon, which are constituents of ground rice hulls (Lee & Cutler 1975). Sharma et al (1984) have produced such whiskers and characterized them by transmission electron microscopy. Another method is the gas-phase reaction of SiCl$_4$, chlorosilane and/or silane in a carbonaceous atmosphere in the presence of Fe and Cr as catalysts (Mazdiyasni & Zangvil 1985). The effect of covalent bond additives, such as AlN, BN and BeO on the structural stability of SiC has been studied by Zangvil & Ruh (1985).

The detailed structure of silicon carbide has been given by Dietzel et al (1960) & Ueltz (1972, p. 1). The crystal structure and mechanical properties of green and black silicon carbides have been discussed by Gasilova & Saksonov (1966, p. 50).

Thermal and chemical properties of silicon carbide which include thermal expansion, thermal conduction and reaction of silicon carbide with various other chemicals have been summarized in the literature. Silicon carbide is attacked at high temperatures by gaseous fluorine, chlorine and hydrogen. It is resistant to mineral acids and is attacked only by a mixture of hydrogen fluoride and nitric acid and/or concentrated phosphoric acid at temperatures above 200°C.

7.2 Industrial production techniques, properties and uses

Silicon carbide based ceramic materials include hot-pressed SiC (HPSiC), reaction-bonded SiC (RBSiC), sintered SiC (SSiC), silicon carbide/silicon composites and chemical vapour deposited SiC (CVD-SiC).

Hot-pressed SiC can be formed with various densification aids, but only the HPSiC
Light element ceramics

Prepared by utilizing Al$_2$O$_3$ additive has been considered for high performance engine applications (Prochazka 1975, p. 171). HPSiC is not as strong as HPSN at low temperatures, however, it retains useful strength up to ~1400°C.

Reaction-bonded silicon carbides cover a wide range of compositions and manufacturing processes (Alliegro 1974). Typical examples of these materials include UKAEA/BNF Rofel, KT, NI-430, NI-435 and Ford siliconized silicon carbide. Each material is formed by a unique proprietary process. In general, a plastic body is formed by SiC powder, graphite and a plasticizer. In some variants of this process, SiC powder and a char-forming plastic binder are used (Whalen et al. 1978). A variety of experimental gas turbine components such as combustors or stators, have been made by this route. Since these materials and the processes are easily adopted to mass production techniques and since the products possess good shape retention, there is a strong incentive to use them for the production of automotive components.

Sintered silicon carbide is a recent development. The pressureless sintering of SiC to full density was thought untenable until Prochazka demonstrated that with boron and carbon additions, β-SiC could be sintered to a maximum density at 2000°C (Prochazka 1974). He also demonstrated that sintered β-SiC could be formed into useful shapes by slip-casting, die-pressing and extrusion. Distribution of the carbon additive and exaggerated grain growth of α-SiC were found to interfere with densification. Coppola & McMurtry (1976) have developed sintered α-SiC partly in an effort to eliminate the problems associated with β-α transformation. The β-SiC structure appears stronger than α-SiC. Bending strengths of α and β forms are of the order of 300–450 MPa (Larsen et al. 1983, pp. 695–710). The temperature variation of the bending strengths of α and β SiC is shown in figure 5.

Reaction-formed SiC/Si composites developed by Hillig (1974) are the first engineering composite ceramic/ceramic materials which offer the possibility of low cost structural components. In this process, the molten silicon reacts with graphite to form polycrystalline SiC fibres in a silicon matrix. This material has been used in a

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**Figure 5.** Flexural strength of silicon carbide materials as a function of temperature (adapted from Larsen et al. 1983, pp. 695–710).
combustion chamber liner application at temperatures above 1400\textdegree\text{C} (Coppola & McMurtry 1976), although it is still in a very early stage of development.

CVD-silicon carbide in contrast to CVD-Si$_3$N$_4$ has been produced in bulk. Fabrication capability of gas turbine components including radial and axial rotors has also been demonstrated. CVD-SiC has proven to be an outstanding creep- and oxidation-resistant material. Its major drawback from an automotive application point of view is likely to be the cost. This process may be useful in coating SiC ceramics formed by more conventional routes. A sintered body consisting of SiC and AlN has 90\% theoretical density, specific resistance of 1–10$^4$ ohm/cm (at room temperature), excellent bending strength and oxidation-resistance. It is useful for heaters, electrical resistors and temperature sensors.

8. Concluding remarks

The ceramics discussed in this article are the most important materials currently in demand for advanced and emerging technologies. Large volume ceramic applications appear to be round the corner in the automotive industry. Adiabatic engines made from advanced ceramics such as Si$_3$N$_4$ have the demonstrated ability to save power upto 20–30\% which is too attractive to ignore by a world faced with an imminent energy crunch.

A variety of advanced technologies also make continuous demand on super hard materials for cutting tools and materials which are capable of standing extremes of temperature, pressure and chemical environment. Metals and alloys have been found to be incapable of answering these challenges, thus making ceramics the only candidates in the field; a ceramic age appears to have been ushered in. As pointed out earlier light element ceramics constitute choice materials for further development and exploration. Nature has distributed the light elements so evenly on our planet that they are there for all progressive countries to harvest for their own benefit.

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S B BHADURI
Defence Metallurgical Research Laboratory, P O Kanchanbagh, Hyderabad 500 258, India

Abstract. In this paper, we comprehensively review the physical principles behind the improvement of mechanical properties of zirconia (ZrO_2) related ceramics. First, the transformation behaviour of different phases in zirconia is discussed. We next present an overview of two zirconia-related commercially important systems e.g. ZrO_2-MgO and ZrO_2-Y_2O_3. The commercial engineering ceramic materials, generated from these systems, are known as partially stabilized zirconia and tetragonal zirconia polycrystal respectively. The third important material is called zirconia toughened alumina. The evolution, characterization and importance of the microstructure in relation to the basic systems are also presented. Attention is then focussed on to three toughening mechanisms e.g. phase transformation toughening, microcrack toughening and crack deflection toughening. We carefully assess the roles they play in improving toughness. We discuss R-curve behaviour arising out of these toughening mechanisms and the implications of R-curve behaviour in engineering applications. Finally, the subcritical crack growth and tribological behaviour of these materials are discussed.

Keywords. Zirconia-related ceramics; partially stabilized zirconia; tetragonal zirconia polycrystal; zirconia toughened alumina; phase transformation toughening; microcrack toughening; crack deflection toughening; R-curve behaviour.

1. Introduction

Since the publication of the seminal paper on toughened zirconia by Garvie et al (1975), this material has become the most important ceramic material of the present. Along with high toughness and strength, zirconia also possesses good hardness, wear resistance, and thermal shock resistance. These superb properties have led to the usage of zirconia-based components in a number of engineering applications such as automobile engine parts, wire drawing dies, cutting tools, in chemical plants for handling corrosive slurries, and in the textile industry as thread guides. An understanding of the peculiar properties of zirconia have made all the applications and improved properties possible. The key to the improvement in properties lies in the controlled phase transformation of the metastable phase to the stabler phase during the crack propagation.
The present paper reviews the current understanding of the scientific aspects of toughened zirconia, emphasizing the role of the system and the microstructure for the development of the mechanical properties. The technological aspects are briefly touched upon.

Therefore, the different phases of zirconia, their stability and the transformation of the metastable phase are first discussed, followed by a review of commercially available systems and their microstructures. Finally, the various mechanical properties are elaborated. The emphasis throughout the paper is on commercially available/viable engineering materials. This is necessitated by the fact that zirconia-related materials have many other uses.

2. Phases and transformation

Polymorphism of zirconia is well-known; three crystallographic modifications exist—cubic (c), tetragonal (t) and monoclinic (m). They are stable at high, intermediate and low temperatures, respectively. Table 1 shows the relevant crystallographic data. Subbarao (1981) reviewed the evidence that clearly established the martensitic nature of the \( t \to m \) transformation. The transformation strain \( \varepsilon^T \) can be expressed in terms of the matrix

\[
\varepsilon^T = \begin{bmatrix}
\frac{a_m \cos (90 - \beta)/2 - a_t}{a_t} & 0 & \frac{\tan (90 - \beta)/2}{\tan (90 - \beta)/2} \\
0 & \frac{b_m - b_t}{b_t} & 0 \\
\frac{\tan (90 - \beta)/2}{\tan (90 - \beta)/2} & 0 & \frac{a_m \cos (90 - \beta)/2 - a_t}{a_t}
\end{bmatrix}
\]

Substituting the lattice parameters in (1), it can be shown that there is 9% shear involved and that the change in volume \( (\varepsilon_{11}^T + \varepsilon_{22}^T + \varepsilon_{33}^T) \) is equal to 4.7%. Therefore, in general, the \( t \to m \) transformation is deleterious to the property of the material. But under controlled conditions, the transformation can lead to enhancement of properties. This is achieved by stabilizing the high temperature \( t \)-phase at room temperature. It has been experimentally shown by Hannink et al. (1981) that there is

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<th>Table 1. Crystallographic data on various phases of zirconia.</th>
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a critical size of the tetragonal particle which is stable at room temperature. The reciprocal of the size of the particle is shown to be linearly proportional to $M_s$, the martensitic start temperature. There are several theoretical attempts to analyse this experimental fact. One of the approaches is to carry out a thermodynamic analysis without looking at the actual processes. Such end-point calculations were undertaken by Lange & Green (1981), Lange (1982), Garvie & Swain (1985). This simple approach provides us with a tangible explanation of the experimental facts. Following Garvie & Swain (1985), the change in free energy of a spherical particle of radius $r$ can be given as

$$
\Delta F_0 = \frac{4}{3} \pi r^3 (\Delta F_{\text{chem}} + \Delta F_{\text{dil}} + \Delta F_{\text{shr}}) + 4 \pi r^2 (\Delta S_{\text{chem}} + \Delta S_{\text{tw}} + \Delta S_{\text{pm}}),
$$

where $F_0$ is the total free energy and $\Delta F$ is the free energy change per unit volume. Subscripts chem, dil and shr denote chemical, dilatational and shear, respectively, $\Delta S$ denotes the change in free energy per unit area, and tw, pm refer to the contributions from twin boundaries and the second phase, respectively. Equation (2) can be written as:

$$
\Delta F_0 / V = \Delta F_{\text{chem}} + \Delta F_{\text{str}} + (3/r) \Sigma \Delta S,
$$

where $V$ is the volume of the particle, $F_{\text{str}}$ is the sum of the strain energies and $S$ is the sum of the interfacial energies. Equation (3) can be conveniently rewritten as

$$
1/r_c = q T/3 \Sigma \Delta S T_b - (9 + \Sigma \Delta S_{\text{str}} )/3 \Sigma \Delta S,
$$

where $c$ denotes a critical value, $q$ is the enthalpy of transformation of an infinitely large crystal and $T_b$ is the transformation start temperature ($M_s$) of a particle of radius $r_c$. It is evident that (4) describes the experimental behaviour perfectly. Garvie & Swain (1985) substituted all the relevant data in the above equation and showed that real systems obey (4). Further, these theories can also predict transformability under stress. They can approximately point out the causes of nucleation of martensite i.e. whether it is by a classical or by a non-classical mode (Burke & Garvie 1977).

Heuer et al (1982), Ruhle & Heuer (1984), Heuer & Ruhle (1985), on the other hand, emphasized the events taking place during transformation i.e. nucleation and the growth of plates. This kind of approach requires a substantial amount of electron microscopy and much more sophisticated modelling involving the nucleation aspect and proper constitutive relations. Modelling work has been initiated along these lines by Lambropoulos (1986, and unpublished work). These models are much more rigorous than the previous ones.

Thus, there is a critical particle size of the tetragonal phase that can remain stable at a given temperature. It undergoes controlled transformation only when the crack propagates in the vicinity of the particles. However, certain alloying elements can increase the stability of tetragonal particles by bringing down $M_s$ temperature. Therefore, in binary systems of other oxides with zirconia, there must be a range of sizes of metastable tetragonal particles which are transformable in the stress field of the propagating crack. It is these particles which are responsible for increasing the toughness. If the tetragonal particle size is less than the critical value, they remain stable even in the stress field of the propagating crack. If they are above the upper bound, they transform spontaneously during cooling without contributing to the toughness.
3. Commercial materials and microstructures

It is known that the \( t \rightarrow m \) transformation leads to severe cracking of the matrix. One solution of the problem known for about fifty years is to form solid solution alloys with CaO, MgO or \( Y_2O_3 \). All of these solutes are supposed to stabilize the cubic structure at room temperature and avoid \( t \rightarrow m \) transformation. Actually, these solutes permit retention of cubic structure at lower temperatures than is possible in undoped material because most of the phase equilibrium diagrams now report eutectoid decomposition reactions at low temperatures. The so-called destabilization phenomenon is this eutectoid reaction. Because of this, cubic or fully stabilized zirconias (CSZ) fail.

Partially stabilized zirconias (PSZ) are two (or more) phase materials, with the matrix phase being cubic. Addition of a limited quantity of solute and proper heat treatment in the two-phase (\( c + t \)) field gives rise to the above microstructure. Usually, the second phase is the metastably-retained tetragonal phase. There are several advantages of this material. During cooling, \( t \rightarrow m \) transformation counteracts the contraction of the cubic phase. Therefore PSZ has better thermal shock resistance than CSZ. Further, the controlled \( t \rightarrow m \) transformation at the crack tip imparts toughness to the material. That is why PSZ is the most important engineering material nowadays.

3.1 The \( \text{ZrO}_2 - \text{MgO} \) system

We now describe the commercially available compositions. Figure 1 shows the phase diagram of the \( \text{ZrO}_2 - \text{MgO} \) binary system. The group at CSIRO, Melbourne, has pioneered the development of commercial PSZ materials based on this system. Typical compositions are also shown in figure 1. A common procedure for producing partially stabilized zirconia is to solutionize and homogenize the desired composition in the cubic phase field, at a temperature of 1700°C or above, and then quench the
material. The phase diagram suggests that the following reactions can take place during cooling/ageing in the $t + c$ phase field.

