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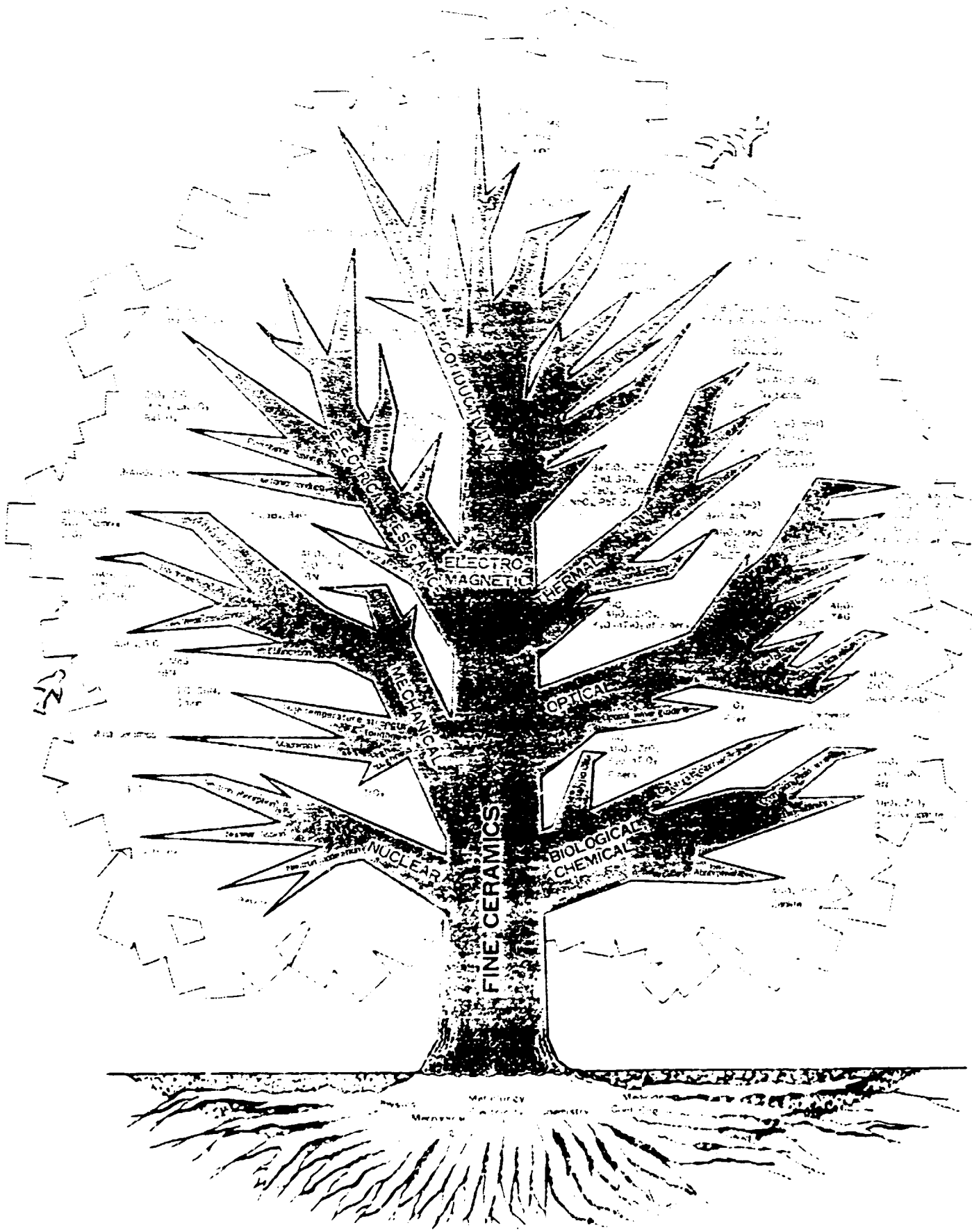
# Advances in Materials Technology: MONITOR

Issue Number 24

March 1991

HIGH-TEMPERATURE CERAMICS

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Dear Reader,

This is number 23 of UNIDO's state-of-the-art series in the field of materials entitled Advances in Materials Technology: Monitor. This issue is devoted to the subject of High-Temperature Ceramics.

The group of materials known as ceramics, with origins dating back to the earliest history of mankind, are today, in their new and advanced form, a competitive alternative to the established engineering materials. Ceramics have been called the "third generation of engineering materials", alongside metals and plastics. An ever-growing number of applications is being found for these high-temperature and high-strength ceramics: in automobile and aerospace components, electronics, cutting tools, wear-resistant materials, communication and computer technologies, and construction work.

The main article for this Monitor has been written for us by Professor L. Cartz, from the Marquette University, Milwaukee, Wisconsin, USA.

We invite our readers also to share with us their experience related to any aspect of production and utilization of materials. Due to paucity of space and other reasons, we reserve the right to abridge the presentation or not publish them at all. We also would be happy to publish your forthcoming meetings, which have to reach us at least 6 months prior to the meeting.

For the interest of those of our readers who may not know, UNIDO also publishes two other Monitors: "Microelectronics Monitor" and "Genetic Engineering and Biotechnology Monitor". For those who would like to receive them please write to the Editor of those Monitors.

Industrial Technology Development Division

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# 1. ADVANCED ENGINEERING MATERIALS AT HIGH TEMPERATURES

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### Abstract

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### Abstract

Materials that are available at the present time for use as engineering components are highly limited in their performance at temperatures above about 1,000°C in corrosive environments. There is probably no satisfactory material for service in air above 1,400°C and there is only a restricted selection of materials in view including silicon nitride based materials, silicon carbide based materials, and carbon-carbon-silicon carbide composites.

This article summarizes the findings of several recent workshops concerned with high-temperature engineering ceramics, and covers nitrogen ceramics, ceramic-ceramic composites, ceramic coatings, ZrO<sub>2</sub>-based ceramics, non-oxide ceramics, ceramic toughening mechanisms, and the micro-structure and processing of engineering ceramics.

Progress towards improved ceramic properties is not automatic, and many severe problems remain. Developments are needed in:

- Oxidation resistant coatings for carbon-carbon composites, and for super alloys;
- Particulate dispersants of controlled morphology suitable for Si<sub>3</sub>N<sub>4</sub>-based and SiC-based materials;
- High-stability fibres with non-reactive interfaces in refractory matrices;
- Sintering mechanisms of monolithic and of composite ceramics;
- Other high-temperature materials such as borides, silicides, carbides;
- Detection of small flaws in ceramics;
- Data on the mechanical properties of ceramics at temperatures above 1,400°C;
- Other methods of preparation of ceramic microstructures;
- Ceramic toughening mechanisms and their interactions.

## 1. Introduction

There is considerable interest in the development of engineering materials for use at temperatures well above 1,000°C, and at temperatures as high as possible. These materials are required for service as components of engineering systems such as gas turbines, reciprocating engines, or energy conversion applications (29,32,34,25). Several workshops and conferences have been held over the past few years to discuss both the progress and the problems facing the preparation and utilization of these advanced materials, particularly ceramics which must be employed once the working temperature exceeds about 1200°C (1-8,10,17,19,42,43).

A workshop "Engineering Materials for Very High Temperatures", which will be referred to as WI, was held in 1987 at the University of Warwick, England, organized by the Office of US Naval Research, (ONRL) in conjunction with the Institute of Physics, UK (1,2). Another workshop, which will be referred to as WII, was held on "Advanced Concepts for Ceramic Toughening" in April 1988 at Stuttgart, Germany (3). Several other meetings have also been held on the topic of ceramics for high temperature engineering purposes and some of these are listed in references 4-18,94.

This review is based in particular on the two workshops WI and WII mentioned above (1-3). The organizing committee of workshop WI included P. Popper (92), D.P. Thompson (67,64), M.H. Lewis (70-76), and L. Cartz (1). The workshop WII was organized by the staff of the research institute directed by G. Petzow (58). The materials and topics covered include nitrogen ceramics, ceramic-ceramic composites, ceramic coatings, ZrO<sub>2</sub>-based ceramics, and non-oxide ceramics. The subjects discussed cover ceramic toughening mechanisms, microstructure, and the processing of engineering ceramics. Some general comments are given on the limitation of present day materials for high temperature uses, as well as an outline of future research initiatives.

A listing is presented of various European research programmes and societies concerned with materials developments.

## 2. High temperature engineering ceramics

A well-balanced review and assessment of the behaviour of ceramics at high-temperatures has been developed by Lewis (1,70-76) in which microstructural mechanisms are described and related to the achievement of improved performance at high temperatures. These microstructural features, and methods of their preparation are illustrated in figures 1-3. In figure 1, the changes of fracture stress with temperature are presented for some of the more interesting high temperature ceramics materials. The properties of solid state sintered SiC are superior at temperatures above approximately 1,000°C though inferior to the properties of Si<sub>3</sub>N<sub>4</sub>- and ZrO<sub>2</sub>-based ceramics at lower temperatures (13,27). In figure 2, microstructural features are illustrated which provide mechanisms of improved mechanical behaviour; micro-cracking (77) of a sub-critical brittle crack, crack-deflection and bifurcation of a sub-critical brittle crack (78),

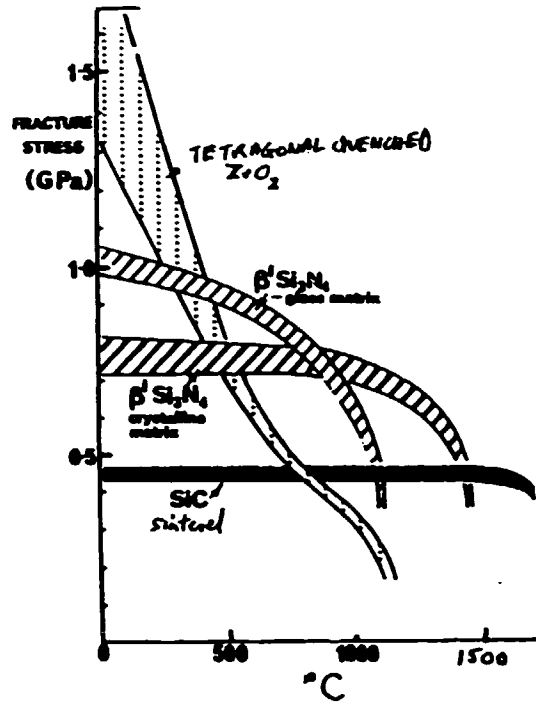


Fig. 1: The variation with temperature of the fracture behaviour of SiC, Si<sub>3</sub>N<sub>4</sub> and ZrO<sub>2</sub>-based ceramics. The sintered SiC has superior properties at high temperature.

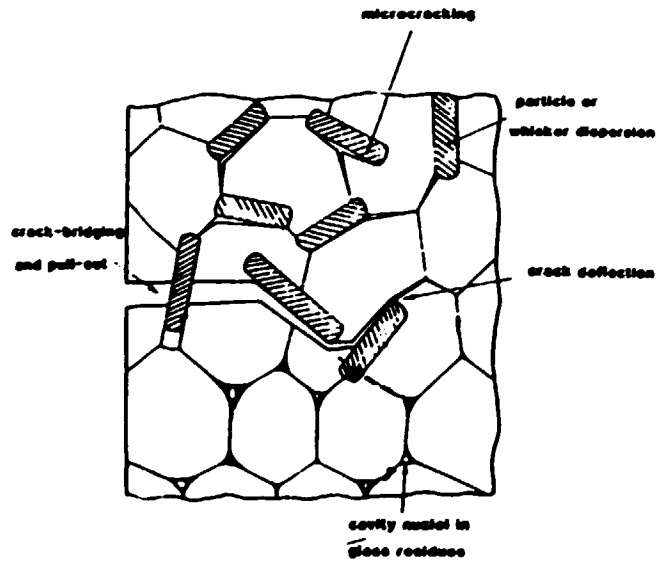


Fig. 2: Illustration of microcracking, crack deflection, crack-bridging, pullout, particle dispersion, whisker dispersion, and glass-residues in ceramic microstructures. These represent mechanisms modifying the mechanical properties of the ceramic material (70-76).

crack-bridging and pull-out by anisotropic particles in the wake of a sub-critical brittle crack (1). Creep deformation at higher temperatures depends on grain-boundary shear and diffusion; creep rates become significant at high temperatures when glassy-phase residues from liquid-phase sintering are present at the grain boundaries.

The microstructure of a ceramic material depends on the fabrication method and many of these are illustrated in figure 3. Solid state sintering (figure 3A) can be used in a limited number of cases, such as SiC with additives of boron and carbon to obtain a nearly equi-dimensional grain morphology. Liquid-phase sintering is necessary for Si<sub>3</sub>N<sub>4</sub>-based ceramics (figure 3B), leaving a glassy phase; an example is the formation of anisotropic grains of Si<sub>3</sub>N<sub>4</sub> with a 10 volume per cent of a silicate phase having a eutectic temperature approaching 1,600°C. This has enhanced fracture toughness but also limited high temperature applications (93). The glassy phase can become fully crystalline as in the case of yttrium aluminum garnet (YAG) (74), or the glass phase can be transient (73) with the formation of a solid solution in the matrix phase. Another method of preparation is by the crystallization of a refractory oxynitride glass to form an oxide-oxynitride ceramic (figure 3C).

Other methods of preparation involve composite structures where random arrangements of short fibres, or woven arrangements of continuous fibres are impregnated with a matrix material by chemical vapour infiltration (CVI) (16,28), or by a glass-ceramic process (81); see figures 3D and E.

The microstructure of a useful ceramic should probably be multiphase, with crystals highly anisotropic in shape, whisker- or needle-like, with no glassy phases present. Liquid phase sintering is a useful method of fabrication, so that methods of crystallizing the glass residues are advantageous. An example of this is the use of a crystallizable M-Si-O-N glass, with hot isostatic pressing to keep the required quantity of glass to a minimum (1).

The presence of intergranular glass can result in increased values of the critical stress-intensity factor  $K_{IC}$  at high temperature due to viscous deformation of the glassy form. However, glass residues lead to time dependent failure, due to creep-cavitation in glass residues (71), limiting use to below 1,000°C. Whisker, fibre and particle dispersions can also improve  $K_{IC}$ , but these particle dispersions tend to degrade at high temperature when the interface fibre-matrix tend to react (85,33). There are high temperature effects on the SiO<sub>2</sub> protective coating which degrades by reactions when oxides are present, such as (YAG) (75), or by reactions with NaCl (86).

### 3. Nitrogen ceramics and silicon carbide

Existing silicon nitride and sialon-based ceramics can currently be used up to 1,300°C and it can be expected to increase the temperature to 1,400°C by improvement in heat-treatment procedures with minimum levels of additives (37,20,65).

The serious problems requiring solution have been discussed in several recent meetings (5,6,37,41,27), and these concern in particular:

- Oxidation problems of nitrogen ceramics;
- The glassy phase in silicon nitride and sialon ceramics;

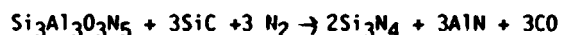
- Chemical compatibility; for example of SiC and sialon (66).

Catastrophic oxidation cracking of nitrogen ceramics occurs at about 1,000°C when yttria, magnesia, or niobia are added as densifiers (35). The microcracking of the ceramic can be related to the volume change on oxidation of the phases of Y, Mg or Nb located usually in the glassy phase at the grain boundaries. Methods of reducing the volume changes decrease the extent of the microcracking, as does the presence of some residual glassy phase at the grain boundary which can tolerate some strain elastically (20,36,38,64).

The mechanical properties of high temperature silicon nitride ceramics deteriorate due to the glassy phase at the grain boundaries. This necessitates using the minimum of sintering additives, changing the wettability of the glassy phase at the grain boundary, and avoiding impurity segregation at the grain boundary. Further improvement to mechanical properties is by forming composite-type structures. The glassy phase at the grain boundary can be reduced by using a glass of lower wettability and lower oxygen content when the glass tends to locate at triple points.

Compositional changes can be made so that no glass phases form, for example by the use of Si-Be-O-N compounds, or by causing the glass to crystallize to a refractory compound, as occurs in the presence of Y<sub>2</sub>O<sub>5</sub>. Improved properties of silicon nitride ceramics at high temperatures depend on the use of the minimum amounts of sintering additives, using pure powders, and by the formation of composite microstructures to cause grain boundary pinning.

Hendry (66) discussed the chemical compatibility of SiC-sialon composites. SiC and Si<sub>3</sub>N<sub>4</sub> are both relatively stable and do not react together at high temperatures so that it had been assumed that SiC with sialon do not react together; this is not so and a reaction does occur, such as:



Other topics reviewed at conferences (5) and (6) include:

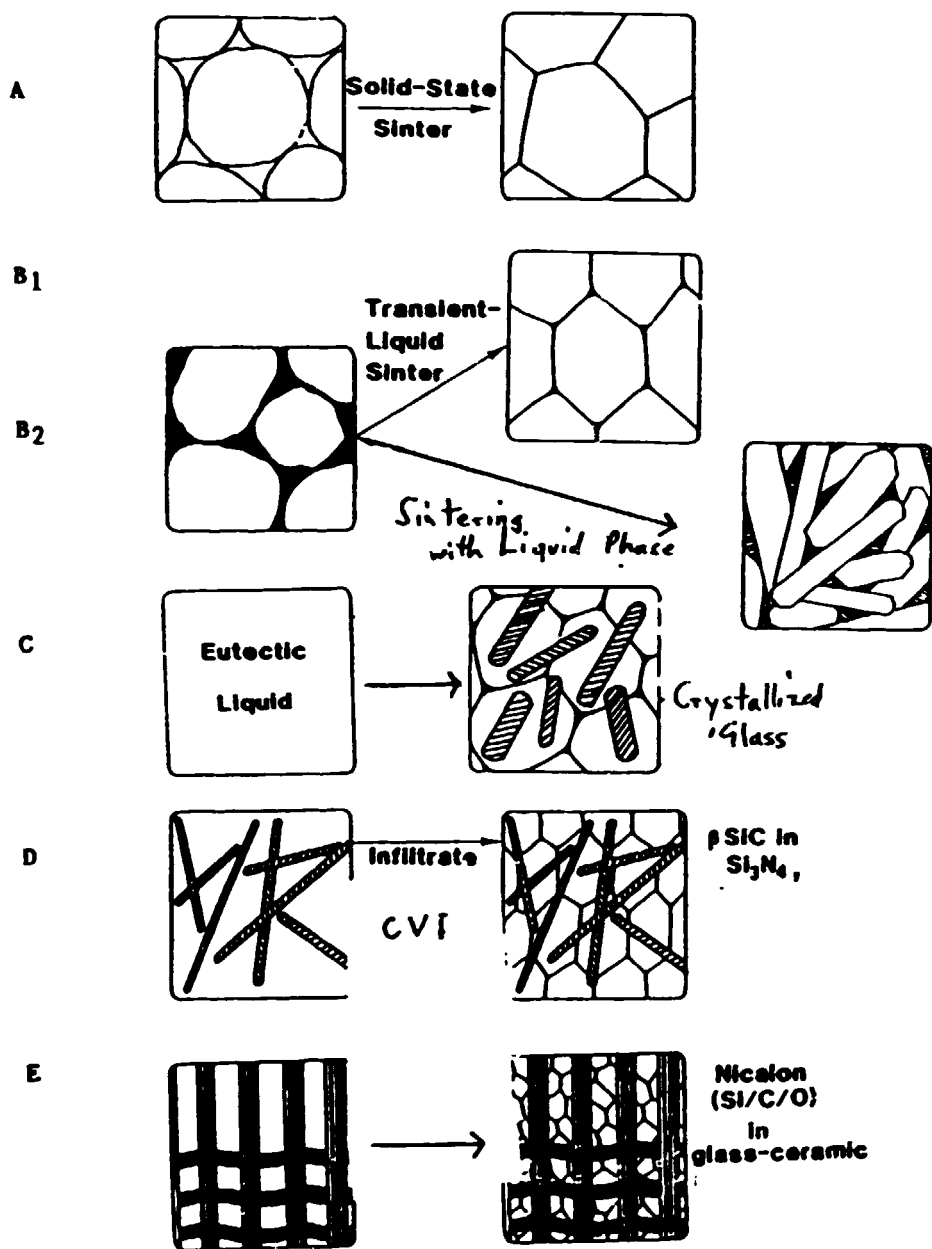
- Transparency of nitrogen ceramics (67)
- Precursors of SiC and Si<sub>3</sub>N<sub>4</sub> (68)
- The Ti-N system (5)
- The reaction of AlN and ZrO<sub>2</sub> (69).

### 4. Ceramic-ceramic composite materials

A range of research studies and technological developments on ceramic-ceramic composite materials have been carried out over the past few decades. The main ceramic-ceramic composite systems under development have been:

- . C-C composites with woven continuous fibre;
- . SiC-SiC;
- . Si nitride with ceramic whiskers;
- . SiC with ceramic whiskers;
- . SiC unidirectional fibres in a SiO<sub>2</sub> matrix;
- . SiC fibre in a refractory silicate glass ceramic.





Ceramic microstructures developed by different fabrication methods (70-76).

- A Solid state sintering; e.g., SiC with B and C additives
- B<sub>1</sub> Liquid phase sintering (transient); e.g., hot pressed Si<sub>3</sub>N<sub>4</sub> with Mg and Al additives
- B<sub>2</sub> Liquid phase sintering; e.g., βSi<sub>3</sub>N<sub>4</sub> and glass
- C Crystallized glass; e.g., Si<sub>2</sub>N<sub>2</sub>O with yttrium aluminum garnet additive
- D Composite of random whiskers with infiltrated matrix; e.g., βSiC in Si<sub>3</sub>N<sub>4</sub> (84)
- E Composite with oriented (woven) continuous fibres, infiltrated by matrix (21); e.g., Nicalon fibres (SiC+O) in glass-ceramic matrix (82) or with vapour infiltration of SiC (83)

Fig. 3

A discussion of the ceramic-ceramic composites development in France has been presented by Jamet (16) as part of the workshop W1, and several of the comments are given here. Recent work in Germany is discussed in reference (92).

Ceramic fibre reinforced ceramic composites have been considered for high temperature applications between 1,200 and 2,500 K which require low weight, high strength, high toughness, high temperature resistance, and damage resistance. High performance fibres, such as C, SiC, Al<sub>2</sub>O<sub>3</sub> (24,30,31) are available and densification of fibrous composites can be carried out by chemical vapour or liquid infiltration. The importance of multidirectional weaving of the fibres in composites has been demonstrated (33). At temperatures up to 2,500 K, survival of the composite requires chemical compatibility of the components with the ability to withstand oxidation (42). Carbon-carbon composites have excellent mechanical characteristics up to 2,500 K in reducing atmospheres but require a protective coating in air (22,25,32,42). Composites using refractory components such as oxides, carbides, or nitrides are limited at high temperatures by:

- The intrinsic stability of the components to grain growth and creep;
- Diffusion or reactions between components requiring the control of the interface;
- Fibre sensitivity to external agents particularly oxidation resistance;
- Diffusion of these external substances through the matrix;
- Reactions between the matrix and external substances.

Several methods exist to protect carbon-carbon composites against oxidation, and the most common method is based on Si-compound coatings chemically compatible with carbon, resulting in the formation of a protective coating of SiO<sub>2</sub> (26,42). This can be achieved using SiC, though there are many limitations including:

- Chemical, thermal, and mechanical bonding between the carbon composite surface and the SiC coating;
- Hermetic sealing of the composite;
- Protection against rapid oxidation leading to catastrophic failure.

The protective coatings can be formed by chemical vapour deposition of SiC at low pressure which gives a good infiltration of the carbon-carbon composite suitable for applications at high temperature, low pressure and low mechanical stress. Another method uses silica or silica glasses prepared by the sol-gel method. Reviews of coatings and surface treatments for high temperature oxidation resistance have been published recently by Saunders and Nichols (22) and Harris and Lutz (25). Ceramic composites using carbide, nitride, silicate, oxycarbonitride matrices with fibres are reviewed in references (59-61). The only composite compositions capable of extended use above 1,000°C are found to be SiC-SiC and C-SiC (61).

Jamet (16) has concluded that carbon and silicon compounds, especially silicon carbide with its silica protective layer, seem to be the two main

materials able to maintain very high temperature stability and thermostructural properties above 1,000°C in spite of their oxidation sensitivity. With additional protection, SiC-SiC chemical vapour infiltration and C-SiC chemical vapour infiltration can be used safely at 1,300°C and 1,600°C respectively. They can also sustain higher temperatures for a brief time. Carbon-carbon composites can be used at 1,600°C with an efficient silicon compound protection and this ceramic-ceramic composite is very promising.

SiC Nicalon continuous fibres and SiC whiskers are the principal ceramic reinforcements used at present with various ceramic matrices. The long fibre may be used up to 1,350°C if its oxidation protection remains intact. The SiC whiskers are very promising for higher temperatures.

Below 1,000°C, several ceramic composites are in use and reinforced glass-ceramic composites show the best performance in this temperature range (62).

At the meeting on ceramic-ceramic composites in Mons, Belgium (1987), see reference (4), the topics discussed included:

- Homogeneous dispersion in multicomponent systems;
- SiC-fibre reinforced composites (62);
- Zr-C-O system (63).

The homogeneity of ceramics of complex compositions depends on obtaining homogeneous dispersions. Sintering rates depend on density composition, and are adversely affected by the presence of non-sintering inclusions such as fibres. Sintering can be improved by inducing comparable shrinkage of the fibres by the application of an organic coating which is driven off at temperature. Other methods are reaction sintering (69), reduced viscosity by employing smaller grain sizes, liquid phase sintering, and by the use of hot isotatic pressing.

SiC-based composites have been investigated by Dawson *et al* (62), and Zr-C-O ceramics by Barnier and Thevenot (63).

## 5. Ceramic toughening mechanisms

The methods available to improve the properties of ceramic materials have been reviewed at the workshop (WII) on "Advanced Concepts for Ceramic Toughening" held in Stuttgart, Germany in (1988). An extensive summary is provided here of the workshop; (3), see also (2), p. 5.

The workshop WII considered toughening mechanisms for ceramics of improved performance, and set out to determine patterns of work required for future improvements. The sessions at the workshop were concerned with:

- Toughening mechanisms; Chairman A.G. Evans (87);
- The role of interfaces; Chairman A.H. Hever (88);
- The requirements of ceramic processing; Chairman R.J. Brook (89);
- Toughness and ceramic applications; Chairman D. Marshall (90).

The toughness mechanisms considered included:

- Transformation of toughening;
- Toughening by ductile phase;
- Toughening by brittle fibres or whiskers;
- Toughening by microcracks and crack bridging.

Transformation toughening discussions covered topics including ferro-elastic transformation, for which little evidence exists at present, twinning transformations, the transformation zone, and the synergism of toughening mechanisms. It is also necessary to determine resistance curves of toughness as a function of crack elongation, R-curves, using standardized specimen geometries.

Toughening by ductile reinforcements require high flow stresses and plastic stretch, possibly involving dislocation pile-up, and the trapping of cracks by ductile particles.

Toughening by brittle fibres and whiskers depends very much on the interface between fibre and matrix. Fibres must be able to debond to some extent from the matrix as a crack propagates. The elastic moduli of fibres and matrix need to be similar, and the debonded layers of matrix and fibres should have low friction coefficients. Special coatings and surface treatments of fibres are important, and the thermal expansion of fibre and matrix should be closely related though some residual stresses are important for good mechanical properties. Aligned fibres are much more effective than random orientations of fibres.

Microcracking and crack-bridging toughen some polycrystalline oxide materials, though there is uncertainty and controversy about the toughening mechanism. Frictional locking, grain boundary locking, and anisotropic grain sizes are considered to play a role. Microcracking is known to toughen alumina-zirconia ceramics.

The role of interfaces (88) is important in glass, alumina and  $\text{Si}_3\text{N}_4$  matrices, reinforced by SiC fibres or whiskers. The whiskers used are frequently Tatcho or Arco of variable diameter, with an amorphous  $\text{SiO}_2$  rich surface layer and low density inner core. SiC whiskers in alumina matrices are under compression, whilst SiC whiskers in  $\text{Si}_3\text{N}_4$  matrices are under tension. Debonding, crack deflection, crack binding, the damage of propagating cracks, and chemical reactions at the interface at temperatures above  $1,000^\circ\text{C}$  all require detailed consideration.

Optimization of the method of applying reinforcement fibres or whiskers are required as well as understanding the diffusion and chemical reactions at the interface. Better methods of testing are required at high temperatures (17).

The nature of the parameter "toughness" used for ceramics needs to be clarified (90). Fatigue in toughened systems, hysteresis in loading/unloading, and fatigue and propagation rates with stress intensity, all of these depend on the toughness mechanism. In continuous fibre composites, multiple cracking mechanisms take place so that failure does not occur by the growth of a single crack. No single parameter of toughness can describe all these properties of ceramics.

Ceramic processing (89,90,40) is required for ceramics with equidimensional grain structures, as

well as for whisker-fibre reinforced structures. Whiskers and fibres present difficulties in achieving high densification due to back stresses arising from the non-sintering components as well as shrinkage anisotropy.

Very fine powder sizes give rise to a dense yttrium doped tetragonal  $\text{ZrO}_2$  of equi-axed grain sizes of about  $0.1 \mu\text{m}$ . Superplasticity  $\text{ZrO}_2$ -mullite can be used to prepare dense components. Reaction sintering ( $\text{ZrN}$  with  $\text{TiO}_2$  to form  $\text{ZrO}_2$  with  $\text{TiN}$ ) has been used to form dense ceramics (69).

It is necessary to obtain good homogeneous suspension of powder-whiskers (or fibre) with additives in order to sinter to a homogeneous ceramic. Control of pH and low fibre loading below 15 volume per cent are generally needed to overcome anisotropic shrinkage and to achieve high densities.

## 6. Present-day materials and future research

General reviews have been presented at several recent workshops and conferences (1-3) on the limitations of present day engineering materials for use at high temperatures, under high stress, and in corrosive environments. Meetham (44) has discussed the future requirements of gas turbine components such as aerofoils, discs and combustors where nickel superalloys permit the use of gas turbines up to about  $700^\circ\text{C}$ . Metselaar and Wolff (45) have described the requirements of a thermionic energy converter operating at  $1,450^\circ\text{C}$  for which a trilayer material has been designed consisting of a tungsten emitter coated with a diffusion barrier of  $\text{TiN}$  and an outer protective shell of  $\text{SiC}$ . Nickel (29) has discussed the requirements of core materials for advanced high temperature reactors. Van der Sluis (3) has reviewed the brazing of oxide and non-oxide ceramics to metals.

At the workshop (WI) on "Engineering Materials for Very High Temperatures", all possible materials and treatments were considered including N-ceramics, ceramic-ceramic composites, carbides, borides, silicides, and refractory silicates. The properties demanded are high strength, toughness, creep resistance, and oxidation resistance at high temperature, but cost-effective processing and reliability are equally important.

The following summary discussions are taken from workshop (WI). Among the ceramic materials silicon nitride-based ceramics allow use up to about  $1,250^\circ\text{C}$ , which might be extended to  $1,400^\circ\text{C}$ . Current ceramics based on  $\text{Si}_3\text{N}_4$  and on sialons have probably the best balance of strength-toughness at temperatures up to  $1,300^\circ\text{C}$ . Monolithic silicon carbide has a better performance at high temperatures but suffers from a low fracture toughness. Carbon-containing materials could be used at temperatures of perhaps  $2,000^\circ\text{C}$ , but for the use of these materials in air, protection against oxidation needs to be provided, which is not an easy problem to solve. The same applies to the protective coatings on refractory metals, which require a better understanding of coating adhesion and diffusion properties.

The fracture toughness of ceramic materials might be increased by the incorporation of fibres and whiskers. This approach is limited by the availability of suitable fibres and whiskers. Current composite materials do not display better fracture toughness properties at high temperatures than monolithic ceramics. The mechanism of sintering without the formation of liquids, as in the sintering of silicon carbide, requires elucidation.

There is a modest understanding of microstructure and property relationships in high-temperature creep, fracture, and oxidation of monolithic ceramics. Monophase ceramics, exemplified by solid-state-sintered SiC, have good time-dependent properties up to 1,600°C (93) but have microstructures with a poor fracture toughness, of the order of 5MPa/m. Some improvement in fracture toughness (6-8 MPa/m) is attainable in liquid-phase-sintered Si<sub>3</sub>N<sub>4</sub> and sialon ceramics, which retain good creep, creep-rupture, and oxidation resistance at 1,300°C provided that the liquid residues are fully crystallized. Instability in oxidizing conditions above 1,350°C may be improved by reducing the residual glass phase content and using hot isostatic pressing (HIP) fabrication, but fracture toughness is generally reduced.

Composites have a potential for removing one of the most important engineering design limits of monolithics, that of microscopic critical flaw sizes associated with low fracture toughness. Useful increments in toughness (10-15 MPa/m) are attainable by the dispersion of whiskers (10-30 volume per cent) in various matrices, retaining conventional fabrication procedures but normally requiring pressurized sintering. Although they exhibit impressive unidirectional fracture properties, there are significant problems in high-temperature stability of non-stoichiometric fibres (such as Nicalon-SiC), in the fabrication of refractory matrices with non-reactive fibre-matrix interfaces, and in the forming of three-dimensional woven-fibre component shapes capable of retaining a large fraction of the unidirectional property. High-temperature deformation and creep-fracture of both fibrous and whisker composites remain a relatively unexplored field.

The more complex, difficult, and hence expensive fabrication processes for high-temperature monolithic ceramics, and especially for composites, must be weighed against the increase in high-temperature performance over the lower temperature superalloys. The "Lanxide" process, in which a liquid metal matrix is converted to an oxide ceramic, is of particular interest in the formation of monolithic and composite ceramic shapes. Incomplete metallic conversion is beneficial for fracture toughness, but it clearly presents problems in relation to high-temperature operation above the liquidus of the metallic residue.

The recommendations made at workshop WI are as follows:

#### Near-term studies

- Increasing the temperature ceiling of Si<sub>3</sub>N<sub>4</sub>-based monolithic ceramics to at least 1,400°C in oxidizing conditions, using stable crystalline sintering residues and HIP processing.
- Improving the fracture toughness and strength of SiC-based ceramics, formed by solid-state sintering, by particulate or whisker dispersions, while retaining the good creep-rupture and oxidation resistance of the sintered matrix.
- Further development of SiC or carbon-based fibrous composites with respect to stability at temperatures of 1,200°C, especially in oxidizing conditions, for example by coatings for carbon-carbon composites and the use of the newly emerging stoichiometric SiC fibres.

