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SPRING COLLEGE IN MATERIALS SCIENCE ON 'CERAMICS AND COMPOSITE MATERIALS'

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BACKGROUND MATERIAL FOR LECTURES ON HIGH TOUGHNESS AND HIGH TEMPERATURE CERAMICS

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NEW DEVELOPMENTS AND APPLICATIONS OF ENGINEERING CERAMICS

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ABSTRACT

The last decade has seen a dramatic improvement in the mechanical properties of structural ceramics. Strengths in excess of 2GPa and fracture toughness values higher than $1KJm^{-2}$ are now possible. These improved properties are possible because of the availability of highly sinterable powders coupled with hot isostatic pressing and the incorporation of new toughening mechanisms such as transformation toughening and fiber and whisker reinforcement. Applications for engineering ceramics continue to diversify, the eventual aim being the large volume market of the automotive industry. However at present the cost and fabrication procedures limit such applications. Instead more limited and less cost competitive markets are being sought such as cutting tools, metal forming dies, seals and components for the chemical engineering industry. The defense area is another where the high performance and cost of ceramic composite materials is finding applications.

INTRODUCTION

The last few years has seen a tremendous upsurge of interest in ceramics. One of the worries of many old hands in the field is whether this is genuine commitment to this, the oldest of all manufacture commodities or whether it is cyclical market hype. No where has this enthusiasm been more evident than in Japan where "ceramic fever" has been diagnosed. Similar but less ambitious ceramic programs are underway in most technologically advanced nations. The market area with the greatest capacity for growth is considered to be in structural ceramics. Various estimates of the market for structural ceramics have been proposed from 0.1 to 3×10^9 US dollars in 1995, with the total ceramic market up to 15 to 20×10^9 US dollars [1].

What has lead to this upsurge of interest in Ceramics? There have been a number of factors, such as: appreciation of new toughening mechanisms, availability of high purity sinter active powders, concern regarding supply and expense of strategic metallic materials such as cobalt, tungsten etc, demand for more fuel efficient and lower maintenance engines. Interest in this area has tended to coincide with high oil prices. Of these the major potential contributor to rapid growth for structural ceramic growth is the automotive industry, however as many commentators have warned it is somewhat speculative and depends upon future free market competitive forces and the price of energy. A significant increase in energy costs will greatly facilitate the improved demand for ceramics in heat engines, particularly insulating and gas turbine componentary. Other areas such as wear resistant components for valves, tappets etc will also find increasing demand when the production cost decreases and volume capacity increases. In the meantime demand for wear resistant ceramics is finding increasing application in the metal fabrication area (extrusion dies, cutting tools etc.) and chemical/mining/petroleum processing areas (valves, pumps, seals etc.) These areas will be discussed in more detail in section 4.

In this paper the emphasis will be on the mechanical properties of structural ceramics particularly on the toughening mechanisms of such materials (Section 2). Some considerations are also given to new developments in materials processing both in the powder synthesis and ceramic fabrication (Section 3). In Section 4 a brief survey of applications of ceramics is given.

2. MECHANICAL PROPERTIES

The two major mechanical properties for engineering ceramics are strength and toughness. Other properties that influence strength, wear resistance and thermo-mechanical behaviour include creep behaviour, hardness, thermal expansion and thermal conductivity. These parameters will not receive attention here as little in terms of new developments has taken place in the last decade but rather the application of the basic mechanisms and procedures.

For engineering design purposes the major consideration is the strength of the ceramic material. However unlike metals, ceramic materials do not have a well defined yield stress or ultimate tensile strength but rather fail catastrophically and show a wide scatter of strengths. It has been known for decades that the tensile strength of fibres of glass, sapphire, etc, may have exceptionally high strength (> 2-3 GPa) [2], but display considerable variability in strength as well as being very vulnerable to damage. Contact with dust particles in the atmosphere may result in 80% reduction of strength. This has necessitated coating of high strength fibres with protective layers as applied currently to telecommunication optical fibre links.

Similar approaches have been applied for polishing surfaces for the improvement in strength of polycrystalline ceramics. Any such gains are usually at great expense and considerable inconvenience and are readily removed when the component enters into service. Other problems associated with strength variability are the influence of pre-existing or introduced flaws (<50µms) and the difficulty of NDE techniques to detect such flaws [3]. Ways that are currently being developed to minimise such defects are discussed in section 3.