1) $c$-ZrO$_2 \rightarrow t$-ZrO$_2 + c$-ZrO$_2$,
   Cool $\rightarrow m$-ZrO$_2 + c$-ZrO$_2$;

2) $c$-ZrO$_2 \rightarrow t$-ZrO$_2 + c$-ZrO$_2$,
   Cool $\rightarrow t$-ZrO$_2$ (metastable) + $c$-ZrO$_2$;

3) $c$-ZrO$_2 \rightarrow t$-ZrO$_2 + MgO$,
   Cool $\rightarrow m$-ZrO$_2 + MgO$;

4) $c$-ZrO$_2 \rightarrow m$-ZrO$_2 + c$-ZrO$_2 (< 1240^\circ C)$,

5) $c$-ZrO$_2 \rightarrow m$-ZrO$_2 + MgO (< 1240^\circ C)$.

Reaction (1) is the typically expected reaction. However, in the case of reaction (2), the size of the tetragonal particles that precipitate out of the cubic matrix is so small that they remain tetragonal when cooled below $M_s$ temperature. Reaction (3) is the eutectoid reaction. Reactions (4) and (5) are the sub-eutectoid reactions. Of all the reactions mentioned above, it is expected that reaction (2) is the most important one, because it tends to retain the tetragonal phase metastably. However, they are optimally aged so that their size range is in between the lower and upper ranges of the transformability limit.

Figure 2a shows a typical microstructure of the optimally aged tetragonal precipitates in the cubic matrix. These precipitates can be easily detected by (111)-type diffraction patterns in the transmission electron microscope (TEM) as shown in figure 2b. The half reflection spots are the cubic forbidden spots and are ascribed to the tetragonal phase present in the cubic matrix. The dark field (DF) imaging technique using one of the tetragonal spots clearly reveals that they arise from the precipitates. These precipitates are lenticular in shape in the ZrO$_2$-MgO system. The tetragonal $c$ axis is parallel to $\langle100\rangle$ of the matrix. This precipitate morphology can now be exactly predicted by the application of the Khachutoriyan (1983) theory as shown by Lanteri et al (1986). The critical particle size of $t$-ZrO$_2$ in Mg-PSZ is around 100 nm. Hannink (1978) explained the critical particle size by assuming that the coherency at the interface is lost if the particle exceeds a certain critical value. He used the one-dimensional Brooks' (1962, pp. 20–25) criterion to analyse the situation. However, the predictions are 2 or 3 times off the experimentally observed values. Clearly, better modelling is needed at the moment. These optimally aged zirconias have high strength and toughness. However, they still lack the high thermal shock resistance that is required in some engineering applications.

Further improvements of the properties were achieved by subeutectoid ageing of a suitably prefired material. This controlled heat treatment does not impart the highest strength but promotes higher toughness values and better thermal shock properties. Hannink & Garvie (1982), and Hannink (1983) have reported that a prefired material containing $t$-precipitates of 100 nm size can be aged at 1100°C to achieve improvement of the above properties.

During the ageing at this temperature, a very complicated reaction takes place. In fact both reactions (2) and (5) operate here simultaneously. Reaction (2) operates inside the grains whereas reaction (5) takes place at the grain boundaries. The reactions can be monitored easily by TEM. Initial ageing at subeutectoid temperature shows tetragonal spots in the diffraction pattern. But additional spots appear in the pattern showing some kind of ordered phase precipitating. This phase has been
Figure 2. (a) Typical microstructure of optimally aged PSZ. (b) corresponding diffraction pattern.

identified by Hannink (1983), and Farmer et al (1983, 1984) as $\text{Mg}_2\text{Zr}_5\text{O}_{12}$. The detailed structure of this phase has been published by Delamarre (1976) who claims that it is a defect fluorite structure of trigonal symmetry. This phase is also called the $\delta$ phase. As opposed to the grain interior, the subeutectoid decomposition goes on along the grain boundary. Detailed microscopy shows that the diffraction pattern has both monoclinic $\text{ZrO}_2$ and MgO spots (Heuer et al 1983) DF imaging can be
performed using one of these spots. The procedure reveals that the grain boundary is full of alternate plates of MgO and \( m \)-ZrO\(_2\). A schematic microstructure is shown in figure 3.

During the ageing treatment, the \( \text{Mg}_2\text{Zr}_5\text{O}_{12} \) phase grows with diffusion of MgO and depletes MgO content in the stable tetragonal precipitates. So the formerly coherent tetragonal precipitates tend to lose coherency and become unstable. Therefore, the number of transformable tetragonal precipitates increases and hence the toughness goes up. Secondly, during the propagation of the crack, it interacts with the grain boundary substantially giving rise to \( R \)-curve behaviour. In other words, resistance to cracking increases as the crack grows. Both of the above processes improve toughness and thermal shock resistance, but with a slight decrease in strength.

3.2 The \( \text{ZrO}_2 - \text{Y}_2\text{O}_3 \) system

The phase diagram of \( \text{ZrO}_2 - \text{Y}_2\text{O}_3 \) is shown in figure 4. It is the single tetragonal phase field that is of commercial interest here. The idea was first proposed by Gupta et al (1977). The material is sintered in the tetragonal phase field with a final grain size of 0.3 \( \mu \)m and is completely (or mostly) tetragonal (figure 5) (Gupta 1978). Such materials are called tetragonal zirconia polycrystals (TZP). This is a very stringent condition indeed. One must choose suitable temperatures and soaking times to avoid grain growth. Second, the initial crystallite size of powders of \( \text{ZrO}_2 - \text{Y}_2\text{O}_3 \) should not be very big. Third, the material has to be sintered in the single tetragonal phase field. Therefore, accurate knowledge of the phase diagram is also essential. Subbarao et al (1974) and Srivastava et al (1975) indicated that the two-phase field extends from 3.9 to 7.5 mol\% \( \text{Y}_2\text{O}_3 \) with \( t \rightarrow m + c \), the eutectoid composition value and temperature at 3.9 mol\% \( \text{Y}_2\text{O}_3 \) and 565\(^\circ\)C, respectively. Scott (1975) reported a eutectoid at 2.6 mol\% \( \text{Y}_2\text{O}_3 \) and at 565\(^\circ\)C. Pascual & Duran (1983) reported that eutectoid is at 4.5 mol\% and at 490\(^\circ\)C.

Such materials possess very high toughness and strength values. Masaki & Sayo

![Figure 3. Schematic microstructure of subeutectoid aged ZrO\(_2\)(MgO).](image)
(1986) report strength values as high as 1700 MPa and fracture toughness values of $K_{IC} = 20$ MPa (m)$^{1/2}$. Detailed TEM characterization results are reported by Ruhle et al (1984a). Most of the materials contain $t$-grains up to 0.8 $\mu$m. $Y_2O_3$ composition in each $t$-$ZrO_2$ grain varies between 1.8 and 4.6 wt%. The grain size and $Y_2O_3$ content do not correlate. Careful studies by Lange (1986) show that as $Y_2O_3$ content is increased from 0 to 4 mol% $Y_2O_3$, grain size decreases from 1.8 to 0.4 $\mu$m. Along with $t$-$ZrO_2$ - $c$-$ZrO_2$ grains are also present in the microstructure. Further studies show that $c$-$ZrO_2$ grains also contain $t$ precipitates. Also, most of the commercial materials contain a glassy grain boundary phase presumably picked up during mechanical milling of powder with $SiO_2$-containing balls. Transformation of $t$-$ZrO_2$ starts at the inhomogeneities at the grain boundaries or at defects present in the grains. Transformation strain frequently causes neighbouring grains to transform autocatalytically. Transformation also leads to some microcracking. A crack always leaves a continuous transformation zone in the wake of the propagating crack. This feature is discussed in §4.1.

3.3 Zirconia toughened alumina

Zirconia toughened aluminas (ZTA) are classic examples of dispersion toughened ceramics. The second phase in these is unstabilized zirconia. Claussen (1976) and Claussen et al (1977) showed that a certain amount of very fine monoclinic zirconia can be well-dispersed in the $Al_2O_3$ matrix, and hot-pressed. Controlled microcracks are formed during cooling. This kind of controlled microcracking increases the toughness of the materials. Furthermore, some of the $ZrO_2$ particles may remain tetragonal in the compression stress field of the matrix. They may transform during
the propagation of the crack. So in this case both phase transformation and microcracking improve toughness. Therefore, the key to the production of ZTA materials is the control of the microstructure during hot-pressing or sintering. Green (1982) studied the critical microstructures and experimentally obtained the lower and upper bounds of the particle sizes which are transformable.

The dilemma now is in deciding which of the two processes, e.g. phase transformation toughening or microcrack toughening, is important in ZTA. Ruhle et al (1984b) addressed the question by performing *in situ* straining experiments in the high voltage electron microscope (HVEM). Recent experimental results by Ruhle et al (1986) show that along with microcracking, phase transformation could also be an important toughening process.

Heuer et al (1982) examined the stability of ZrO$_2$ particles within Al$_2$O$_3$ grains and argued that the stability of ZrO$_2$ particles depends on the nucleation of martensite as well as the solute content. Nucleation can play a significant part in the faceted intergranular particles. The facets act as stress raisers during the cooling of the composites from the fabrication temperature. As opposed to the intergranular particles, the intragranular particles are round shaped and remain quite stable. This is again due to the difficulty of nucleation of the martensite. The typical microstructure of ZTA is shown in figure 6.

Finally we point out the fact that there are several major differences between t-ZrO$_2$ of ZTA and t-ZrO$_2$ of PSZ.

1) The interphase between the second phase and the matrix is coherent in PSZ and incoherent in ZTA (Kraus-Lanteri et al 1986).

2) In PSZ, t-ZrO$_2$ is under compressive stress. The strain field around the particle...
opposes transformation. In ZTA, the thermal mismatch causes tensile stresses in the particle which should encourage transformation.

Notwithstanding the above facts, there is a strong size dependence of \( t-ZrO_2 \) on \( M_s \). The end-point thermodynamic calculations of Garvie & Swain (1985) predict experimentally observed results for PSZ and ZTA, without considering these facts. As noted in § 2 there is still need for better modelling.

4. Mechanical properties

Having described the commercially available materials and their microstructures, we will now concentrate on their important mechanical properties. Naturally, the most important and interesting mechanical property is their toughness. We discuss how the toughness of these materials can be increased by means of different toughening processes. Evans & Cannon (1986) have published a detailed review on this topic. In this paper we will follow their treatise.

Already we have noted that there are two different toughening processes e.g. phase transformation toughening and microcrack toughening. In addition, there is a third process known as crack-deflection. The crack interacts with the second phase and gets deflected. The effect leads to moderate increase in toughness. In the case of phase transformation as well as microcrack toughening, a nonlinear zone ahead of the crack tip is envisaged. One may compare this zone to the plastic zone in metals and crazed zones in polymers. The role of this zone is to reduce the effectiveness of the
4.1 Phase transformation toughening

We begin by quantifying the crack tip shielding concept. The materials that show crack tip shielding have a break in the linearity of their stress–strain curve at a critical stress. In the case of transformation toughening, it is the critical stress of transformation (figures 7a & 7b). This break in stress is also reflected in the strain. The crack tip stress intensity is therefore lowered. That is, even if we apply $K_\infty$ at the far end of the crack, stress at the tip is lowered by amount $K = K_\infty - K_{\text{local}}$. In other words, the zone in front of the crack shields the crack tip from the applied stress intensity. Hence the term 'crack tip shielding'. Since the crack tends to propagate when $K_{\text{local}}$ attains the toughness of the fully transformed material ahead of the crack tip, we can write

$$K_\infty^c = K_\infty^f + \Delta K^c$$

where $\Delta K^c$ is the increase in toughness. Further analysis of the crack tip shielding can be made by taking either a mechanics, thermodynamics or dislocation approach. All the three approaches yield similar results.

Here, we will adopt the mechanics approach as developed by Budianisky et al (1983) and Evans (1984). The methodology is based on the path-independent $J$-integral concept of Rice (1968a), which is discussed in detail in another paper (Rice 1968b, pp. 191–230).

We now examine the development of the zone in front of the crack tip. We distinguish between two types of zones. The first one, called the frontal zone (figure 8a), becomes effective as the crack gets initiated. The frontal zone soon spreads to become the wake zone (figure 8b) as the crack propagates. Since the volume elements within the transformation zone do not experience unloading, the path independent $J$ integral is applicable. We can choose any two paths—one within the frontal zone and...
Figure 8. Schematic drawing of (a) the frontal zone, (b) the wake zone.

the other outside it.

\[ J = \frac{\left(1 - v_1^2\right)K_f^2}{E} = \frac{\left(1 - v_2^2\right)(K_f^*)^2}{E_1} = \frac{\left(1 - v_2^2\right)(K_f^*)^2}{E_2}, \]

where \( v_1, v_2, \) and \( E_1, E_2 \) are Poisson's ratio and the Young's modulii of the frontal zone and the matrix, respectively. Since the \( v \)'s and \( E \)'s are the same in the case of transformation-toughened material, we prove that \( K_f^* = K_f^* \). This shows that the frontal zone does not provide any shielding to the crack tip.

Conversely, we consider a fully developed zone behind the tip that has experienced unloading and path independent \( J \) does not apply. In this case at the tip, the energy balance integral is \( (1 - v^2)(K_f^*)^2/E \). However, far from the tip it becomes

\[ \left[ (1 - v^2)(K_f^*)^2/E \right] - \left[ 2 \int_0^h u(y) \, dy \right], \]

where \( u(y) \) is the residual energy in the wake. We are then left with the calculation of the energy density. This can be evaluated by considering the stress strain relationship as shown in the figure 9a, which takes place during the transformation of an elemental

Figure 9. (a) Stress strain behaviour of transformation toughened material; (b) stress strain curve of microcrack toughened material.
volume as the crack runs through it. Note that each element in the wake is subjected to a residual compression during the transformation. The residual energy density can be evaluated as

\[ u(y) = \sigma_c \varepsilon^T V_f + \left[ \frac{\overline{B} (\varepsilon^T V_f)^2}{1 - \overline{B}/B} + \left[ \frac{E (\varepsilon^T V_f)^2}{9(1-\nu)} \right] \right]. \]  

(8)

Here, \( B \) is the bulk modulus and \( \overline{B} \) is the slope of the transforming material. \( V_f \) is the fraction of transformable tetragonal particles. It is however inherent in the calculation that all the possible transformable particles have transformed during the propagation of the crack.