- Development of coatings on metals, such as superalloys, replacing existing oxide coatings by refractory silicates (celsian, for example) of matched thermal expansion behaviour.

#### Long-term studies

- The development of a range of new particulate dispersants, with controlled morphological anisotropy, and chemical compatibility with Si<sub>3</sub>N<sub>4</sub> and SiC-based matrices, designed to extend the principle of "whisker-toughening".
- Further development of high-stability fibres, such as stoichiometric SiC, and of non-reactive interfaces with refractory matrices. This may be achieved by coatings or by using lower temperature fabrication such as the "sol-gel" route for oxides, or "reaction-bonding" for Si<sub>3</sub>N<sub>4</sub>. The present-day limited choice of fibres is a severe handicap; it would be very useful to have fibres of materials such as BN, BC, and AlN.
- Development of shaping-fabrication procedures, especially for fibrous composites, with an emphasis on specific component applications.
- Develop a better understanding of the basic mechanisms involved in sintering, both of monolithics and composite matrices, and of high-temperature deformation and fracture. In "dispersed-phase" composites, the relative contributions of different toughening mechanisms should be investigated.
- Develop an understanding of coating cohesion and substrate inter-diffusion.
- Examine the properties of other high-temperature materials, such as those based on borides, silicides, and carbides.
- Develop methods of flaw detection in ceramics to permit the study of the smallest flaws under stress and environment, as well as to obtain more consistent properties in ceramic materials.
- There is a lack of data of the mechanical properties of ceramics above 1,400°C, and data is required certainly up to 1,600°C. Measurement techniques to acquire this data need to be developed (9).

At the meeting on engineering ceramics at Coventry, UK, July 1987 (7) the following specific points were made concerning problems arising when metals are replaced by ceramic materials:

- Sharp corners must not be present in the ceramic component so that redesigning of a component is essential;
- Ceramics absorb gases and liquids, and precautions must be taken;
- Catastrophic failures in ceramics do occur so that a very large safety margin must be used in the design;
- There is no standardization in the testing of ceramics;
- It is best if the ceramic component can be held under compressive forces;

- It can be very difficult and expensive to obtain precise shapes or ceramic components; the use of diamond grinding is very expensive and should be avoided if at all possible.

At the workshop WII on "Advanced Concepts for Ceramic Toughening" (3), the following research initiatives were listed:

The nature of fatigue mechanisms in ceramics and the prevalence of fatigue for different ceramic systems are not well understood and are of major significance for applications. The relative importance of fatigue in toughened ceramic microstructures must be assessed to guide microstructural design for such materials;

The use of ceramics at high temperature suffers from the relative lack of characterization of microstructures and failure mechanisms at high temperature. The refinement of high-temperature testing and the specific design of microstructures for high-temperature stability and toughness are important research tasks.

Research requirements identified are as follows (3):

R-curves	Agreed geometry for testing Calculation of curves for specific mechanisms
Synergism	Nature of interaction between different toughening mechanisms
Ductile phase toughening	Plasticity of constrained particles Studies of bridging zone behaviour Control of particle-matrix interface
Fibres, whiskers	Nature of fibre-matrix debonding Design of interface coatings of suitable stability and bonding
Microcracks	Modelling of toughening behaviour Assessment of prevalence of the mechanism
Interface-Microstructure	Debonding phenomena for fibres and particles Characterization and testing at high temperature
Densification of composites	Evaluation of limits for pressureless densification and identification of impediments
Whiskers and fibres	Availability of reinforcement phases of controlled microstructure
Fine grain size	Extension of processing capability to finer powder sizes
Reaction sintering	Preparation of required composite microstructures by <u>in situ</u> reaction

#### 7. European materials research activities

The new European Ceramic Society, ECS, has been established recently with the first European ceramic conference being held in Maastricht, the Netherlands in June 1989. So far, the countries adhering to ECS include France, Italy, Germany, the Netherlands, Belgium, the United Kingdom, and Spain. Further details about ECS can be obtained from the president of the society, Professor R. Metselaar, Secretariat European Ceramic Society, Centre for Technical Ceramics, Eindhoven University of Technology, Eindhoven, the Netherlands.

A new European Society of Materials has recently been established by an agreement signed December 1987 by the Deutsche Gesellschaft für Metalkunde, The Institute of Metals (UK), and la Société Française de Metallurgie. It is hoped that other European societies of metals, ceramics, and other materials will join the federation.

The objectives of the federation are to:

- Improve the dissemination of information about the scientific meetings of the individual national societies;
- Increase the participation in national meetings, including sponsoring European meetings;
- Publish simultaneously scientific reviews of metallurgy in German, English and French;
- Hold an annual major European meeting on materials.

Further information can be obtained from these addresses:

La Société Française de Metallurgie,  
1-5, rue Paul Cezanne, 75008 Paris, France.  
[Secretary-General Yves Francot,  
Tel.: 1-45-63-17-10].

The Institute of Metals, 1, Carlton House  
Terrace, London, SW1Y 5DB, UK. [Secretary  
Sir Geoffrey Ford, Tel.: 1-839-4071].

Deutsche Gesellschaft für Metalkunde,  
Adenauer-Allee 21, D-6370 Oberursel 1, Germany.

A Federation of Materials Institutes has been formed in London, UK, by the amalgamation of the Institute of Metals, the Institute of Ceramics, and the Plastics and Rubber Institute. The new Federation will be able to cover the entire field of Materials, and it is contemplated that eventually a single Institute of Materials will be formed in the UK. The Federation will be governed by a council consisting of the Presidents of the founding societies. Further details may be obtained from Sir Geoffrey Ford, the Institute of Metals, 1, Carlton House Terrace, London SW1Y 5DB, UK.

#### **European programmes on materials science and technology**

There is a wide range of European programmes of collaboration in the fields of science and technology set up by the Commission of the European Communities (CEC) and a selection of these programmes are listed in table I (47,48).

Table I

#### Some Acronyms of the European Scientific and Technological Research Programmes and Organizations

BRITE	Basic Research in Industrial Technologies for Europe
CCFP	Consultative Committee for the Fusion Programme
CEAM	Concerted European Action on Magnets
CEN	European Committee for Standardization
CENELEC	European Committee for Electro-technical Standardization

CERN	European Organization for Nuclear Research	FAST	Forecasting and Assessment in Science and Technology
CERT	European Parliament Committee on Energy, Research and Technology	FEICRO	Federation of European Industrial Co-operative Research Organizations
CIT	Committee on Innovation and Technology Transfer	FP	Framework Programme
CODEST	Committee for the European Development of Science and Technology	FTSC	Fusion Technology Steering Committee
COMETT	Community Action Programme for Education and Training for Technology	IRDAC	Industrial Research and Development Advisory Committee
COST	European Co-operation in the Field of Scientific and Technical Research	JET	Joint European Torus
CREST	Scientific and Technical Research Committee	JRC	Joint Research Centre
CST	Euratom Scientific and Technical Committee	LEP	Large Electron-Positron Collider
DELTA	Developing European Learning through Technological Advance	MTH	Major Technological Hazards Programme
DESY	German Electron Synchrotron	NEA	Nuclear Energy Agency
DIANE	Direct Information Access Network for Europe	NET	Next European Torus
EAEC	European Atomic Energy Community	RACE	Research and Development in Advanced Communications Technologies in Europe
EARN	European Academic and Research Network	RAP	Research Action Programme
ECSC	European Coal and Steel Community	SPRINT	Strategic Programme for Innovation and Technology Transfer
EDPEC	Energy Demonstration Programme of the European Communities	STC	Euratom Scientific and Technical Committee
EIRMA	European Industrial Research Management Association	STD	Science and Technology for Development
EISCAT	European Incoherent Scatter Radar Facility	STIMULATION	European Co-operation between Laboratories
EJOB	European Joint Optical Bistability project	STOA	European Parliament Office for Scientific and Technological Options Assessment
ERASMUS	European Community Action Scheme for Mobility of University Students	TDMS	Technological Developments in the Hydrocarbons Sector
ERS	Earth Resources Satellite	VAMAS	Versailles Project on Advanced Materials and Standards
ESA	European Space Agency		The research programmes concerning Materials are:
ESEP	European Science Exchange Programme	STIMULATION	Stimulation of European Co-operation [see reference 52]
ESF	European Science Foundation	SPRINT	Strategic Programme for Innovation and Technology Transfer [see reference 53]
ESO	European Southern Observatory	EURAM	European Research on Advanced Materials Programme [see references 46,49,51,52]
ESPRIT	European Strategic Program for Research and Development in Information Technology	BRITE	Basic Research in Industrial Technologies for Europe [see references 46,50,52]
ESRC	European Science Research Councils	COST	European Co-operation in the Field of Scientific and Technical Research [see reference 46]
ESRF	European Synchrotron Radiation Facility	EUREKA	European Research Co-ordination Agency [see reference 46]
ESTEC	European Space Research and Technology Centre	VAMAS	Versailles Project on Advanced Materials and Standards [see reference 55]
EURAM	European Research on Advanced Materials		
EUREKA	European Research Co-ordination Agency		
EUROMET	European Collaboration on Measurement Standards		

A short review of the material studies under these programmes is given in reference 2; see also (54).

Some of the projects concerned with high temperature materials are as follows:

BRITE:

- . Plasma reactor for surface deposition of corrosion-resistant layers;
- . SiC-reinforced composite turbine wheel with mechanical strength stability at high temperature.

EURAM:

- . Ceramics intended for future generations of internal combustion engines, especially the adiabatic diesel engine operating at a constant temperature of 1,500°C;
- . Composite materials; synthetic resins with carbon or glass fibres; metal matrix composites;
- . Mechanical properties and corrosion resistance properties of steels, alloys, and engineering ceramics;
- . Data bank of characteristics of high-temperature materials;
- . Processing of monolithic ceramics SiC, Si<sub>3</sub>N<sub>4</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>; whisker-fibre composites.

EUREKA:

- . Precursors for high-performance ceramics by wet chemicals;
- . Coatings for advanced technology.

Reviews of ceramic research in Europe are given in references (46,48,49,55-58).

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## 2. ADVANCED CERAMICS FOR HIGH-TEMPERATURE STRUCTURAL APPLICATIONS - PROBLEMS AND PROSPECTS\*

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### ABSTRACT

In this paper an effort has been made to identify chronologically, the steps used to develop advanced structural ceramics, which can be used in heat engines. Starting with the approach of making very strong ceramics (700 MPa) by identifying and eliminating flaws, and continuing with the development of increased fracture toughness through formation of precipitates and/or introducing a second phase (whiskers or particulates), it has been shown that the future for utilizing advanced ceramics in large scale applications, i.e. in automobile engines, appears to be very good. The activities on advanced ceramics, especially on the plasma synthesis of advanced ceramic powders and ceramic-ceramic composites, at the University of British Columbia are also included in this paper.

### 1.0 Introduction

In this presentation, I shall try to discuss chronologically the development of advanced structural ceramics, the problems encountered and how these problems have been overcome. Finally, I shall deal with "where do we stand" and what are the future prospects?"

Applications of ceramic materials to high performance structural usage refer to systems where components or products made of ceramics are used at high temperature, i.e. 1,000°C and both at high and moderate stresses. These include applications of ceramics to engines or engine components (turbines, diesels, stirlings, etc.). Under moderate and low stresses other structural applications such as heat exchangers can be considered. For such applications, development of very strong ceramics and also tough ceramics is considered essential. For this reason, in this presentation some fundamental concepts in the development of super-strong ceramics and factors such as lifetime prediction and effect of proof-testing on the longevity of components under a certain stress field have to be dealt with. These factors have to be understood before ceramics can be used as high temperature structural components.

The properties and characteristics required of ceramic materials for such high temperature structural applications are:

- (1) Low thermal expansion coefficient
- (2) Good thermal shock resistance
- (3) Good high temperature strength
- (4) Good high temperature creep resistance
- (5) Good stability in environment (e.g. oxidation resistance)

All of these desirable properties can be found in some ceramic materials. That is the reason why ceramics are being highly touted as the materials of the future for high temperature structural applications.

\* This article was given to us by Professor L. Cartz, author of the main article of this Monitor.

### 1.1 Driving force behind development of advanced ceramics

#### 1.1.1 Precursor materials availability:

One of the major driving forces behind these developments is the apparent ease of availability of ceramic materials considered most useful for such applications. These materials can be synthesized from very common natural minerals. Possible materials for high temperature applications (1,000°C) are SiC, Si<sub>3</sub>N<sub>4</sub> and SiAlON, and for moderate temperature applications, Al<sub>2</sub>O<sub>3</sub> and PSZ (Partially Stabilized Zirconia).

In contrast, metals and alloys are used for gas turbines or other engines such as Ni, Cr, Co, Al, Mn, Ti, Fe, etc.

#### 1.1.2 Economic advantages of using ceramics

The other driving forces behind the current interest and feverish effort to develop and commercialize advanced ceramics for engine applications are: the need to improve energy efficiency; the need to achieve multifuel capability without deleterious environmental problems; the need to overcome material cost and supply problems; and most important, to gain significant economic benefits. This is shown in Table 1.

### 1.2 Ceramic applications in engines

The different types of engines under development using ceramic components are identified below:

- (i) Gas turbine engines
- (ii) Diesel engines
- (iii) Gasoline engines

#### (i) Gas turbine engines

Gas turbine engines for three important applications are being developed:

- . Aircraft engines
- . Automotive engines
- . Stationary engines for power generation

### 1.3 Activities on advanced structural ceramics in the United States of America and Japan

The United States has been the world leader in advanced ceramics - in research, development and commercialization - since the 1950s. Although the United States of America developed most of the scientific and technological innovations leading to advanced electronic ceramics, the commercial market leadership is now in the hands of Japan, currently supplying more than 70 per cent of the world market. At present there is concern, both in industry and Government, that in spite of scientific and technological leadership in advanced ceramics for "structural" uses (e.g., automobile engines), commercialization is lagging, mainly because of the technological barriers still to be solved: reproducibility in manufacture, reliability in service, and competitive cost. There is also recognition that, as in Japan, commercialization

**Table 1**  
**Ceramic Technology Payoff of Some Typical Engines 1/**

Engine Type	H.P.	Range Configuration	SFC*	Power
Automotive GT	200	Regenerated, single-shaft 1350°C, TIT**	-27%	0
Truck FT	350	Regenerated, 2-shaft 1250°C, TIT	-27%	+30%
Light Ship GT	1000	Simple cycle, 3-stage, 1350°C, TIT	-10%	+40%
Diesel	500	Adiabatic turbo compound T <sub>max</sub> 1050°C	-22%	+37%

\* SFC - specific fuel consumption - (gm/W-hr), based on current state-of-the-art

\*\* TIT - turbine inlet temperature

should go hand in hand with technological development (i.e., applications should be developed for advanced ceramics, continuously matching technology development to market needs). American industry and Governments have taken a number of new initiatives to regain leadership.

**2.0 General concept of engineering ceramics**

Ceramic materials possess some very useful properties for structural applications, especially at high temperatures. These include strength, hardness, stiffness, lightness (density) and refractoriness (i.e. high melting temperature). But the major weakness or shortcoming in using ceramics for structural applications is their brittleness (i.e. lack of localized stress-relieving mechanisms), which leads to unpredictable behaviour of failure.

In order to design or develop ceramic materials for structural applications, two approaches have been attempted:

- (1) To make ceramics superstrong, and/or,
- (2) To make ceramics tough.

The main thrust of developments in this regard during 1975 to 1985 has been towards producing superstrong ceramics (>700 MPa flexure strength) with somewhat higher predictability of failure.

For this development the following three objectives were considered:

- (i) The first objective is to develop superstrong ceramics. This is to ensure that the total mechanical and thermal stresses in service are always sufficiently low such that fracture is never initiated.
- (ii) The second objective is to develop methods and correspondingly ceramic materials whose failure under a certain stress level can be predicted more accurately.
- (iii) As ceramic materials are susceptible to "delayed failure" (also known as static

fatigue), methods have to be found in developing the relationship between the fracture stress, the probability of failure at that stress and at what time (i.e. after how long) the material has that probability of failure under the stress. This is known as strength-probability-time (S-P-T) diagram and is explained further later on.

It is well known that for brittle solids the strength properties are significantly controlled by the surface finish (i.e. surface flaws) of the components or products. During proof testing a set of components, there is always the possibility of altering the flaw population both on the surface and within the body. So, it is necessary to know the effect of proof testing on the S-P-T relation for that set of components.

All the parameters discussed above are considered essential for structural ceramics.

The following section deals with the basic concepts of fracture mechanics used in achieving the objectives referred to above.

**2.1 Strength**

The weakness in brittle materials arises from the existence of flaws both on the surface and within the bulk of the body, as the theoretical strength of all solids is very high, normally greater than 1 GPa.

For covalent solids, the theoretical strength ( $\sigma_{max}$ ), derived from the potential energy function of Morse potential, is given by 2/

$$\sigma_{max} = \left( \frac{EY}{Nx_0} \right)^{1/2} \tag{1}$$

and for ionic solids, 3/ using the Born Potential equation, the theoretical strength is

$$\sigma_{max} = \frac{E}{2} \left[ \left( \frac{2}{n+1} \right) \left( \frac{n+1}{n-1} \right) \right] \tag{2}$$

where E is the elastic modulus,  $\gamma$  is the surface energy,  $x_0$  is the interatomic distance, n is equal to  $(x_0 E / 2\gamma)$  and N is a numerical constant ( $\approx 4$ ).

Similarly other equations for theoretical shear strength and theoretical cohesive strength  $\sigma_c$  have been developed. All these equations give the values of  $\sigma_{max}$  in the range E/3 to E/10. This means that the theoretical strength of solids are in the range of 2-5 GPa. As a matter of fact, whiskers of alumina, SiC, Fe, Cu, etc., and flame polished silica glass fibres have strength values approaching (within a factor of 5 to 10) the theoretically predicted strength.

### 2.2 Flaw theory of fracture

It is common knowledge that ceramic materials and products are weak. The low strength and brittle behaviour of ceramics are almost entirely due to limitations on the amount and type of plastic deformation (stress-relieving mechanisms) of these materials. An important consequence of this behaviour is the fact that stress concentrations at crack tips or flaws cannot be relieved by generalized plastic flow. As a result any flaw contained within the body or on the surface acts as a stress-raiser and is a potential nucleation site for fracture. It should be noted that even where plastic flow occurs in certain ceramics, (e.g. MgO) the flow itself results in crack nucleation and leads to subsequent failure. 5/

The flaw theory of fracture was originally developed by Griffith 6/ and two equations derived by him are shown below,

$$\sigma_c = 2 \sigma_{app} \sqrt{2/\rho} \quad (3)$$

and 
$$\sigma = (2E\gamma/\pi l)^{1/2} \quad (4)$$

Equation (3) indicates that the stress ( $\sigma_c$ ) acting on a crack tip of radius of curvature ( $\rho$ ) and length ( $l$ ) is the product of twice the stress applied ( $\sigma_{app}$ ) and  $(l/\rho)^{1/2}$ . If it is assumed that the flaw length ( $l$ ) is of the order of  $10^{-6}$  cm and the  $\rho$  is  $\sim 10^{-10}$  m, then the stress concentration at the tip is 200X. This means that if a material has a theoretical strength of 10 GPa, the failure stress for this material having a flaw of the above dimensions would be 50 MPa (7.25 Ksi) such a material is considered to be very weak.

The similarity between equation (1) and equation (4) can be easily seen. If one assumes that crack length is in the order of the interatomic spacing, the rupture stress calculated from equation (4) is in the same order of the theoretical strength.

However, the tensile fracture strength ( $\sigma_f$ ) of a ceramic is more easily understood in terms of a modified classical Griffith equation

$$\sigma_f = \frac{1}{Y} \left( \frac{2E\gamma_1}{C} \right)^{1/2} = \frac{K_{IC}}{Y C^{1/2}} \quad (5)$$

where Y is a geometric constant, E - the elastic modulus,  $\gamma_1$  - effective surface energy,  $K_{IC}$  - critical stress intensity and C is the flaw size.

Equation (5) implies that  $K_{IC}$  or  $\gamma_1$  of the material is a constant, so provided the flaw size is known, the  $\sigma_f$  can be estimated. The effective

surface energy and the stress intensity factor are both measures of the toughness of the ceramics.

Table 2 shows some strength and toughness properties of the advanced ceramics currently being tested in engine applications.

Table 2

Properties of Advanced Structural Ceramics

Material	Strength MPa	Toughness MPa $\sqrt{m}$	Thermal expansion 10 <sup>-6</sup> /C
Types of silicon nitride			
RBSN	300	3.6	3.3
HPSN	1100	6.6	3.5
GPSSN	440	2.9	3.5
Types of silicon carbide			
Alpha SSC	420	2 to 3	4.1
Beta SSC	533	2.4	4.1
HPSC	880	3.9	4.2
Types of transformation-toughened ceramics			
PSZ	700+	8+	10.2
TTA	900	8	7
Ceramic-ceramic composites			
SiC-LAS	620	15	1 to 4

**Key:**

- RBSN Reaction-bonded silicon nitride
- HPSN Hot-pressed silicon nitride
- GPSSN Gas pressure sintered silicon nitride
- Alpha SSC Alpha-phase sintered silicon carbide
- Beta SSC Beta-phase sintered silicon carbide
- HPSC Hot-pressed silicon carbide
- PSZ Partially stabilized zirconia
- TTA Transformation-toughened alumina
- SiC-LAS Silicon carbide fibres in lithium aluminosilicate glass

When fracture strength remains constant with temperature equation (5) can be readily applied. The flaw size can then be related to one of a number of microstructural features, such as grain size or pore size. The experimental evidence of strength dependence on flaw size has been extensive. To improve strength therefore, one needs to reduce the flaw size by controlling the microstructure during fabrication.

The critical flaw sizes 7/ for engineering ceramics are in the range 25 to 75  $\mu$ m (table 3) and it is the largest flaw in a specimen that controls strength.

To achieve the objective of producing very strong ceramic components (breaking strength >700 MPa) efforts are generally made to fabricate flaw-free materials. For controlling bulk properties the grain size of fully dense products is kept as low as possible (<10 $\mu$ m average grain size and preferably <5 $\mu$ m), as the strength of brittle solids also follows a Hall-Petch relationship.

If pore-free specimens cannot be produced both pore size and pore size distribution affect the strength properties. Attempts to narrow the pore-size distribution have been partially successful 8/ (figure 1).

Table 3<sup>26</sup>

**Fracture Toughness and Critical Flaw Sizes of Monolithic and Composite Ceramic Materials Compared with Metals<sup>a</sup> (Al<sub>2</sub>O<sub>3</sub>; LAS; Lithium Aluminosilicate; CVD; Chemical Vapor Deposition)**

Material	Fracture toughness (MPa <sup>1/2</sup> )	Critical flaw size (micrometers)
Conventional microstructure:		
Al <sub>2</sub> O <sub>3</sub>	3.5-4.0	25-33
Sintered Sic	3.0-3.5	18-25
Fibrous or interlocked microstructure:		
Hot pressed Si <sub>3</sub> N <sub>4</sub>	4.0-6.0	33-74
Sintered Si <sub>3</sub> N <sub>4</sub>	4.0-6.0	33-74
SiAlON	4.0-6.0	33-74
Particulate dispersions:		
Al <sub>2</sub> O <sub>3</sub> -TiC	4.2-4.5	36-41
SiC-TiB <sub>2</sub>		
Si <sub>3</sub> N <sub>4</sub> -TiC	4.5	41
Transformation toughening:		
ZrO <sub>2</sub> -MgO	9-12	165-294
ZrO <sub>2</sub> -Y <sub>2</sub> O <sub>3</sub>	6-9	74-165
Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	6.5-15	86-459
Whisker dispersions:		
Al <sub>2</sub> O <sub>3</sub> -SiC	8-10	131-204
Fibre reinforcement:		
SiC in borosilicate glass	15-25	
SiC in LAS	15-25	
SiC in CVD SiC	8-15	
Aluminium <sup>c</sup> :	33-4	
Steel <sup>c</sup> :	44-66	

<sup>a</sup> Assumes a stress of 700 MPa (~100,000 psi).

<sup>b</sup> The strength of these composites is independent of pre-existing flaw size.

<sup>c</sup> The toughness of some alloys can be much higher.

**2.3 Strength variations**

In assessing the capability of a material for a particular engineering application, the generation of design data relative to the operating conditions is essential. Two particularly important aspects of strength properties that have to be considered in designing are:

- (1) Variations in strength for a set of products.
- (2) Time dependent degradation of strength.

One of the distinguishing features of brittle solids is their unpredictable strength behaviour. If two identical sets of metal and ceramic specimens were tested in identical conditions and which had the same mean strength, the data could be presented by a figure, as shown in figure 2, where the frequency of failure at different stress levels are

shown. Whereas no specimen for metals will normally fail below  $\sigma_1$  (see figure 2) which may be within 90 per cent of the  $\sigma_{mean}$ , some specimens of ceramics are expected to fail at as low as 10 per cent of the mean strength (or below). It is this unpredictable behaviour of failure of ceramic materials that prevented their use in engineering applications. To overcome this problem, the statistical variations in strength of brittle solids have been considered equivalent to the probability of failure of a chain at its weakest point. Thus, this statistical variation in strength can be understood in terms of the range of flaw sizes in a piece of material. This is done by applying the Weakest Link Model of Weibull (Weibull Statistics). The failure probability (S) of a chain at its weakest point, which is defined as  $n \times (N+1)^{-1}$  is given by

$$S = 1 - \exp(-K) \tag{6}$$

and 
$$K = V \left(\frac{\sigma}{\sigma_0}\right)^m \tag{7}$$

where n is the n<sup>th</sup> specimen in the order of rank, N is the total number of specimens tested, V is the volume of sample under stress,  $\sigma$  is the applied stress,  $\sigma_0$  is a constant, typical for a material and m is known as the Weibull modulus. Certain materials may have a zero probability of failure up to a stress,  $\sigma_u$  (known as the zero stress), then equation (7), combined with equation (6), becomes,

$$S = 1 - \exp \left[ -V \left(\frac{\sigma - \sigma_u}{\sigma_0}\right)^m \right] \tag{8}$$

The failure probability (S) is related to survival probability P by  $1 - S = P$ . Then equation (8) can be written as:

$$\ln \ln \left(\frac{1}{P}\right) = m \ln (\sigma - \sigma_u) - m \ln \sigma_0 + \ln V \tag{9}$$

A typical plot of  $\log \log (1/P)$  versus  $\log (\sigma)$  which is normally used to calculate 'm', Weibull modulus, the slope of the line, is shown in figure 3.

The value of m, the Weibull modulus, is normally >10 for most ceramics, whereas for metals it is over 50. Thus, the value of m is indicative of the scatter in the strength data. There have been major efforts towards improving the value of m by microstructural control and improved surface finish. Some recent papers have claimed 10/ to have increased the m value for silicon nitride and alumina to ~20. An example of this is shown in figure 4.

**2.4 Time dependent strength (static fatigue)**

This effect has been found to be entirely due to sub-critical crack growth occurring under stress. Failure of brittle solids is essentially due to nucleation of crack (or cracks) and subsequent propagation of these cracks. Sub-critical crack growth is normally assisted by environmental factors. An idealized plot of crack velocity versus stress intensity factor is shown in figure 5.

With respect to this figure the following points should be considered:

(a) There may be a stress level below which no crack growth occurs. However, this stress level is too low to be of any use in structural applications, where the imposed stress is below this value.

(b) There are three stages of crack growth.

(c) In region I, the crack velocity (V) is proportional to  $K_I^n$ , i.e.  $V = A K_I^n$ .

(d) In region II, the crack velocity remains constant but the  $K_I$  value increases. This stage has been identified with a stress induced corrosion mechanism.

(e) At and above  $K_{IC}$  fracture is virtually instantaneous.

### 2.5 Life time prediction

Under conditions where behaviour is controlled either by region I or III (which includes a large number of practical interests) one can calculate the time required for the failure of a ceramic component by using fracture mechanics concepts. The specimen lifetime  $t$  under an applied stress  $\sigma$ , corresponding to an initial stress intensity factor  $K_{Ii}$  is given by 11/12/

$$t = 2 \frac{K_{Ii}^{2-n}}{A \sigma^2 Y^2 (n-2)} \quad (10)$$

If the specimen is subjected to a proof test at a stress  $\sigma_p$ , then the minimum in-service failure time  $t_{min}$  under an applied stress  $\sigma_a$  can be predicted by the following equation 13/

$$t_{min} = \frac{2}{A(n-2) \sigma_a^2 Y^2 K_{IC}^{n-2}} \left[ \left( \frac{\sigma_p}{\sigma_a} \right)^{n-2} - 1 \right] \quad (11)$$

where  $K_{IC}$  is the critical-stress-intensity factor under the proof testing conditions. An S-P-T (time diagram) 14/ for 95 per cent alumina shown in figure 6 and a proof test diagram 12/ for silicon nitride is shown in figure 7.

### 3.0 Elimination of flaw by process control

The major obstacle in using ceramics for critical structural applications is their lack of reliability caused by uncontrolled flaw populations introduced during fabrication. Mechanical reliability has thus become a matter of fabrication reliability. The strengthening that can be achieved by either eliminating or reducing the size of flaw populations through changing either processing or microstructure can be very significant. It is widely recognized that the unreliable behaviour of ceramics is due to the large variation of pre-existing flaw types and sizes. Strength ( $\sigma_c$ ) is proportional to the materials fracture toughness (resistance to crack extension) as measured by the critical stress intensity factor, ( $K_{IC}$ ) and the flaw size (c) of the largest pre-existing crack (or flaw that produces a crack during stressing or testing). The relationship is given by equation (5).

It is well known that flaws are introduced during processing; each processing step, starting with the manufacture of the powder, can introduce one or more strength degrading flaw populations. 15/ Figure 8 schematically illustrates the size frequency of different common flaw populations as a function of potential strength. The order assigned to the different populations in figure 8 is arbitrary, and

depends on both the material and how it is processed. The distribution of strengths for each population will depend on the size uniformity of the inhomogeneity. Different populations can overlap one another. The population that primarily determines the mean strength will be the one that results in the lowest potential strength. Changing processing (or microstructure) to eliminate strength degrading flaw population will increase the mean strength and uncover a new strength determining population. Thus, mechanical reliability is a matter of fabrication reliability which rests with the fabricator who must find new and reliable processing methods that eliminate flaw populations inherent with methods of producing traditional ceramics.

Figure 9 presents the average strength of three transformation toughened materials as a function of the sequential changes made in processing. The progressive strengthening was made by observing fracture surfaces to identify the type of flaw at the fracture origin, relating the flaw to a processing step, and then developing a new processing method that had a high probability of eliminating the strength degrading flaw. This uncovers the next major flaw population which is then treated in the same manner. It should be noted that the flaw type is not always recognizable and once recognized, is difficult to eliminate without innovative processing consistent with processing changes implemented to eliminate previous flaw populations.

The materials used for this study had a high fracture toughness due to stress-induced structural transformation. 16/

The major flaw populations identified and eliminated by process control are as follows:

- (1) Soft agglomerates - are groups of particles held together by mostly Van der Waals forces, which can be easily separated with a surfactant.
- (2) Hard agglomerates - are formed (or retained) when powders are calcined or presintered and then compacted into shapes for sintering.

Note: Since the bulk density of the agglomerates can be different from one another or their surrounding powder matrix, crack like voids can form during sintering due to differential shrinkage. 15b/

- (3) Organic inclusions - lints, fibres, hairs, etc., packed with the powder during consolidation and leave irregular voids when these are burnt out during sintering.

Note: These organic inclusions may arise from bags in which the powder is shipped.

- (4) Inorganic (large) inclusions - these are normally introduced as contaminants during powder manufacture. These inclusions are also commonly observed at fracture origins.

Large second phase inclusions, usually introduced as contaminants during powder manufacture or preparation for consolidation, are commonly observed at fracture origins. Since the thermal expansion and/or elastic properties of the inclusion phase are different from the matrix phase, localized stresses develop within and around the inclusion during cooling the fabrication temperature and/or during subsequent stressing.

When certain conditions are met, a very small flaw at the inclusion/matrix interface can extend into a larger microcrack. Analyses of this problem 17/ have shown that the conditions for microcrack formation not only depend on the magnitude of the maximum tensile stress, but also on the size of the inclusion.

The first step involves both colloidal processing and dry pressing; in the second step colloidal dispersion was used to sediment out the hard agglomerates and then flocced to prevent mass segregation and then dried very carefully. The method used to eliminate flaws produced by organic inclusions was to consolidate the powder by slip casting, burn out the organic matter by heating to a temperature that did not promote sintering, cool to room temperature, iso-press the powder compact to close voids left by organic inclusion, and then sinter. 18/

4.0 Ceramic-ceramic composites

4.1 Partially stabilized zirconia

The first true ceramic-ceramic composite for high technology applications was really discovered by Garvie, 19/ although King and Yavorsky 20/ were the first to draw attention to the fact that partially stabilized zirconia (PSZ) had the capability to relieve stress by localized plastic deformation. Garvie et al. 16a/ were the first to realize that thermal processing of PSZ can give both high stress and toughness, and published a paper in Nature entitled "Ceramic Steel".

A microstructure of a typical tough PSZ ceramic is shown in figure 11. The importance of metastable tetragonal-phase precipitates in a cubic stabilized zirconia matrix for toughening PSZ was noted by Garvie. Various mechanisms have been suggested to account for the strengthening and toughening of PSZ ceramics. This increase in toughness in PSZ has been attributed to the fact that when a crack passes through such a system a significant measure of energy is spent in transforming the tetragonal phase to the monolitic phase.

The most common theory which has been proposed to explain the  $K_{IC}$  values for PSZ is as follows:

$$K_{IC} = K_{matrix} + 2\sigma_A \left( \frac{2r_p^*}{\pi} \right)^{1/2}$$

where  $K_{matrix}$  = fracture toughness of matrix

$r_p^*$  = radius of "Process Zone" ahead of the crack-tip

The second term of the above equation is similar to the plastic zone approach taken by Swain to explain fracture toughness in ductile metals.

In their evaluation of  $r_p^*$ , Porter, Evans and Heuer 22/ incorporated the  $M_s$  temperature (martensitic transformation temperature, which depends on particle size, orientation, composition) and the free energy term into a constant (688). Their equation is as follows:

$$r_p^* = 1/2 \left( \frac{K_{IC}}{688} \right)^2 \left[ \Delta G_{1j}^T f_{1j}(\theta) \right]^2$$

The increase in toughness due to transformation alone can be expressed in terms of transformation zone. 23/

$$\Delta K_{IC} = e_{1j}^T E V_f^{1/2} f(a/h, v)$$

where  $V_f$  = volume fraction of transformed particles  
 $f(a/h, v)$  = function of the crack length to zone thickness  
 $E$  = Elastic modulus

The fracture toughness of fully stabilized zirconia is  $\sim 3 \text{ MPa}\sqrt{\text{m}}$  and the partial stabilized zirconia (MgO-PSZ-8.1 mole% and 25 vol% tetragonal phase) is  $6 \text{ MPa}\sqrt{\text{m}}$ . It is in the same order as predicted by the above equation.