A more appropriate means of improving the mechanical performance of ceramics and reducing the sensitivity to defects, be they intrinsic or generated in service, is to improve the fracture toughness [4]. There have been a number of approaches developed to improve the fracture toughness of ceramics; these inlcude [4,5]

Microcracking
Residual Stress
Crack Bridging
Crack Deflection
Transformation Toughening
Whisker Reinforcement
Fibre Reinforcement

Of these mechanisms the latter three have proved to be the most effective. All of them have evolved both practically and theoretically to the point where they are reasonably well understood.

A plot of the historical trend [6] of the toughness of fabricated ceramics that are commercially available is shown in Figure 1.

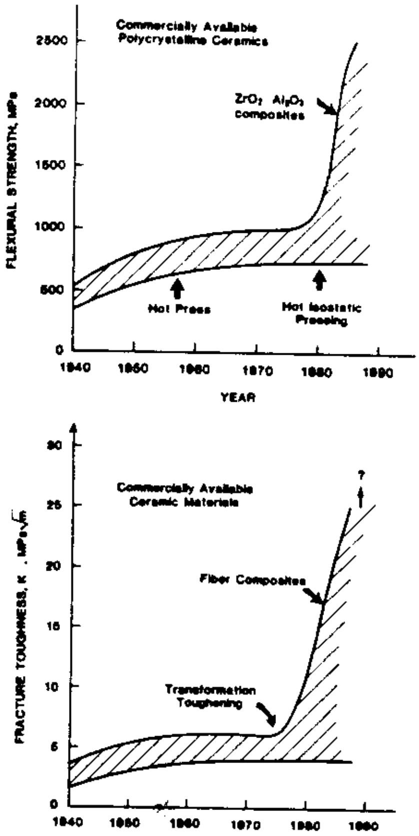

Figure 1. Historical trend of the fracture toughness and strength of commercially available ceramic materials.

This plot highlights the very significant developments that have taken place in the last decade. In many materials more than one toughening mechanism is operating although it is often difficult to quantify the contribution of each mechanism. There is still a considerable degree of development remaining in ceramic systems before the elaborate heirarchy of toughening mechanisms that nature has developed for living organisms are possible [7]. The remainder of this section will deal with recent developments and limitations of the most effective toughening mechanisms listed above. Recent reviews of all these mechanisms have been given elsewhere [5,6].

3.1 Transformation Tougheneing

This mechansims for improving the toughness of ceramics relies upon a stress assisted martensitic volume expanding phase change that takes place about the crack tip. It was first appreciated by Garvie et al [8] in 1975 in zirconia partially stabilized (PSZ) ceramics. Zirconia (ZrO_2) exists in three phases depending upon temperature, namely

$$\underset{\substack{\text{(cubic)}\\ \rho\, =\, 6.09\text{gm/cc}}}{ZrO_2} \xrightleftharpoons{\sim 2300\,°C} \underset{\substack{\text{(tetragonal)}\\ \rho\, =\, 6.10}}{ZrO_2} \xrightleftharpoons{\sim 1200\,°C} \underset{\substack{\text{(monoclinic)}\\ \rho\, =\, 5.83}}{ZrO_2}$$