4.2 Microcrack toughening

The ideas of crack shielding can also be used in explaining microcrack toughening (Faber 1984). However, there are some differences as compared to the previous case. First, since the microcracks are present in the body, the elastic modulus of the microcracked body is slightly smaller than that of the original material. The stress strain curve, therefore, has the configuration shown in figure 9b. It is assumed here that all the potential sites are cracked.

Under such conditions, we apply the principle of path independence around the frontal zone of the microcracked solid. The local stress intensity factor becomes

\[ k^2 = K^2_{\infty} \left( \frac{E}{E_s} \right) \left[ \frac{1 - \nu^2}{(1 - 3
\nu)} \right]. \]  

(9)

However, since the material is damaged now, \( K_{\infty} = k_c (1 - f_s) \) where \( f_s \) is the saturation density of microcracks. O'Connell & Budianisky (1974) have shown

\[ \frac{E}{E_s} = 1 - \left[ \frac{16 (1 - \nu^2)(1 - 3\nu)}{45(2 - \nu)} \right]. \]  

(10)

From the above equations,

\[ k_{\infty}^c = k_c (1 - f_s) \left( \frac{1 - \left[ \frac{16 (1 - \nu^2)(1 - 3\nu)}{45(2 - \nu)} \right]}{16 (1 - \nu^2)(1 - 3\nu)} \right). \]  

(11)

Similar analysis can also be carried out in the wake zone. The energy balance gives an expression for increase in toughness. Proceeding the same way and after simplification, the increase in toughness can be written as

\[ \frac{4 f_s + 25 f_s}{h^3} E \varepsilon^m / K_c. \]  

(12)

This expression implies that for moderate microcrack density, crack shielding is not active and is independent of process zone size. However substantial toughening evolves from dilatation. Specifically, for a zone of 10 \( \mu \)m and a dilatation strain of 0.02 (for ZrO\(_2\)), we have \( \varepsilon^m h^3 E/k_c = 6 \). Toughening levels of this magnitude have been measured in ZTA.

4.3 Crack deflection toughening

This is another toughening mechanism that may take place in zirconia-based materials (Faber & Evans 1983). This mechanism, though less important than the previous two, can be important in some cases. Cracks are usually deflected by the tough second phase or residual stress fields around the second phase particles.
Because of the deflection phenomenon, usually mixed mode propagation of the crack takes place, which in turn reduces the stress intensity.

The modelling of crack deflection is carried out assuming two basic configurations—tilt and twist (figures 10a & b). These are very similar to tilting and twisting defects of grain boundaries. We will now choose a simple case to show how deflection toughening takes place.

To simplify the situation we choose only the tilt configuration. The angle of tilt \( \theta \) is about 0. If mode I loading is applied at 0, the modified intensities can be obtained by transforming from Cartesian to polar coordinates as given by Lawn & Wilshaw (1975). Thus we have

\[
\begin{align*}
\sigma_{yy'} &= \sigma_{0\theta} = [K_1/(2\pi r)^{1/2}] \cos^3(\theta/2) \\
\sigma_{xx'} &= \sigma_{r\theta} = [K_1/(2\pi r)^{1/2}] \sin(\theta/2) \cos^2(\theta/2) \\
\sigma_{x'z'} &= 0.
\end{align*}
\]

The transformed stress intensity factors can be written as

\[ K'_I(\theta) = K_I \cos^3(\theta/2) \quad \text{and} \quad K'_{II}(\theta) = K_I \sin(\theta/2) \cos^2(\theta/2). \]

Therefore, the effective stress intensity becomes

\[ K_{\text{eff}} = K \cos(\theta/2). \]

The angle \( \theta \) is actually an averaged angle through many deflections. The simplified picture can be further expanded by considering the twist configuration and a mixture of tilt and twist configurations. Further, aspect ratios of the different particles can also be examined to check the influence of the aspect ratio on the toughening. We emphasize here that there is not much evidence of occurrence of deflection toughening in \( \text{ZrO}_2 \) bearing ceramics. Increase in toughness of \( \text{ZnO} \), containing monoclinic \( \text{ZrO}_2 \), is attributed to deflection toughening. The increase in toughness with increase in volume fraction of second phase particles shows trends expected in deflection toughening (Ruf & Evans 1983).

Another example of deflection toughening is increase in toughness of PSZ at high temperature where tetragonal precipitates are stable and \( t \rightarrow m \) transformation does not take place (Swain & Hannink 1984).

Figure 10. (a) Tilt, and (b) twist configurations.
4.4 Discussion on mechanisms

Having discussed the various mechanisms in detail it is worthwhile to compare them with one another. We consider phase transformation and microcraking first. We recall, in the case of transformation toughening, that increase in toughness is equal to $E_\varepsilon V_j f_h h^\varepsilon$. In the case of microcrack toughening, the increment is given by $E_\varepsilon^{mc} f_s h^\varepsilon$. Recapitulating the results of phase transformation toughening and microcrack toughening, it is obvious that microcracking is the major toughening mechanism when the zone size is small. However, at larger zone sizes transformation toughening should prevail. The next question is whether these processes are additive. The answer to this question can be illustrated by figure 11. Curve 1 shows the behaviour of the transformation toughened material. Curve 2 shows the behaviour when phase transformation and microcracking take place together. This means that the residual stress is lessened and there is decrease in toughness. Hence these two processes reduce toughness by operating simultaneously. However, crack deflection can still occur along with them thereby giving rise to moderate increase in toughness. Also note here that transformation toughening and microcrack toughening processes are temperature-dependent whereas the deflection process is not. Hence it is always better to utilize the deflection toughening process wherever possible.

The other point is that the above models show toughness determinations depending on the choice of geometry. This is due to the nonlinear behaviour of the material at the crack tip. The notched beam (NB) technique gives lower values than those obtained from the double cantilever beam (DCB) technique. This can be explained in terms of the toughening in frontal zone and wake zone, respectively. In notched beams, cracks propagate from a blunt notch. That is why a frontal zone develops in front of the crack. Hence, the measured increase in toughness is negligible. On the other hand, in the DCB technique, the crack propagates further leaving a wake zone behind. Hence considerable toughness increase can be measured here.

4.5 R-curve behaviour

We have already shown that nonlinearity in the stress–strain relationship of toughened material causes a crack-shielding effect at the crack tip. Also, it is known that the shielding effect is not constant during the growth of the crack. Initially, the increase in shielding (or increase in toughness) starts from a small value. As the crack grows, shielding increases as the frontal zone becomes a fully developed wake zone.

Figure 11. Stress–strain behaviour (hypothetical) of phase transformation toughened and phase transformation + microcrack toughened material.
In other words, the fracture toughness goes on increasing as the crack grows. In fracture mechanics terminology, this is called $R$-curve behaviour. Swain and coworkers (Swain 1983; Swain & Rose 1984, pp. 473–494; Rose & Swain (1986); Burns & Swain 1986) have experimentally obtained $R$-curve behaviour in many of the commercially available ceramic materials. However, we have now begun to realize the far-reaching implications of this property in engineering applications.

Figure 12 schematically represents a system showing $R$-curve behaviour. The stress intensity factor is plotted against the crack length. For the initial crack length $C$, the stress intensity factor is low. As the crack grows, its resistance to growth increases. The condition of failure requires the comparison of $K_R$ to the applied stress intensity. Failure conditions are reached where $K_R(C)$ and $K_a(C)$ curves become tangential to each other. $C^*$ is the critical flaw size and $K_R^*$ is the critical stress intensity factor. Therefore, if a pre-existing flaw is less than $C^*$, it can grow stably, and the material will not fail. The strength in this region is controlled by the $R$-curve. However, if the flaw is greater than $C^*$, the material will fail in the usual brittle manner. The other important feature of these materials is that $K_R^*$ is not a material property but depends on the geometry used for the experimentation. This point was noted earlier by saying that notched beam and double cantilever beam specimens will lead to different fracture toughness values.

Because of the $R$-curve behaviour in $\text{ZrO}_2$-based ceramics, we cannot get a material with both high toughness and strength. In other words, the peak in strength and that of toughness do not match. Swain (1985) demonstrated this aspect in a number of toughened materials. He plotted strength along the $Y$ axis and toughness along the $X$ axis. In all the cases that he examined, the strength increased with the increase in toughness values and then decreased. If the flaw sizes are calculated on both sides of the peak there is a wide difference in their sizes which leads to the fact that the Griffith theory is not valid in at least part of the data considered. Swain argued that the left hand side of the optimum point is still controlled by the Griffith theory whereas the right hand is controlled by $R$-curve behaviour. The optimum point has been interpreted by Swain as the stress required for $t \rightarrow m$ transformation.

![Figure 12. Toughness vs. strength plot of $\text{ZrO}_2$ material showing $R$-curve behaviour.](image-url)
Further experiments by Swain & Rose (1986) divided the materials into two categories, (1) high strength and low toughness ones, and (2) low strength and high toughness ones. While both of them show $R$-curve behaviour it is the $t \rightarrow m$ transformation that is more important in the first case and the $R$-curve behaviour in the second case. S Bhaduri & N E Prasad (unpublished) have expanded this concept further by showing that similar behaviour is also observed in microcracked materials such as ZTA. They have interpreted the optimum point as the criticality point of the $R$-curve. This discussion shows that this kind of strength toughness relationship is fairly common to any ceramic material showing $R$-curve behaviour.

We now discuss the implications of $R$-curve behaviour. It is known that in these materials a flaw can grow stably to the critical flaw size provided it is less than the critical flaw size. Under such circumstances, the statistics of flaw population has no effect on the strength of the material. The strength of the material is not probabilistic but deterministic. Indeed, the Weibull modulus is $\approx 20$ for PSZ as reported by Hannink et al (1984) and Lamon et al (1986). However in the light of the above discussion, application of the Weibull statistics is invalid in the present case. This has a far-reaching effect on the designing aspects with these materials. This concept should revolutionize the manufacturing technology. Currently it is thought that, for reliable components, one has to start with very fine powder, sinter it well and subject it to hot isostatic pressing (HIP) treatment for removing small pores. But in the materials being considered here all such specialized processing is really not necessary. However, what is important is proper heat treatment which leads to $R$-curve behaviour.

Materials showing $R$-curve behaviour have a great deal of resistance to thermal shock. This has been experimentally shown by Hannink & Garvie (1982), Swain (1983) in PSZ. During the thermal shock condition, the thermal stresses generated tend to propagate the flaws, thereby reducing the strength. However, in the present materials, propagation of flaws do not alter the strength. Hence, these materials are more resistant to thermal shock. Therefore, materials on the right hand side of the optimum point in the strength–toughness curve have fantastic engineering applications. We emphasize here that this behaviour is due to the non-linearity of the stress-strain relationship. One can really say that toughened zirconia materials are no longer brittle.

### 4.6 Subcritical crack growth

Subcritical (slow) crack growth behaviour in ceramics is a phenomenon which leads to failure of the bodies at stress levels much lower than the critical stress of fracture. Study of subcritical crack growth is, therefore, important in predicting the life time of a structure. The crack velocity and the applied stress intensity factor are given by a power law relationship

$$ V = A (K_1)^N, $$

where $V$ is the slow crack growth velocity and $K_1$ is the applied stress intensity factor, $N$ is the subcritical crack growth susceptibility coefficient.

Since phase transformation increases $K_{IC}$ it is pertinent to ask whether it affects $K_1$ values that are in the subcritical range. Li & Pabst (1980) carried out experiments to seek an answer to this question. Subcritical crack growth experiments were performed with two different materials e.g. the as-received materials and in annealed
condition where no tetragonal phase was present. The data showed considerable scatter in the experimental curves. Similar experiments with ZTA materials were conducted by Becher (1983). Further, Becher (1986) obtained subcritical crack growth data with high strength PSZ materials recently. All of the data as mentioned above showed that phase transformation affects the mechanical properties in the subcritical region as well. Recently, Bhaduri (1986) has modelled the subcritical crack growth behaviour in PSZ and ZTA in terms of crack deflection mechanisms. This postulate, that crack deflection can explain the experimentally observed data, was motivated by the microstructures of the crack path presented by Becher. The formulation of the model is basically a continuation of the crack deflection model of Faber & Evans (1983) and predicts how lifetimes of the structures could change due to these effects.

4.7 Tribological properties

There are relatively few studies on tribological properties of zirconia and related materials. Scott (1985) performed some experiments with commercial grades of PSZ at very low speeds using a reciprocating slider on a flat sample. At room temperature clean unlubricated zirconia on zirconia has coefficients of friction between 0.2 and 0.3. This value is slightly less than the zirconia on metal case. The presence of water increased the coefficient of friction and long chain fatty acids reduced it. With increase in temperature, the coefficient of friction goes up till 500°C and then drops. The rate of wear with PSZ on PSZ is in the range $10^{-7} - 10^{-8}$ mm$^3$/mN and is similar to alumina and better than sialon. Presence of water increases the wear rate of zirconia. The effect of temperature on wear rate is complicated. At room temperature and above 300°C the wear rate is less. However, in the vicinity of 200°C anomalously high wear rates occur. This has been ascribed to tetragonal to monoclinic transformation around that temperature. Monoclinic phase has much lower hardness and hence the above hypothesis seems to explain the experimental data.

5. Concluding remarks

The discussions, presented above, bring out a clear picture of the interrelationship between the microstructures and the toughening processes. Based on this unified picture one can specify that a particular microstructure is required in order to achieve certain properties. Once the microstructure is agreed upon, one can finalize the raw material and the approximate sintering process, for example, whether to start off with a coarse powder and heat-treat it carefully or to begin with fine powders and sinter them. In between there is a step involving green-shaping. These are uniaxial die pressing, cold isostatic pressing, injection moulding, slip casting etc. Plenty of literature is available on these processes excepting perhaps injection moulding. Hence we have excluded these topics from the review.

We have discussed the different properties that commercial materials have. For example, subeutectoid aged PSZ does not have as high strength as that of optimally aged PSZ. However, the subeutectoid aged material shows more R-curve behaviour as compared to the other materials and therefore is resistant to thermal shock. These materials are used where improved thermal shock resistance is the most important criterion for the choice of the material. Wire drawing is such an application.
Finally, development of these materials is taking place very fast as the science of these materials is advancing at a rapid pace. So every now and then better materials are replacing older ones for a given application. At the same time, many newer applications can be envisaged for such improved materials.