4.2 SiC whisker reinforced ceramics

The partially stabilized zirconia materials can only be used up to a temperature of  $\sim 1000^\circ\text{C}$ , limiting its use to only certain applications. However, this development has led to new ideas of developing tough ceramics using a reinforcing phase, such as strong particulates - platelets, whiskers, etc. Thus, ceramic-ceramic composites incorporating SiC whiskers are extremely attractive materials for possible high temperature structural applications.

The increase in fracture toughness of alumina by addition of SiC whiskers is shown in figure 10. This significant increase in fracture toughness in ceramic-ceramic composites has been attributed to:

- (a) Crack bowing and deflection;
- (b) Crack branching;
- (c) Microcracking of the matrix phase;
- (d) Debonding at the interface of fibres-ceramic matrix;
- (e) Fibre pullout;
- (f) Transformation toughening (if such a phase exists in the composite).

Schematic representations of some of these proposed mechanisms are shown in figures 11 (a-f), and validity of some of these mechanisms have been confirmed experimentally.

Lately there has been considerable theoretical work 24/ to quantitatively correlate the increase in fracture toughness with the proposed mechanisms, especially by debonding and fibre pull-out.

5.0 Advanced ceramic research activities at U.B.C.

Research activities in advanced ceramics can be divided into three groups:

- (1) Plasma synthesis of powders (SiC,  $\text{Si}_3\text{N}_4$ , AlN,  $\text{B}_4\text{C}$  etc.).
- (2) Ceramic-ceramic composites.
- (3) Ceramic superconductors.

5.1 Plasma synthesis activities at U.B.C.

The activities on plasma synthesis of advanced ceramic powder at U.B.C. were started about three years ago for two reasons: (i) the lack of availability of well-characterized sinterable SiC and  $\text{Si}_3\text{N}_4$  powders and (ii) a literature survey

revealed a large number of problems associated with plasma synthesis of powders providing significant research opportunity. Our objectives were therefore twofold; in addition to synthesis of powders we attempted to solve some of the problems encountered in plasma synthesis, especially in the powder collection and handling systems. A 15 kW arc plasma reactor was designed and constructed, the schematic diagram of which is shown in figure 12. Different advanced ceramic powders will be produced as summarized in table 4.

5.1.1 Problems associated with plasma synthesis and possible solutions

In spite of considerable progress over the past two decades on the plasma synthesis of advanced powders, there are a large number of problems which remain to be solved. Before this process can be commercialized, some of these difficulties must be overcome.

**Conversion efficiency.** The conversion efficiency of the reactants in a plasma reactor is not very good. In most publications the conversion efficiency was rarely reported. In our dc arc plasma reactor (1) the maximum yield of SiC powder from a mixture of SiCl<sub>4</sub>+CH<sub>4</sub> was in the order of 55 per cent (silicon basis). The torch thermal efficiency has been reported to be in the order of 80 per cent. This does not imply that this energy, although available, is really used in the formation of the product. We have also calculated the torch efficiency of our plasma reactor, which is in the order of 80 per cent. More fundamental work is needed to increase the yield of the reactors.

**Productivity.** Most of the experimental reactors have ~ 50 kW power supply, producing a few gms of SiC or Si<sub>3</sub>N<sub>4</sub> powder per minute, although a US patent claimed 10-12 gms per minute of SiC powder production.

Table 4

Summary of reactants and chemical reactions for each powder

Powder	Raw Materials	Plasma Chemistry	Proposed Reactions
AlN	Al powder, N <sub>2</sub> , NH <sub>3</sub>	Nitriding	Al <sub>2</sub> +1/2N <sub>2</sub> or NH <sub>3</sub> = AlN, Al <sub>2</sub> +1/2N <sub>2</sub> or NH <sub>3</sub> = AlN,
TiN	TiH <sub>2</sub> or Ti powder, N <sub>2</sub> , NH <sub>3</sub>	Nitriding	Ti <sub>2</sub> +1/2N <sub>2</sub> or NH <sub>3</sub> = TiN, Ti <sub>2</sub> +1/2N <sub>2</sub> or NH <sub>3</sub> = TiN,
TiC	TiH <sub>2</sub> , Ti or TiO <sub>2</sub> powder, CH <sub>4</sub> or C <sub>2</sub> H <sub>2</sub>	Carburizing	TiH <sub>2</sub> +CH <sub>4</sub> = TiC <sub>1</sub> +3H <sub>2</sub> Ti <sub>2</sub> or Ti <sub>2</sub> +CH <sub>4</sub> = TiC, TiO <sub>2</sub> +3CH <sub>4</sub> =TiC <sub>1</sub> +3CO <sub>1</sub> +12H <sub>2</sub>
TiB <sub>2</sub>	ferrotitanium, ferroboron	Neutral	Ti <sub>sol</sub> +B <sub>sol</sub> = TiB <sub>2precipitate</sub> (Ti and B in solution in Fe.)
B <sub>2</sub> C	B or B <sub>2</sub> O <sub>3</sub> powder, CH <sub>4</sub> or C <sub>2</sub> H <sub>2</sub>	Carburizing	4B+CH <sub>4</sub> = B <sub>2</sub> C+2H <sub>2</sub> 2B <sub>2</sub> O <sub>3</sub> +7CH <sub>4</sub> =B <sub>2</sub> C+6CO+14H <sub>2</sub>
WC	W or WO <sub>3</sub> powder, CH <sub>4</sub> or C <sub>2</sub> H <sub>2</sub>	Carburizing	W <sub>2</sub> or W <sub>2</sub> +CH <sub>4</sub> = WC <sub>1</sub> +2H <sub>2</sub> WO <sub>3</sub> +4CH <sub>4</sub> = WC <sub>1</sub> +3CO+8H <sub>2</sub>
TaC	TaO <sub>2</sub> powder, CH <sub>4</sub> or C <sub>2</sub> H <sub>2</sub>	Carburizing	TaO <sub>2</sub> +3CH <sub>4</sub> = TaC <sub>1</sub> +2CO+6H <sub>2</sub>
SiC	Si or SiO <sub>2</sub> powder, CH <sub>4</sub> or C <sub>2</sub> H <sub>2</sub>	Carburizing	Si <sub>2</sub> or Si <sub>2</sub> +CH <sub>4</sub> = SiC <sub>1</sub> +2H <sub>2</sub> SiO <sub>2</sub> +3CH <sub>4</sub> = SiC <sub>1</sub> +2CO+6H <sub>2</sub>



One of the difficulties encountered in increasing the productivity of the rf torch is the problem of quenching the flame when it is loaded with a very high concentration of reactants. In order to overcome this problem, the hybrid plasma torch was developed with the intention of using the DC arc to start and stabilize the RF component of the torch.

**Collection system.** Another major difficulty which prevented large scale and continuous production of powder was the collection system. The regular glass-filter system normally got plugged-up, resulting in back-pressure shutting down the reactor system. Multiple parallel glass-filter systems may help to overcome this problem, but one of the most convenient collection systems is a high boiling point organic fluid system. Using a fluid collection system coupled with a heat exchanger, as shown schematically in figure 11, the plasma reactor can be run continuously. We have been able to run such a system for more than an hour. With some modifications, in which fresh fluid can be injected into the system, while some of the fluid with suspended powder can be withdrawn, the system made can be designed for continuous operation.

**Oxygen free powder.** Benefits of fluid collection systems are manifold. It has been known for a long time that very fine particles of SiC and Si<sub>3</sub>N<sub>4</sub> oxidize very easily even at ambient temperatures, even if they can be made oxygen free in the reactors. The collection of powder in an organic fluid resulted in coating the particles with the fluid and it appears that some type of reaction occurred with the particles. A thermogravimetric analysis of such a powder shows that this organic reactant can only be removed at ~370°C. This organic layer prevents immediate oxidation of particles and can be retained for a considerable period of time if the powder is kept in a fluid such as hexane.

**Handling and packing of ultrafine powder.** It is well known that ultrafine powder is very difficult to handle and also to compact. Ultrafine powders of SiC and Si<sub>3</sub>N<sub>4</sub> also pose a health hazard. Collection of ultrafine powders using a fluid within the reactor itself eliminates all these problems. For example, the 40-100nm powders of SiC were found to be easy to handle, as no particles were found to be floating in air. The powder collected with an organic fluid was subsequently washed with a solvent, such as hexane, and filtered on a glass filter (while exposed to air). The powder, as obtained on the filter paper, was in the form of a cake. This cake can be dried and lightly pulverized and compacted to 0.5 to 0.6 of the relative density at a very moderate pressure (200 MPa). Thus, the powder collection by a fluid eliminates both the handling and compaction problems.

#### 5.1.2 Powder production and characteristics

The particle size distribution of SiC powder produced in our plasma torch using SiCl<sub>4</sub>+CH<sub>4</sub> is shown in figure 13 (a) and similarly AlN powder produced using Al powder and NH<sub>3</sub> is shown in figure 13 (b).

We are currently working on doping and sinterability of these powders.

#### 5.2 Ceramic-ceramic composite activities at U.B.C.

Silicon carbide whiskers are carcinogenic and considerable precautions, and innumerable steps have to be taken to uniformly distribute the whiskers in

alumina or other matrices (mostly done by colloidal processing). Although mostly theoretical predictions and experimental tests for increase in toughness are made on the basis of whisker toughening, the potential for SiC platelets toughening has not been thoroughly studied. At U.B.C. we are investigating both the SiC platelets and SiC whiskers in Al<sub>2</sub>O<sub>3</sub> toughening and trying to compare these effects. Preliminary indications are that platelet toughening may be as effective. We are also investigating *in situ* formation of SiC in Al<sub>2</sub>O<sub>3</sub> by converting SiO<sub>2</sub> in aluminosilicate systems 25/ (both natural and synthetic). Other studies in this field are on the kinetics of sintering and hot-pressing of Al<sub>2</sub>O<sub>3</sub> with a second phase. It is known that the presence of a second phase in alumina impedes sintering as shown in figure 14.

In the presentation more results will be given to illustrate some of the activities at U.B.C.

#### 6.0 Future of advanced structural ceramics

With the development of high strength (>700 MPa) ceramics incorporating high toughness (~7 to 10 MPa√m), there is no doubt that the prospect of utilizing these materials in critical structural applications, such as in automobile engines, is very good.

Because of the high rejection rate (20 to 30 per cent) of monolithic ceramics after fabrication, these components are still not cost effective. However, significant improvement has been made over the last five years. The prognosis is that over the next five years, the use of ceramic-ceramic composites (which are less sensitive to inherent flaws) will result in further reduction (from original 50 to 70 per cent to current 20 to 30 per cent to ~10 per cent) of rejection during proof testing. If this goal can be achieved, ceramic components will be definitely used in different types of engines, which would eventually result in so-called "ceramic-engines".

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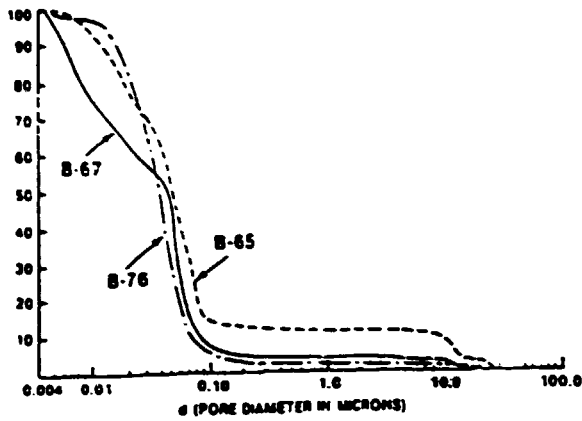


Figure 1: Typical pore size distribution for RBSN (from Rolls Royce Ltd. Report 1971). (8).

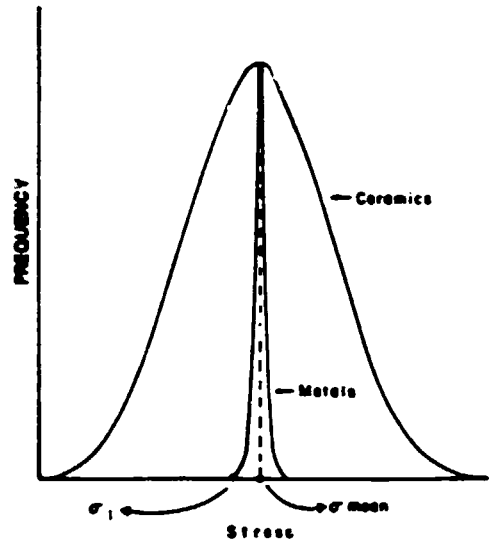


Figure 2: Schematic plot of frequency of failure vs. stress.

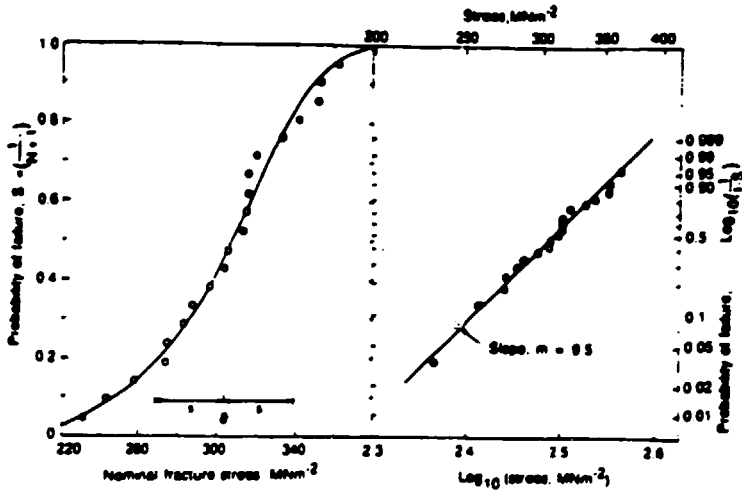


Figure 3: Typical failure analysis for ceramic bend test pieces (after Morrell). (9)

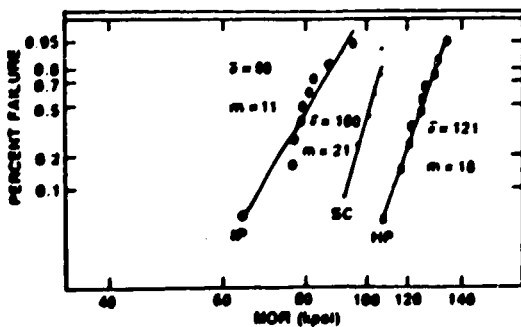


Figure 4: Strength distribution of dense silicon nitrides. (IP-isopressed, SC-slip cast and HP-hot-pressed). (10).

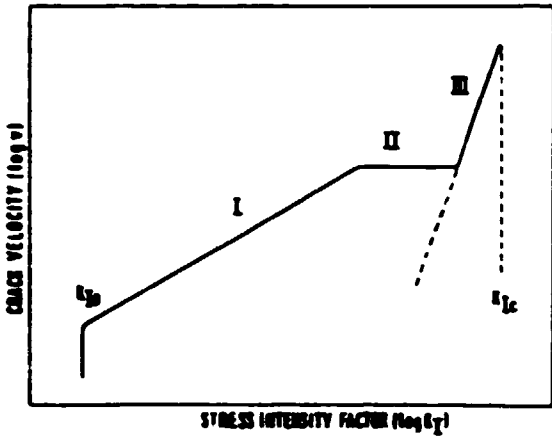


Figure 5: Typical V-K plot for ceramics.

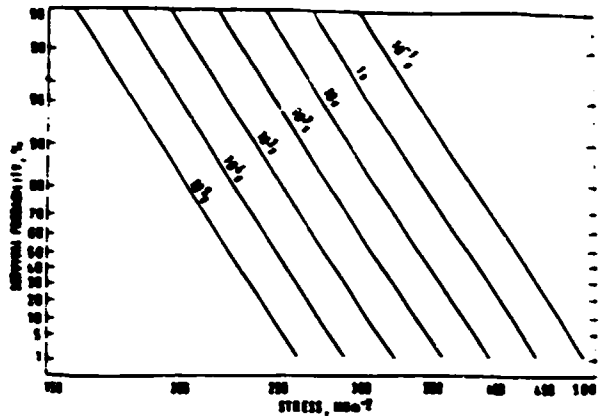


Figure 6: Strength-Probability-Time diagram for alumina. (14).

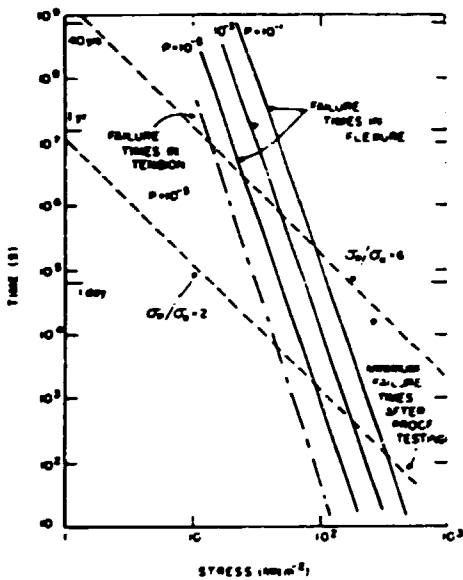


Figure 7: Probability related failure time for high purity  $Si_3N_4$  after proof testing at twice and six times of service stress. (12).

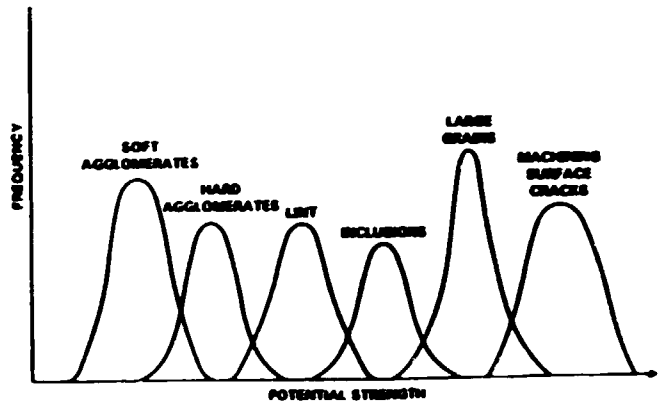


Figure 8: Common flaw population distribution. (15).

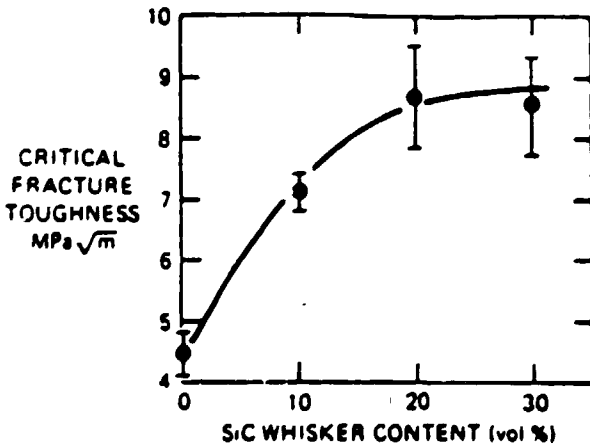


Figure 10: Increase in fracture toughness of  $Al_2O_3-SiC_n$  composites with increasing whisker content. (26).

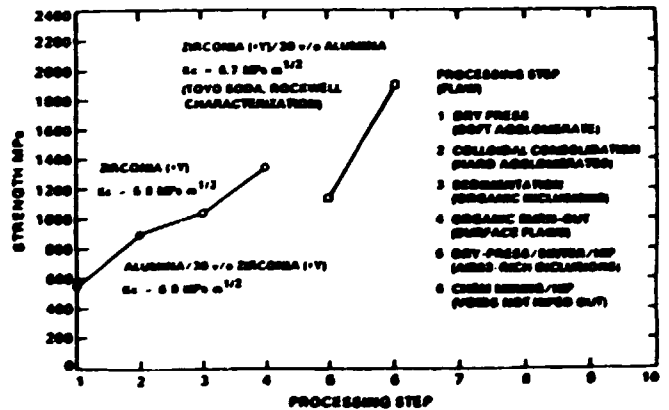


Figure 9: Increase of fracture strength due to elimination of flaw populations by processing steps. (15).

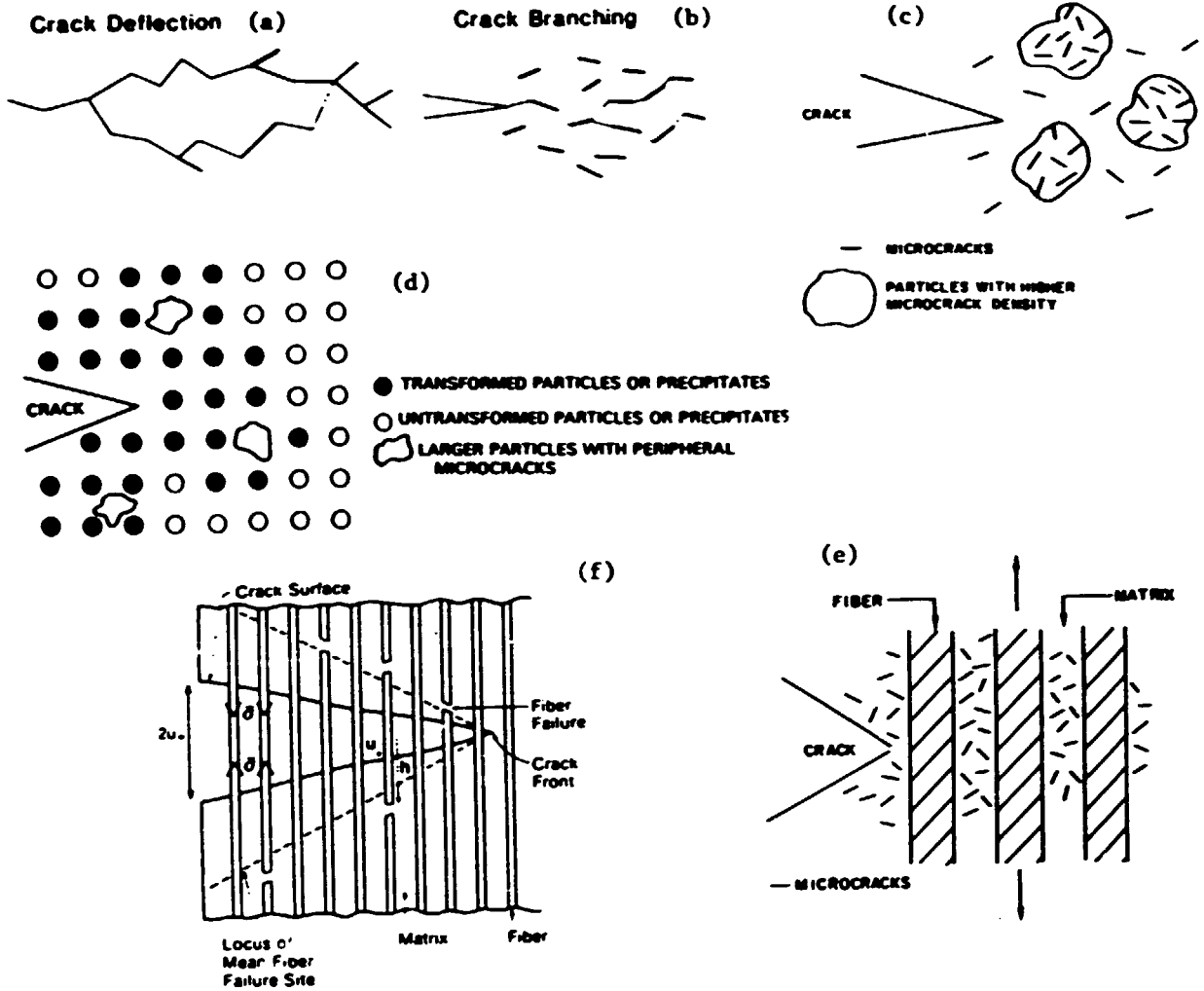


Figure 11 (a-f). Proposed mechanisms for increase in fracture toughness with the addition of a second phase.

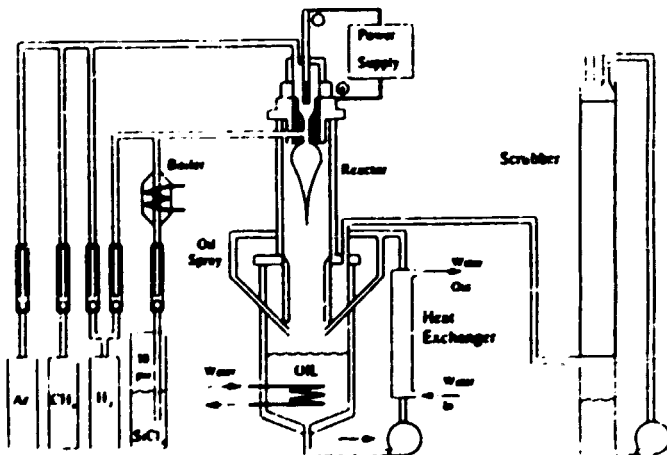
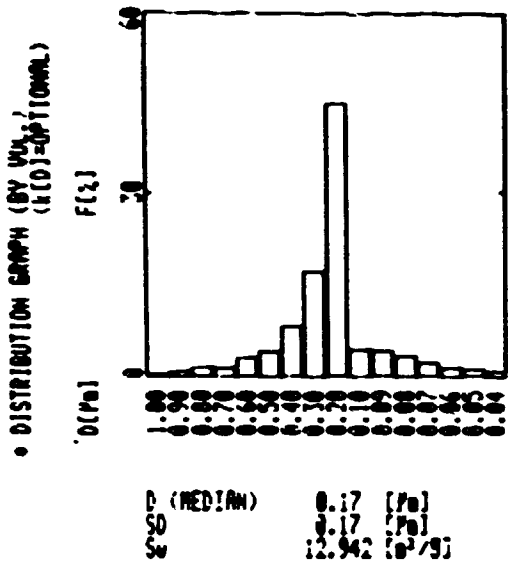
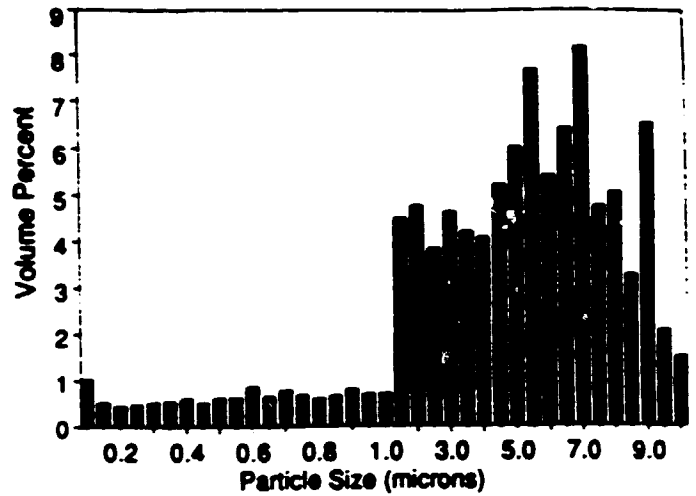


Figure 12: Schematic diagram of U.B.C. DC plasma torch.



(a)



(b)

Figure 13: Particle size distribution of plasma synthesized ceramic powder, (a) SiC powder, (b) AlN powder.

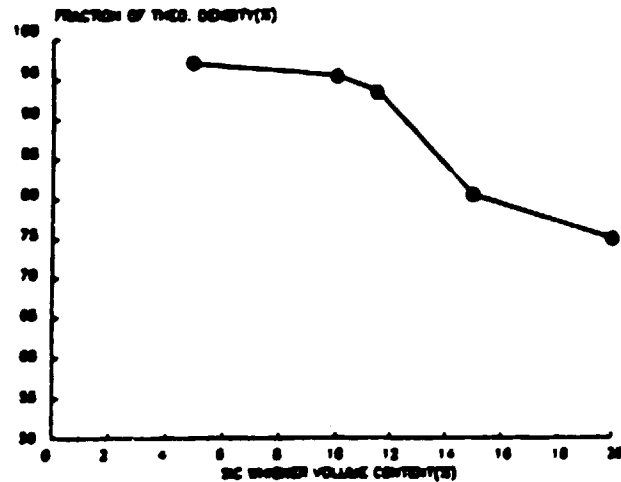


Figure 14: Pressure has sintering of alumina - SiC<sub>v</sub> composites. (26).

### 3. CERAMICS AS HIGH-TECHNOLOGY MATERIALS

Just as in pottery, advanced ceramics of the twentieth century are also formed by "calcination" at high temperatures. This involves sintering, a sort of "compacting" of fine oxide, carbide or nitride powders produced by synthesis using raw materials such as quartz clay, kaolin and feldspar as base. The development of the electronics and aerospace industries has only been possible through the growth of advanced ceramics sometimes called fine, technical, special, or even engineering ceramics. Computers, solar collectors, nuclear and chemical reactors, spacecraft, and even terrestrial engines, are all examples of equipment or devices that have benefited from advances in new ceramics over the past 30 years or so. This will also be the case in regard to the technologies of the twenty-first century. This type of material of the future divides for the moment into two principal groups: structural ceramics, and electronic and electro-technical ceramics, also called functional ceramics.

#### Structural ceramics

This type of ceramic material, which includes nitrides, carbides, aluminium oxide of alumina ( $Al_2O_3$ ) and zirconium oxide or zirconia ( $ZrO_2$ ), is also called thermomechanical because of resistance to thermal and mechanical shocks, and has exceptional characteristics (see table 1 on page 30).

#### Functional ceramics

A large number of functional ceramics, such as the silicon used in semiconductors, have microstructures which allow the passage of electrons if they are excited. This is the case of cobalt and zirconium oxides and the phenomenon is employed in a wide range of functions - hence the name - especially in the use of various sensors, varistor etc. (see table 2 on page 30).

#### Ceramics for engines

Many of the structural ceramics have a better resistance to high temperatures than superalloys, even above  $1000^\circ C$ , as well as to natural wear and corrosion under severe weather conditions. They are, for the most part, half as dense as modern-day steels, so much so that the ceramic parts of automobile or aeroplane engines reduce engine weight considerably, thus resulting in fuel economy. The weight of a cooling system can also be dispensed with in an engine even partially ceramic, thanks to the excellent thermal conductivity of this material leading to rapid heat elimination. This is a characteristic which has already been used in aluminium oxide or nitride casings to carry away the heat given off by micro-miniaturized electronic circuits.

One of the oldest ceramic products, though not quite belonging to the class of high-performance ceramics, is the sparking plug in internal combustion engines. In fact, it is still the automotive industry, with its demands for more efficient engines with lower emissions and multi-fuel capability, which is leading the development. New material concepts have had to be adopted to meet increased requirements made on different engine parts. And higher operating temperatures are aimed at in order to raise the efficiency of engines. Here, ceramic materials have proved to be superior to metals.

It is silicon nitride that is used to the greatest extent, particularly in the turbocompressor turbines of diesel engines, for the insulation of the hot parts of the engines, or for parts subject to friction and heavy wear. The operating conditions are then much higher with the turbine operating at up to 15,000 rpm. Whatever the type of engine, operation at higher temperatures means improved efficiency; engines are also much lighter inasmuch as certain versions have no need of a cooling system. The Japanese estimate that the penetration of ceramic parts in their engines will be about 7 to 8 kg by 1992, with the Europeans using only around 1 to 2 kg; this process is then still very slow.

#### High-temperature ceramic materials for the superconductor industry

Although many companies in the superconductor industry have great expectations for high-temperature superconductive ceramic materials, they are still plagued by two problems. Superconductive ceramics are very brittle and hard to work with, and they cannot carry large electrical current, which is the key to generating strong magnetic fields. Several companies are working to improve the current flow of ceramic superconductors, but with limited success. Both the Americans and the Japanese have made very thin films, a micron or less in thickness, with current capacities comparable to niobium alloys. However, the usefulness of such films as bulk current-carriers is very doubtful. As a result, materials research increasingly focuses on learning more about the properties of ceramics' high-temperature superconductivity. Because of its hefty cost, such fundamental research remains primarily with large companies who are also developing techniques for large-scale production of superconductive ceramics.

#### Ceramic wires and tapes

Wires and conducting tapes are essential if ceramic superconductors are to become useful products. Therefore, a number of companies in the US, Europe and Japan are attacking this problem. A US firm, one of the front-runners in the race, makes flexible ribbon from superconductive materials by mixing them with molten silver, then putting the mixture onto a chilled spinning wheel. The metal rapidly solidifies and rolls off the wheels as continuous ribbon. Backed by \$4 million in venture-capital funding, the company is now running a pilot plant and claims it will begin selling its superconductive tape very soon.

#### Ceramic coatings, thin films and electronics

Ceramics can easily be formed into coatings and thin films that can be processed with standard microelectronic fabrication techniques used to make silicon chips. Ceramic coatings already have been used to produce electronic devices such as SQUIDS in laboratories by American and Japanese companies. But many technical difficulties remain. For example, ceramic SQUIDS are as much as 1,000 times less sensitive than their niobium counterparts.

A US firm engaged in superconductor electronic research is studying the use of ceramics not in chips, but in electronic inter-connects that would tie conventional computer chips together. Superconductive ceramics would provide much faster

signal transmission between chips in a multiple-chip device.

In yet another attempt to apply superconductive ceramics to electronics, another US firm is developing coatings that would provide electronic shielding for supercomputers. The coating would absorb signals generated by the computer which, when picked up by an outside receiver, can be deciphered to reveal its computations - a threat to security. The computer already uses liquid nitrogen to chill its circuits, setting up the perfect environment for ceramic superconductor coating. Because of this synergism, shielding is expected to be one of the earliest commercial products from the new ceramics.

#### The emergence of ceramic composites

Although most advanced ceramic materials, such as the bricks used in a furnace, are refractory and can withstand very high temperatures, rapid temperature variations or thermal shocks cause them to crack as easily as a simple plate. This is also the case with mechanical shock. One of the weak points is, in fact, a low ductility, or expansion coefficient, with a possible lengthening of only 0.1 per cent, whereas modern steels stretch several percentage points before breaking. This poor ability to sustain deformation without fracture due to the rigidity of this very hard material can even be seen when two ceramic pieces are bolted together: in most cases, they break. This "Achilles' heel", the fragility of ceramics - above all, of structural ceramics - is at the origin of the development of composites. The French have acquired a good deal of know-how in this field; the Americans have been working in this area for only a few years, whereas the Japanese, right from the beginning, have remained faithful to structural ceramics which are commercially profitable, especially for engine parts.