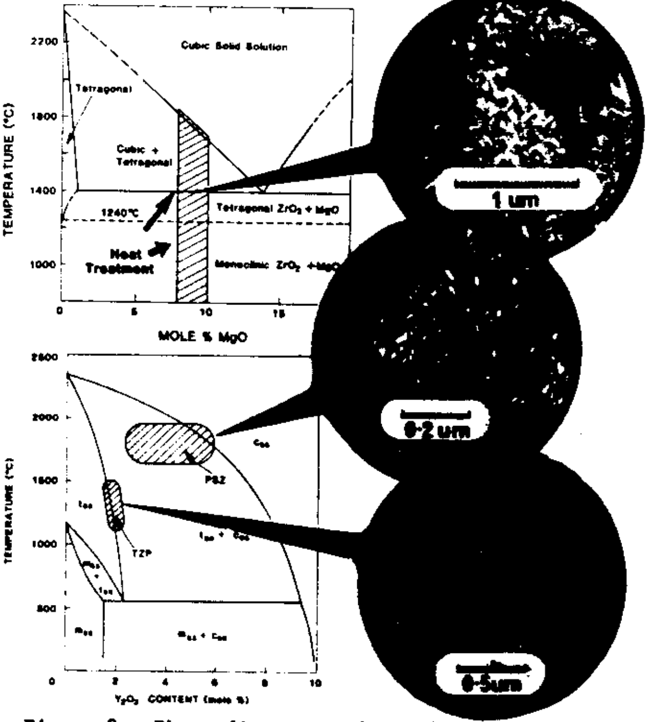

Figure 2. Phase diagrams and resulting microstructures of two binary PSZ systems [9]. The hatched area is the usual range of commercial compositions, also shown are the regions where heat treatment is possible.

The massive transformation strains, both dilational and shear, of the tetragonal → monoclinic transformation cause destruction of articles fabricated of pure zirconia. This feature is overcome by the addition of various stabilizers such as MgO, CaO and various rare earth oxides. Judicious selection of stabiliser content and sintering - heat treatment conditions leads to retention of the tetragonal zirconia phase at room temperature. Then the application of stress may lead to the following reaction.

$$ZrO_2\ (\text{tetragonal}) \xrightleftharpoons[\text{heat}]{\text{stress}} ZrO_2\ (\text{monoclinic})$$

A wide range of microstructures containing tetragonal zirconia may be fabricated varying in grain sizes from 0.2μm completely tetragonal zirconia polycrystals (TZP) to 50μm grain size with lenticular tetragonal precipitates in a cubic zirconia matrix in PSZ materials. A third group containing tetragonal zirconia dispersed ceramics (ZDC) in another matrix e.g. alumina, mullite etc [9]. Features of these latter materials will be discussed in more detail later this section. Phase diagrams, typical compositions and microstructures achievable in two such PSZ systems are shown in Figure 2. The hatched areas are the usual range of composition used to achieve high strengths and toughness and typical examples of the microstructures developed at different conditions inserted. Often additional heat treatments of the materials are given to optimise the toughness. Examples of such modifications of toughness of a $MgO-ZrO_2$ material heat treated at two different temperatures [10], are shown in Figure 3. Similar types of variations maybe achieved in Y-PSZ or Y-TZP materials [11].

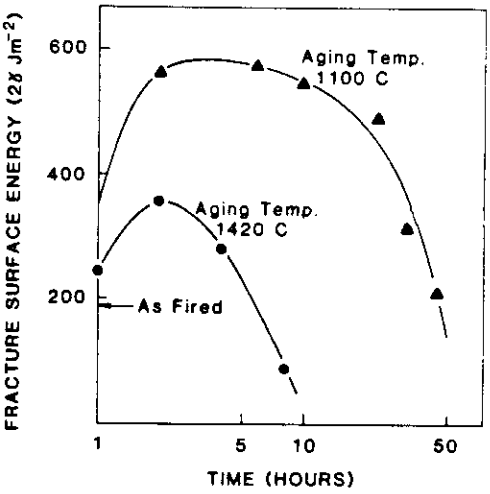

Figure 3. Variation in toughness of Mg-PSZ with heat treatment temperature and time.

The toughening increments achievable in transformation toughened materials have been discussed from the basis of energetics or mechanics perspectives [12,13]. To date the theoretical arguments have taken the materials as essentially isotropic with a smeared out zone of transformation about the crack tip area. More detailed models are required to fully appreciate the toughening mechanisms. Both approaches predict comparable relationships, and are of the form [14]

$$K_c = K_o + \Delta K^T$$

$$\text{and} \quad \Delta K^T = \eta E^* e^T V_f \sqrt{h} \qquad (1)$$

where ΔK^T is the transformation toughening increment, K_o the toughness of the matrix material, h the size of the transformation zone normal to the crack, e^T the dilational strain, E^* the effective modulus of the material and η a constant determined by the transformation zone shape. The effective modulus E^* as pointed out by McMeeking [15] plays a very important role in determining the effectiveness of the dilational strain of the zirconia phase (E~210GPa, ν = 0.3) on that the matrix in ZDC materials. The influence of the dilation in an alumina matrix (E ~380GPA, ν = 0.2) is only one third as effective as in a PSZ material.