The author thanks Dr P Rama Rao, for his keen interest and encouragement in the development of zirconia-related materials. Thanks are also due to his colleagues—D Banerjee, J Subrahmanyam, Y Mahajan, J A Sekhar, R Mohan Rao, N Eswara Prasad, K Muraleedharan and A Chakraborti for their respective inputs—both intellectual and physical.

List of symbols

- $a_m, b_m$: lattice parameters of monoclinic lattice;
- $a_t, b_t$: lattice parameters of tetragonal lattice;
- $c$: critical flow size;
- $E_1, E_2, E$: elastic moduli of the frontal zone, matrix and microcracked material, respectively;
- $\Delta F_0$: change in total free energy;
- $\Delta F_{chem}, \Delta F_{dil}, \Delta F_{shr}$: change in free energy/volume due to chemical, dilatational and shear energies, respectively;
- $f$: saturation density of microcrack;
- $h$: process zone dimension;
- $J$: ‘J’ integral of Rice (1968);
- $K, K_\infty, K_{local}$: stress intensity factors at a given point, at infinity and near the crack tip, respectively;
- $\Delta K$: change in stress intensity factor;
- $K_i^I, K_i^\infty$: mode I stress intensity factors in the vicinity of the crack tip and away from it;
- $K_{c, \infty}, K_T^c, \Delta K^c$: critical fracture toughness at the tip, near crack tip, and difference between the two, respectively;
- $K_{R(c)}, K_{a(c)}$: stress intensity factors due to $R$ curve and applied stress intensity factor, respectively;
- $M_s$: martensite start temperature;
- $r, r_c$: radius and critical radius of martensite particles, respectively;
- $\Delta S_{chem}, \Delta S_{tw}, \Delta S_{pm}$: change in free energy/area due to chemical, twinning and second phases, respectively;
- $T, T_b$: given temperature and critical temperature, respectively;
- $V$: volume of the martensite;
- $V_f$: volume fraction of second phase;
- $\varepsilon^T$: transformation strain;
- $\varepsilon_{11}^T, \varepsilon_{22}^T, \varepsilon_{33}^T$: transformation strains along three principal directions;
- $\sigma_c$: critical stress of transformation;
- $\nu, \bar{\nu}$: Poisson’s ratio of original material and microcracked material, respectively;
- $\theta$: angle of tilt.
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Advanced ceramic tool materials for machining

RANGA KOMANDURI*

Division of Design, Manufacturing, and Computer-Integrated Engineering, National Science Foundation, Washington, DC 20550, USA

*On research sabbatical from General Electric Co. Corporate Research and Development, Schenectady, NY 12309, USA

Abstract. Cutting tools made of advanced ceramics have the potential for high-speed finish machining as well as for high-removal-rate machining of difficult-to-machine materials. The raw materials used in these ceramics are abundant, inexpensive, and free from strategic materials. In spite of this, solid or monolithic ceramic tools are currently used only to a limited extent partly due to certain limitations of these materials and partly due to the inadequacy of the machine tools used. The advances in ceramic materials and processing technology, the need to use materials that are increasingly more difficult to machine, increasing competition, and the rapidly rising manufacturing costs, have opened new vistas for ceramics in machining applications. The development of ceramic tool materials can be broadly categorized into three types: monolithic forms, thin coatings, and whisker-reinforced composites. Such a classification provides a totally new perspective on ceramic tool materials and broadens their scope considerably, and is justified on the basis that it is the ceramic addition that makes the tool material more effective. A brief overview of these materials is presented in this paper.

Keywords. Ceramic tools; coatings; high-speed machining; SiAlON; SiC whisker-reinforced alumina; cubic boron nitride; SiC whisker-reinforced silicon nitride.

1. Introduction

Ceramics are the newest upcoming class of tool materials with potential for a wide range of high-speed finishing operations as well as for high-removal-rate machining of difficult-to-machine materials. Advances in the ceramic tool materials are partially a spin-off of the high temperature structural ceramics technology developed in the 1970’s for automotive gas turbine and other high temperature structural applications. Of the advanced ceramics, namely, alumina, partially stabilized zirconia (PSZ), silicon carbide, and silicon nitride, PSZ in bulk form is not used as a cutting tool in machining because of its limited hardness (Knoop hardness ~ 1500 kg/mm²) and neither is silicon carbide for its brittleness as well as its reactivity with ferrous work materials. However, all these materials as well as others are used in various forms for cutting tool applications as will be elaborated in this paper. Other ceramic
tool materials include the super-abrasives, namely, the single crystal and polycrystalline diamond and the polycrystalline cubic boron nitride (CBN).

The development of ceramic tool materials for machining applications can be classified into the following three broad categories:

- monolithic forms;
- thin coatings;
- whisker-reinforced composites.

Hot pressed alumina and alumina-TiC, SiAlON, Si$_3$N$_4$, polycrystalline diamond or cubic boron nitride (CBN), and CBN-TiC come under the first category. Thin coatings (2–10 $\mu$m) of Al$_2$O$_3$, TiC, and TiN, singly or in combination, on substrates of cemented carbide, high-speed steel or ceramic fall under the second category. Silicon carbide whisker-reinforced-alumina and -silicon nitride belong to the third category.

2. Factors to be considered in the choice of ceramic tool materials

The following factors have to be considered for the appropriateness of a ceramic tool material for machining (Komanduri 1986a):

(i) Which cutting processes can employ ceramic tools to advantage or, alternatively, which processes are unsuitable for ceramic tools?
(ii) Which work materials can or cannot be machined by ceramics?
(iii) What are the machine tool limitations with regard to the use of ceramic tools?
(iv) What are the strengths and weaknesses of ceramic tools? How can some of the drawbacks be overcome?

These questions will be addressed in the following sections. Successful implementation of the solutions can lead to wider use of ceramic cutting tools.

2.1 Machining process limitations

Figure 1 is a pie chart showing the percentage cost distribution in the United States of various machining operations (Machinability data handbook 1980, pp. 21–23). In grinding, polishing, and cut-off operations, ceramics (alumina, silicon carbide, diamond, and CBN abrasives) are invariably used. Of the other operations, drilling is generally not amenable to the use of ceramic tools because of small-diameter holes and consequent lower cutting speeds at which ceramics are not efficient. Of the other operations, turning (~22%) and milling (~13%), together account for a substantial portion (~1/3) of the cutting processes. The strength and fracture toughness limitations of current ceramics somewhat restrict their application to milling, although some recently introduced ceramics are being applied successfully in milling of selected work materials. Rapid advances in ceramic tool technology by way of toughened ceramics should, however, enable wider application of ceramics to turning operations.

2.2 Work material limitations

Not all materials can be machined presently with ceramics. Ceramic tools can be
used successfully to machine most steels, cast iron, and nickel-base superalloys, even in their hardened condition, as well as many nonferrous alloys and composites. Titanium alloys, aluminum alloys, and some stainless steels cannot be machined with most ceramic tools available today due to chemical interactions between the ceramic tools and these work materials.

In contrast, both high speed steels (HSS) and cemented carbides (e.g., WC base and TiC base) are capable of machining a wide range of work materials. This is because both classes of materials were developed to exhibit a range of hardness and toughness for a variety of applications. They are, therefore, very versatile.

Unless ceramic tools can also be developed to broaden the field of applications, their use will be limited to niche areas. The challenge lies in the ability to develop ceramic tool materials for machining a wide range of work materials, at cutting speeds significantly higher than those currently used. It should, however, be realized that both economics and machinability needs dictate the final choice of tool materials for a given application.

2.3 Machine tool limitations

Ceramic tools, being brittle (low strength and fracture toughness), require rigid, high precision machine tools for best performance. This is because even the smallest amplitude of vibration of the machine tool system can lead to chipping and failure of
the tool, thus abruptly terminating its useful life. Further, many of the older machine tools were not designed for ceramic tool applications. As a result, they are inadequate in terms of cutting speed capability, power, precision, and rigidity requirements for this application. A new generation of machine tools with the above requirements are required to take full advantage of ceramic tools.

2.4 Potential strengths and limitations of ceramic tools

Ceramic tools have great potential for the following applications:

- High-speed (> 15 m/s or 1000 ft/min) finish-machining of many hard and difficult-to-machine materials;
- High-removal-rate (up to several thousand cm³/min or several hundred in.³/min) machining of some of the above materials with high-horsepower, high-rigidity machine tools using low to conventional cutting speeds;
- Machining of extremely difficult-to-machine materials such as hardened steels, alloy and white cast irons, and nickel-base superalloys;
- Producing superior finish and accuracy of parts. This potential exists because ceramics have the following characteristics:
  - high room temperature and elevated temperature hardness;
  - high strength in compression;
  - good chemical stability up to high temperatures.

An additional advantage of ceramics is that the raw materials used in their synthesis include the elements Si, Al, O, N, and C, which are abundant in nature, inexpensive, and free from dependence on strategic materials. In spite of these advantages, monolithic or solid ceramic tools are currently used in industry only to a limited extent. This is due partly to certain limitations of current ceramic tools (e.g., fracture toughness, strength, and hardness, chemical stability and reactivity with work materials), and partly to the lack of adequate machine tools (e.g., rigidity, precision and power). Also, there is a lack of training on the use and application of ceramic tools and on their proper industrial implementation. The inadequate strength and inconsistency in performance of some of the earlier ceramics did not help in promoting their use, especially when they were used in conjunction with low-power, low-speed, and less rigid machine tools.

The main limitations of the ceramics as compared to cemented carbides are listed below:

- lower transverse rupture strength (TRS);
- lower edge strength;
- lower fracture toughness;
- greater proneness to chipping, both micro- and macro-, and even gross chipping;
- high processing and finishing costs of the ceramic cutting tools, even though raw materials are relatively inexpensive. If these costs can be reduced by technological advances, then it would result in less expensive ceramic tools;
- lack of amenability to forming complex shapes in some cases;
- lack of consistency of the product and of predictability in performance;
- proneness to notching at the depth-of-cut line and at the point at which the tool edge leaves the finish surface;
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- abrupt ending of tool life without prior warning, compared to gradual tool wear at the end of tool life in the case of carbide tools;
- more limited scope for machining of a variety of work materials, or for use in different machining operations;
- competition among ceramic tools and consequent replacement of one for another;
- need for high-power, high-speed, rigid machine tools.

While the cutting tool is a vital element of the machining system, there are other elements that affect the overall performance (Komanduri 1986b, pp. 1003-1112). These elements include:

- work material characteristics (chemical and metallurgical state);
- part characteristics (geometry, accuracy, finish, and surface-integrity requirements);
- machine tool characteristics (adequate rigidity with high horsepower and high-speed capabilities);
- support systems (operator's ability, sensors, controls, method of lubrication, and chip control);
- cutting conditions and tool geometry.

In the case of ceramics, improved (high-speed, high-power, rigid) machine tools and the development of tougher ceramics (together with sensors to monitor the tool condition and give warning of tool failure) are two significant areas of concern for increasing the efficient use of ceramics. Implementation of the former and research on the latter are crucial for extensive application of ceramic tools.

3. Historical background

The use of ceramic tools dates back to the dawn of civilization when man used stone as a tool to aid in achieving his basic needs of food, shelter and protection (Suh 1980). Although ceramic tools were considered for certain machining applications as early as 1905, strength under the conditions of cutting was inadequate and the performance inconsistent (King & Wheildon 1966). In the mid-1950's, ceramic tools were reintroduced for high-speed machining of gray cast iron for the automobile industry, and for slow-speed, high-removal-rate machining of extremely hard (and difficult-to-machine) cast or forged steel rolls in the steel industry. These materials were typically fine grain (< 5 \mu m) alumina-based materials, either almost pure or alloyed with suboxides of titanium or chromium to form solid solutions, and containing small amounts of magnesia as a sintering aid and as a grain growth inhibitor. For example, Goliber (1960) developed an alumina-TiO ceramic made by cold pressing and liquid phase sintering. It is characterized by fine grain size (> 3 – 5 \mu m) and uniform microstructure. TiO constitutes about 10% of the material. A hardness of 93–94 R_A and a transverse rupture strength (TRS) > 550 MPa (~80 ksi) were achieved. However, due to limited strength and inconsistency, the applications of these materials were extremely limited. The main success stories include the high removal-rate machining of chill cast iron rolls on an extremely rigid, high powered (up to 450 kW or 600 hp), high precision Binns Superlathe (figure 2) (Binns 1963) and the selective high-speed, finishing application on carbon steels and cast iron for automotive applications.

Several factors have recently rejuvenated interest in the development and
application of ceramic cutting tools. These include the introduction of new ceramic materials, advances in the ceramic-processing technology, new opportunities (higher cutting speeds and removal rates) for reducing manufacturing costs, the need to use materials that are increasingly difficult to machine, advances in machining science and technology, rapidly rising manufacturing costs, and global competition.

4. Advanced ceramic tool materials

Advanced ceramic tool materials can be broadly classified into the following three categories, which will be discussed in the next section: monolithic forms, thin film coatings, and fibre-reinforced composites.

4.1 Monolithic forms

Over the past two decades, several monolithic ceramic tool materials were developed. These include:

- hot pressed alumina and alumina-TiC;
- polycrystalline diamond or CBN and CBN-TiC;
- SiAlON;
- silicon nitride.

These materials will be discussed briefly below.

4.1a Alumina and alumina-TiC ceramics: Advances in ceramic processing technology, such as hot pressing and hot isostatic pressing (HIP) and the development of pure, fine grain (micron size) ceramic powders led to the introduction of tougher (TRS ≈ 750 MPa or 110 ksi) ceramic tools in the early 1970’s. The first tool material introduced was the hot-pressed, fully dense (>99.5%) fine grain
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alumina which is significantly tougher (TRS $> 685$ MPa or 100 ksi) than the alumina-TiO tools (TRS $\sim 550$ MPa or 80 ksi) (Hatschek 1981). This was soon followed by another hot-pressed ceramic tool material, alumina-TiC (alumina with 30% by volume of TiC and small amounts of yttria as a sintering aid) with enhanced mechanical and thermal shock resistance (figure 3). These two materials are used for high-speed, finish machining of steel and high temperature superalloys.