The ceramic composite is formed from a matrix with the inclusion of fibres. Tailor-made, so to speak, it has the advantage of allowing the use of the advantageous characteristic of ceramics "combined" in this way for a given application. The SiC-SiC composite for thermomechanical applications is one example, and the zirconia-fibre reinforced aluminium oxide cutting tool is another. In the chemical formula of a composite, SiC-SiC, for example, the first silicon carbide represents the fibres and the second, the matrix material.

Composites have aroused considerable interest, for they possess a toughness two to three times greater than many structural ceramics. But their industrial production is even more difficult for a great many reasons. Successful marriages of matrix and fibre are not numerous, the problem of interfaces being difficult to overcome. Manufacturing is a long and complex process, especially when it involves complicated parts with great differences in thickness. Few materials are, as yet, manufactured in the form of fibres. They are rare, expensive, and their quality is not always satisfactory.

However, shorter monocrystalline fibres (whiskers) are easier to use. There is already a promising manufacturing technique for silicon carbide whiskers using controlled combustion of a product which is very rich in calcium - rice husks. But, generally speaking, the new fibres currently available lose their properties at the high temperature necessary for sintering with the matrix to form the composite part.

The development of composites is thus for the moment still too expensive for civil applications, and is limited to the military and aerospace fields,

where cost is of secondary importance; ceramics, moreover, cannot be detected by radar. Current programmes in the US, for instance, concern three types of composites in the main: composites with a ceramic matrix, those with a metallic matrix and ceramic fibres, and carbon-carbon composites.

Already, the 33,000 tiles made from silica fibre covered with borosilicate or silicon carbide have made the American space shuttle's re-entry into the atmosphere possible by limiting wall-heating to 180°C, whereas friction produces more than 1,200°C. The thermal barrier of the future will perhaps be a ceramic composite made of borosilicate fibre in an aluminium oxide (alumina) matrix. Of particular note is the Alumina Enhanced Thermal Barrier (AETB) currently being developed by the Americans as much for the space shuttle as for the aerospace industry.

In fact, it is the metallic matrix composites that have been developed for aerospace and aviation applications in the United States and Europe, even if the heat-shield for the European space shuttle Hermes is to be made entirely in SiC-SiC ceramics. The European Space Agency is concentrating, in co-operation with several companies, on the research and development of composites with a matrix in aluminium, magnesium or titanium, and silicon carbide, graphite, or boron fibres.

#### High performance ceramics for construction purposes

The last two decades have seen innovative designs ranging from high technology structures to consumer goods being driven by advancements and exploitation of increasingly higher performance materials. Many examples could be found which illustrate that innovative structural designs are often made possible in the construction industry by the availability of high performance materials. Steel reinforcement, for instance, made possible the design of taller buildings with concrete. Recent years have seen improvement in concrete properties and the arrival of reinforced and several types of specialized concrete. However, the use of these concrete-based materials is not trouble-free. In contrast, high-performance ceramics, as a construction material, are found to have several advantages over concrete:

- Improved durability against freeze-thaw action, due to possibility of much better controlled porosity;
- Improved durability against chemical (chloride sulphate) attacks, as proper choice of ceramics could be inert to these chemicals;
- Improved durability against mechanical wear due to ceramic hardness and wear resistance;
- Higher elastic stiffness, compressive and tensile strength and modulus of rupture;
- Higher dimensional stability in certain glass ceramics, resulting in reduction in thermal cracking related to temperature cycling;
- Higher temperature resistance, which may be useful to prevent heat spalls, such as due to hot jet exhaust on airfield pavements from vertical takeoff/landing aircraft.

The market for ceramics in the construction industry derives from the need to address current construction problems as well as to position for future innovative structural designs. The



mechanisms in which ceramics may be initially introduced into the construction market involves simple substitution of materials, applications in structures operating under demanding environments, and in the possibility of fundamental changes in construction (see table 3 on page 30).

#### Challenges in research

Ongoing and future research directly related to the application of ceramics in construction may be divided into five major areas:

##### Research in processing

Research emphasis is on the low-temperature synthesis of ceramics. One of the main reasons for the high processing cost of ceramics is the large demand of energy for high-temperature processes. Various techniques for low-temperature ceramic powder production have been successfully developed in the laboratory.

##### Improvement in mechanical properties

As mentioned earlier, while very strong, most ceramics are also very brittle, with fracture toughness ranging from  $0.5-5 \text{ MPa}\sqrt{\text{m}}$  (concrete has  $0.1-0.2$ ). Among the toughening mechanisms presently available, the most promising appears to be fibre reinforcement, which gives over  $20 \text{ MPa}\sqrt{\text{m}}$ . Also, fibre reinforcement is more generally applicable as mechanisms like transformation toughening and micro-crack toughening only occur in some special ceramic systems. As a reference, structural steels range from  $20-200 \text{ MPa}\sqrt{\text{m}}$ . However, the technology trend is such that the toughness will continue to be improved over the next several years.

With advantages discussed above, fibre-reinforced ceramics is probably the most prospective group of ceramic materials to be developed for use in construction.

##### Performance evaluation of ceramics under severe conditions

Most initial applications of ceramics in construction are expected to be under severe conditions such as high thermal blast, large range of temperature cycling, heavy traffic or corrosive environment. The performance of ceramics under such conditions is being studied to work out techniques for further improvement of ceramic properties under severe environments.

##### Development of new techniques in construction

To carry out actual construction with ceramics, new construction techniques have to be developed. Research issues include the joining of prefabricated ceramic parts, the possibility of *in situ* processing of ceramics with good quality control and the application of ceramic layers on other construction materials (e.g. chemical tanks). Research has already been carried out on the joining of ceramics and on the coating of ceramics on metals. These findings may be exploited in the research of ceramic construction components.

##### Innovative ideas in the application of ceramics in construction

Besides its use as a structural material, the full potential of ceramics should be exploited. New ideas that can use ceramics to full advantage should be developed. Two examples of such innovative ideas have been included in table 3 under item 3 on page 30.

#### Prospects of ceramics in construction

While cost-performance comparison has shown that for some applications the use of ceramics is actually more economical than concrete in the long run, the initial cost of ceramics is at present still too high for it to be widely used. However, the past decade has witnessed the reduction in ceramics cost with volume produced, the increase in ceramics toughness through better understanding of toughening mechanisms, as well as the success of processing techniques at increasingly lower temperatures. These are all encouraging facts which strongly suggest that in the future ceramics with better performance can be produced at a much lower cost.

Continued research on processing and toughening of ceramics, as well as research on special issues relating to construction, are expected to gradually bring about the widespread use of ceramics in the construction industry.

#### Co-operation in advanced ceramics research: the European example

In Europe well-known industries as well as groups recently set up for the purpose, together with official research laboratories and universities in various countries, have been working hand in hand in the domain of advanced ceramics. This co-operation is being stepped up, especially in the context of the European Economic Community's "EURAM" and "EUREKA" programmes which have been operating for almost three years.

"EURAM" (European Research on Advanced Materials) brings together the partners that are developing such materials, and is concerned with stimulating research in Europe so that countries may equip themselves with the means of producing sophisticated materials, instead of importing them or manufacturing them under Japanese or American licence. Among the three major fields of co-operation, two concern advanced ceramics: high-temperature internal combustion engines and gas turbines, and composites with different types of matrix materials for aviation and biomedical uses. The initial budget is only 30 million Ecus, but once the programme is well under way, funds for the projects will probably increase quite considerably.

At the end of 1987, "EUREKA" consisted of 165 projects launched jointly by 19 European countries, their funding amounting to 4.3 thousand million Ecus. Technical ceramics quite logically form part of this venture. European researchers are also collaborating on a number of other projects. These include: (i) development of new ceramic materials for "the car of the future" with better bodywork and structural design; (ii) a ceramic diesel engine using SiC-SiC composite; (iii) two low-output radial gas turbine ceramic prototypes; and (iv) small ceramic aero-engines in the medium power range.

#### Present markets and the future

As for functional ceramics, they have made rapid strides since 1980, to a much greater extent than structural ceramics, even in engine applications. Constraints in their use are, in fact, much less severe than those of structural ceramics, and more than electronics. In fact, several European industries are finally following in the footsteps of Japan and the US. The present world market stands at somewhere around \$25 thousand million. Structural or thermomechanical ceramics

cover only 25 per cent of this market, the lion's share going to functional ceramics; the future market for these ceramics is, moreover, very promising, according to forecasts in these two countries.

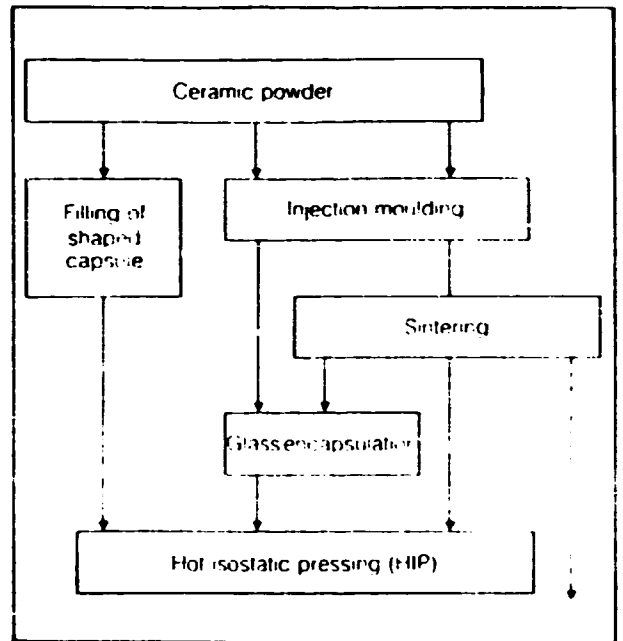
**Postscript**

Many of the developing countries are among the world's principal producers of metals and raw materials such as copper, bauxite, zinc, lead, iron ore and tin. They are finding that in the rush for leaner, less-materials-intensive production in the United States, Japan and Western Europe, their industries and institutions are farther than ever from the cutting edge of technology, and that the economies of some nations are immediately threatened by the declining demand for raw materials. Some fear that a new industrial wave, made possible by metal composites, polymers, glass fibres and ceramics, will impact on their markets for traditional metals in much the same way as petroleum-based synthetics overran commodities like rubber, cotton and fibres three decades ago.

It is expected that by the turn of the century, fibre-reinforced composites or aluminium lithium alloys will have replaced most of the conventional alloys in aircraft structure, and ceramics are likely to replace metal turbines in aircraft engines. Because of their hardness and high-temperature strength, cutting tools made from silicon nitride-based materials are reducing machining costs in industry. The wear and corrosion of metallic parts in machinery has been estimated to cost the US more than \$10 billion a year, and the expanded use of ceramics in components like seals and bearings seems assured.

The quantum leap in the development of new materials like advanced ceramics and innovative manufacturing processes in the industrialized world has made the threat of a possible decline in the demand for commodities very real. The developing countries are beginning to realize the need for

joining forces in evolving appropriate mechanisms to alert them on the new frontiers of technology of the benefits they offer as well as the dangers they pose to them as primary commodity producers.



*A Swedish firm, one of the world leaders in advanced engineering ceramics, has developed and commercialized the technology for glass encapsulation and hot isostatic pressing (HIP) of advanced ceramic components. With the technology it is possible to manufacture near net shape components, such as integrated turbine and turbocharger wheels, from silicon nitride powder. This process is also being used increasingly for critical wear parts used in, for example, flu gas cleaning systems and the textile industry.*

(Source: Asia-Pacific Tech Monitor, May-June 1989)

**TABLE 1: STRUCTURAL CERAMICS**

Characteristics	Materials	Uses
<b>Mechanical properties</b>		
Resistance to high temperatures	Nitrides	Gas turbines
Resistance to friction	Alumina, boron carbide	Diesel engines
Resistance to shearing	TiC, TiN, CW, carbon boron	Cutting tools, heavy duty parts
Lubricants	Boron nitride	Solid lubricants, friction parts, bearings
Armour plating	Alumina, carbides	Military and other applications
<b>Thermal properties</b>		
Thermal resistance	Carbides, nitrides, MgO	MHD (Magneto hydrodynamics)
Thermal insulators	Potassium oxide, titanium oxide, alumina, zirconia	Industrial furnaces, heat shields in nuclear power stations
Thermal conductors	Boron oxide, carbides, aluminum nitride, alumina	Electronic equipment elements, radiators

**TABLE 2: FUNCTIONAL CERAMICS**

Characteristics	Materials	Uses
<b>Electrical properties</b>		
Electrical resistance	Alumina, carbides, beryllium oxide	Semi-conductor sockets
Piezoelectricity	Lead zirconates and titanates, PLTZ, perovskites, lithium niobates, quartz, lanthanum chromates	Electric oscillators, printers, ignition devices
Electrical conductors	Zirconia, carbides	Exothermal resistors, miniature capacitors
Dielectrics	Beryllium titanate, strontium titanate	High-voltage capacitors
Ionic conductors	Zirconia, alumina	Oxygen detectors, solid electrolytes
Semi-conductors	Zirconia, beryllium titanate	Gas detectors, solar batteries, varistors
Electron emitters	Lanthanum boride	Electron cathode guns, flat screens
<b>Magnetic properties</b>		
Magnetic quality	Fe <sub>2</sub> O <sub>3</sub> , MnO, BaO	Ferrites, magnetic recording, data storage
<b>Optical properties</b>		
Transparency	Alumina, yttrium oxide, MgO	High temperature optical lenses, sodium lamps
Optical transmission	SiO <sub>2</sub>	Optical fibres, internal observation, cameras, optical detectors
Polarizers	Zirconium oxide, titanium oxide, lead oxide, lanthanum oxide	Optical memories (reversible)
Fluorescence	Rare earth ceramics and potassium arsenide, Nd glass, YAG	Semi-conductor lasers, luminescent diodes
Photosensitivity	Silver halogenated glass	Lens shield glass, image storage
Infrared optics	Chalcogenide, fluoride glass	Military and other applications
<b>Biological properties</b>		
Chemical properties	Alumina, apatites	Artificial teeth, prostheses, artificial bones
Absorption	Multiporous silica, multiporous alumina glass	Absorbants, catalysers, bioreactors
Catalysis	Zeolites	Catalysers for environmental protection
Anticorrosion	Zirconia, alumina	High temperature reactors

**TABLE 3: PROPOSED APPLICATIONS FOR ADVANCED CERAMICS IN CONSTRUCTION USING THREE MECHANISMS OF INTRODUCTION**

Mechanism	Applications
(1) Simple substitution	Road pavement and bridge decks, fire protection for steel, pipe and pipe linings
(2) Demanding environments	Airfield pavements (esp. those for vertical take off/landing aircraft), walls for engine testing facility and other high heat environment, structures in marine or severe industrial atmosphere, arctic, offshore and space structures, vessels, reactors and conduits for high purity and hazardous substances
(3) Fundamental changes in construction	Self monitoring containment or reactor (employing the ability of some ceramics to detect the presence of particular ions), chloride trapping bridge deck (some ceramics can trap chloride ions)

(Source: Asia-Pacific Tech Monitor, May-June 1989)

#### 4. NEW ACHIEVEMENTS AND DEVELOPMENTS

##### High interest in ceramics at Toyota

Toyota Central Research and Development Laboratories are actively involved in ceramics research aimed at improving processing, properties, and the reliability of structural ceramics. Research areas of interest include:

- Improving special clay minerals, high temperature ceramics such as silicon nitride ( $\text{Si}_3\text{N}_4$ ) and silicon carbide (SiC), and ceramic fibre-reinforced ceramics;
- Improving processing techniques such as injection moulding and slip casting;
- Developing new methods to modify ceramic surfaces and enhance their properties by ion implantation;
- Studying fatigue fracture mechanisms;
- Developing a methodology for the life prediction of ceramics, composites, and polymers;
- Studying tribological characteristics (the wear behaviour) of ceramics and ceramic-matrix composites.

##### Positive results in several areas

Researchers have evaluated the mechanical properties of metal/ceramic surface composites formed by high-energy ion irradiation. The adhesive strength of a 200-nm zirconium film on sapphire is increased by  $\text{N}^+$  ion irradiation. Adhesive tensile stress increased to over 75 MPa (11,000 psi) after the specimen was irradiated to a dose of  $5 \times 10^{16}$  ions/cm<sup>2</sup> or higher. Zirconium film deposition and subsequent ion irradiation reportedly also increase, by a factor of six, the resistance to surface-crack initiation from scratches produced by a diamond stylus under a specific load. Irradiation causes an interdiffusion of elements at the interface, which is confirmed by Rutherford back-scattering analysis and transmission electron microscopy. Compressive stresses at the sapphire surface are believed to be promoted by the generation of defects.

A technique has been developed to form Si-Al-O-N (sialon) ceramics by implanting  $\text{Si}^+$  and  $\text{N}^+$  ions into sapphire. Single-crystal sapphire ( $\text{Al}_2\text{O}_3$ ) is implanted first with 400-keV  $\text{Si}^+$  ions and then with  $\text{N}^+$  ions, followed by annealing at 1,400°C (2,550°F) in a nitrogen atmosphere. Annealing sapphire that was implanted at ambient temperature resulted in the formation of  $\beta$ -sialon, a solid solution of  $\beta$ -silicon nitride and alumina in the substrate layer. By comparison, implantation at approximately -175°C (-280°F) resulted in the formation of aluminum oxynitride in the surface layer. At the lower temperature, implanted silicon ions are believed to react with substrate oxygen atoms, not with the implanted nitrogen ions. These crystalline precipitates have an epitaxial relationship with the sapphire substrate.

Researchers also are studying the effects of solid-particle erosion of ceramics and ceramic composites. Erosive wear by solid-particle impingement was evaluated for 16 different types of  $\text{Si}_3\text{N}_4$ . The specimens, made of different starting powders containing various amounts of

additives, were gas-pressure sintered at different temperatures. The erodant was #30 SiC abrasive grains, impinging at an angle of 80 degrees with respect to the incident surface at a velocity of 250 to 300 m/sec (820 to 980 ft/sec). The erosion rate for four brittle materials (gas-pressure sintered  $\text{Si}_3\text{N}_4$ , partially stabilized zirconia, sintered SiC, and soda-lime silica glass) depends on the ratio of particle hardness to target hardness.

Erosive wear of 13 types of commercial  $\text{Al}_2\text{O}_3$  also has been evaluated. The erosion rate, V, was described by using a multiple regression analysis. SiC-reinforced  $\text{Al}_2\text{O}_3$  composites containing up to 30-wt per cent SiC particles or whiskers were hot pressed at 1,500 to 1,850°C (2,730 to 3,360°F) for one hour at a pressure of 25 MPa (3,625 psi). Erosive wear was studied using SiC and  $\text{Al}_2\text{O}_3$ -SiC composites decreases with increasing SiC content regardless of the type of abrasive used. The erosion rate of  $\text{Al}_2\text{O}_3$  containing 30wt per cent SiC whiskers is one-fourth of that for pure  $\text{Al}_2\text{O}_3$ . The decrease in erosion rate is related to an increase in hardness and fracture toughness of the composites due to the presence of SiC. SiC whiskers, in any concentration, result in a lower composite-erosion rate than for the same concentration of SiC in the form of equiaxed particulates.

SiC-reinforced  $\text{Si}_3\text{N}_4$  composites containing up to 30-wt per cent SiC particulates or whiskers were hot pressed at two different temperatures. Pressing at 1,650°C (3,000°F) for one hour under a pressure of 25 MPa (3,625 psi) produced  $\alpha$  and  $\beta$  phases of  $\text{Si}_3\text{N}_4$ . Pressing at 1,800°C (3,270°F) for one hour under the same pressure produced  $\text{Si}_3\text{N}_4$  consisting of 100 per cent  $\beta$  phase. The erosive material-removal rate of these composites was evaluated using both SiC and  $\text{Al}_2\text{O}_3$  abrasives. For  $\text{Al}_2\text{O}_3$  abrasives, the erosion mechanism was characterized as elastic/plastic deformation followed by lateral-crack formation when the ratio of substrate to abrasive hardnesses is less than one. When the ratio is greater than one, the erosion mechanism is associated with scratching or ploughing.

Friction and wear characteristics of niobium (Nb) deposited on SiC and the effects of high-energy ion irradiation on the coated substrate have been evaluated. SiC with and without a Nb surface film, and  $\text{Ar}^+$  ion-irradiated Nb-coated SiC were subjected to a pin-on-disk friction and wear-tests for 40 hrs using a diamond pin. The metal-film reduces both the friction coefficient and wear. No wear is detected on the irradiated Nb/SiC specimens.  $\text{Ar}^+$  ion implantation enhances Nb-film adhesion to SiC and improves wear resistance.

Ion irradiation also has an effect on crack healing and crack initiation in a sapphire surface. Sapphire plates that suffered a reduction in strength caused by Vickers indentation were irradiated with 300 keV  $\text{Ni}^+$  ion and 400 keV  $\text{Mn}^+$  ions to determine strength recovery as a function of ion dose. Sapphire plates that lost about 50 per cent of their original strength after indentation recovered to about 90 per cent of the original strength after  $\text{Ni}^+$  or  $\text{Mn}^+$  ion irradiation of  $5 \times 10^{17}$  ions/cm<sup>2</sup>. Crack initiation in sapphire caused by Vickers indentation is largely retarded by ion irradiation; this effect is attributed to the formation of an amorphous layer during  $\text{Mn}^+$  ion irradiation.

Researchers also have studied the effects of Cr<sup>+</sup> ion implantation on the oxidation behaviour of sintered Si<sub>3</sub>N<sub>4</sub> containing a MgAl<sub>2</sub>O<sub>4</sub> sintering additive. Si<sub>3</sub>N<sub>4</sub> was implanted with 200 keV Cr<sup>+</sup> ions and oxidized at temperatures from 1,000 to 1,200°C (1,830 to 2,190°F) in air. Below 1,100°C (2,010°F), implanted Cr<sup>+</sup> ions are predominantly oxidized to Cr<sub>2</sub>O<sub>3</sub>, resulting in increased resistance to oxidation of Si<sub>3</sub>N<sub>4</sub> to SiO<sub>2</sub>; the diffusion of impurity cations to the surface oxide also was retarded. There is little difference in oxidation behaviour of Cr<sup>+</sup> implanted and unimplanted specimens at 1,200°C (2,190°F). Preoxidation of the implanted specimen at 1,000°C (1,830°F) provides slightly better resistance to subsequent oxidation at 1,200°C.

Automotive-ceramics development continues

Toyota Central Research and Development Laboratories is a participant in the multiorganization-sponsored Japanese National Gas Turbine Project initiated in 1988. The planned total project budget is ¥16,000 million (~\$US 114 million) over a nine-year period. Development of methods to fabricate and machine ceramic components will continue until 1995. Development of a small ceramic gas turbine including the combustor, turbine, and heat exchanger, will continue through 1996.

The engine will be tested in four stages. The engine will be tested at 900°C (1,650°F) from 1989 through 1991; at 1,200°C (2,190°F) from 1991 through 1993; and at 1,350°C (2,460°F) from 1993 through 1996. A cogeneration system is planned for development and evaluation from 1993 through 1996.

Toyota, Nissan, and Mitsubishi will work on the development of a 100-kW ceramic gas turbine for a passenger car, and Ishikawajima-Harima Industries, Kawasaki, and Yanmar Diesel will work on a ceramic gas turbine for a 300-kW cogeneration system. (Source: Advanced Materials and Processes, September 1989)

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Toyota introduces ceramic rotors

Regarding ceramics for car engines, silicon nitride (Si<sub>3</sub>N<sub>4</sub>) is already a production reality for turbocharger rotors at Toyota and it may be close to that as a face material for aluminium tappets at Mitsubishi. Respectively, these applications point out two key advantages of ceramics over metals: lightweight, mainly for improved engine performance, and wear resistance.

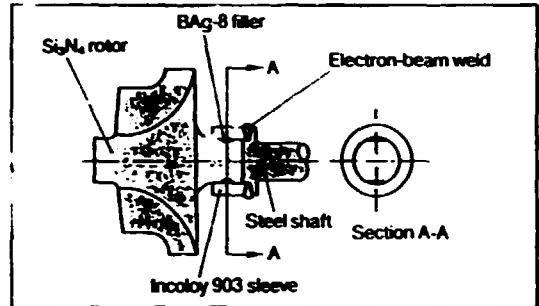
The rotors, for Celica and MR-2 cars, reduce the moment of inertia by 60 per cent, reducing turbocharger response to boost pressure by 30 per cent, according to Tetsuji Shimizu. They are mass-produced by injection moulding a powder mixture of the ceramic, Y<sub>2</sub>O<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> sintering aids, and binder, then sintering.

One of the critical concerns regarding the use of ceramics is ensuring sound joints to mating metal parts. To join the rotor to the steel turbocharger shaft (see drawing), a sleeve of iron-based-superalloy Incoloy 903 with layers of a ductile, low-temperature-melting brazing alloy (BAg-8) on the ID, is first fused to the rotor. Then the sleeve is electron-beam welded to the shaft.

As a face material for aluminium tappets, the ceramic has demonstrated 30 times the wear resistance (against chilled cast-iron cams) of current chilled cast-iron tappets, according to

Mitsubishi's Toshiharu Matsui. The composite tappet, which is interchangeable with those currently used, is also two-thirds lighter in weight.

The face is made by mechanical pressing and sintering a mixture of the ceramic, MgO-CeO<sub>2</sub>-SrO sintering aids, and binder. It is then used as an insert in pressure-mould casting the hypereutectic aluminum-silicon alloy that serves as the tappet body.



How ceramic rotor is joined to turbocharger shaft

(Source: American Machinist, April 1990)

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High-performance ceramics

ABB ranks among the world leaders in advanced technology for engineering ceramics. The company has developed in-house a unique technology for producing components from advanced heat-resistant ceramics for use in demanding environments in which erosion and corrosion may occur.

These ceramics are so important today that they are beginning to be referred to as the "third generation" of engineering materials.

Near net shape parts requiring only a minimum of machining can be produced at competitive prices.

ABB Cerama in Robertsfors, northern Sweden, is a high-tech development company in the Asea Brown Boveri Group. Its activities focus on R and D in the field of high-strength ceramics. For more than 15 years, work has been carried out with ceramics based on materials such as silicon nitride, boron carbide, boron nitride, zirconium oxide, titanium diboride and aluminium oxide.

ABB Cerama has developed a complete process technology for the manufacture of ceramic engineering materials using hot isostatic pressing (HIP). This yields fully dense, high-strength products with a very high uniformity and precision directly after the high-pressure sintering step.

Licence agreements covering the use of ABB Cerama's patented technology have been signed with several leading companies in the United States, Japan and Sweden. The company also conducts projects in the form of research assignments and manufactures prototype components. New applications are constantly being found.

The group of materials known as ceramics, with origins dating back to the earliest history of mankind, are today in their new and advanced form a competitive alternative to the established engineering materials.

An ever-growing number of applications is being found for high-temperature and high-strength ceramics. Components highly resistant to heat, wear and corrosion are being produced today from fully dense ceramic materials based on covalent bonded compounds such as silicon nitride and silicon carbide.

Typical products include ball bearings, valves, pumps, precision nozzles, gas-turbine rotors, turbocharger rotors, cutting tools and heat exchangers.

Near net shape parts requiring only a minimum of finish machining can be made from ceramics using HIP technology. Such products feature the following characteristics:

- High service temperatures, up to 1,400°C;
- Low density, being only 30-40 per cent of that of metals and other heat-resistant alloys;
- High strength;
- Extreme hardness;
- Low friction;
- Good wear properties;
- Excellent thermal shock resistance;
- High corrosion resistance;
- Need no or only limited finish machining;
- Can be produced at competitive prices.

Intensive materials development work conducted over the last decade has led to the market introduction of the first high-strength ceramics. This group of materials has been called the "third generation of engineering materials", alongside metals and plastics.

The new ceramics are generally based on non-oxidic materials such as silicon nitride, silicon carbide and boron carbide. The raw materials are supplied in the form of powder with particle sizes of about 1 micron and less.

One of the oldest ceramic products, though not quite belonging to the class of high-performance ceramics, is the sparking plug in internal combustion engines. In fact, it is still the automotive industry, with its demands for more efficient engines with lower emissions and multifuel capability, that is leading the development.

New materials concepts have had to be adopted to meet increased requirements made on different engine parts. And higher operating temperatures are aimed at in order to raise the efficiency of engines. For example, by raising the temperature by 280°C, it is possible to improve output by 40 per cent and reduce fuel consumption by 20 per cent. Here, ceramic materials have proved to be superior to metals. Current development work in Sweden and other countries focuses on building CMgas-turbine engine with numerous components made of ceramics.

#### Competitive alternative

Ceramics' main potential lies primarily in the possibilities they offer for development and improvement in advanced applications for example in components for car engines, gas turbines and other combustion systems, as well as cutting tools and ball bearings. A characteristic feature of compounds formed from elements around carbon in the periodic system (B, Al, Si, C, O and N) is the great binding force between atoms (with potential for high strength), light elements (providing a relatively low density), great hardness and high melting

point. Such materials exhibit a high resistance to erosion and corrosion.

However, materials or components made from these compounds are very difficult to produce. Melting processes, for example, are not practical due to melting points approaching 3000°C, and would anyway result in products with inferior properties.

The densification process involves sintering, i.e. the fusing together of powder bodies. The HIP technology developed by ABB provides a method by which outstanding properties can be achieved for many ceramics.

Among nitrides, silicon nitride constitutes the most important material for a number of applications, particularly those where high temperatures and rapid temperature changes occur. The oxidation resistance of HIPed silicon nitride with a low doping-additive content is very high. This is due on the one hand to the excellent oxidation behaviour of the silicon nitride itself, and on the other to low contents of yttrium silicate and any glass phase which might occur.

#### Extremely high strengths

Aluminium oxide is today the most important commercial material for industrial ceramics. Its greatest limitation is the low thermal shock resistance it offers, due above all to the high thermal expansion coefficient.

Significant development work has been carried out at ABB Cerama on aluminium oxide. The most publicized achievement is the manufacture of what is believed to be the world's largest individual ceramic component with very high purity and density, namely aluminium oxide canisters for the final storage of spent nuclear fuel.

Zirconium oxide is another oxide with important technical significance. The reason for this is its different crystalline modifications: monoclinic, tetragonal or cubic. Transitions between them may be utilized for controlled and favourable microcrack formation or to absorb energy to prevent crack propagation - so-called transformation toughening. It is possible to achieve extremely high strength values exceeding 2GPa with these materials. (Source: International Licensing, November 1990)

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#### Ceramics put to stressful use

A desire to understand high temperature ceramic materials is accelerating the development of integrated, or concurrent engineering, where design, development and production engineering proceed in parallel.

This is evident in a new collaborative venture between Rolls-Royce, the aero-engine company, and the manufacturing systems engineering department at the University of Warwick, Coventry. Rolls-Royce has established an Advanced Ceramics Centre at the university to develop ceramic materials technology for future Rolls-Royce gas turbine engines.

The aim is to strengthen the company's competitive position in world markets against the powerful US engine makers, General Electric and Pratt and Whitney, through the improvements in engine performance that are possible through the greater use of ceramic materials.

Some of these substances are based on silicon and carbon compounds such as silicon nitride and silicon carbide. They are resistant to high temperatures and have high strength-to-weight properties. This makes them suitable for aero-engines and other applications where metals are at the limit of their properties. Rolls-Royce says "reinforced ceramic composites are the most promising successors to the metals currently in gas turbines."

Rolls-Royce says that the incorporation of ceramic materials demands the development of a wide range of new technologies.

A totally new design system is required which will allow the design engineer to design and specify internal material architecture and composition in conjunction with component geometry. The loading of the components can be matched by introducing and orientating fibres in a ceramic material.

The Centre is also working on the manufacturing technology to produce complex fibre architecture by weaving, braiding and knitting fibre-reinforced composites in two and three dimensions.

Another of the Centre's activities is the development of fibre-reinforced glasses and ceramics and single material "monolithic" ceramics that will be capable of operating in more demanding environments than those in which current materials are used. Laboratory scale manufacture is also being carried out to study the behaviour of a component. (Extracted from Financial Times, 2 August 1990)

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#### Engine maker seeks out ceramics

In its bid to develop new materials for aircraft engines, Rolls-Royce installed a team of

materials and stress engineers and designers in the technology park of Warwick University last year, and the team is now beginning to start work.

The advantage of ceramics is that they will work at higher temperatures than metals, which reach their limit at between 850 and 950°C. Above that temperature, metal components must be cooled using air passing through the engine, thus reducing the engine's efficiency. With ceramic components the cooling can be omitted. Ceramics are also lighter.

The disadvantage of ceramics is that they are more brittle than metals. To increase their strength, they can be reinforced with fibres, but this makes them more complex to manufacture and design than metals.

Rolls-Royce hopes its first composite ceramic components, made from silicon carbide for the Eurofighter engine, will be developed in three to five years. The components will not be load bearing and would operate at about 1,000°C.

The next step will be to replace static components in the engine turbines with ceramics. At first, these would work at about 1,000°C. Eventually, static components in hotter parts of the turbine - at temperatures up to 1,400°C - would be replaced by composite ceramics.

The eventual goal, though not until the next century, would be to make moving, load-bearing parts, such as turbine blades, from ceramic composites. But the stress on these components currently rules out the use of such brittle materials. (Extracted from New Scientist, 8 September 1990)

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## 5. MANUFACTURING

### Engineering ceramics FMS factory

Fine ceramics, a new type of advanced materials, have now established themselves as key materials for high-tech industries, and are increasingly being used by the electronics, machinery and other industries due to their excellent heat, corrosion and wear resistance, and also intrinsic properties such as lightness, superhardness and electrical insulation.

Functional ceramics produced by mass production (mainly for IC packages and capacitors) account for about 70 per cent of the total output, while structural ceramics mainly for mechanical parts and other fine ceramics, manufactured primarily by the multi-type/small lot production, account for the remaining 30 per cent. Engineering ceramics, in particular, must conform to various user specifications for manufacturing a broad range of products from miniature (mm size) bolts to large items.

This emphasizes the uniqueness of each particular product.

This issue introduces Nihon Ceratec Co. Ltd.'s modern FMS factory constructed and presently operating as Japan's only specialized engineering ceramics factory capable of producing a wide variety of products. The company is a fully owned subsidiary of Nihon Cement Co. Ltd., Japan's leading cement manufacturer.