4.1b Ultrahard ceramic tools: The synthesis of diamond, the hardest material (8000 kg/mm$^2$) known, and the discovery of the cubic form of boron nitride (CBN), the second hardest ($\sim 4700$ kg/mm$^2$) material, by a high temperature-high pressure process and in the presence of catalyst-solvents led to the development of ultrahard ceramic tools, namely, polycrystalline diamond and polycrystalline CBN (Wentorf et al 1980).

The polycrystalline diamond/CBN tools consist of a thin layer (0.5 to 1.5 mm) of fine grain (1–30 $\mu$m) diamond/CBN powder sintered together and metallurgically bonded to a cemented carbide substrate (figure 4). The cemented carbide substrate provides the necessary elastic support for the hard and brittle diamond/CBN layer above it. At the appropriate conditions of pressure ($\sim 5$ MPa or 50 kbar) and temperature ($\sim 1500^\circ$C), full densification, extensive diamond-to-diamond bonding, and bonding between diamond/CBN and the tungsten carbide substrate takes place (figure 5). In addition, small amounts of binder phase, predominantly cobalt, present at the grain boundaries, infiltrate throughout the body. Because of this, both diamond and CBN tools can be thermally affected at temperatures above 700$^\circ$C. The
resistance to thermal degradation can, however, be improved significantly by leaching the infiltrant using aqua regia (Bovenkerk & Gigl 1980). The issue of thermal degradation assumes importance when the cutting temperatures are high as in the machining of hardened steels, alloyed cast iron, and nickel-iron base superalloys at higher speeds.

Polycrystalline diamond tools are used for machining of polymer and glass epoxy composites, aluminum-silicon alloys, cast iron, and other nonferrous and nonmetallic materials. Due to high reactivity with ferrous alloys, diamond tools are not recommended for machining carbon steel. Polycrystalline CBN tools, on the other hand, are less reactive with ferrous alloys. They are recommended for machining of hardened (>55 R_c) steels, alloyed cast iron, and nickel-iron base superalloys.

To increase the toughness and to extend the fields of application of polycrystalline diamond/CBN tools, diamond or CBN is alloyed with TiB_2, TiC, TiN, etc. although this addition is at the expense of hardness (Hara & Yazu 1980, 1982). Polycrystalline CBN tools alloyed with TiC can be used for machining medium hard (~40–50 R_c) steels (Tabuchi et al. 1978).

Sintered polycrystalline diamond or CBN tools can be fabricated in an assortment of shapes (squares, rounds, triangles, and sectors of a circle of different included angles) and sizes from round blanks. These tools are more expensive (an order of magnitude or more) than the conventional cemented carbides or ceramic tools because of the high cost of both the processing techniques, which involve high-temperature and high-pressure sintering, final shaping etc., and the finishing
methods. In spite of the higher cost, these tools are used for specific applications because they increase productivity, provide long tool life, and are economical on the basis of overall cost per part.

4.1c Silicon nitride and SiAlON ceramics: Yttria (or magnesia) stabilized, dense silicon nitride is one of the more attractive ceramic tool materials recently introduced for the high-speed machining (>25 m/s or 5000 ft/min) and/or high-removal-rate machining (several thousand cm$^3$/s or several hundred to a thousand in.$^3$/min) of gray cast iron for automotive and other applications, thus opening new opportunities for ceramic tool materials (Ezia et al 1983, 1984; Samanta & Subramanian 1985).

New machine tools with high power (up to 375 kW or 500 hp), high r.p.m. (to provide cutting speeds of up to 50 m/s or 10,000 ft/min), high rigidity, and high precision are being built specifically for this purpose. Silicon nitride is, unfortunately, not suitable for machining other ferrous materials or high temperature superalloys, thus limiting its application to the machining of cast iron.

Fully dense silicon nitride has an unique combination of properties, namely, high strength and toughness, moderate hardness, good wear resistance, and low thermal expansion coefficient and consequent excellent thermal shock resistance. It is a covalently bonded material with a small self-diffusivity and hence cannot be easily densified by sintering without a sintering aid. Dense material of $\beta$-$\text{Si}_3\text{N}_4$ is fabricated by hot pressing $\alpha$-$\text{Si}_3\text{N}_4$ powder with a suitable densification additive (e.g., yttria or MgO) at 30 MPa in a graphite die at 1700–1800°C. The $\text{Si}_3\text{N}_4$ powder is generally
covered with a thin layer of silica. The purpose of the additive is to react with this silica and a small amount of $\text{Si}_3\text{N}_4$ at the high hot-pressing temperature to form an oxynitride liquid in which $\alpha$-$\text{Si}_3\text{N}_4$ dissolves and from which $\beta$-$\text{Si}_3\text{N}_4$ is precipitated.

Densification occurs by liquid-phase mechanisms; but, unfortunately, the liquid that is necessary for densification cools to give secondary crystalline or vitreous phases which affect the properties of the hot pressed material at the glass softening temperature (900°C). For example, with the yttria stabilized $\beta$-$\text{Si}_3\text{N}_4$, yttrium-silicon oxynitride is formed at elevated temperature (> 900°C) with a pronounced change in specific volume that causes microcracking. It is somewhat difficult, if not impossible, to produce dense, pure $\beta$-$\text{Si}_3\text{N}_4$ without any additive. Yttria- or MgO-stabilized silicon nitride material, produced by hot pressing and subsequently fabricated into cutting tools by dicing and shaping with diamond grinding, is rather expensive. Need, therefore, exists for a less expensive near net-shape processing technique for this material.

Since additives degrade the properties of $\text{Si}_3\text{N}_4$ at elevated temperatures, the alternative is to alloy $\text{Si}_3\text{N}_4$ with other inorganic compounds. This led to the development of another exciting, tough ceramic tool material, SiAlON, for machining of nickel-iron base superalloys (Oyama & Kamigaito 1971; Jack & Wilson 1972; Bhattacharyya & Jawaid 1981; Jack 1982). This material is yttria-stabilized silicon aluminum oxynitride (SiAlON) which is isostructural with $\beta$-$\text{Si}_3\text{N}_4$. Because of the similarity of crystal structure, $\beta'$-SiAlON has physical and mechanical properties similar to those of silicon nitride; because of its composition, its chemical properties approach those of alumina (Jack 1982).

![Figure 6. Micrograph of a SiAlON tool showing $\beta'$-SiAlON grains and presence of glassy phase at the grain boundaries (courtesy, S K Bhattacharyya).](image-url)
To produce $\beta'$-SiAlON, a mixture of alumina (~13%), silicon nitride (~77%), yttria (~10%), and aluminum nitride is used as the starting material. Since this mixture produces, during sintering, a larger volume of lower viscosity liquid than in the synthesis of yttria-stabilized silicon nitride and its surface silica under similar conditions, $\beta'$-SiAlON can be fully densified by pressureless sintering. The powder mix for $\beta'$-SiAlON is first ball-milled, then preformed by cold isostatic pressing, and subsequently sintered at a maximum temperature of ~1800°C under isothermal conditions for ~1 h before it is allowed to cool slowly. The microstructure of $\beta'$-SiAlON consists of $\beta'$ grains cemented by a glassy phase (figure 6) (Bhattacharyya et al 1984, pp. 245-262).

SiAlON tools were originally developed by Joseph Lucas Industries Ltd. of the UK. It is marketed under licence by Kennametal, Inc. in the US and by Sandvik in Sweden. It is much tougher than alumina-TiC and is used for rough machining of nickel-iron base superalloys. Further developments in microstructure and composition of SiAlON are likely to yield an even tougher material consisting of $\beta'$ SiAlON and an intergranular phase of yttrium aluminum garnet (YAG) without any intergranular glassy phase. Similarly, addition of TiC is likely to yield a much harder and tougher SiAlON with enhanced mechanical and thermal shock resistance. The introduction of SiAlON tool material was for a time very exciting since it led major tool manufacturers to concentrate on developing a similar material till another tool material, SiC whisker-reinforced alumina, a far tougher material, was introduced.

4.2 Thin ceramic coatings

An analysis of the cutting process indicates that the characteristics of the tool at or near the surface should be different from those of the bulk. To be abrasive-resistant, the surface has to be hard; to be chemically wear-resistant, it has to shield the constituents of the tool and the work material from each other under the conditions of cutting, especially at high cutting speeds. The bulk of the material, by contrast, should be tough enough to withstand high-temperature plastic deformation and resist breakage under the conditions of cutting. Since the surface and bulk requirements are markedly different, it is logical to consider engineered tool materials. This was the basis for the development of thin (2-10 $\mu$m) ceramic coatings on cemented carbide tools in the late 1960's and on HSS in the late 1970's which are now used very extensively.

In cemented tungsten carbide cutting tools, cobalt metal is used as the binder. The cutting speed capability of these tools is limited primarily by the binder phase. Reducing the volume fraction of the binder phase increases the refractoriness of the tool material, at the expense of strength. It is somewhat difficult to develop a bulk material with the above diverse characteristics. If, however, a binderless ceramic coating were deposited on a tough cemented carbide tool such that the coating is thin enough and strongly bonded metallurgically to the substrate, then such a coating may not affect the strength significantly, resulting in longer tool life and/or higher cutting speed capability. This idea has led to the development of single and multiple, hard, refractory ceramic coatings on cemented carbide tools by the chemical vapour deposition (CVD) technique (Whalen 1971).

To be effective, the coatings should be

- hard;
- refractory;
- chemically stable;
- chemically inert, to shield the constituents of the tool and the work material from interacting chemically under cutting conditions;
- binder-free;
- of fine grain size with no porosity;
- metallurgically bonded to the substrate with a graded interface to match the properties of the coating and the substrate;
- thick enough to prolong tool life, but thin enough to prevent brittleness;
- free from the tendency of the chip to adhere (or seize) to the tool face;
- easy to deposit in bulk quantities;
- inexpensive.

Several hard, refractory, ceramic coatings, including single coatings of TiC, Al₂O₃, TiN etc.; double coatings of Al₂O₃ on TiC, TiN on Al₂O₃ or TiC; and triple coatings of TiN on Al₂O₃ on TiC were developed by the CVD process. To deposit a coating of TiC, the tools are heated to 1000°C, and TiCl₄ and methane (CH₄) are reacted in hydrogen at a pressure of ≤ one atmosphere. The hard reaction product, TiC, deposits on the tool and forms a metallurgical bond with the substrate at high temperature. A coating thickness of 5 μm is found to be optimum from the standpoint of best performance and requires about 8 h of processing time.

Multiple coatings are developed with the following objectives:
- prolong the life of the tool by building up the thickness without encountering the deleterious effects of thick, hard coatings, such as delamination and chipping;
- form a stronger metallurgical bond with a graded interface;
- take advantage of the desirable features of each coating material without causing delamination.

Figure 7 is a micrograph of a representative multiple coating of Al₂O₃ on TiC on a cemented carbide tool. The microprobe traces of Al and Ti show clearly the graded interface between the substrate and TiC as well as between TiC and Al₂O₃. Currently, titanium nitride coating is deposited as the upper layer on most coated tools because it minimizes metal build-up and reduces friction.

At the cutting speeds at which HSS tools (e.g., drills, end mills) operate, metal build-up or periodic seizure between the chip and the tool is the main problem limiting tool life and productivity. To overcome this problem and to reduce friction, a titanium nitride (TiN) ceramic coating has been developed successfully for HSS tools. However, the CVD technique (used for coating cemented carbide tools) cannot be used for this application as the substrate temperature used (~1000°C) is too high, resulting in alterations of the metallurgical structure of HSS. Hence, only those coatings and processes that require heating below the HSS transformation temperature (~400°C) is increasingly used for HSS tools. The attractive golden colour of the coating is an added aesthetic feature.

To take full advantage of the coating potential, substrate materials are being carefully matched with the coatings or appropriately altered to optimize properties, resulting in significant gains in productivity. Also, for strong bonding between the
coating and the substrate, there should be good chemical and metallurgical compatibility between them. Since the mode of wear is different on the rake face and on the clearance face, coated-tool technology is advancing in the direction of selective compositions and/or modifications of the substrate in these areas to further prolong tool life and to make the coated tool more versatile for special or general purpose applications. An example in this direction is the recent development of a multilayer-coated (TiC-TiCN-TiN or TiC-Al$_2$O$_3$-TiN), cemented carbide tool that has a cobalt-enriched layer (25 μm deep) on the rake face to provide superior edge strength and a cobalt depleted layer in the clearance face for high abrasion resistance and high temperature deformation resistance (figure 8) (Nemeth et al 1981, pp. 613–627).

Ceramic coatings are also being developed on ceramic substrates mainly to limit chemical interactions between the tool and the work material. For example, silicon nitride tools are used successfully for high-speed machining of cast iron. However, they react significantly with steels and hence cannot be used for this application as such. To take advantage of the high-temperature deformation resistance of this material and to minimize chemical interactions when machining steels at high-speeds, multiple coatings of TiC-TiN, or Al$_2$O$_3$-TiC on silicon nitride, and SiAlON substrates were developed similar to those for cemented carbides (Sarin & Buljan 1983, 1984). Figure 9 is a cross-section of multiple coatings of TiN on TiC on silicon nitride tool material. However, the extent to which such coated ceramic tools will be used as compared to other competing materials for high-speed machining of steels depends upon the need and the economics of machining.

4.3 Fibre-reinforced composites

Recently, a fibre-reinforced ceramic composite material possessing improved fracture
toughness \( K_{IC} \approx 9 \text{ MN} \text{ m}^{-3/2} \) has been introduced as a cutting tool for machining of nickel-iron base superalloys used in aircraft engines (Wei 1985; Smith 1986). This

Figure 8. (a) and (b). (Caption on facing page.)
Figure 8. Micrograph of a multicoating of TiN-Ti (C, N)-TiC on an engineered cemented carbide substrate (note the top layer is TiN). (a) A low magnification micrograph showing the areas around the rake face and the clearance face of the tool. (b) Micrograph at higher magnification of an area around the rake face showing a thin cobalt-enriched straight WC layer near the rake face for increased toughness and edge strength, and (c) micrograph at higher magnification of an area around the clearance face showing a thin layer of cobalt-depleted multicarbide near the clearance face for increased wear resistance and high temperature deformation-resistance (courtesy, A T Santanam).

material is silicon carbide (SiC) whisker-reinforced alumina (figure 10). Single-crystal whiskers of SiC possess very high tensile strength (7 GPa). SiC also has higher thermal conductivity and coefficient of thermal expansion than alumina. Consequently, the composite exhibits higher strength and thermal shock resistance.