### Factory site and outline

The new ceramics production factory lies on the outskirts of Sendai City, situated about two hours away from Tokyo by Tohoku Shinkansen. This region is designated a Technopolis Region, a national project, consisting of a research park for promoting R&D in the field of advanced technologies, and is a new industrial zone in Japan concentrating on advanced industries such as the semiconductor and electronics industries.

The factory, situated in this high-tech industrial complex, has a land area of 19,614 m<sup>2</sup>, building area of 3,524 m<sup>2</sup> and a labour force of about 100 workers. A wide variety of engineering ceramics exceeding 400 different types are manufactured each month using materials such as alumina (Al<sub>2</sub>O<sub>3</sub>), zirconia (ZrO<sub>2</sub>), silicon nitride (Si<sub>3</sub>N<sub>4</sub>), silicon carbide (SiC), mullite (3Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>) and sialon (SiAlON). At the present stage, roughly 4 tons of raw materials are used monthly, 70 per cent of which is alumina.

Orders have been pouring in for the immediate manufacture of many small parts in small lots including one-off orders, each with unique specifications. This factory was specifically constructed to manufacture such products in small lots, to respond to this need. All processes from raw material mixing and conditioning, moulding, product moulding, sintering and machining involved in the manufacture of these engineering ceramics are based on the batch system concept.

### Production lines

Personal computer networks are used to prepare the product design and specifications, determine the raw material mixing ratios, selection of product machining methods, and for management of orders, sales, etc.

The production lines, broadly classified, consist of two parallel lines in the factory building. One is for raw materials mixing and conditioning, moulding and machining, and the other is a firing and sintering line matched to various modes and capacities.

A wide variety of advanced machines are installed here. A ball mill is used for raw materials mixing and conditioning, and casting, extrusion and injection moulding machines are used for wet type moulding in diverse modes and sizes. Cold isostatic presses (CIPs) and mechanical presses are used for dry type moulding. Several types of machine tools are also provided for green mould machining. Sintered semi-finished products are machined by the most modern NC lathes, machining centres (MCs), NC plane and cylindrical grinders and super-precision grinders. For feasible operation of the sintering line at a broad range of sintering temperatures and product sizes, numerous large, medium and small electric furnaces, vacuum sintering furnaces, compact high-performance tunnel kilns and others are also installed.

### Production processes

Raw materials are slurried by adding water, then atomized and dried to obtain ceramic particles of 70-80 m. Depending on the required accuracy and moulding method, finer particles of micron order can be prepared. These raw materials are fed to the moulding process where they are processed by casting, extrusion moulding or injection moulding machines, or to the dry moulding process for working with CIPs and mechanical presses.

The moulded semi-finished products, after drying, are sent either to the sintering process or green machining before sintering. By combining these various moulding methods and green machining methods, it is possible to produce green products of highly complicated shapes.

Green mouldings are usually designed with the sintering contraction of 13-20 per cent taken into account, but  $\pm 0.3$  per cent final accuracy can still be predicted after sintering. 20-30 per cent of products, therefore, can be shipped out of furnace after inspection, the rest being processed further by precision machining to attain the required shape and dimensional accuracies. Subsequently, shapes, dimensions, injuries, stains, impurities and other items are inspected, then products are shipped out. Since engineering ceramics are generally small, they are shipped by the rapid door-to-door delivery system. (Nihon Ceratec Co. Ltd., 3-5 Ake-dori, Izumi-ku, Sendai City, Miyagi Pref. Tel.: 022-378-9231. Fax: 022-378-9236) (Source: JETRO, October 1990)

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### Ceramic tile developed for European space shuttle

MAN Technologie AG (Munich, Germany) has developed a ceramic heat shield material for the European space shuttle Hermes. This material is an SiC-SiC composite and must withstand temperatures to 1,700°C. To produce this composite, carbon fibre mats are embedded in an SiC matrix by means of a vapour process. This solid matrix is obtained from an organic silicon compound in liquid form, which is



boiled and then mixed with hydrogen as the carrier gas and catalyst. The carbon vapour is then heated to  $\approx 1,100^{\circ}\text{C}$  and passed through a pile of carbon fibre mats. At this temperature, the carbon components of the gas mixture are baked into the mats thus producing a solid carbon composite.

(D. Forschungsdienst, Ahrstrasse 45, D-5300 Bonn 2, Germany) (Source: Ceramic Bulletin, Vol. 69, No. 6, 1990. Copyright A.Cer.S.)

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## 6. APPLICATIONS

### Joining of non-oxide ceramics for high-temperature applications

Silicon nitride and silicon carbide are of great interest for high-temperature structural applications in advanced heat engines because of their strength, toughness, creep and oxidation resistance, and thermal shock properties. Although interest in  $\text{Si}_3\text{N}_4$  and  $\text{SiC}$  remains high, the use of both materials has been inhibited by the difficulty and cost of manufacturing components of complex shape. Limitations in size and geometry can be potentially overcome by joining small and simple parts together to form a complex-shaped aggregate. However, improved joining techniques are required so that the join is not the performance-limiting "weak link" in the aggregate body. In this study, joining methods were developed that will be used later to generate complex shapes.

#### High-temperature joins are needed

The mechanical and chemical material properties necessary for advanced heat engine applications are at the limit and often exceed the present capabilities of  $\text{Si}_3\text{N}_4$  and  $\text{SiC}$  materials. The objective of this research is to develop reliable techniques to join  $\text{Si}_3\text{N}_4$  to  $\text{Si}_3\text{N}_4$  and  $\text{SiC}$  to  $\text{SiC}$  without affecting the attractive material properties inherent in these non-oxide ceramics. Ideally, the join must have similar material properties and mechanical behaviour to unjoined monoliths to be of interest for high-temperature structural applications.

Methods by which complex-shaped  $\text{Si}_3\text{N}_4$  and  $\text{SiC}$  components may be formed are numerous, but each has its limitations. Injection moulding has shown promise, but difficulties with defects, removal of binders/lubricants from thick cross sections without cracking, control of warpage, and lengthy debinderization cycles limiting fast throughput have been encountered. Conventional slip-casting and pressure-casting methods have difficulties with intricate shapes of varying cross section, mould release, drying shrinkage cracking, and lengthy drying cycles.

Extensive work has been performed on joining dense  $\text{Si}_3\text{N}_4$  to  $\text{Si}_3\text{N}_4$  using a brazing technique, with either a metallic or glassy interlayer. Although some of these joins have exhibited good mechanical properties at low temperatures, the performance at high temperatures found in heat engines is expected to be unsatisfactory because of oxidation of the metal/alloy and creep, both in the metallic and in the glassy interlayers. In contrast with  $\text{Si}_3\text{N}_4$ , comparatively fewer data are available on joining dense  $\text{SiC}$  to itself. It appears that the best results have been obtained by brazing, using metal borides or silicides. Researchers have claimed that a  $\text{SiC}/\text{SiC}$  bond resistant to 1,300°C can be obtained by an electric welding method, in which a rare-earth element, as adhesive, is put between dense  $\text{SiC}$  parts, and the parts are joined by applying a high voltage near the interlayer. As in the case of  $\text{Si}_3\text{N}_4$ , high-temperature oxidation, creep, and differential stresses due to the dissimilar nature of interlayer and adherend are expected to adversely affect the performance of the joined part.

In this study, joining techniques were developed for  $\text{Si}_3\text{N}_4$  and  $\text{SiC}$  to achieve optimum high-temperature strength and to avoid the problems associated with earlier methods. The techniques

consisted of joining green parts, using an interlayer of the same nominal composition as the green adherend pieces, followed by codensification of the aggregate body. The four main advantages are as follows:

- (1) Stresses due to compositional and microstructural differences between the join region and bulk can be reduced. Such stresses can arise during either fabrication or use.
- (2) The joining operation can be accomplished in one firing step.
- (3) Defects (such as cracks and pores) that may form from differential shrinkage between a green interlayer and dense bulk materials can be minimized.
- (4) Preferential oxidation and creep in the join region usually found at high temperatures in ceramics joined with metallic or glassy interlayers can be eliminated.

Current capabilities in the manufacture of structural ceramics are bound by the limitations of the forming process. The potential for high-temperature materials has not been entirely realized because only small size and simple geometries can be manufactured reliably and cost effectively. The following work is an initial attempt toward overcoming such manufacturing limitations.

In the following sections, the joining techniques are described and the results of flexural tests on joined and control modulus of rupture (MOR) bars are presented, with microstructural and fractographic data. The work in this paper is the result of an ongoing research activity sponsored by the Oak Ridge National Laboratory/US Department of Energy (ORNL/DOE) in the Ceramic Technology for Advanced Heat Engines Project. Final results will be available in future publications.

#### Joining techniques for $\text{Si}_3\text{N}_4$

The  $\text{Si}_3\text{N}_4$  to be joined (designated NCX-5100) contained 4 wt. per cent  $\text{Y}_2\text{O}_3$ . This composition was chosen for its high-temperature strength and creep resistance. Two grades were used during the preliminary experiments, designated A (fine-grain size) and B (coarse-grain size). The parts to be joined were green billets obtained by cold isostatic pressing (CIP) of the powder.

Three join interlayers were evaluated: self-bonded, slip, and injection-moulding compound. The interlayer of the self-bonded joins was formed by the bare, flat surfaces of the parent material placed in contact. Surfaces to be joined were not perfectly flat and were limited by the capability of green machining practice. The slip and injection-moulding compound interlayers were used in case the clearance between the self-bonded join surfaces was not eliminated by hot isostatic pressing (HIP). The slip and injection-moulding compound consisted of the 4 wt per cent  $\text{Y}_2\text{O}_3$  -  $\text{Si}_3\text{N}_4$  composition of the parent material as a powder suspended in their respective media. Both the slip and the injection-moulding compound provided a plastic interlayer in the green state to fill voids between the mating surfaces.

The advantage of the slip interlayer is that the slip, being plastic, conforms itself to the asperities of the green surface, so that minor

defects introduced by machining, such as scratches, can be filled. The injection-moulding compound can, in theory, fill voids and scratches of the mating surfaces, but was not successful and was abandoned.

For all three joining techniques, densification was accomplished by glass encapsulation HIP, using the HIP technology licensed by Allmannä Svenska Elektriska Aktiebolaget-Cerama. The size of the dense joined billets was approximately 2.8 cm by 3.6 cm by 8.4 cm, with the join plane parallel to the 2.8-cm x 3.6-cm face.

#### Joining techniques for SiC

The SiC used in this study (designated NCX-4500) was a pressureless-sintered  $\alpha$ -SiC material densified with boron and carbon as sintering aids (General Electric Co. licence). Two joining techniques were used in the preliminary stage of this work. The first one, similar to that used for  $\text{Si}_3\text{N}_4$ , used a slip between two flat surfaces of green billets. After the application of the slip, the two parts were pressed together by hand and cold isostatically pressed. The joined green SiC parts were densified by pressureless sintering. This is referred to as the slip/CIP method. The size of the dense, joined billets was approximately 1.8 cm by 2.4 cm by 6.3 cm, with the join plane parallel to the 1.8-cm by 2.4-cm face.

The second technique consisted of grinding and polishing two dense SiC parts with diamond pastes of increasing fineness to a mirror-like finish, cleaning the surfaces from debris, and drying and friction fitting the mating surfaces by hand. This method was successful when applied to disks of about 2 cm in diameter. The two disks stuck to each other, and a good bond was formed after sintering. However, when billets with a square cross section of about 2.5 cm by 2.5 cm were used, they did not bond strongly after firing. The failure was thought to be due to insufficient flatness and smoothness of the polished surfaces. This technique was therefore abandoned in favour of the slip/CIP method previously described. Patent applications for both methods of joining SiC have been filed.

#### Characterization methods

Both  $\text{Si}_3\text{N}_4$  and SiC joins were analysed and characterized during and after the join development stage. Optical microscopy and SEM were used for microstructural characterization, and microfocus X-radiography was used to detect the presence of flaws such as delaminations, debonding, and cracking. All flexural specimens were made to and tested by the MIL-STD-1942(MR) B geometry specifications. The join plane was located at the centre of the bar, perpendicular to the long axis of the specimen. Fractography was performed optically and by SEM in both  $\text{Si}_3\text{N}_4$  and SiC specimens. Preliminary room-temperature (22°C) and high-temperature fast-fracture tests were performed during join development at 1,370°C for  $\text{Si}_3\text{N}_4$  and 1,530°C for SiC to select the best joining technique.

Flexural stress rupture tests were conducted on joined and control (unjoined)  $\text{Si}_3\text{N}_4$  bars at 1,370°C under constant stresses of 200, 250 and 300 MPa. These tests were interrupted either upon fracture or after 200 h, whichever occurred first. In addition to the real-time measurement of strain during creep tests, the curvature of the specimens after stress rupture testing was used to calculate the strain to failure (or, if the sample survived, the maximum strain at 200 h). This test was not performed on SiC since differences in the quality of the joining technique could be determined by flexural strength comparison.

Fast-fracture tests originally used four-point span lengths of 20 mm by 40 mm, but, after experiencing few failures at the join area, the inner span was changed to 5 mm. All of the fast-fracture tests conducted after the completion of the join development used this new configuration. This reduction of the inner span length enhances the probability of failure in the vicinity of the join. Consequently, the fast-fracture experimental results reported, although consistent throughout this paper, should be compared using the appropriate statistical material parameters.

#### Joining $\text{Si}_3\text{N}_4$ to $\text{Si}_3\text{N}_4$ results

During the join development stage, theoretically dense joined bodies were obtained by HIP with the self-bonding and slip interlayer methods. The joins could not be discerned visually and were difficult to detect optically. Identification of the join interlayer by metallography was possible in approximately 90 per cent of the as-ground flexure specimens.

Tables I and II on pages 39 and 40 show the average strength values obtained at 22° and 1,300°C for control, self-bonded, and slip-bonded MDR bars of material A and for control and self-bonded bars of material B. Testing of slip-bonded material B was not performed. The flexural strength evaluation (Tables I and II) could not clearly indicate which of the four possible material/join interlayer combinations was the best. For example, material A (self-bonded) had a higher average strength than material B (self-bonded) at room temperature, but the opposite was true at 1,300°C. Alternately, the slip method in material A gave higher average strengths over the self-bonded at 1,300°C although this was not statistically significant. Also, material A had a few failures at the join, whereas material B did not. The join fractures originated at clearance voids that were not completely eliminated during densification. These could have been caused by inadequate shear at the join interface during HIP, grinding scratches of greater depth than desired, or inadequate filling of the surface topography by the slip during sample preparation.

The results of the stress rupture tests at 1,370°C showed that material A did not perform satisfactorily. The control sample's failure times exceeded 200 h at 200 MPa, but at 250 MPa, variable times were observed, and all specimens failed in less than 2 h at 300 MPa. The joined bars of material A accommodated more strain than the control ones, but all samples failed before 200 h at a stress of 250 MPa. Fracture never originated at the join. Self-bonded and slip-bonded samples of material A exhibited similar creep rates, but the latter samples had longer times to failure. This variability in failure time is under investigation. On the other hand, stress rupture tests on material B gave much better results. Control bars consistently survived 200 h at 1,370°C under stresses of 250 and 300 MPa. Self-bonded joined specimens exhibited superior survival times and creep resistances relative to material A joins. Material B joins survived a 200-h exposure at 250 MPa with a maximum strain of 0.006, the lowest measured in all joined samples. Figure 1 on page 40 shows the maximum strain as a function of time in the creep test at 1,370°C under a stress of 250 MPa.

Flexural and creep test results provided sufficient evidence that the best combination was material B with the slip interlayer and, therefore, was chosen for extensive mechanical characterization. Material B was tested by fast fracture at room

temperature, 750°C, and 1,370°C, with the 5-mm inner span and a crosshead speed of 0.5 mm/min (table III). The average room-temperature strength of the control bars was 967 MPa whereas that of the joined bars was 941 MPa. A drop in the average strength was experienced at high temperature for both control and joined bars (570 and 526 MPa, respectively). At 1,370°C, MCX-5100 Si<sub>3</sub>N<sub>4</sub> joined and control samples retained approximately 60 per cent of their room-temperature strength. Figure 2 shows the Weibull plots for all tested temperatures. Although the Weibull modulus of the controls was not affected by the test temperature, the joined samples showed an increase in scatter (decrease in Weibull modulus), with the lowest Weibull modulus at 750°C. However, the error of the Weibull modulus increased as the number of samples tested decreased. Further statistical analysis is underway.

The statistical significance of the difference in the mean strength of joins and controls was calculated using the t-test distribution of means (table IV). This analysis indicated that the joined samples had a flaw population different from the control samples. Confidence levels of dissimilarity were 91.93 per cent and 99.91 per cent for room temperature and high temperature, respectively.

Fractographic analysis showed that failures at the joined region were still scarce, less than 20 per cent of the total, even though the fast-fracture average strength was marginally lower than the controls. Failure origins were located at the surface, but the origins were too small to be confirmed by optical microscopy. SEM results were unavailable at the time of publication.

#### Joining of SiC to SiC results

As previously mentioned, two methods were evaluated for joining SiC. Preliminary attempts to bond pressureless-sintered disks with mirror-like surfaces directly to each other showed shear strengths of about 20 MPa. After post-sintering HIP, a strength of approximately 110 MPa was achieved. Partially fractured samples of the latter method also indicated a much stronger bond. Unfortunately, larger billets were unsuccessfully joined, and, therefore, this method was not pursued further. The second joining method (slip/CIP) produced an interlayer about 100 μm thick. Unlike Si<sub>3</sub>N<sub>4</sub>, the join could be clearly seen in all specimens that were polished. The billets had densities consistently around 96 per cent to 97 per cent of theoretical. A microstructure at higher magnification revealed the presence of elongated, high aspect ratio, grains which are very likely α-SiC from the presence of α and β polytypes in the XRD analysis.

The fast-fracture flexural strength data are reported in table III. The average room-temperature strength of the control bars was 397 MPa whereas the joined bars had an average strength of 351 MPa. This difference was not as pronounced at 1,530°C for control and joined bars (347 to 338 MPa, respectively). The confidence level of dissimilarity (CLD) between joins and controls was 99.82 per cent at room temperature whereas no statistically significant difference (table IV) can be associated at 1,530°C (CLD of 47.22 per cent).

There was a slight variation between the Weibull diagrams of joined and control samples tested at different temperatures (figure 3). SiC joins showed lower strength and Weibull modulus than the controls. Optical fractography showed

failure origins both at the surface and in the volume. The defects were mostly of the inclusion/agglomerate type.

The SiC samples exhibited both lower Weibull modulus and strength compared with Si<sub>3</sub>N<sub>4</sub>. These properties, however, are likely to be improved by high-pressure and high-temperature post-sintering HIP.

#### Additional characterization planned

A joining method based on the application of a slip to green parts has been developed and demonstrated for joining Si<sub>3</sub>N<sub>4</sub> to Si<sub>3</sub>N<sub>4</sub> and SiC to SiC. An important result of this work is the achievement of a high-temperature joining technique that does not greatly alter the mechanical properties, such as strength and creep resistance, from the original parent material. The mechanical properties of the joined specimens were sufficient to show promise for heat engine applications. Future work will determine the mechanical behaviour and the feasibility of complex-shape component manufacture using the joining methods developed in this study.

The Si<sub>3</sub>N<sub>4</sub>-joined billets were densified by glass-encapsulated ASEA HIP to theoretical density and the SiC-joined billets by pressureless sintering to about 97 per cent of theoretical density. A second joining method was successfully used to join dense SiC disks with polished mating surfaces, but could not be applied to larger billets presumably because of insufficient flatness and smoothness of the two surfaces. Excellent join strengths were obtained, both at room temperature and at high temperature, for Si<sub>3</sub>N<sub>4</sub> and SiC. For Si<sub>3</sub>N<sub>4</sub>, the average room-temperature strength of the control body (without a join) was 967 MPa whereas that for the joined bars was 941 MPa. A drop in the average strength in Si<sub>3</sub>N<sub>4</sub> was experienced at 1,370°C for both control and join bars (570 and 526 MPa, respectively). For SiC, the average room-temperature strength of the control bars was 397 MPa whereas the joined bars had 351 MPa. This difference was not as pronounced at 1,530°C for control and joined SiC bars (347 to 338 MPa, respectively). Although only a minor fraction of the breaks occurred in the join plane, in the fast-fracture tests of MOR bars, the joined samples showed a slightly lower average strength than the controls. The only exception was SiC at 1,530°C, which had similar joined and control average strengths.

An important objective of this contract was to obtain 140-MPa tensile strength in joined specimens at 1,370°C for Si<sub>3</sub>N<sub>4</sub> and 1,530°C for SiC. A more detailed and complete characterization study is planned to determine grain-boundary chemistry and phase composition of the joined and control samples. Stress/strain, creep, oxidation, thermal cycling, and cyclic fatigue testing will be performed. Analytical modeling using the characterization data will predict the probability of survival in various environments, stresses, and temperatures.

Table I Si<sub>3</sub>N<sub>4</sub> Flexure Strength at 22°C

Material	Mean (MPa)	Standard deviation (MPa)	Failures (No.)
A self bonded	881.4	221.4	2
A slip interlayer	881.8	202.2	1
A control (unjoined)	1010.1	70.1	0
B self bonded	786.8	84.4	0
B control (unjoined)	841.0	68.2	0

Table II Si<sub>3</sub>N<sub>4</sub> Flexure Strength at 1300°C

Material	Mean (MPa)	Standard deviation (MPa)	Failures at joint (No.)
A self bonded	610.9	33.8	0
A slip interlayer	649.5	35.2	0
A control (unjoined)	704.8	24.1	
B self bonded	713.6	36.5	0

Table III. Fast-Fracture Statistical Data

Material	Temperature (°C)	$\bar{\sigma}$ (ksi (MPa))	Standard deviation (ksi (MPa))	$\sigma_{max}$ (ksi (MPa))	Weibull modulus (m)	No. of samples
NCX 5100 joined	Room	136.4 (940.7)	9.0 (61.8)	140.5 (968.7)	17.0	45
	750	98.2 (676.8)	15.3 (105.4)	104.5 (720.8)	7.4	30
	1370	76.3 (526.3)	7.8 (54.1)	79.7 (549.8)	11.3	45
NCX 5100 control	Room	140.2 (966.7)	9.1 (62.9)	144.5 (996.5)	15.8	30
	1370	82.6 (569.6)	7.4 (50.9)	85.7 (590.6)	16.2	30
NCX 4500 joined	Room	50.9 (351.2)	8.3 (57.2)	54.4 (374.9)	6.8	45
	750	49.0 (338.1)	6.6 (45.3)	51.8 (356.9)	9.2	30
	1530	49.0 (337.6)	8.9 (61.2)	52.7 (363.4)	5.4	45
NCX 4500 control	Room	57.6 (397.2)	9.3 (64.2)	61.4 (423.7)	7.2	30
	1530	50.1 (346.7)	8.8 (60.9)	54.0 (372.4)	6.2	30

\*These strengths are for 5-mm by 40-mm spans

Table IV. Confidence Level of Dissimilarity between Joined and Control Samples

Material	Temperature (°C)	CLD (%)
NCX 5100	Room	91.93
	1370	99.91
NCX 4500	Room	99.82
	1530	47.22

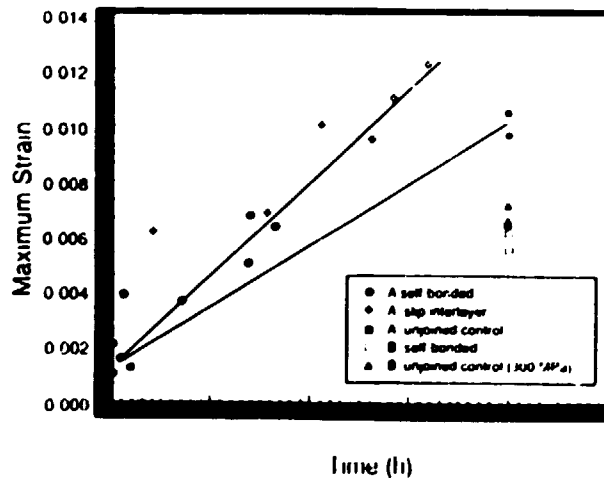


Fig. 1. Maximum strain as a function of time of the poststress rupture of Si<sub>3</sub>N<sub>4</sub> specimens (1370°C and 250 MPa)

WEIBULL FAILURE DIAGRAM OF NORTON'S NCX-5100  
(MOR Bars Based on 40 mm x 5 mm Spans)

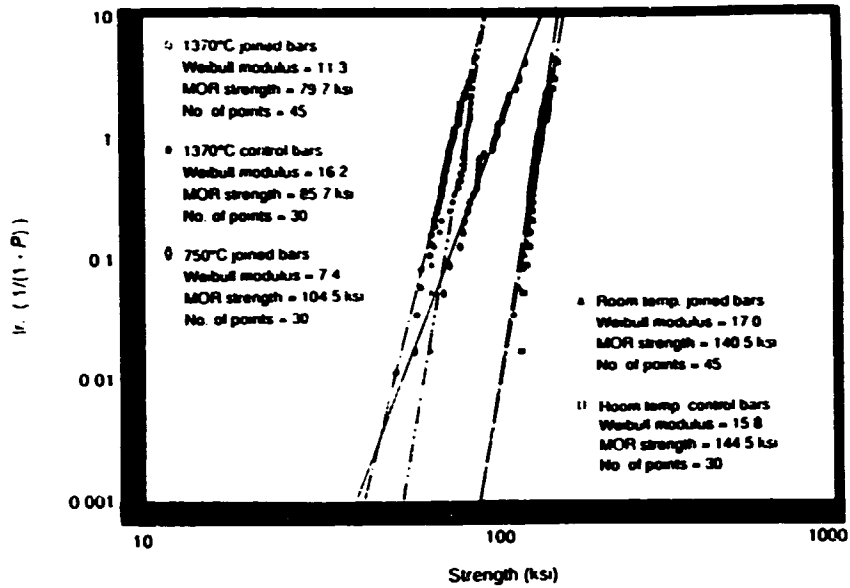


Fig. 2. Weibull failure diagram for Norton's NCX-5100 Si<sub>3</sub>N<sub>4</sub> (MOR bars based on 40-mm by 5-mm spans).

WEIBULL FAILURE DIAGRAM OF NORTON'S NCX-4500  
(MOR Bars Based on 40 mm x 5 mm Spans)

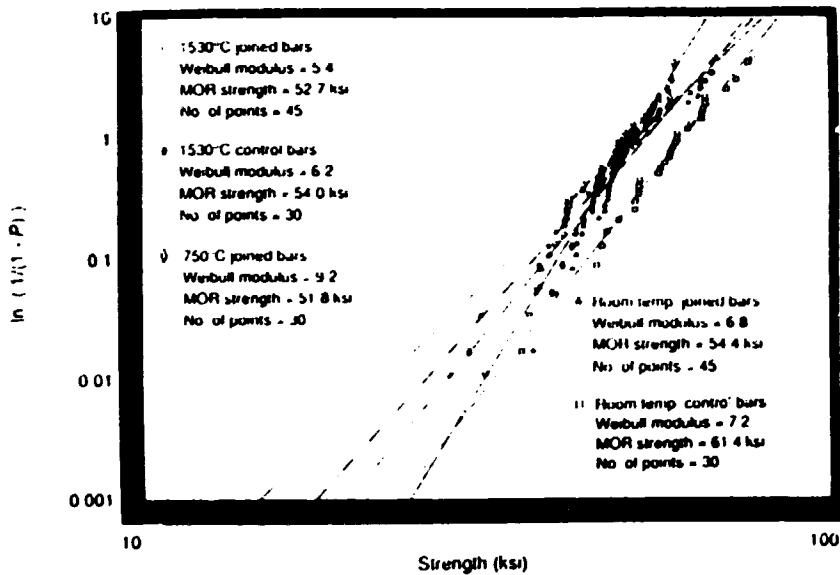


Fig. 3. Weibull failure diagram for Norton's NCX-4500 SiC (MOR bars based on 40-mm by 5-mm spans).

(Extracted from *Ceramic Bulletin*, Vol. 69, No. 3, 1990 (©ACerS). Article written by Carl H. Bates, Michael R. Foley, Giulio A. Rossi, Glenn J. Sundberg, and Francisco J. Wu, Norton Company, Advanced Ceramics, Northborough, Massachusetts 01532-1545)

### Selecting ceramics for temperature resistance

One of the advantages of engineering ceramics over metals is their ability to withstand service temperatures to 1,650°C (3,000°F). The temperature resistance of ceramics is characterized by several thermal properties, including creep resistance, thermal expansion, thermal conductivity, and thermal shock resistance.

Creep resistance must be taken into consideration when designing dynamic components because high creep rates can lead to excessive deformation and uncontrolled stress.

For structural ceramics, especially hot-pressed silicon nitride ( $\text{Si}_3\text{N}_4$ ), creep rate can be controlled by adjusting the composition and, thus, the properties of grain boundary phases. In  $\text{Si}_3\text{N}_4$  doped with magnesia ( $\text{MgO}$ ), for example, an amorphous inter-granular phase can cause grain-boundary plasticity, and cavity nucleation and growth, with corresponding high creep rates. Creep resistance is improved by controlled crystallization of the inter-granular phase. Stress dependence can be reduced by doping  $\text{Si}_3\text{N}_4$  with yttria ( $\text{Y}_2\text{O}_3$ ) and zirconia ( $\text{ZrO}_2$ ), which produce a deformation-resistant grain-boundary phase. Reaction-sintered  $\text{Si}_3\text{N}_4$  has good creep resistance due to a lack of oxide impurity phases. The rate-controlling process has been attributed to both grain-boundary sliding and microcracking.

Creep resistance of silicon carbide ( $\text{SiC}$ ) also is affected by inter-granular phases, but, in general, creep rates are extremely low. Siliconized  $\text{SiC}$ , however, has higher creep rates due to the presence of the continuous silicon phase. The rate-controlling process may be a carbon-vacancy diffusion mechanism.

Polycrystalline ceramics generally have high activation energies associated with non-viscous creep or dislocation movements. Glasses and glass-ceramics, on the other hand, have low activation energies that are associated with viscous-flow mechanisms due to the amorphous phase present. Consequently, the creep rate of glass-ceramics is influenced by the morphology and composition of the crystalline phase. Refractory phases reduce deformation or creep. Most of the glass phase in glass-ceramics is removed by further heat treatment, and the material then behaves more like a polycrystalline ceramic.

#### **Thermal expansion**

Compared with oxides, silicon-base ceramics have low coefficients of thermal expansion (CTEs), which help to increase thermal-shock resistance.

Like creep resistance, thermal expansion for silicon-base ceramics is a function of the solid phase, and is not affected much by porosity and minor impurities.  $\text{SiC}$  has a thermal expansion 50 per cent higher than that of  $\text{Si}_3\text{N}_4$ .

Thermal expansion of  $\text{Si}_3\text{N}_4$  is a function of the amount of inter-granular oxide present. Minimizing this phase, as in pure reaction-sintered  $\text{Si}_3\text{N}_4$ , minimizes thermal expansion. Hot-pressed  $\text{Si}_3\text{N}_4$  contains larger amounts of high-expansion oxide phases. Thermal expansion of a reaction-sintered  $\text{Si}_3\text{N}_4$  and a hot-pressed  $\text{Si}_3\text{N}_4$  can differ by as much as 30 per cent, which indicates the influence of processing methods.  $\text{SiC}$  materials are not affected as much by processing - the difference in thermal expansion is only about 5 per cent.

Variation of thermal expansion with temperature also is important with glasses because thermally induced stresses are a function of the rate of

expansion. Both linear dimensions and volume of glass change with temperature; the rate of volume increase is three times the linear rate of expansion. Up to 300°C (570°F), the total expansion is linear, with increases occurring after annealing. The addition of oxides to conventional glasses usually increases CTE significantly, except for some borosilicate glasses.

Heat-treatment of glass-ceramics or glasses, which determines the volume fraction and nature of the crystalline phases present, also can influence thermal-expansion characteristics. For example, if crystalline forms of silicon are present, different treatments can result in different CTEs. This occurs because the material undergoes structural changes at different temperatures. Quartz is one type of silica structure that has a high CTE.

Heat capacity and thermal conductivity also must be considered for high-temperature applications, since both properties are indicative of thermal-stress resistance.

For most oxides and carbides, heat capacity increases with temperature to about 1,000°C (1,830°F). Further increase in temperature have little effect on heat capacity. Heat capacities of glasses and glass-ceramics also increase with increasing temperature.

Thermal conductivity of glasses decreases with decreasing temperature, while those of crystalline ceramics and glass-ceramics increase. Thermal conductivity values for glass-ceramics are lower than those for oxide ceramics and higher than those for glasses.

The thermal conductivity of single-phase ceramics is influenced by structure and composition. Complex structures with wide atomic-size variations have lower thermal conductivity. Impurity atoms in solid solution also decrease conductivity. Thermal conductivity of multiphase ceramics is more complicated, because the amount and distribution of each phase (including porosity) also must be taken into consideration.

Thermal shock resistance indicates the ability to withstand thermal stresses generated by large temperature gradients. Such stresses can cause catastrophic failure, or growth of existing flaws, reducing strength and component integrity.

Resistance to thermal shock usually is determined by quenching heated samples in water. The initiation of thermal-shock damage is determined by internal-friction measurements.

For structural ceramics, thermal-shock resistance is dependent on both material type and processing method. For example, hot-pressed  $\text{Si}_3\text{N}_4$  usually has higher resistance than reaction-sintered  $\text{Si}_3\text{N}_4$ . Thermal-shock resistance also is affected by the type of dopants incorporated in the ceramic. However,  $\text{SiC}$  materials have lower resistance than the nitrides because of their high thermal expansions and elastic moduli. Processing methods do not influence these properties.

Oxidation resistance is important for certain high-temperature applications. The higher purity and higher density of  $\text{SiC}$  materials generally make them more oxidation resistant and, therefore, more stable in long-term service than  $\text{Si}_3\text{N}_4$ . Hot-pressed  $\text{Si}_3\text{N}_4$  is affected by alkali impurities that segregate at grain boundaries and increase oxidation rates. This effect can be reduced by adding  $\text{Y}_2\text{O}_3$  and silica ( $\text{SiO}_2$ ). Reaction-sintered  $\text{Si}_3\text{N}_4$  usually contains more porosity, which also lowers oxidation resistance.

## High-performance structural ceramics vs conventional metals

Material	Room-temperature strength, MPa	Strength at 1,095°C, MPa	Density, g/cm <sup>3</sup>
Various sintered SiC materials	340-550 (flexure)	340-550	3.2
Various sintered Si <sub>3</sub> N <sub>4</sub> materials	205-690 (flexure)	205-690	2.7-3.2
Transformation-toughened ZrO <sub>2</sub>	345-620 (flexure)	150-400	5.8
SiC whisker-toughened Al <sub>2</sub> O <sub>3</sub>	500-600 (flexure)	Not well known	3.5
SiC-lithium aluminosilicate composites	380-825 (flexure)	485-895	2.6
Steels (4100, 4300, 8600, and 5600 series)	1,035-1,380 (tensile yield)	Insignificant (690-1,035 at 540°C)	7.8
Cast irons	205-550 (tensile yield)	Insignificant (170 at 480°C)	7-7.5
Aluminum alloys	415-895 (tensile yield)	Insignificant (140 at 315°C)	2.5

(Extracted from the Guide to Selecting Engineered Materials, Advanced Materials and Processes, June 1990)

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### Tests on new fibre-reinforced ceramics

High-temperature resistant materials are the prerequisite for many tasks in the aviation, space, and defence fields. Certain structural parts of space gliders of hypersonic aircraft, for example, must withstand temperatures of more than 1,200°C in oxidizing or reducing (propulsions) atmospheres. Only ceramic materials are suitable for such tasks. The specific drawback of ceramics, their brittleness, can be limited by reinforcing them with continuous fibres to achieve a satisfactory damage tolerance. This new type of material is still at the beginning of its career although some applications have already been implemented. Intensive comparative studies of different production technologies at Dornier (P.O. Box 1420, D-7990, Friedrichshafen, Germany) showed that the combination of continuous fibres and a matrix of pyrolyzed organic Si polymers may yield the best economic and technical potential.

The developments in the space and aviation fields aiming at weight-saving designs, a better use of energy, longer operating lifetimes, and the planned use of the hypersonic range for future aircraft have led to component specifications which by far exceed the possibilities of conventional materials. Especially primary structures on the outside of hypersonic aircraft or space gliders are subject to high thermal and mechanical loads. Only ceramic materials can guarantee sufficient strength at temperatures of more than 1,200°C and can resist to oxidation by atmospheric oxygen. Ceramic materials, as a rule, also have a weight advantage over metals, but their brittleness, which may lead to catastrophic failure, makes them unsuitable for use in airborne systems. Therefore, about 15 years of effort has been invested (by SEP, France) to obtain a sufficient damage tolerance of the material by combining continuous fibres and a ceramic matrix.

### Presentation of damage tolerance

The CFC (carbonfibre-reinforced ceramics) material was proven to be damage tolerant in a non-oxidizing atmosphere. When compared with non-reinforced brittle materials, additional energy absorbing mechanisms become effective. Besides the activation of additional crack systems depending on the fibre layers, it is above all the delamination and the friction when fibres are pulled out of the matrix, combined with the possibility of load transfer over long ranges, that leads to a quasi-plastical material behaviour. Excessive tension thus does not lead to catastrophic failure but can be coped with locally. The load-elongation curve thus clearly differs from that of non-reinforced ceramics and resembles more that of metals. The defined failure behaviour while maintaining a residual strength allows to use fibre-reinforced ceramic components for primary structures as well.

So far, oxidation-resistant composite ceramics are predominantly made by preparing the ceramic matrix from the gaseous phase (Chemical Vapour Infiltration, CVI). In this way, the French company SEP has manufactured big structural parts of silicon carbide (SiC) reinforced by C or SiC fibres (C-SiC or SiC-SiC). This procedure requires very long process times, however.

### New infiltration procedures

In the past five years, increasing efforts have become obvious internationally that aim at developing more economic procedures for the production of more efficient structures of ceramic with continuous-fibre reinforcement. Dornier has studied the following promising technologies:

- CVI (p, T-gradient process) C-SiC, SiC-SiC
- pyrolysis of organic Si polymers C-SiC, SiC-SiC
- pressure-infiltration of ultrafine powders Al<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>

These processes differ by the aggregate states and the processing technologies for the materials



employed. In the CVI process, a ceramic product is deposited in the voids of a preformed fibre prepreg by the reaction of process gases. A pressure and temperature gradient is used to considerably shorten the process time.

The use of liquid organic Si polymers opens up further possibilities for impregnating fibre bodies or for producing layups consisting of parallel fibre layers. In this field of work, the Dornier experience with fibre-reinforced plastics is put to use. Fibre layups impregnated with polymer are laminated, and these laminates will be cured under high pressure (approx. 15 bar) and temperature (approx. 200 to 400°C). The Si polymer is converted into a ceramic material without pressure at 800 to 1200°C. In this field, Dornier co-operates closely with Wacker Chemie who develops suitable Si polymers specially for this purpose.

With the pyrolysis of Si polymers, Dornier has already succeeded to make tiles of 25 by 25 cm and big thin-walled pipes. The special advantage of the laminating technology becomes obvious when making complete parts and fasteners. The manufacturing process here closely resembles that of plastic processing.

Pressure infiltration with ultrafine powders works with solid materials in suspension, called slip. Ultrafine powders (with a grain size of less than 1 micrometer) are produced by means of the reaction-spray process (RSV). Other than in the two procedures mentioned above, oxidic powders and fibres are used in this process. The slips are dehydrated together with the fibres under pressure, and the composite is subsequently hardened while pressure and temperature are increased.

After intensive studies and experimental work since early 1986, clear advantages have been recognized for the pyrolysis of organic Si polymers for matrix production:

- damage-tolerant behaviour at 1,100°C with strengths of up to 400 MPa could be proven
- "scaling-up" is easily feasible with the production technologies available for fibre-reinforced plastics
- comparatively low production price. As the two other procedures offer no comparable technical and economic potential, work will concentrate on developing the pyrolysis of organic polymers. Studies for CVI technology are also continued as this technology is suitable for post-impregnation and improvement of the surface characteristics.

Besides continuous fibres in the form of filaments or fabrics, shortcut fibres are studied as reinforcement material. This requires, however, a completely different processing technology. Work is concentrated mainly on the production of homogeneous mixtures of short fibres, powder, and polymer. We have succeeded in developing a promising production procedure, and we have already manufactured ceramic tiles with short-fibre reinforcement.

#### Applications

According to international market studies, fibre-reinforced ceramics have very good development chances in the aerospace sector. Engines with increased thrust-to-weight ratio, for example, will require parts made of fibre-reinforced ceramics. Dornier is conducting promising studies of the use

of fibre-reinforced ceramic heat shields of space transporters. Applications in turbine and vehicle engine construction are also under discussion.

The development of ceramic fibre composites is very important for Dornier's specific fields of activity as in this way a key position for the future can be occupied. At the same time, application possibilities in other fields can be pursued and put to use. (Source: Dornier Post, No.1, 1990)

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#### Ceramic fibres insulate to 1600°C

Despite being around for many years, ceramic fibres did not assume a significant role in furnace refractories until the late 1970s. The characteristics of high insulating value, good refractoriness and low density were not fully utilized because of the absence of adequate techniques of application in furnace linings.

The first breakthrough came with the introduction of "stack-bonding". This consists of a ceramic fibre blanket edge-on to the furnace wall, thereby creating a fibre lining with good tensile strength in the direction normal to the wall. This enables the lining to be attached at its back face and so avoids the use of anchors reaching through to the hot face. Further benefits in the form of the virtual elimination of gas erosion problems, improved resistance to shrinkage, simpler installation techniques and neater finishes, result.

#### Benefits

Ceramic fibres are completely asbestos-free, totally inorganic and non-combustible. They offer the following benefits in furnace installation:

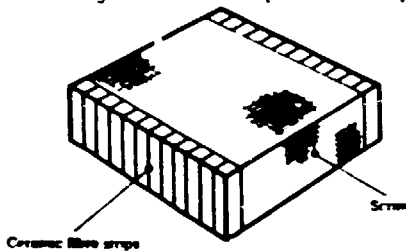
- Ceramic fibres have much lower thermal conductivities and densities compared with firebricks resulting in better insulation, significantly lower heat storage, faster cycling times and consequently savings in fuel and production time.
- Ceramic fibre is resistant to thermal shock and will not crack or spall with rapid heating or cooling. The low mass and resilient nature of ceramic fibre enable it to stand up to conditions of vibration such as encountered in forges.
- The product is easily handled and can be cut with basic tools for rapid installation and minimum downtime.
- Significant fuel savings from 10% to more than 50% have been achieved giving most acceptable short capital payback periods. Further savings result from minimal repair work following the elimination of thermal shock.

#### Products

The range of products available include blocks for veneering to furnace walls and anchorblocks, both of which are suitable for use up to 1,600°C.

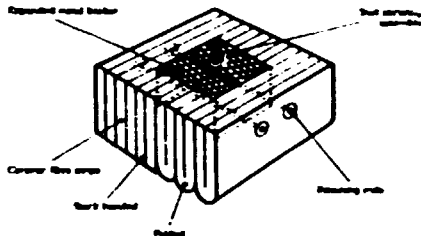
Blocks known as Clinoblocks comprise strips of ceramic fibre formed into a flexible stack-bonded block under compression in a combustible scrim (figure 1). They are ideal for veneering on to

brickwork, monolithic, metal and ceramic fibre surfaces. They are nominally 300 mm square in various thicknesses and grades for temperatures up to 1,600°C.



1 Clinoblocks are strips of ceramic fibre formed into a stack-bonded block and held in a combustible scrim.

Anchorblocks are strips of ceramic fibre formed into a block held in a stainless steel expanded metal basket and secured with twin retaining rods (Fig. 2). The front face can be either stack-bonded or folded. They are suitable for roof and door linings. Fast reheating is possible since the drying out of a cement is avoided.



2 Anchorblocks are strips of ceramic fibre held in a stainless steel expanded metal basket.

Anchorblocks are also nominally 300 mm square and available in various thicknesses and grades for temperatures up to 1,600°C.

Also available are steel clad modules designed for speed of installation. These Clinotherm Modules can be bolted together to form sidewalls, roofs or even complete furnaces. A suitable supporting frame for the panels is all that is required. Each panel has an insulation lining to suit the application. In all cases the fibres are at right angles to the hot face to give maximum mechanical strength to withstand high gas velocities.

In many cases a roof can be prefabricated with a few lightweight supporting members and lifted on to the furnace in one piece. Special shaped roofs can be accommodated by using standard modules for the greater part of the roof surrounded by suitably shaped edge modules to suit the furnace layout.

Clinotherm modular roofs will sit on level brick wall heads and produce a satisfactory seal without recourse to special jointing materials or flanges. This feature can be exploited to even greater advantage on furnace doors to provide high quality sealing.

#### Cements

A range of cements have been developed to secure ceramic fibre to a variety of surfaces. Each type of cement is generally particularly suitable for a given application. For example, Clinotherm LT cement is produced in thin and thick versions. The thin cement is ideal for securing fibre to dense refractories, while the thick cement is used for metal substrates. HT cement has been developed for veneering to hot face substrates, porous structures and stack-bonded fibre. It can be used up to 1,600°C in continuous service.

The economics of fibre lining thickness involve many factors including capital cost, fuel cost,

plant life and capital available. Further influences may be exerted by considerations of potential damage and acceptable cold face temperatures. Clinotherm Limited can be contacted at: Low Road, Earlsheaton, Dewsbury, West Yorkshire WF12 8BU, UK. Telephone: (0924) 462272. Telex: 556352. Fax: (0924) 452201. (Source: Steel Times, June 1989)

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#### Hi-Q Resonators

Siemens has developed ceramic coaxial resonators for the 400 to 4,500 MHz range which achieved a quality factor (Q) of over 1,000. They are especially suited for applications in which high Q takes precedence over the need for small dimensions. For example, mobile radio stations or filters with extremely low insertion loss.

The edges of these new cuboid coaxial resonators are either 12 mm or 20 mm in length. At 1,000 MHz the 12 mm versions achieve a (frequency-dependent) Q of approximately 1,000; at the same frequency, the 20 mm version yields a Q of 1,300. In comparison, standard coaxial resonators, such as the Siemens 6 mm version - also suitable for the 400 to 4,500 MHz frequency range - have a Q between 300 and 900 and the 4 mm versions between 240 and 260.

As with the standard versions, filters can be constructed by coupling a number of 12 mm version resonators. The bandpass filters comprising the new coaxial resonators are suitable for frequencies from 400 MHz to 1,700 MHz and achieve insertion losses of less than 1 dB.

With these new versions, Siemens offers the widest range of coaxial ceramic resonators. Six-millimetre standard resonators are also available in cylindrical style and in packages with soldering lugs. Developers can design filters for specific frequencies by grinding down the resonators and so write specifications for the subsequent production of individual resonators. (For further details, contact: Siemens Infoservice, Postfach 2348, D-8510 Fuerth 2, Germany.) (Source: Technology Ireland, September 1990)

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#### Machinable ceramic with high dielectric strength

A machinable glass-ceramic with temperature resistance to 1,100°F has been developed which is recommended for use in RF insulation applications such as fixtures for medical bag sealing equipment. It is known as Aremcolox(R) 502-600 and used as fixtures in applications where good RF insulation is required because of its excellent dielectric strength of 380 V/mil and high dielectric constant of 6.8 at 1 MHz. The combination of high temperature resistance and electrical insulation means that it can replace many plastics that cannot withstand temperatures above 600°F. In medical bag sealing equipment these fixtures provide excellent RF insulation under 27 MHz.

Aremcolox(R) 502-600 is easily machined using conventional tooling, can be threaded and tapped and metal inserts can be used as fasteners. (Aremco Products Inc., 23 Snowden Avenue, Ossining, NY 10562-3218, USA. Tel: (914) 762-0685. Telex: 137442. Fax: 914 762 1663.) (Source: New Materials World, August 1989)

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### Ceramic fibres of high tensile strength replace asbestos

Development continues of asbestos-free materials for high temperature uses. A flexible ceramic textile fabric has been produced with particularly high tensile strength and stability for temperatures up to 1,430°C, and a melting point of about 1,800°C, as an asbestos-free product.

The material consists of an ultra-pure aluminium oxide ceramic fibre and allows for weaving of bands, tubes, sheets. The fibre is resistant against liquid metal spray, most chemicals and solvents and guarantees outstanding chemical and electrical resistance in high temperature applications for continuous operations. Fibre diameter is 11 µm. Areas of application are seen as protection and screening of tubes, jointing, wire and cable coatings, thermoelement coatings. (Kager GmbH, Postfach 610324, 6000 Frankfurt 61, Germany. Tel: (06104) 2098. Fax: (06104) 5943.) (Source: New Materials World, September 1989)

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### Ceramic fibres and CMCs from readily-available precursors

Ceramic fibres and ceramic matrix composites (CMCs) have been successfully produced from polymeric precursors including polysilazane, polycarbosilane, and polysilane, yielding continuous filaments of high strength, stiffness, and thermal stability. These polymers require somewhat complex synthesis, however, and the stoichiometry of the resulting ceramic is difficult to control. Recently, researchers at NASA Lewis have successfully produced ceramic fibres and CMCs from silsesquioxanes, an easily-synthesized polymer already used commercially for such applications as paint surfactants. Silsesquioxanes have the general formula  $RSiO$ , where R can be a methyl, ethyl, propyl, vinyl, phenyl, or alkyl group.

In the NASA process, which is available for commercial licensing, silsesquioxane powders are blended to achieve the desired silicon/carbon ratio. This blend is heated, causing excess silanol groups to condense out with the evolution of water. When the melt reaches a suitable viscosity, it may be extruded or drawn into fibres. These, in turn, are cured and then fired to yield ceramic fibres. Melt stability is good, so very narrow filaments may be spun. Composites may be produced by first winding the reinforcement fibre onto a mandrel, and then spraying it with the silsesquioxane melt. Alternatively, reinforcement preforms may be melt-infiltrated. After cooling, the pre-impregnated fibres may be cut into plies and stacked in the desired configuration in a metal mould, where they are heated under pressure according to a sequence designed to eliminate any residual void-causing volatiles. The laminate is then cured and heat treated. This new process avoids the problems of solvent removal, shrinkage, and void formation that have accompanied conventional ceramic matrix composite fabrication. (Technology Utilization Officer, Mail Stop 7-3, 21000 Brookpark Road, Cleveland, OH 44135, USA. Tel: (216) 433-5567. Fax: (216) 433-8000.) (Source: New Materials World, September 1989)

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### High-temperature metal/ceramic bond coatings

A new class of bond coatings with reduced thermal expansion has been developed for use in high-temperature thermal-barrier-coating systems. Composed of low-pressure plasma-sprayed metallic matrices combined with a dispersion of low thermal-expansion/high bulk-modulus ceramic particles. This coating method is better than the conventional practice of applying a ceramic coating directly over a metallic bond coat, in that the composite coating lowers the strain of thermal-expansion-coefficient mismatch and retains its integrity at high temperatures.

The ceramic particle dispersoids are processed to possess high cohesive strength, low porosity, and roughly spherical shape. Optimum microstructure is obtained through adjustment of plasma spraying conditions so that the metal component melts completely while the dispersoids undergo only surface melting to preserve their spherical shape.

The resulting coat consists of a dense matrix of metal with well-bonded spherical ceramic inclusions. In practice, however, the ceramic particles often melt and thus flatten on impact. The level of ceramic is therefore kept sufficiently low to prevent dispersoid-dispersoid contact. In this way, the thermal expansion characteristics of the matrix metal are preserved, in combination with the oxidation resistance of the dispersoids. (Technology Utilization Officer, Mail Stop 7-3 (re: Lew-14541/TN), NASA Lewis Research Center, 21000 Brookpark Road, Cleveland, OH 44135, USA. Tel: (216) 433-5567. Fax: (216) 297-8000 or (216) 433-8000.) (Source: New Materials World, March 1989)

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### Ceramics made as artificial lattice

Ceramic artificial lattices have been developed as regular layered structures of molybdenum nitrides and titanium nitrides. However, there is no combination among monolayers. The material is made under vacuum by electron beam deposition.

Metal and semiconductor artificial lattices exist, but this is claimed to be the first time that ceramic artificial lattices have been made. The development is still in its basic stage and its application is not clear. However, there seems to be a possibility of applying the new material in the search for superconductors, magnetic recording materials and development of high-performance X-ray mirrors.

The synthesizing method begins by preparing Mo and Ti in two crucibles. They are subjected to irradiation by electron beam under vacuum; the pressure is  $10^{-8}$  to  $10^{-9}$  Torr. Then they are irradiated by an  $NH_3$  pulse beam near the substrate as the nitrogen source. The partial pressure of  $NH_3$  pulse beam is  $10^{-3}$  to  $10^{-4}$  Torr.  $MgO$  single crystal is the most suitable material for the substrate. Its temperature is 500°C. Then the experimenters deposit the vapour that develops from the crucibles containing Mo and Ti onto the substrate. While depositing this vapour they alternately shut off the crucibles by using shutters. The Mo and Ti then react with N on the substrate, and Mo nitride layers and Ti nitride layers alternately develop. (National Chemical

Laboratory for Industry Planning Div., 1-1, Higashi, Tsukuba-Shi, Ibaraki-Ken 305, Japan. Tel: (0298) 54-4434.) (Source: New Materials World, April 1989)

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#### Castable ceramic for "extreme" heat resistance

Based on zirconia, a castable ceramic, trade-named Ceramacast(c) 646 is claimed to be resistant to temperatures up to 4000°F and recommended for use in ultra high temperature casting and potting applications. This ceramic has the advantage of a high compressive strength of 11,500 psi, making it suitable for cast tooling applications such as brazing fixtures, sintering boats, furnace parts and potting large RF heating coils where good structural strength is required. It is also used for encapsulating thermocouple and electrical gear and has a dielectric strength of 250 volts/mil. In use, it is mixed with water and requires a low heat cure of 200°F. (Aremco Products Inc., 23 Snowden Avenue, Ossining, New York 10562-3218, USA. Tel: (914) 762-0685. Telex: 137442. Fax: (914) 762-1663.) (Source: New Materials World, March 1989)

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#### Ceramic matrix composites by CVI

It is likely that net shape ceramic composite components with continuous fibre reinforcement will be needed for the next generation gas turbine engines and rocket motors; space vehicle thermal protection systems; and high efficiency heat exchangers in power generation. The composites can operate at temperatures higher than dense refractory metals, whilst the fibres confer a form of pseudo ductility to the otherwise brittle ceramics. Chemical Vapour Infiltration (CVI) offers a means of forming composites by infiltrating and depositing ceramic within a continuous fibre preform. This provides close control of matrix chemistry and guarantees fibre alignment and continuity. Instead of carbon fibres, refractory fibres based on silicon carbide, titanocarborane, alumina, and aluminosilicate are appropriate for use with silicon carbide or alumina matrices for example. Fulmer Research has used CVI to work on oxidation protection systems for carbon-carbon composites. CVI also allows dopant gases to be introduced as a means of modifying matrix composition and microstructure. From this experience Fulmer is moving on to work on silicon carbide-silicon carbide composites. (Fulmer Research Limited, Hollybush Hill, Stoke Poges, Slough, Berkshire SL2 4QD, UK. Tel: (02816) 2181. Telex: 849374. Fax: (02816) 3178.) (Source: New Materials World, June 1989)

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#### High-temperature thread locking adhesive

A single component alumina based adhesive is now available for locking metal threads at temperatures above 500°F. This adhesive, known as Ceramabond<sup>TM</sup> 569 is stated to have temperature resistance to 3,000°F. Most thread locking adhesives are organic systems such as silicones and epoxies which can be used to only 500°F. The present product comes in a pre-mixed paste and is easily applied by spatula, brush or injected with syringes on to the threaded area to be sealed. It will cure in place requiring no further treatment after its application, and then has excellent chemical corrosion and oxidation resistance. The

product is useful in locking threads in chemical process equipment, petrochemical equipment, waste treatment units, and aerospace applications where operating temperatures exceed 500°F. (Aremco Products Inc., P. O. Box 429, Ossining, New York 10562-0429, USA. Tel: (914) 762-0685. Tlx: 137442. Fax: (914) 762 1663.) (Source: New Materials World, January 1989)

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#### Engineered ceramic that resists shock

In co-operation with Birmingham University, Foseco Limited have developed an engineered ceramic which can be shaped to close dimensional tolerances. It is known as Deltek and the major advantages are: excellent thermal shock resistance, high refractoriness, high strengths, facility to be tailor-made to complex shapes, good dimensional tolerances, thermal stability, high modulus of rupture at elevated temperature, and excellent surface finish. A component produced through this route can be dipped into liquid steel up to 30 times without thermal cracking. A Deltek range has been produced for the low pressure die casting of aluminium, where it is replacing the iron riser tubes which have long been a source of contamination.

In this operation, the tube does not react with the liquid aluminium; it is not wetted; it is impermeable; it is cost effective; it is insulating; it is maintenance free and reduces the tendency for dross to build up on the internal bore of the tube.

Now the project team is developing a range of nozzles, shrouds, tubes, and dam plates for a variety of metal casting operations. (Foseco (FS) Limited, Tamworth B78 3TL, UK. Fax: 0827 250806. Tlx: 34357 FOSECO-G.) (Source: New Materials World, February 1989)

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#### Alumina ceramic based tape

An asbestos free, flexible, insulating, high temperature ceramic in convenient and economical tape form has been developed made from asbestos free, aluminium oxide based high purity refractory fibres, with a melting point of 3,200°F. It can be cut with ordinary hand scissors and formed into complex shapes. Designed to replace asbestos, based products which were limited to use at 1,200°F, this tape can be used to temperatures exceeding 2,500°F. It is claimed to be especially suited for high temperature gaskets, combustion, furnace and induction linings, handling molten metals, brazing, heat treatment, heat treating and metal forming operations and is an electrical insulator. Further properties claimed are high temperature stability at continuous use temperatures of 2,500°F, low specific heat, low thermal conductivity, resistance to thermal shock, electrical insulation, good dielectric strength and excellent corrosion resistance. (Cotronics Corporation, 3379 Shore Parkway, Brooklyn, NY 11235, USA. Tel: (718) 646-7996 Fax (718) 646-3028.) (Source: New Materials World, February 1989)

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#### Silicon carbide-coated ceramic fabric

A ceramic fabric coated with silicon carbide (SiC) has been developed to serve as a tough,

heat-resistant cover for other refractory materials. Developed to protect the reusable insulating tiles on advanced space transport systems, the covering can also be used on furnace bricks, as engine insulation, and other more conventional uses.

To make the covering, fabric is woven from fibres of alumina/boria/silica and formed into a top-hat shape (or other desired configuration). Silicon carbide is applied to this preformed fabric by chemical vapour deposition (CVD). The amount of SiC applied depends on the temperature of the vapour reaction, the time in the reactor, and the nature of the substrate material. The finished rigid covering, which has a mass of about 0.4 lbm per square foot of surface area, is attached to the tile or other object to be protected by integral pins or clips of ceramic similar to the protected material.

The SiC-coated fabric adds virtually no weight to the tile, and can withstand temperatures up to 3,000°F, whereas glazed protective coatings can only tolerate 2,300 to 2,700°F. Further, because of their brittle nature, glazes afford only minimal protection against impact, and can crack and spall, exposing the tile substrate. The coated fabric can be formulated to meet specific emissivity requirements, and the attachment method compensates for any differences in thermal expansion coefficients. (Technology Utilization Officer, Mail Code 223-3, NASA Ames Research Center, Moffett Field, CA 94035, USA. Tel: (415) 694-6471. Fax: (415) 694-4004.) (Source: New Materials World, February 1989)

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## 7. TRENDS

### Engineering ceramics

Several significant trends in the field of advanced engineering ceramics are projected for the 1990s including:

**Electronic ceramics:** Presently, alumina is the dominant material, while beryllia accounts for about 5 per cent of integrated-circuit (IC) packaging applications. However, aluminium nitride is expected to become commercially important as ICs become faster, smaller, and generate considerably more heat. Electrically resistive silicon carbide with high thermal conductivity also may provide heat dissipation for ICs, particularly in multichip modules. Similarly, the demand for barium-titanate and strontium-titanate ceramic capacitors, used to electrically isolate individual IC chips, is expected to parallel the growth of ICs.

Systematic development of advanced ferro-electrics will continue in the 1990s. Current co-fired dielectric/metal systems for multilayer capacitors and substrates are expected to improve further, leading to lower costs for capacitors and higher speeds and greater circuit densities for substrates. For capacitors, one goal is to reduce the sintering temperature of the dielectric so that lower cost metallization (silver or base metals instead of silver-palladium) can be used while improving dielectric properties and stability.

For substrates, sinterable compositions with reduced dielectric constant will improve speed by decreasing capacitive signal delays. Reduced firing temperatures will allow more conductive metallization (copper versus tungsten or molybdenum) to be used. However, the development of very large multilayer transducers for undersea use will remain a technical challenge.

Perhaps the most tantalizing "new" electronic material is diamond - considered the ideal semiconductor - if its intrinsic properties can be exploited in actual devices, although large-scale devices still are years away.

The role of ceramics in chemical sensing will grow as new compositions and structures are developed. The power of integrated sensors can be enhanced further by mating them to advanced information-processing or signature-analysis techniques such as neural networks.

**High-temperature superconductors:** Worldwide research of superconductor science and technology in response to the discovery of high- $T_c$  superconducting oxide ceramics has provided a clearer understanding of the problems presented by these materials and a more sober assessment of the time scales required for practical applications. Nevertheless, the 1990s will see a continued strong effort in superconductor technology and significant advances in commercialization of devices using oxide superconductors.

The key factor limiting bulk applications of oxide superconductors is the poor current-carrying ability of powder-processed polycrystalline materials. Critical current densities in the presence of magnetic fields must be improved by a factor of  $10^2$  to  $10^4$  in many applications. Solutions to this complex problem will require an understanding of the physical and chemical origins of the so-called "weak link" behaviour, which limits

critical current densities. In addition, researchers must devise methods of installing microstructural defects that can "pin" magnetic flux effectively, and thus increase critical current density, even at operating temperatures near 77K. Ceramic process engineering also will be required to fabricate the materials as composites in conductor form.

Recent research has demonstrated that melt-processed Bi-Sr-Ca-Cu-O can carry even higher currents at 4.2 K in magnetic fields greater than 15 tesla than the present commercial materials, NbTi and Nb<sub>3</sub>Sn. This indicates that low critical currents are not intrinsic to polycrystalline material, and may lead to the first high-field applications of oxide superconductors. At higher temperatures, the first bulk applications are expected to involve low magnetic fields and simple fabrication geometries, such as magnetic shielding.

Electronic devices involving superconductor thin films, such as superconducting quantum devices (SQUIDs and Josephson devices), infrared sensors, and integrated circuits, are expected to precede most bulk applications. A major difficulty in this area is the requirement that films be smooth on the scale of a few angstroms. Continuing efforts to find higher transition-temperature materials may well be successful. However, current understanding suggests that the major benefit of such discoveries would be improved material properties at 77 K rather than increased operating temperatures for devices.

**High-temperature corrosion applications:** Current ceramic recuperators are only marginally economical because of the high cost of ceramic components and relatively low energy prices. However, the inevitable rise in fossil-fuel costs and development of oxide-ceramic composites will combine to make ceramic recuperators economical. Oxide-ceramic components, which include whisker- and continuous fibre-toughened materials, will offer the strength, thermal-shock resistance, and corrosion resistance needed for use in aggressive flue gases.

**Advanced processing:** Increasing use of Jeming-type statistical quality-control programmes is expected to raise the quality of ceramic products, both in the US and other countries. Improvements in process control have reduced dimensional control tolerances from nominally  $\pm 1$  per cent to  $\pm 0.5$  per cent. Tolerances of  $\pm 0.1$  per cent are expected to become common. Product purity levels will be in the parts-per-billion range by the year 2000.

Microstructure/property control requires major changes in traditional ceramic-processing flow-sheets. For example, clean-room technology, already common in electronic-ceramic processing, is necessary to control strength-limiting flaws in structural ceramics. Net-shape processing, requiring only minimal surface finishing, will be required to remain cost competitive. The high cost (~90 per cent of the cost of precision parts) of hard machining is likely to decrease through better control of all forming and firing operations.

**Advanced forming processes:** Advanced net-shape or near-net-shape ceramic-forming processes can improve properties and reliability by minimizing structural defects, while reducing overall manufacturing costs. Frequently, the forming process is the source of many strength-limiting defects including inadequately milled and dispersed

powder agglomerates, voids from trapped gas bubbles, foreign inclusions from contaminants in the powder or introduced during processing, and gross defects such as knit lines arising from the forming process.

Development must focus on fluid processes that control impurities and produce micro and macro-homogeneous parts without introducing voids, cracks, or other physical discontinuities. The goal is to improve existing injection-moulding and slip-casting processes through powder characterization and treatment, better dispersion, and better control of heat and mass-transfer steps. The use of SPC and on-line NDE methods will assure process control and provide early warning of problems.

New processing and forming methods also are under development. Colloidal processing, applicable to any slurry-type process, provides more effective distribution of sintering aids, which allows a reduction in the amount of additives leading to improved high-temperature properties.

New forming methods include slip casting under pressure, centrifugal force, or organic gelation. Pressure-assisted casting offers advantages over conventional slip casting by accelerating the forming step, eliminating mould contamination, and increasing green density, which improves green strength and sintering behaviour.

Organic-gelation casting (gelcasting), which uses a polymerizable monomer in solution, affords all of the advantages of colloidal slurry processing. In addition, it forms a dimensionally stable green body with application of heat. Because liquid transport is not involved, there is no redistribution of fine particles or soluble salts, which improves microstructural homogeneity. Unlike injection moulding, gelcasting does not require high-pressure dies, and leaves a much smaller amount of organic material for the critical binder-removal step.

Polymer-derived ceramics: These materials will continue to increase in significance through the 1990s. Pyrolysis of polymeric metal-organic compounds leads to a wide variety of ceramic materials and promises to be an important method not only for engineering ceramics, but also for electronic ceramics. This technology has led to a variety of silicon-carbide and silicon-oxycarbide fibres. Powder-preparation methods by sol-gel processing have produced fine oxide powders such as

spherical alumina, as well as porous and impervious monolithic forms.

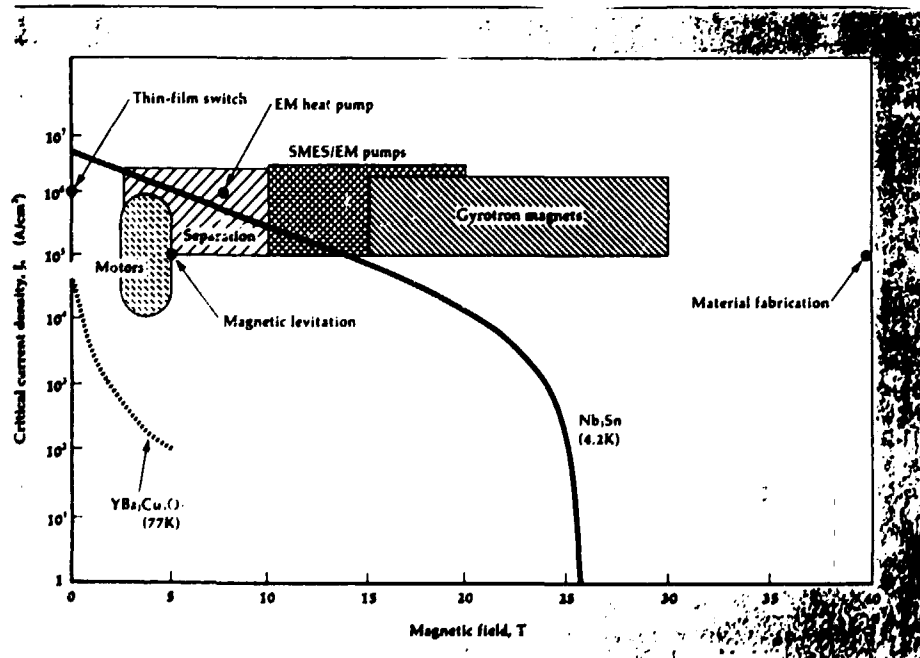
Organic polysilazanes, depending on structure, silicon/nitrogen ratio, and melting properties, pyrolyze to various silicon-nitride products. Some contain finely dispersed silicon carbide, qualifying them as a new type of composite. Strong monoliths of reduced density (70 per cent theoretical) and some foam materials also have been created. Generally, pyrolysis is carried out at lower temperatures than normally required for ceramic materials. Therefore, micrometre-thick wear- or oxidation-resistant coatings can be applied in the field.

The complex chemistry of the polysilazane system may lead to the development of new oxides, nitrides, and borides, both as monolithic ceramics and as composites, although current processing costs are high. The novel, controllable properties of these materials will generate new applications.