In the preparation of this composite material, SiC whiskers (0.5 to 1 μm in diameter and 10 to 80 μm long) about 20% volume fraction are mixed homogeneously with micron-sized fine powder of alumina. The mixture is then hot-pressed to over 99% of the theoretical density at a pressure in the range of 28-70 MPa and temperature in the range of 1600-1950°C for pressing times varying from about 0.75 to 2.5 h. The fracture toughness of this material is by far the highest among ceramic cutting tools, nearly twice that of its closest ceramic, namely, Si₃N₄ and SiAlON. Although details of the micromechanisms for improved fracture toughness of this ceramic composite tool material are not clearly established at this time, a plausible mechanism for the toughness is given in the following paragraph based on current knowledge of the behaviour of composite materials in general (Lewis 1986).

As a crack propagates through the ceramic matrix, bonds between the matrix and the whiskers are broken. However, the SiC whiskers, because of their inherently high
strength (7 GPa) remain essentially intact. Consequently, whisker pullout occurs due to the separation of the matrix from the whiskers. Interfacial shear stress resisting the whisker pullout absorbs a substantial amount of this fracture energy and inhibits crack propagation. For improved fracture toughness, a strong metallurgical bond between the fibres and the matrix is not desirable for it causes the whiskers to fail along with the matrix. This is the case with SiC whisker-reinforced alumina composites because the bond between the matrix and the fibres is not particularly strong. The bonding is weak because alumina and SiC are not metallurgically compatible. For best results, the fracture energy of the interface ($J_i$) is recommended not to exceed a fraction (0-1) of the fracture energy of the matrix ($J_0$). Although $\text{Si}_3\text{N}_4$ is a tough ceramic, its fracture toughness is not sufficiently high for interrupted cutting such as milling of cast iron. So, using the above approach a tougher SiC whisker-reinforced silicon nitride was developed for high-speed milling applications. When whiskers of other refractory materials become available, new tool materials incorporating them may be developed. The SiC whisker-reinforced alumina composite has opened new vistas for tool material development. One can consider this material as a model engineered material and develop other composites for machining different work materials and for different applications. However, to accomplish this it is necessary to thoroughly analyse this material and its performance. For example, why is this tool not suitable for machining ferrous materials, such as steel or cast iron? What is the role of SiC whiskers? Can they be replaced with whiskers of other materials such as TiC, $\text{Al}_2\text{O}_3$, $\text{ZrO}_2$, $\text{Si}_3\text{N}_4$, and SiAlON? What is the optimum size (diameter and aspect ratio), volume fraction, and geometric distribution of the fibres? Can ceramic coatings be applied to shield the

Figure 9. Micrograph of the cross-section of $\text{Al}_2\text{O}_3$-TiC coating on a silicon nitride-based ceramic tool (courtesy, V Sarin).
ingredients of the tool and work material from each other? Can one design a composite ceramic tool material based on the knowledge of the properties of the various ingredients of the tool and work materials as well as the cutting conditions for a given application?

5. Concluding remarks

Significant innovations and technological advances were made in the last three decades in the adaptation of ceramic materials for many cutting tool applications. Thin ceramic coatings, synthesis of diamond and CBN, whisker-reinforced ceramic composites, processing techniques that produce ceramics close to the theoretical density, and toughened ceramics presented in this paper are examples in that direction. Basically many advanced ceramics are hard enough to machine a range of work materials with the possible exception of hard ceramics themselves. To extend the field of applications and to open up new opportunities, ceramic cutting tools have to be developed even further, as future applications are bound to be more challenging than at present. Some of the future directions in the development of ceramic tools include the following:

(1) Ceramics with considerable increase in transverse rupture strength (TRS) and fracture toughness than currently available.
(2) A class of ceramics with a range of hardness, and improved strength and fracture toughness characteristics, similar to HSS and cemented carbide tools.
(3) Ceramics that are relatively inert chemically for machining a range of work materials at higher cutting speeds. For example, the development of a cutting tool material for high-speed machining of titanium alloys. This is not an esoteric problem since titanium is very reactive chemically with most tool materials at elevated temperatures. However, in the event that such a material is developed, it may revolutionize the way we make cutting tools in general.

(4) New ceramic tool materials developed on the basis of fundamental understanding on the nature and performance of current toughened ceramics, whisker-reinforced ceramics etc.

(5) New engineered ceramics with hierarchical structures, nano grain size, amorphous structures and artificially layered structures.

The author wishes to thank the National Science Foundation for the opportunity to prepare this paper. Thanks are also due to Sri Komanduri and Prof. Ephraim M Sparrow for patience, inspiration and advice, and to the General Electric Corporate Research and Development, Schenectady, New York, for permission to publish this work. The author would like to thank Drs A T Santanam, V Sarin and S K Bhattacharyya for providing some of the micrographs presented in this paper.

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Ceramic coating technology

J KARTHIKEYAN¹ and M M MAYURAM²

¹Plasma Physics Division, Bhabha Atomic Research Centre, Bombay 400 085, India
²Machine Elements Laboratory, Mechanical Engineering Department, Indian Institute of Technology, Madras 600 036, India

Abstract. Modern technology calls for systems performing satisfactorily under extreme and often adverse operating conditions; hence it has become a technical and economic necessity to protect structural materials from the hostile environment. Thus ceramic coating technology (CCT) has found widespread applications in many diverse industries for the protection of structural materials. Ceramic coatings are used to minimise effects such as high temperature degradation, corrosion, erosion and wear.

Two techniques, viz. thermal spray and chemical vapour deposition, are well-developed and commercially established for preparing coatings of almost all ceramic materials. Each process has its own advantages and disadvantages and the choice of any particular method depends on the application, economics etc.

CCT is both technically and commercially well-established abroad. Commercial equipment suitable for general application in coating shops as well as custom-engineered ones to suit specific requirements are readily available. Raw materials such as powders, wires, rods, gases, chemicals etc. are readily available and are moderately priced. R & D is continuously in progress adding new materials, techniques and applications every year.

In India, the full potential of the technology has not been tapped as yet. A few governmental organisations such as BARC, BHEL, DMRL, HAL, Air India etc., have exploited the application potential of the technology, while the private industry has begun to adopt the technology only recently. Such a situation is due to a variety of reasons including limited awareness of these new techniques amongst our user industries, non-availability of raw materials and equipment indigenously etc.

Keywords. Ceramic; coating; thermal spray; protection; chemical vapour deposition.

1. Introduction

The development of the nation through science and technology is essentially determined by the possibility of creating and of producing, in sufficient quantities, structural materials meeting the requirements of technology. As the frontiers of
Science and technology expand into complex and more sophisticated areas, operating systems face more and more severe environments, which they have to withstand.

1.1 Importance of ceramic coatings

Any high technology system—nuclear, space, power, missile, aeronautics etc. operates under extreme conditions—like very high and very low temperatures, very high and very low pressures, high rates of gas flow, highly corrosive-erosive fluids and concentrated energy fluxes—which take a severe toll of the materials of construction. Considerable amount of work is being carried out to find new materials which can withstand severe environments. Ceramics, with their excellent properties such as high temperature stability, resistance to corrosion, erosion and wear, chemical inertness etc., have found increasing use in high technology systems. However, it is not always possible to replace structural parts made of metals and alloys with ceramic ones, since ceramics have poor mechanical properties. Moreover in many applications, properties desired at the surface are different from those required at the core of many engineering components. For instance, a shaft requires good toughness at the core, wear resistance at the seal and fatigue resistance on the outer surface.

Ceramic coating technology, the process of preparing or depositing a ceramic layer on a surface, offers the best solution in such situations. Ceramic coatings have found use, not as a substitute for metals and alloys, but in complementing metal characteristics by imparting additional refractoriness, insulation, erosion resistance, oxidation and corrosion resistance, electrical resistance or different optical characteristics. Moreover, coating technology allows the design engineer to select the base material on mechanical and other design considerations and then prepare the surface for meeting requirements simply by making a ceramic coat on it.

1.2 Applications of ceramic coatings

Ceramic coating technology is used to prepare coatings for various applications. They can be broadly classified as follows:

a) Protective coatings—corrosion, erosion and wear resistant surfaces and high temperature and electrical insulation coatings etc.

b) Process improvement and control coatings—thermal barrier coatings on internal combustion engine components, coatings with specific optical characteristics on space vehicles, neutron absorbing coatings on nuclear components etc.

c) Free standing structures—fabrication of complex thin-wall components for various applications by the coating process.

d) Reclamation coatings—preparation of coatings on worn-out components for reclamation.

2. Ceramic coating processes

Ceramic coatings are required in various industries for different applications and hence the requirements and specifications of the coatings vary with a particular
application. It can be summarised that an ideal ceramic coating should have the following properties:

(i) good mechanical properties over a wide temperature range;
(ii) resistance to thermal and mechanical cycling;
(iii) good dense layers;
(iv) hardness and resistance to wear;
(v) chemical inertness and thus resistance to corrosion and high temperature oxidation;
(vi) resistance to erosion;
(vii) resistance to atomic diffusion and inter-diffusion at high temperatures.

Such an ideal coating material does not exist, and it is often necessary to find a suitable coating such that the combined coating/substrate system can satisfy the operating conditions. The choice of any coating for a given application depends on the operating environment, the substrate material, the coating availability and economics. Fortunately, a large number of ceramic materials are available that can be prepared in the form of coatings by the thermal spray (TS) or the chemical vapour deposition (CVD) process which show satisfactory performance in many applications.

2.1 Thermal spray process

The thermal spray process is the most versatile one for preparing ceramic coatings. In this process (Hecht & Gerdeman 1972) any material which melts without decomposing or vapourising can be spray-coated. Moreover there is no limitation on the size and shape of the substrate and, as required in some special applications, the coatings can be prepared in situ. Hence this process has found widespread applications in many diverse industries. Though some exotic techniques like pulse arc spray (Rykalin & Kudinov 1976), liquid fuel gun spray (Hecht & Gerdeman 1972) etc. have been tried for spray coating, only two processes, viz. combustion flame spray and plasma spray are commercially used as routine techniques (Chagnon & Fauchais 1984).

2.1a Principles and techniques: In the thermal spray process (Zaat 1983) a ceramic coating is created by a solid or powdered ceramic material, which is heated in a flame, atomized and projected, while still in the form of molten particles, by a stream of gas moving at a high velocity onto the relatively cold surface of the article to be coated.

These impacting particles flatten, interlock and overlap one another, so that they are securely bonded together to form a dense coherent coating which is built up to the desired thickness. The adherence of the coating to the surface results primarily from the mechanical fastening of spray particles as they deform to take the shape of the suitably prepared surface being coated.

The basic systems for thermal spray application of ceramic coatings may be classified as follows:

(i) combustion flame-spray using a (a) powder torch, (b) rod or wire torch, or (c) detonation gun;
(ii) plasma spray using a (a) powder torch, (b) rod or wire torch, or (c) plasma transferred arc torch.
Figure 1 gives the schematic of different torches used for spraying ceramic materials and these are discussed below.

Combustion flame spray process—In the combustion flame spray process, oxygen and a fuel gas are ignited and the exhaust gas is used as the heat source for melting and for projecting the spray material (figure 2). The fuel gases used in this process are acetylene, hydrogen and propane. The flame temperature achieved by this process is approximately 3000 K. Material to be sprayed is introduced into the hot flame in powder, rod or wire form.

In the flame powder (FP) spray system, ceramic powder is introduced directly into a portion of the oxygen flow, which aspirates it through the centre of the burner.
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nozzle where it is heated and carried to the substrate with an average velocity between 50 and 150 m/s. Ceramics with melting points less than 3000 K can be sprayed (Hecht & Gerdeman 1972).

In the combustion flame-rod or wire (FR) spray system the rod or wire is fed into the high temperature flame where the end of the rod is melted, the molten material is disintegrated by a rapid flow of compressed gas and the resulting spray is delivered by the high velocity flow of gases to the substrates (Chagnon & Fauchais 1984). Such a system has the advantage that the spray material cannot be propelled with the effluent until it is completely molten as opposed to powder particles which may remain incompletely melted on impact. The spray rate is controlled by the melting rate of the rod, which in turn is a function of the gas enthalpy and melting characteristics of the rod. The viscosity of the liquid phase is also an important factor. The average particle velocity in the rod spray system is 150–200 m/s, which is higher than the velocity of the powder-sprayed particles. The biggest disadvantage of the rod spray process is that not all materials can be fabricated in wire or rod form, and only a few ceramics like Al₂O₃, ZrO₂, CrO₂, ZrSiO₄ and MgAl₂O₄ can be coated by this process.

In the detonation gun (D-gun) process (Hecht & Gerdeman 1972) a mixture of acetylene, oxygen and powdered coating material is pressure-fed into a chamber and detonated by a spark plug. The detonation wave heats and accelerates the particles onto the substrate. The barrel is detonated approximately four times per second. The detonated gas accelerates the powder to a velocity of about 750 m/s. The detonation-gun process has been used to spray a number of ceramics including Al₂O₃, Cr₂O₃, WC, CrC, NiC etc. Of all thermally sprayed coatings the detonation-gun sprayed ones have the highest density (99%, which is not normally possible by other conventional powder metallurgy techniques) and very high bond strength (40–65 MPa). However, the detonation equipment should be operated in a sound-proof, explosion-proof room because of the high sound levels of about 150 dB and the danger of explosion. Hence the detonation process has not found wide use in industrial applications in spite of the superiority of the properties of the coatings.

Figure 2. Schematic of combustion flame spray system.
**Plasma spray process**—In the plasma spray process (Fauchais et al 1983), a high current arc (300–600 A) is formed between a tungsten-tipped conical cathode and a copper nozzle anode (figure 1d). The plasma gas (usually inert gases like argon, helium, nitrogen and hydrogen) flowing through the arc is heated to an average temperature of approximately 10,000 K and jets out of the nozzle at a high velocity. The coating material, introduced either in the powder form or in wire or rod form into this flame, melts and sprays the coating material onto the substrate with velocities around 200 m/s. Figure 3 gives a schematic of the plasma spray system.