Microwave processing: Recent research into high-temperature processing with microwave energy has shown promising results in other applications. Ceramics including alumina, zirconia, silicon nitride, and lithium hydride have been microwave sintered to high densities at temperatures significantly lower than those required in a conventional furnace. The accelerated densification with shorter times and lower temperatures produces much finer microstructures compared with conventional heating. This provides flexibility for tailoring microstructures that offer potential property improvements.

Nitriding silicon to form reaction-bonded silicon nitride (RBSN) also proceeds more rapidly in a microwave furnace than with conventional heating. This suggests the possibility of producing large RBSN components economically.

Potentially, microwave processing may lead to new technological approaches to fabricate ceramic-composite systems that are otherwise impossible. For example, practical alumina-metal composites such as alumina-copper substrate packages may be produced by microwave sintering alumina at temperatures below 1,000°C (1,830°F). Or, ceramic-ceramic composites containing second phases that normally degrade or are incompatible with the matrix at conventional sintering temperatures may be produced by microwave firing. (Source: *Advanced Materials and Processes*, January 1990. Article written by Dr. James O. Stiegler, Director, Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tenn., USA)



The 1990s will see some significant applications for oxide-ceramic superconductors. Researchers must resolve a number of problems, however, including raising the critical current density of high-temperature superconducting materials. Estimated critical current densities that will be needed are shown for potential superconducting applications. (Source: *Advanced Materials and Processes*, January 1990)

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## Structural CERAMICS R&D

### Bright future for ceramic composites

The commercial availability of relatively stable, high-modulus ceramic fibres, such as Nippon Carbon Co.'s Nicalon SiC material, has made possible the development of ceramic-matrix composites that behave pseudoplastically, rather than undergoing the rapid, catastrophic failure normally associated with ceramic materials.

The fabrication of continuous-filament ceramic-ceramic composites is highly constrained due to the fragility of the  $<10\ \mu\text{m}$ -diameter fibres. Thus, only relatively low-stress processes, in which the ceramic matrix is formed from liquid or gaseous precursors, can be used. The most highly commercialized of these methods is chemical vapour infiltration (CVI), in which the matrix material is created at the surface of the fibre when vapour species react at elevated temperatures. The European Propulsion Society in France is the most successful producer of this material, and recently licensed its process to Du Pont, which is now producing it in the United States. However, this process is extremely slow and limited to relatively thin components because it depends on gas-phase diffusion to bring reactants into contact with the fibres.

Continuous-filament ceramic composites are attractive because they combine high strength and toughness with the typical ceramic attributes of refractoriness and resistance to erosion corrosion, and wear. Mechanical behaviour of the composite can be tailored to a significant degree by modifying the friction between fibre and matrix. This property is fundamentally controlled by the fibre/matrix bond.

Applications of continuous-filament composites range from corrosion-resistant, high-temperature heat-exchanger tubes to high-performance jet-engine thrust deflectors. Further refinements to the CVI process should drive down the cost of these materials and create additional applications.

**Whiskers:** Reinforcement of ceramics with microscopic whiskers, as opposed to continuous fibres, substantially increases fracture toughness, even though the materials remain nominally brittle. For example, the toughness of very fine-grain alumina increases from less than 3 MPa<sup>1/2</sup> (2.7 ksi.in.<sup>1/2</sup>) to more than 9 MPa<sup>1/2</sup> (8.2 ksi.in.<sup>1/2</sup>) with the addition of SiC whiskers. Comparable increases in toughness are obtained in other whisker-reinforced ceramics. Whisker reinforcement also can improve a ceramic's resistance to thermal shock, creep, and loss of strength at elevated temperatures.

The mechanisms by which whiskers toughen the composite include both whisker bridging and whisker pullout within the region immediately beyond the crack tip. A theoretical model of the toughening process reveals that composite toughness is determined by a variety of matrix and whisker properties, including volume fraction of whiskers, elastic properties of the matrix, relative fracture energy of the fibre/matrix interface, and whisker diameter and strength.

### Polymer-derived ceramics

Development of advanced ceramic forming processes is aimed at improving properties and reliability by minimizing structural defects, and reducing overall manufacturing costs. The forming process is frequently the source of many

strength-limiting defects including powder agglomerates not adequately milled and dispersed, voids resulting from trapped gas bubbles, foreign inclusions due to contaminants not removed from the powder or introduced during processing by lack of cleanliness control, and gross defects such as knit lines arising from the forming process itself. Forming-process improvements, therefore, must seek to minimize these defects via reliable, cost-effective methods. Minimization of defective parts to maximize yield through processing control also is the most important single factor for achieving cost reduction.

Polymer-precursor routes for fabricating ceramics offer one potential means of reliable, cost-effective ceramics. Pyrolysis of polymeric metallo-organic compounds can be used to produce a wide variety of ceramic materials, and promises to be an important process for both structural and electronic ceramics. Silicon-carbide and silicon-oxycarbide fibres already have been produced and marketed, and sol-gel methods have been used to prepare fine oxide-ceramic powders, such as spherical alumina, as well as porous and fully dense monolithic forms.

Polysilazanes, which contain the (-Si-N-) unit, typify the type of product that can be expected to result from this merging of ceramic science with organic- and inorganic-preparation chemistry. Depending on molecular structure, Si:N ratio, and melting properties, these polymers pyrolyze to many different silicon-nitride products. Some contain silicon carbide dispersed on such a fine scale that the materials can be considered new types of composites. Strong monoliths of reduced density (70 per cent of theoretical) and foam materials also have been created. And, because pyrolysis generally is performed at temperatures lower than those normally required to manufacture ceramics, the process can be used to apply micrometer-thick protective coatings in the field. A major application of these materials, due to their low gas emissions, is binders for conventional ceramic powders to help control shrinkage.

Work on polysilazanes and other complex-chemistry systems is expected to result in the development of new oxides, nitrides, and borides, as both monolithic ceramics and composites.

### Getting a better understanding

Microanalysis plays an important role in improving the mechanical properties of ceramics. For example, it was microanalysis that led to the crucial insight that most ceramic-component failures initiate at relatively large defects (10  $\mu\text{m}$ , 400 microin., or larger). By characterizing the morphology and chemical nature of these defects, it has been possible to identify their causes and to recommend improvements to manufacturing practices and the purity and uniformity of feed materials. As a result, today's ceramic parts are stronger and more reliable.

The mechanical and thermal properties of a ceramic part are governed primarily by micro-structure, if no gross defects exist. Important microstructural features include phases, crystallite morphology, and the crystallography and chemistry of interfaces. Ceramics typically contain small amounts of minor phases that reside at major-phase grain boundaries, and result from impurities, sintering aids, and chemical reactions associated with processing. These secondary phases often control high-temperature properties such as creep resistance



and thermal conductivity. Ceramic-process research is focusing on ceramic chemistry and crystallography, with particular emphasis on tailoring these grain-boundary phases to improve high-temperature performance. Among the expected results are the development of intergranular phases that resist the void formation and crack propagation associated with creep, and the development of interface layers in ceramic composites that control interfacial shear strengths and, thus, improve fracture toughness.

Microstructural and surface-chemistry characterization of new materials before and after use or testing is a necessary step in ceramic-materials development. Techniques such as ultrahigh-resolution transmission-electron microscopy, high-spatial-resolution Auger electron spectroscopy, and secondary-ion mass spectrometry incorporating liquid-metal-ion sources are used extensively. New and improved analytical techniques such as imaging X-ray photoelectron spectroscopy and even higher resolution transmission-electron microscopy using small-gap objective pole-pieces and/or electron holography are being developed.

**Property data:** Widespread use of advanced ceramics will require the development of readily accessible engineering data on properties such as thermal expansion, heat capacity, thermal conductivity, and thermal-shock resistance. New and improved instruments are now available for the rapid and accurate measurement of thermophysical properties at high temperatures. For example, thermal diffusivity can be measured from room temperature to 2,000°C (3,630°F) in less than 8 hours using an automated laser-flash system.

Such thermophysical-property data will be used extensively to improve forming processes. Microstructural-based, finite-element analysis modeling, in its infancy today, also will eventually be used to optimize ceramic-forming methods, as well as to design materials from knowledge of the properties of their phases and microstructural morphology.

#### Service in extreme environments

Energy-saving ceramic-recuperator projects have been sponsored by DoE in recent years. The devices transfer heat from the flue gases of industrial furnaces to the combustion air. The preheated air produces higher flame temperatures for a given amount of fuel, which results in decreased fuel consumption. Alternatively, more product can be processed for a given amount of fuel. Recuperator applications include aluminium-remelting furnaces, steel-soaking pits, municipal and hazardous-waste incinerators and other high-temperature, corrosive, and/or fouling environments. In these applications, maximum flue-gas temperatures are about 1,200°C (2,190°F), and the design preheat-air temperatures are 1,000 to 1,100°C (1,830 to 2,010°F). Because these conditions are too severe for metallic alloys, ceramic components are specified.

Silicon-carbide (SiC) ceramics often are selected for recuperator tubes because of their high strength, oxidation resistance, thermal-shock resistance, and availability; however, these materials are susceptible to corrosion by atmospheres containing alkali compounds, such as NaCl, KCl, Na<sub>3</sub>AlF<sub>6</sub>, Na<sub>2</sub>SO<sub>4</sub>, and Na<sub>2</sub>CO<sub>3</sub>. Oxide ceramics are much more corrosion resistant in these atmospheres, but corrosion increases with increasing silica (SiO<sub>2</sub>) content. Thus, alumina (Al<sub>2</sub>O<sub>3</sub>) and zirconia (ZrO<sub>2</sub>) are more corrosion resistant than mullite (3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>) and zircon (ZrO<sub>2</sub>·SiO<sub>2</sub>).

Ceramic recuperators currently have only marginal economic viability because of the high cost of ceramic components and the relatively low cost of energy. The inevitable rise in fossil-fuel prices and continuing development of oxide-ceramic composites will combine to improve the economics of using ceramic recuperators. Ceramic-composite tubes and other components, toughened with whiskers or other particles, chopped fibres, and continuous filaments, can provide the strength, thermal-shock resistance, and corrosion resistance needed for use in aggressive flue gases. The current high cost of whiskers and fibres will fall with increasing production capability. A DoE-funded project with a major ceramic manufacturer involves developing generic fabrication technology (such as extrusion) for large-diameter, toughened oxide ceramic tubes, while an ongoing DoE-sponsored heat-exchanger project involves developing sol-gel fabrication technology specifically for heat-exchanger tubes.

**Wear resistance:** Friction and wear applications, such as cutting-tool tips, valve trim, seal rings, and pump plungers, represent much of the current market for structural ceramics. Alumina has been the traditional material of choice, followed by silicon carbide. In recent years, partially stabilized zirconia has replaced alumina in many applications as performance requirements have increased. Most recently, whisker-toughened alumina composites have made major inroads into the cutting-tool market for machining superalloys, and may replace tungsten-carbide/cobalt cermets in dies for drawing aluminium cans.

During the past two decades, R&D on friction and wear of engineering ceramics was driven primarily by the needs of new, energy-efficient, high-operating-temperature engine designs for both civilian and military vehicles. The initial expectation was that unlubricated, sliding ceramic couples could be used in piston-ring/cylinder-liner applications. Monolithic, poly-crystalline ceramics like alumina, silicon carbide, silicon nitride, and partially stabilized zirconia were among the first candidates to be investigated, and results of these initial studies suggested that the unlubricated approach was unrealistic for engine applications. This led to high interest in studying the compatibility of ceramics with existing liquid lubricants, and in extending the operating range of liquid lubricants to higher temperatures where ceramics can offer major advantages.

During the period when tribology of engineering ceramics was the focus of a great deal of research, several technological breakthroughs were achieved in developing ceramic-matrix, whisker-reinforced composites and ordered intermetallic alloys. Whisker composites are now used in cutting tools, pump gears, and other wear parts. Friction and wear applications of ordered intermetallics are still emerging as a result of encouraging preliminary results of laboratory wear tests at elevated temperatures. It is possible, however, that high-temperature bearings will be developed before the end of the century that combine ceramic and intermetallic components, especially if the intermetallic component is used to promote beneficial lubricant surface-film formation, which it then transfers to the ceramic. Other approaches, such as using lubricious oxides and chalcogenides as solid lubricants, or redesigning engines to operate with vapor-phase-deposited lubricants, also may be used.

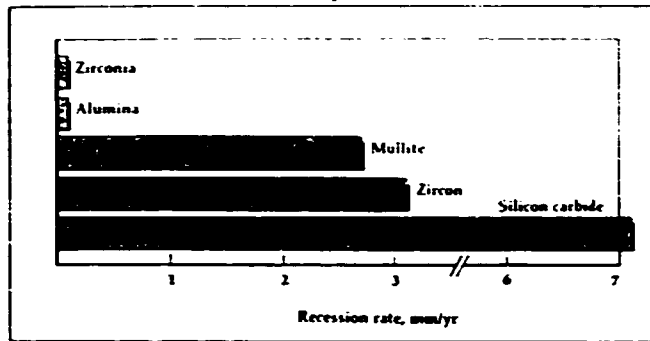
There are many forms of surface-contact damage besides sliding wear. Rolling-contact fatigue resistance, for example, is an important issue in the use of ceramics in rolling-element bearings.

Silicon-nitride materials are among the most successful ceramics introduced to date for use in rolling-contact applications.

The development of toughened ceramics has overcome the limitation of using ceramics under conditions of impact and wear, and more impact-critical applications are emerging. Ceramic coatings, in the meantime, will continue to be used to reduce damage to metal components by fretting, sliding, abrasive, and erosive wear, particularly at elevated temperatures and in corrosive

environments. Many of the next-generation tribological ceramics may find use as coatings or inserts rather than as bulk parts.

Expanded friction- and wear-critical applications of engineering ceramics depend on advances in processing that drive down their cost, the development of new nondestructive evaluation methods that make ceramics more reliable, and continued strong demand for longer-lasting, energy-efficient machine components.



Potential applications of ceramic recuperators include aluminum-remelting furnaces, steel-soaking pits, and waste incinerators. These recession-rate data show why oxide ceramics (zirconia and alumina, for example) are the preferred recuperator-tube materials. The ceramics were exposed for 2,500 hr to remelting-furnace flue gases at 750 to 1,250°C.

(Extracted from Advanced Materials and Processes, September 1990)

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8. MARKETING

Ceramics toughened simply, at low cost

A team of British researchers has invented a simple, inexpensive way to toughen ceramics so that they resist cracking. The new process counters the intrinsic brittleness of ceramics and thus promises to help them fulfil their potential as structural materials.

The new process is noteworthy because it creates a very tough, laminated material by layering a strong component - silicon carbide (SiC) - with a thinner, weaker layer of graphite. Cracks tend to get deflected along the weak SiC/graphite interface, making the composite less prone to catastrophic failure.

Scientists have made other crack-resistant composites by, for example, infiltrating ceramic fibres with a gaseous ceramic precursor or by encasing ceramic fibres in a ceramic or polymer matrix. But ceramic/ceramic composites have been difficult and expensive to fabricate, while polymer/ceramic composites cannot withstand high temperatures.

The new SiC/graphite composite does not have these disadvantages. It is made from inexpensive ceramic powders, and the process is fast. The composite was prepared by coating thin, doughlike sheets of a SiC/polymer paste with graphite. The coated sheets were stacked, pressed, heated to pyrolyze the polymer, and then sintered at about 2,000°C.

The resulting laminate requires 100 times as much work to break as uncoated SiC sheets. Any cracks that form find it easier to grow along the weak interface than through the SiC layers. Such crack formation, however, does weaken the material. (Extracted from C&EN, 8 October 1990)

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Advanced ceramic powder market on rise

Western world market seen to jump 65 per cent: study

The Western world market for advanced ceramic powder materials is expected to grow 65 per cent in the seven years between 1988 and 1995, according to the Micron Powder Systems unit of Hosokawa Micron International Inc.

The estimates were made in an analysis prepared for the company by Ibis Associates Inc., which is affiliated with the Massachusetts Institute of Technology. It defined the advanced ceramic materials covered by the study as electronic and optical ceramics, high-performance structural ceramics and ceramic composites and specialty refractories.

Sales of structural ceramics - which include ceramic cutting tools, wear-resistant crucibles for metal smelting and armour for military vehicles - are expected to grow 15 per cent per year between 1990 and the year 2000.

Ceramic electronic materials make up the largest dollar volume of advanced ceramic material sales. They include ceramic capacitors, gas sensors, ferrite memories and heating elements.

New York-based Hosokawa Micron is a producer of powder processing equipment and systems for a variety of industries.

Sharp growth expected in advanced ceramics  
(in thousands of dollars)

Industry	1985	1990	2000	Annual growth 1985-1990	Annual growth 1990-2000
	\$	\$	\$	%	%
Automotive	53	634	5,700	64	25
Electronics	1,708	3,740	11,360	17	12
Integrated optics	1	111	-	60	-
Cutting tools	14	92	500	46	18
Other industrial	80	225	690	23	12
Other aerospace	20	30	65	8	8
Bioceramics	10	30	-	12	-
<b>TOTAL</b>	<b>1,875</b>	<b>4,372</b>	<b>18,816</b>	<b>20</b>	<b>15</b>

Source: Ibis Associates Inc.

(Extracted from American Metal Market, 10 October 1990)

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For ceramics players reality is setting in

Analysts and people working in the ceramics industry are becoming more realistic. Ceramics are important, they say, markets and applications are growing, but ceramics are not the miracle materials that people once believed them to be.

Speculation about a ceramic engine for passenger cars is a good example of over-optimistic wishful thinking.

World wide, the current advanced ceramics market is valued at \$14 billion, according to analysts at Kline & Co., in Fairfield, N.J., mainly due to the large electronic ceramics market in Asia.

In the US the total advanced ceramics market is \$5 billion, a compounded annual growth rate of 8 per cent to a total of \$11 billion in constant 1989 dollars by the year 2000 is predicted.

The largest advanced ceramics market is in electronic applications such as capacitors, substrates, integrated circuit packages and superconducting materials.

Strategic Analysis predicts an annual growth rate for this market segment of 7 per cent, from \$3.8 billion in 1989 to \$8 billion in the year 2000. Structural applications, including wear parts and cutting tools, will increase by 9 per cent annually, from \$1.2 billion to \$3.0 billion.

And although advanced ceramics may not have taken off as predicted, there is plenty of activity. Many players, however, are finding that

developing and bringing advanced ceramics to market is too difficult and too expensive for a single company. This leads to mergers and joint ventures.

For example, Coors Ceramics Company in Golden, Colo., a subsidiary of New York City-based W. R. Grace, recently signed a letter of intent to jointly work on ceramic packaging technology for multichip modules. The companies want to develop multilayer, co-fired aluminium nitride packages for use by the Navy.

Hercules Advanced Materials & Systems Company in Wilmington, Del., in April contracted with Rhone-Poulenc Inc. to market and sell the silicon-carbon-tri-oxide fibre made by the French company in the US.

There were a number of acquisitions in recent years, including, in 1989, Kyocera of Japan buying AVX, Tokuyama Soda acquiring General Ceramics and Coors Ceramics buying GE Ceramics.

Developing advanced ceramics is a long-range undertaking according to Oakridge National Laboratory in Oakridge, Tenn., which is currently trying to start a research project on continuous fibres ceramics composites.

The composite is an advanced material that has unique and different properties. The material also has potential uses in pollution abatement systems. Still, the cost and risk associated with developing these materials are such that no company wants to undertake the research and development by itself.

Advanced ceramics research and development efforts are focusing on the material's many advantages, such as resistance to corrosion, thermal shock and high temperatures while offering excellent wear and low surface resistance. At the same time efforts are being made to overcome disadvantages: such as brittleness and a propensity to crack.

The result is a steady stream of new mixtures and manufacturing processes where advanced ceramics are coupled with other advanced composites to produce structural ceramics which combine the best characteristics of both materials. For example, ICI Advanced Materials in Wilmington, Del., uses a process called "viscous plastic processing" (VPP) to make high-strength superconductive materials.

VPP involves mixing a ceramic powder with a viscous polymer, resulting in a mixture that is easy to shape, has a high degree of uniformity and has fewer cracks and other defects. ICI uses the VPP process to manufacture superconductive short-dipole antennas for such radio frequency devices as waveguides, antennas, resonant cavities and flux transformers. Lanxide Corporation in Newark, Del., overcomes the brittleness problem by literally "growing" ceramic matrix composites from a mixture of ceramic powder and a metal. By combining aluminium and ceramics, for example, Lanxide produces alumina with about 10 per cent of residual metal.

Applications are as parts for pumps, valves and other high-wear applications. Additional advantages of this process are that it avoids "the huge shrinkage which you normally get when you fire a ceramic. And this material grows exactly in the shape you want, even in complicated large shapes".

In another application, E.I. du Pont de Nemours & Co. is using these Lanxide "engineered ceramics" in developing armour, heat-exchangers and aerospace components.

According to the materials systems reliability department with Ford Motor Company in Dearborn, Mich., the main problems are still cost and

reliability. But Ford continues with ceramics research "trying to replace some of the valve train parts, for example, where there is a need to improve the Company Average Fuel Economy (CAFE)". One way to achieve the fuel standard is to take weight out of the engine.

Meanwhile, Japanese auto makers are applying more ceramics in higher-end cars. The Nissan equivalent of the 300 ZX has a ceramic turbo charger. Using this material is a little more expensive, but it provides a lot more power in a comparatively small engine.

The field of energy-generating equipment offers many current applications of structural advanced ceramics. In coal fired generating plants, for example, ceramics are used to protect coal chutes and corrosion-prone places exposed to sulphur from the burnt coal.

Biomedical applications are also coming on line. Advanced ceramics are increasingly used to manufacture internal prostheses to braces.

ICI Advanced Materials sees chances for high temperature applications, for the national aerospace plane or for other areas where you want to shield components from the high temperature in the engines or in a high corrosion environment.

Dow Chemical Company agrees that ceramics face tough competition for applications in engines with materials that might not be as good but are a lot cheaper. Consequently, the organization is concentrating on structural materials: ballistic applications, cutting tools and wear products.

Despite all their promising applications, advanced ceramics have to overcome a major catch-22: production is still relatively small, which makes the material expensive. And until ceramics become cheaper, industry will not seriously look at them as alternatives for current, cheaper materials. (Extracted from Chemical Marketing Reporter, 30 April 1990)

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#### Kline tracks growth for specialty ceramics

The global market for precursor-derived ceramics, consisting of high-performance structural and electronic products, will exceed \$500 million by the year 2000, according to the advanced materials group of Kline & Co., Fairfield, N.J., USA. The firm places the world market for these products at \$200 million in 1989 and says chemical vapour deposition (CVD) accounted for 86 per cent of it. CVD-derived ceramics are used primarily in structural coatings and should grow at 9 per cent per year. Ceramics produced by chemical vapour infiltration, sol-gel, and polymer pyrolysis are growing even faster, between 13 and 17 per cent annually.

The advanced ceramics industry reached \$14 billion in 1989, Kline says. Structural products, such as wear parts, accounted for over 20 per cent of the market, but these, despite earlier forecasts of 20 per cent annual growth, failed to keep pace with electronic ceramics. The future of the market depends on whether ceramics can overcome several inherent flaws, particularly catastrophic failure. Chemically-derived ceramics have the potential to solve these through close control of purity and microstructure. (Source: Chemical Marketing Reporter, 19 May 1990)

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## 9. PUBLICATIONS

### Superalloys, supercomposites and superceramics

Edited by John K. Tien and Thomas Caulfield, Boston: Acad. Pr. 1989. 755 pages. \$129.95.  
620. 1'18 TA485 88-30261 ISBN 0-12-690845-1

Contents, abridged. Resources - supply and availability. Metallurgy of investment cast superalloy components. Thermomechanical processing of superalloys. Powder metallurgy and oxide dispersion processing of superalloys. Creep-fatigue interaction in structural alloys. Cyclic deformation, fatigue and fatigue crack propagation in Ni-base alloys. High temperature corrosion. Strength and ductility of intermetallic compounds. Structural ceramics: processing and properties. Index.

Note: Reviews the state-of-the-art superalloy technology along with discussion of superceramics and supercomposites, alternative high temperature systems. Twenty-two contributions prepared by experts in the field, including researchers from Taiwan and Japan. Not meant to be comprehensive but does consider significant issues. Includes chapter references and many helpful illustrations. For research level collections.

To obtain: Academic Press Inc.,  
465 South Lincoln Drive, Troy, MO 63379, USA.  
Phone: (800) 321-5068.

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The following three books can be ordered through The American Ceramic Society, Inc., Book Service Dept., 757 Brookside Plaza Drive, Westerville, OH 43081. Fax: 614-899-6109. Phone: 614-890-4700.

Ceramics and Civilization, Vol. V.  
The changing roles of ceramics in society:  
26,000 BP to the present  
W. D. Kingery, ed.

Several of the essays included here were presented at a 1988 American Ceramic Society symposium on the changing roles and functions of ceramics in society. Others were presented at a 1989 symposium that focused on cultures in contact as a source of ceramic change. Copyright 1990. Hardbound; 388 pages. ISBN 0-944904-11-4.

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Sintering of advanced ceramic materials. Ceramic transactions, Vol. 7  
Carol A. Handwerker, John E. Blendell and Wolfgang Kaysser, eds.

The International Symposium, Sintering of Advanced Ceramics, held at the American Ceramic Society Annual Meeting, Cincinnati, Ohio, on 2-4 May 1988, served two purposes. First, the Symposium was held to recognize Professor Robert L. Coble for his pioneering work on sintering, grain growth, creep and other diffusion-controlled processes. Second, the Symposium provided a forum for discussion of the state of sintering theory and experiment. As seen in the papers from the Symposium, these two purposes are intimately connected. In almost every sintering paper, not just in the ones here, Bob Coble's influence can be found.

The 45 papers included in these proceedings cover such topics as sintering paradigms; current

status; models of sintering and grain growth; model experiments; liquid phase sintering and creep of two phase materials; sintering and microstructure development in multi-component ceramics; and ceramic-ceramic composites.

Copyright 1990; hardbound; 800 pages.  
ISBN 0-944904-20-3.

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Mullite and mullite matrix composites  
Ceramic transactions, Vol. 6  
Shigeyuki Somiya, Robert F. Davis,  
Joseph A. Pask, eds.

Mullite is now considered to be a strong candidate material for structural applications at high temperatures because of its intrinsic strength, low thermal expansion and good chemical stability at such temperatures. Mullite is the only compound in the  $Al_2O_3-SiO_2$  system under standard conditions. Most traditional ceramic products have mullite as part of their final phase composition, since they usually contain some clay and silicon as starting materials. The microstructures of the materials also contain a relatively low melting glass. Thus, the significance of the inherently favourable properties of mullite was not recognized until about 15 years ago when the mechanical behaviour in compression at high temperature (1,500°C) of mullite specimens free or nearly free of a glassy phase was first studied.

These proceedings, from the First International Conference on Mullite, Japan, 1987, cover such topics as: phase equilibria and immiscibility in the  $Al_2O_3-SiO_2$  system; crystal growth, crystalline and amorphous structures and impurity distribution; reactions and mechanisms of mullitization; starting powder preparation and characterization; forming and sintering of mullite and composites containing mullite; mullite matrix composites; mechanical properties and behaviour; and applications and process characterization. Copyright 1990; hardbound; 665 pages. ISBN 0-944904-05-X.

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Artificial composites for high temperature applications, by M. U. Islam, W. Wallace and A. Y. Kandell, reviews developments in metal and ceramic matrix composites containing metal or ceramic fibres or whiskers for high temperature applications. The composites are categorized as ductile-ductile (metal matrix composites reinforced with refractory fibres, e.g. tungsten wire reinforced superalloys); brittle-ductile (metal matrix composites reinforced with ceramic fibres, e.g. the iron alloy FeCrAlY reinforced with silicon carbide fibre); ductile-brittle (ceramic matrix composites reinforced with relatively ductile, refractory metal wires, e.g. tantalum wire reinforced silicon nitride); and brittle-brittle (ceramic fibre reinforced ceramic, glass, or glass ceramic matrices, e.g. silicon carbide fibre-reinforced silicon carbide, silicon nitride, or lithium aluminosilicate glasses). Significant problems in each of the composite systems are identified and research directions for the future suggested. The information was originally prepared as a review sponsored by the National Research Council of Canada. While the emphasis is placed on developments between 1975 and 1986 (the last date in the references), the status of the composite systems before 1975 is summarized.

To obtain: Noyes Publications, Mill Road at Grand Ave., Park Ridge, NJ 07656, USA. Phone: (201) 391-8484. Fax: (201) 391-6383.

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Advanced Technical Ceramics, edited by Shigeyuki Somiya, is an updated English translation of the 1984 Japanese edition. The term technical ceramics as defined by Dr. Somiya refers to "ceramics that exhibit a high degree of industrial efficiency through their carefully designed microstructure and superb dimensional precision ... Rigorously selected materials are used in products with a precisely regulated chemical composition, fabricated under strictly controlled conditions of shaping and firing." The 23 contributors are largely from Japanese industrial laboratories, with several, including the editor, from technical institutes. The book is divided into three major sections. The introduction includes chapters on definitions and types of ceramics; synthetic raw materials; production processes; and methods of evaluating mechanical and thermal properties. The section on properties and applications covers electrical, electronic, magnetic, thermal, chemical, optical and mechanical properties in separate chapters, plus a chapter on biological applications. The final section covers precision machining methods. An appendix that presents a chronology of the development of advanced electronic and engineering ceramics from 1893 to 1982 is a novel and informative addition.

To obtain: Academic Press Inc., 465 South Lincoln Drive, Troy, MO 63379, USA. Phone: (800) 321-5068.

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Basic research in superconductor, ceramic, and semiconductor sciences at selected Japanese laboratories, by Robert J. Gottschall, is a report based on visits in 1988 to 14 major industrial, governmental, and university R&D organizations and laboratories. The subjects covered in this most interesting and informative 194-page report are: superconductivity; diamonds; cubic boron nitrides; synchrotron radiation, accelerators, and applications; beam technology and lithography; semiconductor sciences; ceramic process science; high pressure and bonding ceramic process science; mechanical behaviour and characterization of ceramics; ceramic design and engine applications; ceramic surface modification and behaviour; ceramic superplasticity; ceramic matrix composites; carbon; ordered alloys; metal matrix composites; and advanced instruments and facilities. This is highly recommended for obtaining an overall picture of the thrust and scope of materials R&D in Japan.

To obtain: Dr. Robert J. Gottschall, Division of Materials Sciences, Office of Basic Energy Sciences. Mail Stop G-256 GTN, Washington, DC 20545. Phone: (301) 353-3428. Also available for purchase: The National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161 as PB89-174264/WFT. Phone: (800) 336-4700.

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Advanced ceramic matrix, metal matrix and carbon-carbon composites by Dr. John Briggs, published by Materials Technology Publications, February 1990, 177 pages. World Business Publications Ltd., 4th Floor, Britannia House, 960 High Road, London N12 9RY, UK.

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Advanced Structural Ceramics prepared by Innovations 128, Paris, published February 1990, 230 pages. May be obtained through World Business Publications Ltd., 4th Floor, Britannia House, 960 High Road, London N12 9RY, UK.

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High Tech Ceramics P. Vicenzini, Elsevier Science Publishers BV 1987. ISBN: 0 444 42776 7 (set). Price: \$770.

High Tech Ceramics is a new publication containing the proceedings of the sixth International Meeting on Modern Ceramics Technology (6th CIMTEC) held in Milan, Italy from 24 to 28 June 1986. The opening section of the three-volume compilation concentrates on the economic implications and strategies for the new ceramics and their growing impact on key industrial sectors. Forecasts are provided for various market growths and the criteria for these evaluations are clearly explained. Over 300 fully-referenced scientific papers are then presented, each containing in-depth accounts of methods, results and conclusions spanning a wide range of state-of-the-art advanced ceramic research. The key sections include basic ceramic science, process technology, materials characterization, and investigation into the properties and functions of ceramics in magnetic, optical, chemical, thermal, mechanical, electronic and nuclear applications. Drawing from a wide range of international expertise, High Tech Ceramics will be of particular relevance to personnel currently involved in research and development, whatever the application.

The 3,000-page treatise concludes with an authoritative overview given by leading representatives from the US, Japan, Western Europe and Australia who are all involved in major national advanced ceramic research programmes.

For further details contact: Elsevier Science Publishers BV, Sara Bargerhartstraat 25, PO Box 211, 1000 AE Amsterdam, Netherlands.

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Hardness estimation of minerals, rocks and ceramic materials

A. Szymanski of the Institute of Electronic Materials Technology, Warsaw, Poland, and J. Szymanski of the Union of Whiteware Ceramic Producers, Warsaw, Poland, authored this volume, which is No. 49 of the Materials Science Monographs. This book provides a survey of hardness test methods in current world-wide use and includes examples indicating the merits and deficiencies of these methods. The tables found at the end of the book, as well as the hardness test results from various methods included in the text itself, are meant to serve as a rough guide in the choice of appropriate test methods. Included are a list of symbols, appendix, bibliography and subject index. 350 pages, \$122, ISBN 0-444-98898-X. Order from Elsevier Science Publishers Co. Inc., Box 882, Madison Square Sta., New York, NY 10159, USA.

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2nd European Symposium on Engineering Ceramics Edited by F. L. Riley, Elsevier Science Publishing Co. Inc., 655 Avenue of the Americas, New York, NY 10010. 1989, xiii, 285 pages. ISBN 1-85166-295-2.

This book is the proceedings of a meeting held in London, England in 1987. Unlike most conference

proceedings, this book contains only papers by invited speakers that presented authoritative overviews of work since the first European Symposium on Engineering Ceramics in 1985. It does not contain detailed technical information. It is directed towards current and potential users of engineering ceramics, and provides an excellent review of the European perspective on the status of engineering ceramics at the time of the symposium, although one presentation from the United States and one from Japan give an overview of the perspective in these regions.

Twelve papers are included in the book. The first provides an excellent overview of the European Communities programmes that include work on engineering ceramics. The second is a review of the status of standardization activities for engineering ceramics, and the third is an overview of the developments in engineering ceramics since the first meeting in 1985. Other papers provide overviews on coatings for thermal barrier and wear resistance applications, production technology, non-destructive evaluation, non-oxides, ceramic matrix composites and ceramics in internal combustion engines.

The last three papers are regional in scope. One reviews the ceramic heat engine programmes in the United States; one reviews the developments in the UK engine ceramic programmes; and the final paper reviews the attitude towards high technology ceramics in Japan. The book contains a large number of references and provides an excellent overview of European activities in engineering ceramics.

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Plasma spraying of metallic and ceramic materials.  
Dusan Matejka and Bernard Benko. John Wiley & Sons, Inc., Baffins Lane, Chichester, West Sussex, PO19 1UD, England. 1989, 280 pages.  
ISBN 0-471-918768. \$119.

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Ceramics and Civilization: Vol. IV: Cross-craft and cross-cultural interactions in ceramics  
Edited by P. E. McGovern, M. D. Notis and W. D. Kingery. American Ceramic Society, 757 Brooksedge Plaza Drive, Westerville, OH 43081. 1989, ii, 390 pages. ISBN 0-916094-48-0.

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Advances in ceramics, Vol. 22: Fractography of glasses and ceramics  
Edited by J. R. Varner and V. D. Frechette. American Ceramic Society, 757 Brooksedge Plaza Drive, Westerville, OH 43081. 1988, vi, 442 pages. ISBN 0-916094-85-5.

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#### High performance materials

This report provides a broad review of key trends and developments in high performance materials, highlighting selected topics such as metal- and ceramic-matrix composites, engineering ceramics, ceramic fibres, superconducting ceramics and fibre reinforcements. Problem areas in materials performance and fabrication are identified. The market situation and growth prospects for many materials are assessed. An international directory of companies and research laboratories involved in the development of these materials is included. 230 pages, 1988, \$480.

Order from Innovation 128, 24 rue du Quatre Septembre, 75002 Paris, France.

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Plastics-Ceramics-Metals  
Edited by H. L. Hornfeld. Published by Society for the Advancement of Material and Process Engineering (SAMPE), European Chapter, c/o Ernst Schiantarelli, Glasslistrasse 11, CH-8172 Niederglatt/ZH, Switzerland. 545 pages.

Proceedings of the 11th SAMPE international conference held in May 1990 in Basle, Switzerland. Sections cover global issues in advanced composites, with contributions from industry specialists. Specific chapters deal with high temperature/high toughness matrix materials, hybrid design and engineering, non-destructive testing of composite structures, and joining, adhesion and interface phenomena. Aerospace topics include a new approach to complex aircraft composite structures, and design and fabrication of a compression-moulded graphite-reinforced epoxy SMC ram air turbine blade.

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#### Structural ceramics data base formed

To speed the application of high-temperature advanced ceramics from laboratories to market, a new structural ceramics data base for personal computers has been developed by materials scientists at the National Institute of Standards and Technology with help from the Center for Advanced Materials at Pennsylvania State University, USA. (Source: American Metal Market, 19 November 1990)

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Ceramics: applications in manufacturing  
Edited by David W. Richerson, Society of Manufacturing Engineers, 1 SME Drive, Dearborn, Michigan 48121. 1988, 217 pages, hardcover.

The use of ceramics in industrial applications has suffered from the perception that they are fragile and not very reliable. Recent dramatic improvements in the properties of ceramics has outdated this perception, and advanced ceramics now can perform effectively in a multitude of applications. By publicizing more widely the many cases where ceramics have been used successfully, it is hoped that some of the traditional reluctance to use these materials can be overcome. This volume is a compilation of 24 journal articles and conference papers, selected by a well-respected figure in the ceramics field to introduce industrial personnel to some of the successful applications of ceramics in manufacturing. It is part of the "Manufacturing Update Series" of SME publications, designed to provide up-to-date background information for engineers reviewing the subject for the first time, and offer solutions to practical shop problems.

The introductory chapter sets the stage with two papers co-authored by Richerson that provide a general description of ceramic materials and an overview of possible applications in manufacturing. The second chapter follows with two papers that refer to ceramics applications in two specific metal-forming operations: investment casting and extrusion, but the first of these papers is really a history of the development of investment casting of turbine components and refers to the role of ceramics only in passing. Chapter 3 consists of a number of articles on the use of ceramics in high

temperature manufacturing equipment, including heat exchangers and furnaces, and chapter 4 comprises articles on the use of ceramics in metal-cutting operations. These two chapters are the highlight of the volume, with numerous specific examples of successful applications that exploit appealing characteristics of ceramics (e.g. high temperature capability, high hardness, high resistance to chemical attack). Chapter 5 is entitled "Ceramics in non-traditional manufacturing operations", but this is somewhat misleading because the articles in this chapter really deal with various novel methods for machining ceramics (e.g. laser cutting, water jet cutting) rather than with the use of ceramics in any of these operations. In chapter 6 the book finishes off with the paper by Lumby on the evolution of "sialon" ceramic materials and some of their specific uses in manufacturing applications, and with an excerpt from Richerson's textbook "Modern Ceramic Engineering: properties, processing, and use in design" that provides another overview of possible applications.

On the whole the volume is an interesting collection of articles, and serves as a useful starting-point for manufacturing personnel thinking about utilizing ceramics in their operations.

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C2C Abstracts: Japan is a new monthly series containing abstracts in English of the leading scientific, technical and business publications of Japan. The series offers coverage of chemistry, the chemical industry, materials sciences and materials production.

The publisher, SCAN C2C, reportedly maintains a data base consisting of over 140,000 abstracts from more than 500 Japanese publications, and adds 4,000 new abstracts to this data base each month. Future plans include data base access through leading on-line hosts, customized research and English language directories. SCAN C2C is located at 500 E St., SW, Suite 800, Washington DC 20024, USA.

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#### Concise Encyclopedia of Building & Construction Materials

Edited by Fred Moavenzadeh, this book presents the work of numerous specialists in the field. There are articles covering general building materials, their mechanical properties, and economic and historical aspects, as well as those dealing specifically with the use of materials such as clays, ceramics, cement, sand, gravels, glass, metals, wood, polymers, plastics and composites. Intended primarily for those interested in having a useful reference source in building and construction materials, the work would also be the ideal course reference for students in architecture, civil and structural engineering and related disciplines. Hardcover, 650 pages, \$175. Order No. 0 08 034728 2 from Pergamon Press, Inc., Maxwell House, Fairview Park, Elmsford, NY 10523, USA.

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#### Thermoset powder coatings

Edited by J. Ward. Published by FMJ International Publications Ltd., Queensway House, Redhill, Surrey RH1 1QS, England. 140 pages.

Industry specialists contribute chapters on raw materials and their manufacture, coatings and their

applications, surface pretreatment, and curing and stripping.

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Glass science and technology, Vol. 4A: Structure, microstructure and properties  
Edited by D. R. Uhlmann and N. J. Kreidl, Academic Press, 1250 Sixth Ave., San Diego, CA 92101. 1990, xviii, 346 pages. ISBN 0-12-706704-3.

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#### Superconductivity: A guide for industrial applications

This report provides a realistic picture of both high and low temperature superconducting materials and products, reviewing the state of the art of the technology and updating developments, including processing advances and electrical property improvements. Key research activities in Europe, the United States and Japan are provided. 190 pages, 1989, \$500. Order from Innovation 128, 24, rue du Quatre Septembre, 75002 Paris, France.

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Advanced materials: The challenge for the next decade is available in two volumes and contains the proceedings of the 35th International Society for the Advancement of Material and Process Engineering (SAMPE) Symposium and exhibition, held in April. The technical sessions and papers presented include developments in materials fibres and matrix materials, tooling materials, adhesives and bonding, metal and ceramic matrix composites, health and safety, quality control, coatings, and the National Aero-Space Plane materials development programme.

Price \$80. SAMPE, 1055 W. San Bernardino Rd., Box 2459, Covina, CA 91722, USA.

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#### Polymer alloys and blends

by L. A. Utracki. Published by Carl Hanser Verlag, Postfach 860420, Kolbergerstrasse 22, W-8000 Munich 86, Germany. 356 pages.

Following an introduction and historical outline of alloys and blends, the book describes principles of miscibility and phase equilibria phenomena, and crystallinity considerations, then goes on to discuss rheology of specific systems. Appendices list commercial polymer alloys and blends, survey the patent literature, and cite selected monographs.

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#### Concise encyclopaedia of composite materials

Anthony Kelly edited this volume. The 55 articles in this encyclopaedia provide a full and up-to-date account of all aspects of composite materials, including fibre composites, particulate composites, and naturally occurring composite materials and their properties. Current coverage also is given to metal-matrix composites and thermoplastic resins reinforced with fibres. Each article is extensively cross-referenced to other related topics. Hardcover, 350 pages, 250 illustrations and tables, \$135. Order No. 0 08 0347185 from Pergamon Press, Inc., Maxwell House, Fairview Park, Elmsford, NY 10523, USA.

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Proceedings of the American Society for Composites,  
Fifth Technical Conference: Composite Materials in  
Transition

This is a collection of 96 reports on composite materials processes, performance and applications from North America, Great Britain and Japan. Report topics include vibration and damping; joining, fastening and fabrication; interfaces; biotechnology applications; toughness and damage tolerance; control and modelling; structural mechanics; metal matrix, cementitious and ceramic composites; design; impact and compression; thermal aspects; and non-destructive testing. Hardcover, 1,049 pages, illustrations, \$165. ISBN 0-87762-767-3. Order from Technomic Publishing Co. Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604, USA.

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Composites: an insider's technical guide to  
corporate America's activities  
437 pages, \$127.

A fine overview of the 249 most significant companies (465 entities, including subsidiaries) that comprise the US composites industry. Each company's description includes address and phone number, ownership, product lines, key executives, types of professionals employed, and facilities and equipment. Equally valuable are lists of companies by product, materials, process capabilities and research activities.

Turner Moss Co., PO Box 1885 W. Murray Hill Station, New York, NY 10156-0611, USA. Phone: 212-481-8666.

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High-temperature superconductivity in perspective  
Gregory Eyring (Office of Technology Assessment Project Director), 136 pages, \$6.50.

High-T<sub>c</sub> technology moves fast enough to turn today's definitive study into yesterday's news. Still, the outline of potential applications has become increasingly clear, and the Office of Technology Assessment has done a fine job of pulling the pieces together. It also provides an excellent comparison of US, Japanese and other R&D efforts, and discusses policy options.

(Refer to GPO No. 052-003-01187-5: Supt. of Documents, Government Printing Office, Washington, DC 20402-9325. Phone: 202-783-3238. Fax: 202-275-0019.)

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Advanced materials source book  
by Jon Binner, Paul Hogg and John Sweeney,  
367 pages, \$135.

Short takes on new ceramic, polymer and composite technology that provide excellent depth, though with a mostly European slant. Most of the information has been published by Elsevier before, but its availability in a single volume will let you more readily discern trends.

(Elsevier Science Publishers Ltd., Crown House, Lindton Road, Barking, Essex, IG11 8JU, England. Phone: 01-594-7272. Fax: 081-594-5942.)

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Adhesion and bonding in composites  
Edited by Ryutoku Yosomiya et al., NY: Dekker, 1990.  
357 pages, \$99.75. 620.1'18 TA418.9 89-36669,  
ISBN 0-8247-8149-X.

Contents, abridged: interfacial characteristics of composite materials. Surface modification of matrix polymer for adhesion. Modification of inorganic fillers for composite materials. Adhesion of resin to metal. Interfacial modifications and bonding of fibre-reinforced metal composite material. Interface analyses of composite materials. Index.

Note: The editors emphasize methods used to improve the adhesion and bonding between composite materials. Contributions by Japanese experts discuss topics such as the relationship between wetting properties and adhesion, surface modifications of matrices or fillers, adhesion of plastics onto metals, and methods of measuring the interfacial strength of fibre-reinforced composites. Includes over 250 diagrams and tables and about 450 literature references. For polymer scientists and technologists, plastics engineers, adhesives chemists and graduate students.

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Bonding and repair of composites: papers from a  
one-day seminar organized jointly by Butterworth  
Scientific Ltd. and Rapra Technology Ltd.,  
14 July 1989

Edited by John Herriot, London: Butterworth, 1989,  
106 pages, \$89.95. 620.1'18 TA418.9 89-15832,  
ISBN 0-408-04863-8.

Contents, abridged: adhesives for composite joints. Frictional coupling for bonding of composites. Adhesive bonded joint between a fibre composite wing blade and the steel hub of a wind turbine. Structural adhesive bonding of thermoplastic fibre composites. Fatigue crack growth in adhesively bonded and co-cured CFRP joints. FDEMS sensors: in-situ monitoring of adhesive bondline and resin cure during repair. Low energy cured composite repair systems. A new low-temperature rapid curing composite material for structural repair.

Note: Bonding, which covers the extensive use of adhesives, welding and frictional coupling, is a major theme. Non-destructive testing of composite bonds and composite repairs are also covered. The techniques described herein may be applied to plastic, cement, metals and ceramics, among other materials. For specialists in polymer engineering, materials science, composites and non-destructive testing.

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Processing of plastics

A concise reference book on processing of plastics covering major processing methods with emphasis on newer developments, processing parameters, trouble-shooting, etc. was published in December 1990 by Popular Plastics & Packaging.

The book is edited by our Editor Mr. A. S. Athalye, who has been actively associated with the industry for over 30 years and knows exactly the information needs of the industry.

Colour Publications Pvt. Ltd., 126-A Dhuruwadi, Off Dr. Nariman Road, Prabhadevi, Bombay 400 025,

India. Phone: 430 9318, 430 6319. Telex: 011-71242 CEPE IN.

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Who's who in world petrochemicals & plastics

It lists the names, titles, addresses, telephone, telex and fax numbers of 2,700 corporate offices and 7,900 top persons. The directory costs \$125 per copy from Who's Who Information Services, 17 South Briar Hollow Lane, #401, Houston, Texas 77027, USA. Phone: (713) 623-4627. Fax: (713) 623-4628.

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Handbook of plastic material and technology answers the most frequently asked questions by engineers, designers, manufacturers, processors, mould makers and purchasing agents. The book covers 70 materials and fillers and 17 primary processes. Thirty-two additional chapters detail such plastics-related information as assembly, decorating and process control. Appendices provide a ranking of materials according to properties (density, tensile strength and modulus, flexural modulus, elongation at break, notched Izod impact strength, heat distortion temperature and electrical properties), as well as abbreviations, conversion tables to and from standard and metric units, and commonly used metric conversions. Contributors to the Handbook are experts in their subject areas with business experience in the field.

1,750 pages, \$99.95. John Wiley & Sons, 605 Third Ave., New York, NY 10158, USA.

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International Conference on Advances in the Stabilization and Controlled Degradation of Polymers, Vols. 1 and 2.

By A. V. Patsis, 1989, Lancaster, PA/Basel, Technomic. ISBN 87762 572 7 (Vol. 1), 588 3 (Vol. 2).

These volumes contain the proceedings of conferences held in May of the years 1985-1987 at Lucerne, Switzerland. Papers covering aspects of polymers, polypropylenes, UV-cured coatings and thermoplastic elastomers are among those presented.

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Handbook of polymer science and technology, Vols. 1-4.

N. P. Cheremisinoff (ed.), 1989, New York/Basel, Marcel Dekker. ISBN 0 82478 173 2 (Vol. 1), 174 0 (Vol. 2), 004 3 (Vol. 3), 021 3 (Vol. 4).

This handbook comprises four volumes: "Synthesis and properties", "Performance properties of plastics and elastomers", "Applications and processing operations", and "Composites and speciality applications", and provides a comprehensive, authoritative guide to the field of polymer science and the technologies related to their engineering applications - bridging the gap between the theoretical foundations of polymer science and practical manufacturing concepts.

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Engineering polymer sourcebook

Raymond B. Seymour, xvii + 300 pages. McGraw-Hill, 1221 Ave. of the Americas, New York, NY 10020. 1989, \$42.50.

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Materials science of concrete I

Jan P. Skalny, editor. American Ceramic Society, 757 Brookside Plaza Dr., Westerville, OH 43081. 1989, 332 pages. ISBN 0-944904-01-7, \$75 non-members, \$60 members.

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Metallurgical dictionary

J. A. Wanderer (ed.). Part 1: English-German, Part 2: German-English; 1989, Wanderer Verlag Heere, ISBN 3 92772 600 1.

The dictionary contains traditional vocabulary from both the ferrous and non-ferrous fields of metallurgy. It also includes the "keywords" of allied professions and industries, from geology, process mineralogy, mining, ore treatment, and beneficiation to recycling, remelting, pouring or casting, deformation, heat treatment and machining of metals, chemical and quality analysis, material testing and maintenance.

Helpful explanations for acronyms, abbreviations, chemical formulae for minerals, chemical compounds and alloys relevant to metallurgy are also provided.

At least 20,000 essential terms are given in each part of the dictionary which should assist users in all branches of the metallurgical and allied industries world-wide. It should also prove invaluable to learning and research institutions as well as to professionals in industry.

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Studies of high temperature superconductors, Vols. 1-3

A. Narlikar, 1989, Commack, NY, Nova Science Publishers, ISBN 0 94174 354 3 (Vol. 1), 355 1 (Vol. 2), 356 X (Vol. 3).

These three volumes introduce a new international series of in-depth research studies devoted exclusively to high temperature superconductivity. Further volumes are to be published. The series is intended to fill the gap between journal articles and conference proceedings. Both research and applications are covered in these volumes.

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Metal matrix composites - thermomechanical behaviour

M. Taya and R. J. Arsenault, 1989, Oxford/New York, Pergamon Press. ISBN 0 08036 984 7 (hardcover)/ 0 08036 983 9 (flexicover)

Metal matrix composites (MMCs) are one of the strongest candidates for use as structural materials in many high temperature and aerospace applications. Their strength and high temperature performance are related to their thermomechanical behaviour. In this book, the effects of thermal strains on the materials' properties are examined at microscopic and macroscopic levels, by combining continuum mechanics and dislocation mechanisms. Literature coverage is comprehensive, and each chapter includes a set of problems.

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Indian Journal of Technology

Special issue: Materials Science and Engineering Vol. 28, June-August 1990. ISSN: 0019-5669

Indian Journal of Technology has brought out a special issue on materials science and engineering. It is well known that materials science is an area

of strength of S&T research in India. A few years ago, a study conducted by the US National Science Foundation on the strengths and weaknesses of Indian science identified materials science research as an area of great strength. This special issue is being brought out at a time when there is an upsurge in the world-wide awareness of the key role that materials play in the modern-day technological world. The selection of papers represents a comprehensive but not exhaustive overview of the current Indian research focus.

Guest edited by three of India's outstanding metallurgists/materials scientists, the special issue carries 26 invited articles written by internationally known experts, and four book reviews. Among the authors are Prof. Michael Ashby of Cambridge University, Dr. J. T. Staley of Alcoa, Dr. K. H. Kuo of the Chinese Academy of Sciences, Dr. Shalini Menezes of Rockwell International, Prof. P. Rama Rao of Defence Metallurgical Research Laboratory, Prof. P. Ramachandrarao of Banaras Hindu University, Dr. Sanak Mishra of SAIL R&D Centre at Ranchi, Professors K. T. Jacob and S. Ranganathan of the Indian Institute of Science, Bangalore, Dr. Subrata Ray of the University of Roorkee, Prof. S. B. Ogale of the University of Poona, Prof. B. K. Dhindaw of IIT, Kharagpur, Dr. C. Ganguly of Bhabha Atomic Research Centre and Prof. O. Prabhakar of IIT, Madras.

The topics covered include: selection of materials in mechanical design, aluminium alloy development special steels for breeder reactors, ceramic materials for superconductors, polymer, metal and ceramic matrix composites, quasicrystals, thermodynamics of metastable liquids, solid-state electrochemical sensors, ion implantation and Auger electron spectroscopy and non-destructive testing of materials.

Guest editors: P. Rama Rao, S. Ranganathan, Subrata Ray.

308 pages; price Rs 160, \$54, £35.

(Sales and Distribution Officer, Publications & Information Directorate, Hillside Road, New Delhi 110012, India.)

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Powder metallurgy and related high temperature materials

Ed. P. Ramakrishnan. Proceedings of the 4th International Conference held at the IIT, Bombay, December 1987. Previously published in Key Engineering Materials, ISBN 0-87849-577-0; 1988, 862 pages, SFr 270 (about \$US 184)

The proceedings present approximately 60 papers, including a number of invited review papers, on the topics of powder preparation and characterization, powder consolidation methods and mechanisms, sintering theories, novel consolidation processes, rapid solidification, carbides and wear-resistant materials, structural materials, nuclear materials, structure and property evaluation, special ceramics, and computer applications.

Some highlights:

- Surface oxidation of steel powder during atomization investigated by ESCA, L. Nyborg and I. Oleffjord;
- Chemical characterization of ultrapure refractory metals for the electronics industry, H. M. Ortner and P. Wilhartitz;

- Progress in understanding sintering, W. Schatt and E. Friedrich;
- Sintering on the electronic level, M. M. Ristic and L. F. Pryadko;
- Consolidation of rapidly solidified magnesium-rare earth alloy powder, S. Krishnamurthy;
- Lightweight metals using rapid solidification, F. H. Froes et al.;
- Characterization of rapidly solidified Ti<sub>3</sub>Al base alloys, G. Venkataraman;
- Processing-properties relationships in cemented carbide, B. Aronsson;
- Gel processed transparent alumina, V. Saraswati;
- Microstructure analysis by morphological analysis, J. K. Beddow;
- Iron base alloys sintered with composite powders prepared by electroless plating, S. Kohara and K. Tatsuzawa;
- Mechanically alloyed aluminium-SiC particulate composites, G. Mahanty et al.;
- Processing and mechanical properties of carbon/carbon composites, L. M. Manocha et al.;
- Microstructural development and densification during HIPing of ceramics and metals, G. Petzow et al.

TransTech Publications Ltd., Segatini-strasse 216, CH-8049 Zurich, Switzerland, or Old Post Road, Brookfield, VT 05036, USA.

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Powder metallurgy opportunities for engineering industries

Edited by P. Ramakrishnan, Professor, Department of Metallurgical Engineering, Indian Institute of Technology, Bombay, 1987, 144 pages, Oxford & IBH Publishing Co. Pvt. Ltd., 17 Park Street, Calcutta-700016/66 Janpath, New Delhi-110001, India.

This book, the first of its kind, provides the latest developments in the field and state-of-the-art by leading experts in the chosen field of specialization. This book can serve as a reference book for undergraduate, post-graduate and research students of powder metallurgy, ceramics, materials science and engineering, metallurgy, manufacturing and production engineering.

Contents:

- Powder metallurgy progress and opportunities: Dr. P. Ramakrishnan, Professor, Department of Metallurgical Engineering, Indian Institute of Technology, Bombay;
- Ferrous metal powders and their applications: Mr. B. M. Kataria, Executive Director, Mr. N. Nagarjuna, Metallurgist/Sales Engineer, Mahindra Sintered Products Ltd., Pune;

- Perspectives in sintered friction materials for power absorption: Mr. S. L. N. Acharyulu, Deputy Director, Defence Metallurgical Research Laboratory, Hyderabad;
- Cemented carbide tools and wearparts: Dr. Sanjay Basu, General Manager, Research & Development, Sandvik Asia Ltd., Pune;
- Developments and trends in tungsten carbide tooling: Mr. R. Srinivasan, Managing Director, Wildia (India) Ltd., Bangalore;
- Application of P/M for the production of contact materials with special reference to India: Dr. G. S. Tendolkar, Director, Research & Development, Modison Metal Refiners, Bombay;
- Some aspects of powder metallurgy processed electronic ceramics and their applications: Dr. G. S. Nadkarni, Shri B. Sarkar Memorial, Research and Development Centre, Elpro International Ltd., Pune;
- Special powders for wear and corrosion resistant coatings: Dr. R. Chattopadhyar, Deputy General Manager, Research and Development, EWAC Alloys, Larsen and Toubro Ltd., Bombay;
- New technique of thin film coatings for wear resistance: Mr. A. K. Jani, Technical Director, Dura Coaters Pvt. Ltd., Bombay;
- Natural diamonds and their industrial applications: Mr. Kailas Zaveri, Solar Diamond, Bombay;
- Diamond tools for modern industry: Mr. P. K. Goon, Technical Manager, Greaves Cotton & Co. Ltd., Bombay;
- Polycrystalline diamond compacts and their industrial applications: Dr. H. J. Modi, Director, Research and Development, Bhukhanvala Diamond Tools Pvt. Ltd., Bombay.

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Measuring the dynamics of technological change  
Edited by Jon Sigurdson. Available at bookstores  
July 1990, 220 pages; hardback £33;  
ISBN 0 86187 842 6

This volume, published by Pinter Publishers, is an output from a comprehensive research collaboration

between researchers in Sweden (Research Policy Institute, University of Lund), Germany (Fraunhofer Institut für Systemtechnik und Innovationsforschung) and Japan (Institute for Policy Studies, Saitama University).

Significant changes in national R&D systems are the focal point of this volume which suggests new ways of applying quantitative indicators to study current shifts. The technique, called technometrics, is seen as a major new development in measuring change. The difficulties of applying new methods to insufficient data bases is covered in depth and finally the importance of the environmental and social contexts of change is analysed.

Contents:

**Introduction:** Jon Sigurdson;

**Dimensions of technical change:**

Basic technologies and the innovation process - Rikard Stankiewicz;

The growing importance of technology fusion - Fumio Kodama;

**Measuring science and technology:**

Technometrics as a missing link in science and technology indicators - Hariolf Grupp;

Laser research in Sweden, Germany and Japan - Anders Granberg;

Developing industrial robot technology in Sweden, Germany, Japan and the USA - Hariolf Grupp, Beatrix Schwitalla, Ulrich Schmoch and Anders Granberg;

Japanese R&D in robotics and generic engineering - Masayuki Kondo;

Dynamics of national R&D programs - Fumio Kodama;

**Organizing technical change:**

Joint research and networking - Jon Sigurdson;

A vision of S&T policy in a resource-conscious society - Helmar Krupp.

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10. PAST EVENTS AND FUTURE MEETINGS

JANUARY 1991

23-26  
Marseille,  
France

3rd INTERNATIONAL EXHIBITION FOR NORTH-SOUTH CO-OPERATION - SICAD '91 (Glahe International KG, PF 800349, D-5000 Köln, Germany)

APRIL

18-19  
Brussels,  
Belgium

THERMOPLASTIC ELASTOMERS - III Conference (RAPRA Technology Ltd., Shawbury, Shrewsbury, Shropshire SY4 4NR, UK)

MAY

6-7  
Indianapolis, IN.,  
USA

4th Symposium on Composite Materials: Fatigue and Fracture (Sponsored by ASTM, 1916 Race Street, Philadelphia, PA 19103, USA)

7-9  
Balatonaliya,  
Hungary

14th Conference on Materials Testing in Metallurgy (Hungarian Mining and Metallurgical Society, H-1371 Budapest, P.O. Box 433. Fax: 361 156 1215)

14-16  
Carlsbad,  
Czechoslovakia

REINFORCED PLASTICS Exhibition (Dun techniky CSVTS, Ing. J. Svitakova, Nejedleho Sady 6, 303 40 Pilzen, Czechoslovakia)

15-17  
Amsterdam,  
Netherlands

ENVIRONMENTAL ISSUES - THEIR IMPACT ON THE METALS PROCESSING AND USER INDUSTRIES (BNF Metals Technology Centre, Wantage Business Park, Denchworth Road, Wantage, Oxon, OX12 9BJ; Fax: 0235-771144)

20-24  
Long Beach,  
Calif., USA

ADVANCED AEROSPACE MATERIALS (American Society for Metals International, Metals Park, OH 44073, USA)

21-24  
Amsterdam,  
Netherlands

1st ASM European Heat Treatment Conference and Exhibition (ECCO, rue de l'Orme 19, B-1040 Brussels, Belgium, TX: 61473)

JUNE

3-6  
Osaka, Japan

Superplasticity in Advanced Materials, Prof. N. Furushiro, Osaka University, Fax: 81-6-876-4729

10-12  
Goeteborg,  
Sweden

CERAMIC MATERIALS & COMPOSITES FOR ENGINES (Swedish Ceramic Society, Box 5403, S-402 29 Goeteborg, Sweden)

18-19  
Warrington, UK

Characterization of engineering alloys 2: mechanical testing and non-destructive testing (Institute of Metals, 1 Carlton House Terrace, London SW1Y 5DB)

JUNE

18-21  
Valexp0, Oyonnax  
France

3rd International Plasturgy Forum (Sogexpo, B.P. 219, F-01106 Oyonnax Cedex, France)

19-21  
San Diego, Calif.,  
USA

International Symposium on Environmental Effects on Advanced Materials (NACE = National Association of Corrosion Engineers, P.O. Box 218340, Houston, Texas 77218)

JULY

8-12  
Hong Kong

13th IOCU World Congress (IOCU = International Organization of Consumer Unions, 250-A Jalan Air Itam, 10460 Penang, Malaysia; for more information: Rajeswari Kanniah (Ms.), Congress Co-ordinator, 13th IOCU World Congress Secretariat. Address as above, Tel/Fax: (60-4)376955, TX: 40164)

JULY

14-19  
Haifa,  
Israel

The Strength of Metals and Alloys - International Conference (Unitours Israel Ltd., 90A Hayarkon Street, P.O. Box 3190, Tel Aviv 61031, Israel)

15-19  
Honolulu,  
USA

International Conference on Composite Materials (EACM = European Association for Composite Materials, 2 Place de la Bourse, 33076 Bordeaux Cedex, France)

22-24  
Cambridge, UK

EUROMAT '91 - 2nd European Conference on Advanced Materials and Processes (Institute of Metals & Materials Science for the Federation of European Materials Societies, 1 Carlton House Terrace, London SW1Y 5DB, UK)

22-26  
Kanazawa, Japan

International Conference on Materials and Mechanisms of Superconductivity - High Temperature Superconductors (University of Tokyo, Department of Industrial Chemistry, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan)

AUGUST

17-24  
Denver, Colo.,  
USA

ISES SOLAR WORLD CONGRESS 1991 (International Solar Energy Society)

18-21  
Ottawa, Canada

COPPER '91 (Inco Ltd., Sheridan Park, Mississauga, Ontario, Canada. Fax: 416-822 3922, TX: 069-82263)

SEPTEMBER

9-11  
Detroit, MI., USA  
ADVANCED COMPOSITES - 7th Annual Conference  
(Engineering Society of Detroit, 100 Farnsworth Avenue, Detroit, MI 48202, USA)

15-18  
Glasgow, UK  
THE SECOND EUROPEAN IRONMAKING CONGRESS  
(Iron and Steel Division of the Institute of Metals, 1 Carlton House Terrace, London SW1Y 5DB, UK)

15-19  
Islamabad, Pakistan  
Second Int'l Symposium on Advanced Materials,  
(Dr. Nazeer Ahmad, Dr. A. Q. Khan Research Laboratories, Fax: 051-841987)

15-20  
Brussels, Belgium  
EMC '91 - First European Metals Conference - Nonferrous Metallurgy - Present and Future  
(Universiteit Brussel, Department of Metallurgy, Pleinlaan 2, 1050 Brussels, Belgium. Fax: 32-2/641.32.00)

17-19  
Leuven, Belgium  
2nd International Conference on Interfacial Phenomena in Composite Materials '91  
(Butterworth Scientific Ltd., P.O. Box 63, Westbury House, Bury Street, Guildford, Surrey GU2 5BH, UK. Fax: 44-483-301563)

OCTOBER

1-3  
Zurich, Switzerland  
ENGINEERED COMPOSITE MATERIALS - 1st International Conference  
(ECCO, rue de l'Orme 19, B-1040 Brussels, Belgium)

2-4  
Stuttgart, Germany  
Reliability of Advanced Materials  
(Max Planck Institut für Eisenforschung, ASM Int. Rhein-Ruhr, Max Planck Strasse 1, D-4000 Düsseldorf, Germany)

7-11  
Cadiz, Spain  
Sixth International Workshop on Glasses and Ceramics from Gels (Group of Gels, University of Cadiz, Departamento de Estructura y Propiedades de los Materiales, Apartado 40-11510, Puerto Real (Cadiz), Spain)

24-25  
Berlin, Germany  
TyreTech '91 (org. by European Rubber Journal and Rapra Technical Ltd.; European Rubber Journal, Crain Communications Ltd., 20-22 Bedford Row, London WC1R 4EW, TX: 28544 CRAINS G; Fax: +44(0)71 430 2176)

NOVEMBER

Bordeaux, France  
Conference on Computer Applications in Production and Engineering  
(CAPE '91 Conference Secretariat, GRAI Laboratory, 351 Course de la Liberation, 33405 Talence Cedex, France)

DECEMBER

10-11  
London, UK  
Metal Matrix Composites  
(Institute of Metals, 1 Carlton House Terrace, London SW1Y 5DB)

Previous Issues

- Issue No. 1      Steel
- Issue No. 2      New Ceramics
- Issue No. 3      Fibre Optics
- Issue No. 4      Powder Metallurgy
- Issue No. 5      Composites
- Issue No. 6      Plastics
- Issue No. 7      Aluminium Alloys
- Issue No. 8      Materials Testing and Quality Control
- Issue No. 9      Solar Cells Materials
- Issue No. 10     Space-related Materials
- Issue No. 11     High Temperature Superconductive Materials
- Issue No. 12     Materials for Cutting Tools
- Issue No. 13     Materials for Packaging, Storage and Transportation
- Issue No. 14     Industrial Sensors
- Issue No. 15     Non-destructive Testing
- Issue No. 16     Materials Developments in Selected Countries
- Issue No. 17     Metal-matrix Composites
- Issue No. 18     Plastics Recycling
- Issue No. 19/20   Advanced Materials Technology: CAD/CAM Application
- Issue No. 21     New Materials Technology and CIM
- Issue No. 22     Powder Metallurgy

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Advances in Materials Technology: Monitor  
Reader Survey

The Advances in Materials Technology: Monitor has now been published since 1983. Although its mailing list is continuously updated as new requests for inclusion are received and changes of address are made as soon as notifications of such changes are received, I would be grateful if readers could reconfirm their interest in receiving this newsletter. Kindly, therefore, answer the questions below and mail this form to: The Editor, Advances in Materials Technology: Monitor, UNIDO Technology Programme at the above address.

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How many issues of this newsletter have you read?

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Optional

Which section in the Monitor is of particular interest to you?

---

Which additional subjects would you suggest be included?

---

Would you like to see any sections deleted?

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Have you access to some/most of the journals from which the information contained in the Monitor is drawn?

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Is your copy of the Monitor passed on to friends/colleagues etc.?

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Please make any other comments or suggestions for improving the quality and usefulness of this newsletter.

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Reader's comments

We should appreciate it if readers could take the time to tell us in this space what they think of the 23rd issue of Advances in Materials Technology: Monitor. Comments on the usefulness of the information and the way it has been organized will help-us in preparing future issues of the Monitor. We thank you for your co-operation and look forward to hearing from you.