Since the temperature in the plasma flame is an order of magnitude greater than in the combustion flame, all materials with well-defined melting points can be sprayed. In the plasma spray process, the spray efficiency and the coating quality are affected by a large number of variables and table 1 gives a list of important variables. Many of these variables are inter-related, and hence, careful optimization of the spray parameters is of paramount importance for obtaining coatings with the desired properties (Fisher 1972).

Almost all oxides, nitrides, carbides and borides can be coated by use of the plasma spray powder gun, since the plasma temperature is higher than the melting point of any known material (Fauchais et al 1983). However, since the dwell time of the powders in the plasma is only a few milliseconds, coatings with inadequate qualities will be obtained if extreme care is not taken while preparing coatings (Hecht & Gerdeman 1972).

Though some systems with rod feed have been introduced, because of the difficulties in preparing ceramic rods, the rod-fed plasma spray system has not been commercially successful.

The plasma transferred arc (PTA) process is more of a weld surfacing technique than a spray process. This process effectively combines the plasma spraying and plasma welding techniques in a semitransferred arc mode (Shull et al 1984, pp. 297–301). In this system a pilot arc, the same as in a normal plasma spray process, is used to melt and spray the coating material while a transferred arc is used to form a puddle at the surface where the coating material is welded resulting in a metallurgi-
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Table 1. Plasma spray variables.

<table>
<thead>
<tr>
<th>Plasma</th>
<th>Spraying procedure</th>
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<tbody>
<tr>
<td>Power input</td>
<td>Torch to work distance</td>
</tr>
<tr>
<td>Type of arc gas</td>
<td>Traverse rate</td>
</tr>
<tr>
<td>Flow of arc gas</td>
<td>Angle of torch to work</td>
</tr>
<tr>
<td>Plasma torch geometry</td>
<td>Cover gas</td>
</tr>
<tr>
<td>Type of arc</td>
<td>Spray atmosphere</td>
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<tr>
<td>Powder</td>
<td>Substrate</td>
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<tr>
<td>Composition</td>
<td>Composition</td>
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<tr>
<td>Physical properties</td>
<td>Surface preparation</td>
</tr>
<tr>
<td>Method of manufacture</td>
<td>Surface roughness</td>
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<tr>
<td>Powder size</td>
<td>Temperature</td>
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<tr>
<td>Size distribution</td>
<td></td>
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<tr>
<td>Powder feed</td>
<td></td>
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<tr>
<td>Type of feed system</td>
<td></td>
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<tr>
<td>Rate of powder addition</td>
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<td>to carrier gas</td>
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<td>Type of carrier gas</td>
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<td>Angle and position of</td>
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<td>powder entry port</td>
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</table>

cally bonded (or welded) coating. This process is used in general for preparing hard surfaces with refractory carbides like TiC, WC, CrC etc. with or without binder materials.

2.1b Thermal spray coated ceramics: Though a general statement that materials which do not vaporize or sublime can be sprayed is often made, because of the short dwell time of the particles, some materials which have high specific heat and low thermal conductivity yield poor quality coatings. Moreover, other materials, such as pure carbides of tungsten and boron produce coatings with weak particle-bonding due to the inability of the material to wet itself or because of loss of stoichiometry. Still the widest range of ceramics have been thermal spray coated.

2.1c Properties of TS coatings: Microscopic properties

(i) Structure—In the thermal spray process the powder particles melt in the flame and then solidify as they impinge on the substrate. Hence, the properties of the coatings depend on both the melting and the solidification process. It has been found that unless the melting point of the powder is well-separated, by at least 200 to 300 K, from the decomposition or evaporation temperature the material can not be coated onto a surface.

Heat transfer calculations (Zaat 1980) have shown that:
(a) the heating and melting of the powder particles take place in about 1–10 ms. (b) the entire cooling cycle takes less than 100 μs, (c) the particles are always deposited on already solidified layers, (d) the temperature gradients during cooling reach around $10^5$ K/cm. Since the coating is formed by the flattening of the particles on impact (which occurs only when the particle is still in the molten or plastic state), the liquid density ($\rho$), viscosity ($\mu$) and surface tension ($J$) of the particles play an important role in determining the properties of the coating (e.g. density, adhesion etc.). The degree of flattening (the ratio of diameter on the flattened disc, $D$, to the
diameter of the particle, \( d \) is given by
\[
D/d = 1.29 \left( \rho v d / \mu \right)^{0.2}. \tag{1}
\]

As can be seen, lower values of viscosity and higher values of \( \rho \) and particle impact velocity \( v \) give higher degrees of flattening, resulting in dense and strong coatings.

(ii) Composition—Compositional changes in the particle may occur during melting in the flame. However, this requires diffusion of hot gas towards the condensed phase and reverse diffusion of gaseous products. This diffusion occurs at a lower rate \((10^{-2}-10^{-1} \text{ s})\) compared to the melting time \((10^{-4}-10^{-2} \text{ s})\). Hence, stable compounds like oxides are sprayable even in reducing atmospheres while surface reactions may occur during spraying of carbides, nitrides and borides.

Rapid quenching of molten particles result in the formation of metastable high temperature phases in the coatings, like \( \eta, \gamma, \delta \) and \( \theta \) Al\(_2\)O\(_3\) while spraying \( \alpha \) Al\(_2\)O\(_3\). The formation of various metastable phases depends on the rate of transformation from one metastable phase to another and to the stable phase, which in turn strongly depends on spraying conditions, size and shape of the particles, temperature of the substrate etc.

(iii) Residual stresses—There are two types of residual stresses in coating, viz. the microstresses within the individual particles and the macrostresses in the coating as a whole. The microstresses arise because of the restraint on the thermal contraction of the individual particles when they cool in the solid state as they are bound to the relatively cold underlying layer which is at constant temperature. These stresses depend on the thermal expansion coefficient and the elastic constants of the coating material (as well as the substrate for the first layer of the coating).

The macrostresses arise due to the difference in the thermal expansion coefficients between the coating and the substrate material and the temperature gradient during the formation of the coating. Interfacial stresses increase with increasing coating thickness resulting in the peeling off of the coating when the coating thickness reaches about 0.3 to 0.4 mm. High tensile stresses in the coating result in cracking of the coatings.

(iv) Adhesion—The most important phenomenon responsible for adhesion of the coatings is believed to be mechanical i.e. interlocking of the particles as they deform to take the shape of the underlying surface.

Two factors which result in high physical adhesion of two surfaces on contact are:
(a) an intensive and permanent contact, and (b) a decreasing Gibb’s free energy of the substrate–particle system. Zaat (1981) has shown that when contact occurs between two surfaces the total decrease in Gibb’s free energy is given by
\[
\Delta G = \Delta H_s - (T_{\text{cont}} \Delta S_s) + \Delta G_{\text{surf}}, \tag{2}
\]
where \( \Delta H_s \) is the change of the enthalpy because of different potential curves for the atom combinations \( SS, CC \) and \( SC \) (\( SS, CC \) and \( SC \) are the atom configurations in the substrate, coating and interface, respectively); \( T_{\text{cont}} \) is the contact temperature; \( \Delta S_s \) is the increase in the entropy due to surface diffusion and \( \Delta G_{\text{surf}} \) is the decrease in Gibb’s free energy due to surface energy.

The first two terms represent the change in Gibb’s free energy due to the enthalpy and the entropy of formation of the solid solution of the substrate-coating material system. The formation of solid solution requires the interdiffusion of the two
materials and ordering which take place at the slow rate of \(10^{-2} - 10^{-1}\) s whereas the quenching of the solid particles takes place at about \(10^{-4}\) s. Hence the resultant fall in Gibb's free energy due to these two terms is negligible in the case of ceramic coatings.

The last term \(\Delta G_{\text{surf}}\) represents the decrease in Gibb's free energy when two surfaces are brought in intimate contact and can be written as

\[
\Delta G_{\text{surf}} = \gamma_{\text{sc}} - (\gamma_s + \gamma_c),
\]

where \(\gamma_s\) is the substrate surface energy; \(\gamma_c\) is the surface energy of the coating particle and \(\gamma_{\text{sc}}\) is the interface energy when contact occurs between substrate and coating particle. This term will have a large negative value if (a) the substrate surface is clean and plastically deformed (\(\gamma_s\) is large); (b) the particle is impinged with high velocity and its surface is clean (\(\gamma_c\) is large); (c) the contact is intimate (\(\gamma_{\text{sc}}\) is small).

As can be seen, cleaning, degreasing and sand blasting of the substrate prior to spraying not only increase the surface area (for contact to be increased) but also increase the surface energy by cleaning and plastic deformation.

Bulk properties—The bulk properties of thermal-sprayed coatings vary with coating and substrate materials, spray process variables, pre- and post-spray treatments as well as the applications. For instance, the density of the coatings can be changed by changing the spray parameters as can be seen in figure 4. Again the spray process variables are selected to obtain a highly dense tungsten carbide coating if it is to be used as a wear-resistant surface or a highly porous coating if required for an abrasive surface.

An exhaustive list of physical, mechanical, optical, electrical and chemical properties of various thermally sprayed coatings has been given in Hecht &

![Figure 4. Variation of density of the coating with spray parameters.](image-url)
Gerdeman (1972), Fisher (1972), and Fauchais et al (1983). The following general comments can be made on data published by various authors.

(i) Though it is possible to obtain coatings with less than 1% porosity using the D-gun process, typical thermal-sprayed coatings have about 5-20% porosity.

(ii) The adhesion of the coatings to the substrate is only mechanical though some degree of metallurgical bonding has been reported in some cases. However, in case of PTA coatings, definite metallurgical bonding is obtained. The majority of the literature quotes adhesion values of about 35 MPa. The adhesion of the coating to the substrate strongly depends on (a) the substrate surface preparation before spray, (b) thermal and physical properties of the coating and substrate, (c) thickness of the coating, and (d) post-spray heat-treatment. Usually, under-coat and/or graded coatings have been used successfully to increase adhesion.

(iii) Since the coatings are developed by quenching the molten particles, they can have hardness values even higher than the bulk properties of the material. For the same reason, the as-sprayed coatings have high internal stresses.

(iv) Since the general physical and mechanical properties of the coatings strongly depend on the strength of the bonding between the quenched particles (cohesive strength), it has been found that, in general, the physical and mechanical properties of the coatings are slightly inferior to those of bulk materials.

2.1d Comparison of thermal spray processes: Table 2 presents a compilation of selected characteristics of different spray processes (Hecht & Gerdeman 1972). As compared to the combustion flame process, the plasma process is more expensive and requires more complex equipment. However, the combustion process is limited to materials which melt below 3000 K and which are not severely deteriorated by an oxidising atmosphere. Combustion flame-produced coatings tend to have lower densities and bond strengths, and looser tolerances than plasma-sprayed ones.

Coatings prepared by the detonation process have higher density and greater bond strength than those normally found for plasma-sprayed coatings. In addition the tolerances are closer and the surface finish and physical properties are somewhat better. However, the cost of the detonation process is greater and is not effective for

Table 2. Comparison of thermal spray processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Plasma</th>
<th>Combustion powder</th>
<th>Combustion rod</th>
<th>D-gun</th>
<th>PTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating material</td>
<td>All</td>
<td>Ceramics</td>
<td>Selected oxides</td>
<td>Selected oxides + carbides</td>
<td>Selected carbides</td>
</tr>
<tr>
<td>Coating thickness</td>
<td>0.05-2.5</td>
<td>0.1-5.0</td>
<td>0.03-0.5</td>
<td>0.03-0.04</td>
<td>2.5-12.5</td>
</tr>
<tr>
<td>and tolerances (mm)</td>
<td>0.025</td>
<td>0.075</td>
<td>—</td>
<td>0.025</td>
<td>Variable</td>
</tr>
<tr>
<td>Porosity of coating</td>
<td>5-15</td>
<td>10-20</td>
<td>5-10</td>
<td>1-5</td>
<td>—</td>
</tr>
<tr>
<td>(%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Base material</td>
<td>All</td>
<td>All</td>
<td>All</td>
<td>All</td>
<td>Weldable material</td>
</tr>
<tr>
<td>Base temperature (°C)</td>
<td>50-200</td>
<td>250-320</td>
<td>200-350</td>
<td>200</td>
<td>Locally 1000 to m.p.</td>
</tr>
<tr>
<td>Type of bond</td>
<td>Mechanical</td>
<td>Mechanical</td>
<td>Mechanical</td>
<td>Intimate mechanical</td>
<td>Metallurgical</td>
</tr>
<tr>
<td>Particle velocity (m/s)</td>
<td>200</td>
<td>50-150</td>
<td>150-200</td>
<td>750</td>
<td>—</td>
</tr>
</tbody>
</table>
large surface area coverage or coverage of complex shapes. Moreover D-gun coatings require post-spray finishing as well.

Rod-sprayed coatings have better properties as compared to powder-sprayed ones. However, the primary limitation is the necessity of obtaining the ceramic materials in the rod form. All rod-sprayed coatings have been obtained only with combustion flames and plasma-based units have not been commercialised though some lab-based units are in operation.

PTA processed coatings have excellent adhesive strength and can take the higher wear load. The disadvantage is that the high local heating may cause distortions and thus nonconductors and low melting point materials are not suitable as substrates. Deposits are usually applied in thick sections to heavy machinery rather than to precision pieces, since welded parts are generally not subsequently ground to close tolerances. The deposits usually contain some blow holes or pores.

2.2 Chemical vapour deposition process

This is perhaps the oldest technique for preparing coatings. Well-known case-hardening processes like carburizing, nitriding and carbonitriding are the most popular CVD coating processes. Recently many techniques to produce overlay coatings have been developed and a few have found immediate industrial applications as well.

2.2a Principles and techniques: The CVD process is defined as the deposition of a solid material onto a (usually) heated substrate surface as a result of chemical reactions in the gas phase (Yee 1978). These reactions may occur on, at or near the substrate surface. A unified classification of the various CVD processes is given in table 3. These processes are differentiated by the principal mode of supply of chemicals and activation of the chemical reactants. Figure 5 gives schematic diagrams of various CVD processes.

In the conventional CVD (CCVD) process stable gaseous chemical reactants are transported to the reaction chamber, activated thermally in the vicinity of the heated substrate and made to react under controlled conditions to form a solid deposit on the substrate surface. A schematic diagram of the system for the deposition of tungsten carbide coatings is shown in figure 6. The most widely used case-hardening

<table>
<thead>
<tr>
<th>Table 3. Classification of CVD processes.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Principal mode of reactants</strong></td>
</tr>
<tr>
<td>-----------------------------------</td>
</tr>
<tr>
<td>Gaseous</td>
</tr>
<tr>
<td>P (with or without T)</td>
</tr>
<tr>
<td>P (with or without T)</td>
</tr>
<tr>
<td>Liquid</td>
</tr>
<tr>
<td>Evaporation</td>
</tr>
<tr>
<td>P, T (or EB)</td>
</tr>
<tr>
<td>P, T (or EB)</td>
</tr>
<tr>
<td>Sputtering</td>
</tr>
</tbody>
</table>

Abbreviations: T-thermal; P-plasma; EB-electron beam
processes such as carburizing, nitriding, and carbo-nitriding are well-known CCVD processes.

Most chemical reactions in CCVD are endothermic, so that thermal energy must be supplied by the heated substrate and/or by the environment in the neighbourhood of the substrate. There are several established methods of heating the substrate like direct-resistance heating, RF induction heating, thermal radiation heating, photoradiation heating etc.

The high temperature (>600°C) of the substrate material places an undesirable limitation on the types of substrate material which may be coated. Though recently many techniques like selection of suitable chemical systems, plasma activation etc. have been incorporated in order to reduce coating temperatures, many of the established CCVD coatings still use high substrate temperature.

In the chemical spray deposition (CSD) process, instead of gases, reactants enter the
reaction chamber in the form of atomized liquid spray. CSD is very similar to CCVD, the main difference being the mode of transport of the chemicals. Deposition can be carried out in vacuum, at atmospheric pressure and in some cases even in air. CSD is capable of depositing coatings at relatively low temperatures. Its utility depends, however, on the price and availability of suitable liquid reactants.

In the reactive evaporation (RE) method, the reactive metal atoms are evaporated either by resistance-heating or by an electron-beam gun. These metal atoms react with the reactant gas at the heated substrate surface to form a chemical compound coating. TiO$_2$, Al$_2$O$_3$, Y$_2$O$_3$, AlN and TiN are some of the materials that have been coated by the RE process. In principle, this technique is suitable for low temperature depositions.

Activated reactive evaporation (ARE) is essentially an RE process with plasma activation. The plasma in the activation zone can be generated by a microwave, RF or electrical discharge. Various metal carbides, nitrides, and oxides have been deposited using the ARE technique at relatively low temperatures.

A more generalised ARE is called the plasma activated CVD (PACVD) process. Here the starting chemical includes non-reactive as well as reactive species. SiO$_2$, SiN and BN have been deposited by the PACVD process using stable starting chemicals.

In the reactive sputtering (RS), the negatively biased coating material (the target) is bombarded by positively charged inert gas ions, usually Ar$^+$. The chemical species ejected from the target surface react with the reactant gas, which is activated in the plasma zone, to form a coating on the substrate surface. RS, like ARE, is thus very suitable for deposition at low temperatures. Both d.c. and RF sputtering systems have been used to deposit SiN, TiO$_2$, TiN, SiC etc.

The reactive ion plating (RIP) is a hybrid CVD process, combining ion plating and ARE. As in the ARE process both vaporized reactive atoms and the reactant gas are activated in a plasma flame. However, in RIP, the reactive atoms are ionised as well in the plasma flame and accelerated towards the surface of the negatively biased substrate, resulting in strongly adherent deposits. Various compound coatings have been made using the RIP process. Typical examples are TiC, ZrC, TiN, ZrN, Cr$_2$C$_2$ and SiN.
A variation of RIP is the use of stable, gaseous reactants instead of a combination of evaporated atoms and a reactant gas. This variation, which, in principle, may be considered as a generalisation of RIP, is called chemical ion plating (CIP).

2.2b CVD coated ceramics

Many CVD processes for depositing metals, non-metals and metal carbides, nitrides, oxides, borides and silicides have been reported in the literature (Yee 1978).

2.2c Properties of CVD coatings: In any CVD process, there are several inter-related deposition parameters which collectively decide the properties of the deposited coatings. These parameters include not only the temperature, pressure, chemical concentration and velocity of gas flow, but also the geometry of the gas inlet and the substrate, and the configuration of the reactor. Therefore, the desired properties of the coatings can be obtained by careful optimization of the deposition parameters. For instance, the chemical composition of the coatings can even be tailored to meet requirements by suitably varying the concentration of the reactants in the chamber.

In general, CVD coatings have been reported to have very high density and very low porosity, and thus are highly resistant to corrosion, erosion and wear. The microhardness values of various CVD coatings have been presented in figure 7 (Yee 1978).

![Figure 7. Microhardness of CVD coatings.](image-url)
Adhesion or bonding of the coatings to the substrate, which is one of the most important properties on which the successful application of coatings depends, has been the subject of investigation in many reports. However, the reported adhesion values vary from one another, showing the strong dependence of adhesion on various coating process parameters. However, the following general comments can be made:

(i) stresses are invariably produced at the coating/substrate interface during the cooling period after deposition and during service, because of the differences in the thermal properties of coatings and substrate;
(ii) higher internal stresses tend to build up in thick coatings, which result in weaker bonding;
(iii) these stresses can be reduced by using intermediate layer (under-coat) and/or graded coating procedures;
(iv) coatings deposited at high temperatures generally have better adhesion than those produced at low temperatures because of diffusion bonding.

2.2d Comparison of CVD processes: As can be seen from table 4, each process has its own advantages and disadvantages. For instance, the CCVD process is well-established and coatings of almost all ceramic materials have been obtained with very good density and excellent adhesion. Moreover, CCVD gives good uniform coating over the entire substrate surface unlike other processes which are mostly line-of-sight techniques only. But CCVD coatings are deposited at high temperature and hence the selection of substrate materials is limited.

2.3 Comparison of ceramic coating processes

Both thermal spray and CVD are well-established and coatings prepared by these techniques are already in standard usage in almost all branches of science and engineering.

Each process has its own advantages and disadvantages. The selection of a particular process is entirely decided by the particular application. For instance, if the application demands a near-theoretical-density coating with as high an adhesion value as possible, then CVD is the best process. However, the CVD process sets

<table>
<thead>
<tr>
<th>Process</th>
<th>CCVD</th>
<th>CSD</th>
<th>PACVD</th>
<th>RE</th>
<th>ARE</th>
<th>RS</th>
<th>RIP</th>
<th>CIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating materials</td>
<td>Almost all</td>
<td>Proper solution</td>
<td>Almost all</td>
<td>Good VP materials</td>
<td>Target EC</td>
<td>Same as RE</td>
<td>Almost all</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>High temperature material</td>
<td>All materials</td>
<td>Mostly EC</td>
<td>EC</td>
<td>EC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>400-1600</td>
<td>25-1000</td>
<td>25-300</td>
<td>20-1200</td>
<td>~500</td>
<td>25-1100</td>
<td>~100</td>
<td>100-900</td>
</tr>
<tr>
<td>Size limitation</td>
<td>Reactor size</td>
<td>Vacuum chamber size</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Throwing power</td>
<td>Very good</td>
<td>Mostly line-of-sight</td>
<td>Good</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Abbreviations: VP: vapour pressure; EC: electrical conductor.
limitations on the size of the substrate and the normal coating process takes place at fairly high temperature. These factors should also be taken into account while selecting the CVD process.

Salient aspects of various ceramic coating processes have been compared in table 5, which in a way summarizes the advantages and disadvantages of each technique.

3. Applications of ceramic coating technology

The general range of applications of ceramic coatings is as follows:

(a) thermal barrier coatings;
(b) heat and oxidation resistance surfaces;
(c) high temperature wear and abrasion resistance surfaces;
(d) corrosion and erosion resistance layers;
(e) electrical insulation coatings;
(f) diffusion barrier coatings.

Though thermal barrier coatings are usually prepared by thermal spray, and wear-resistant coating on tools and tool inserts is a speciality of the CVD process, in most cases both processes have been used to prepare ceramic coatings on various industrial components. A sampling of industry-wise applications is given in table 6.

4. Present status of the technology abroad and in India

4.1 Thermal spray process

4.1a Status abroad: Commercial equipment suitable for general application in coating shops as well as custom-built ones to suit specific needs are readily available. Special systems (Muehllerberger 1975) like high power systems, supersonic flame facilities, controlled environment and vacuum deposition systems etc., have also been commercialised.

Table 5. Comparison of ceramic coating processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Thermal spray</th>
<th>CVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating Material</td>
<td>All</td>
<td>Almost all</td>
</tr>
<tr>
<td>Thickness (μm)</td>
<td>25–3000</td>
<td>10–500</td>
</tr>
<tr>
<td>Porosity</td>
<td>Slightly porous</td>
<td>Almost non-porous</td>
</tr>
<tr>
<td>Substrate Material</td>
<td>All</td>
<td>Mostly high temperature</td>
</tr>
<tr>
<td>Size limited by</td>
<td>Nil</td>
<td>Reactor size</td>
</tr>
<tr>
<td>Process temperature (°C)</td>
<td>50–200</td>
<td>400–1600</td>
</tr>
<tr>
<td>Type of bond</td>
<td>Mechanical</td>
<td>Metallurgical</td>
</tr>
<tr>
<td>Throwing power</td>
<td>Line-of-sight</td>
<td>Very good</td>
</tr>
<tr>
<td>Coating speed</td>
<td>Fast</td>
<td>Slow</td>
</tr>
<tr>
<td>Main application area</td>
<td>Thermal barrier; corrosion, erosion and wear resistance; electrical and thermal insulation</td>
<td>Wear, erosion and corrosion resistance; diffusion barrier</td>
</tr>
</tbody>
</table>
Ceramic coating technology

Table 6. Industrial applications of coatings.

<table>
<thead>
<tr>
<th>Industry</th>
<th>Environment</th>
<th>Typical coated parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aircraft and space</td>
<td>Vibration, fretting, impact, hammerwear</td>
<td>Compressor and turbine blades, mechanical seals, compressor and fan casings, combustion chamber lining</td>
</tr>
<tr>
<td>Automotive</td>
<td>Vibration, fretting, impact, hammerwear</td>
<td>Cylinder heads and walls, piston walls, crowns and rings, valves and valve stems</td>
</tr>
<tr>
<td>Chemical</td>
<td>Corrosion, wet and dry particle abrasion, high pressure and temperature, friction</td>
<td>Pumps, pistons, turbine rotors, valves</td>
</tr>
<tr>
<td>Textile</td>
<td>Abrasion, corrosion</td>
<td>Rollers, guides, tensioners</td>
</tr>
<tr>
<td>Paper</td>
<td>Precision, corrosion</td>
<td>Surfaces</td>
</tr>
<tr>
<td>Iron &amp; steel</td>
<td>Wear, abrasion, oxidation, heat, corrosion</td>
<td>Furnace rolls, shrouds, pumps, shafts</td>
</tr>
<tr>
<td>Nuclear</td>
<td></td>
<td>Fuel handling, machine parts, boiler and circulation seals, core rod drives</td>
</tr>
<tr>
<td>Machine tools</td>
<td>Wear, high temperature</td>
<td>HSS drills, end mills, reamers, broaches, form tools, hobs, shapers, slitting saws, milling cutters, routers, punches, dies</td>
</tr>
<tr>
<td>Electronics</td>
<td></td>
<td>Oxide coatings on LSI and VLSI</td>
</tr>
</tbody>
</table>

Robot-controlled job-handling systems, microprocessor based powder feeders and similar novel ancillary equipment are also being marketed (Kaczmerek et al 1984, pp. 205–215). Raw materials such as spray quality powders, rods, wires etc., are readily available and are moderately priced. User industries are very well aware of the potentialities and a large number of industries have incorporated coating systems for routine in-house applications and in research and development.

4.1b Status in India: Equipment—Bhabha Atomic Research Centre (BARC) has developed a plasma spray system consisting of 40 kW plasma torch with necessary power, gas and water cables, constant current power supply, screw feed powder feeder and a control console for safe and easy operation of the system. This technology has been transferred to the Vikram Sarabhai Space Centre (VSSC), Trivandrum, Gas Turbine Research Establishment (GTRE), Bangalore, and M/s Kirloskar Electric Co., Bangalore.

M/s Metallizing Equipment Co. (P) Ltd., Jodhpur, has commercialised rod or cord-fed combustion flame systems. It has also recently introduced powder flame type units to the market. M/s Ewac Alloys Ltd. has marketed a rod-fed flame-spray system to spray tungsten carbide coatings.

Coatings—A few organisations like BARC (Karthikeyan 1983; Karthikeyan et al 1985), VSSC, Defence Metallurgical Research Laboratory (DMRL), Hyderabad, Bharat Heavy Electricals Ltd. (BHEL), Trichy, Air India, Bombay etc., are using the plasma spray process for a variety of their own in-house applications. A private company, Plasma Spray Processors, has come to the market recently to undertake jobs on commercial basis.

In the Metallizing Equipment Co. wear-resistant coatings have been prepared over piston rods, plungers, pump shafts, compressor blades and extrusion dies. They have observed a 4–10 fold increase in life of the items because of the coatings.
4.2 Chemical Vapour Deposition Process

4.2a Status abroad: Various equipments and systems of thermal and plasma activated CVD processes are commercially available. Diffusion bonded case hardening processes like carburizing, nitriding etc., have been incorporated in most of the engineering industries.

4.2b Status in India: A few commercial organisations like M/s Sandvik Asia, Pune, M/s Indicarb Ltd., Hosur, have CVD systems for in-house coating of tools and tool inserts. M/s Dura Coaters of Bombay prepare coatings on a commercial basis. Coated machine tools such as drills, broachers, end mills, punches etc. are available in the market.

5. Conclusions

The tremendous potential of the ceramic coating technology has been well-proved, and many industries abroad have used ceramic coatings for both life elongation and process improvement. However, in India, the full potential of the technology has not been tapped as yet.

This article is based on a report co-authored with three other scientists and submitted to the Department of Science and Technology, New Delhi. We are thankful to the DST as well as the Bhabha Atomic Research Centre, Bombay, for assistance. We appreciate the help of scientists from different organisations, working on coating technology, who responded to our queries and sent us technical details about their work. We are grateful to Prof. E C Subbarao for continued guidance and encouragement.

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