Substantial experimental support for the simple relationship in equation (1) has been obtained for a range of transformation toughened ceramics both PSZ and TZP materials [16]. This is shown in Figure 4 which plots the toughness of 3 different systems, Mg-PSZ, Y-TZP and Ce-TZP against volume fraction and width of the transformed zone. The latter have been measured with a Raman microprobe system which enables volume fraction and zone width to be measured very accurately. The observations show that a five fold increase in toughness is possible in PSZ materials. The difference in slope of the Ce-TZP material from the other materials suggests a different η value and is suggestive of a different zone shape for the Ce-TZP material.

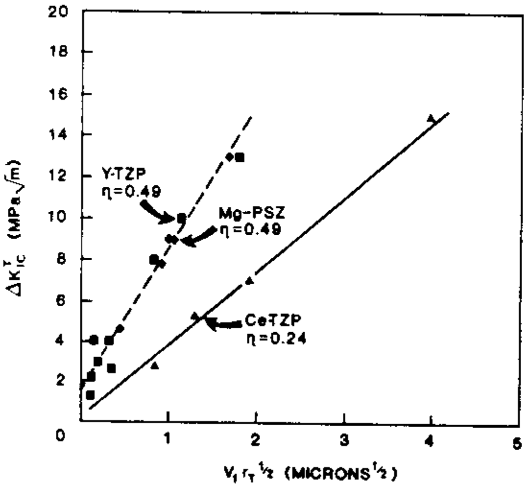

Figure 4. Dependence of K_c of PSZ and TZP ceramics on dimensions of the transformation zone size and volume fraction of transformed monoclinic zirconia.

This is indeed found to be the case as shown in Figure 5 which compares the transformation zone about a crack in Mg-PSZ and Ce-TZP material [17]. The former is almost as predicted on the basis of a "small scale" transformed zone modified by anisotropy in various grains along the crack front. Whereas the zone shape in Ce-TZP material is closer to a craze zone in a polymer or Dugdale stretch zone in a metal. This similarity is currently being explored to elucidate the basic transformation mechanisms in TZP materials [18].

Another parameter that significantly influences the toughness of transformation materials is temperature. With increasing temperature the tetragonal phase becomes more stable making transformation energetically more difficult and hence the zone size and toughness decreases. Recently Becher et al [19] have shown that the critical normalising parameter is the M_s

temperature at which the tetragonal phase spontaneously transforms to the monoclinic phase. The toughening increment ΔK^T (equation 1) may then be modified to the following relation [19]

$$\Delta K^T = \frac{\Omega\, n(e^T)^2\, V_f\, E^* K_0}{\Delta s\ (T-M_s)} \qquad (2)$$

where Ω and n are constants, Δs is the entropy difference between tetragonal and monoclinic zirconia.

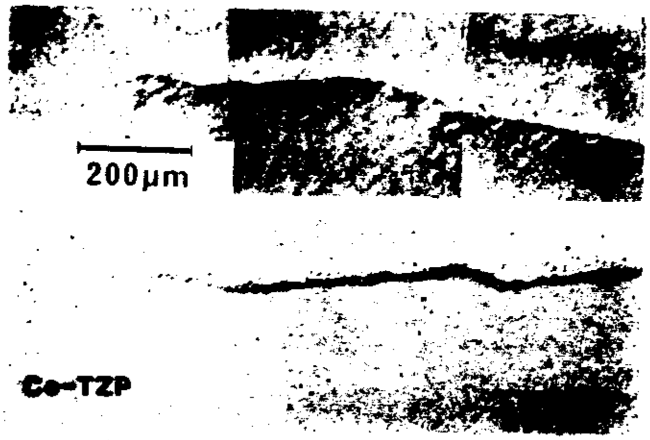

Figure 5. Comparison of the transformtion zones about the crack tip in Mg-PSZ and Ce-TZP materials.

Experimental evidence in support of this expression is shown in Figure 6 which plots K_c versus temperature for Mg-PSZ materials [19]. The maxima in toughness corresponds with the M_s temperature and thereafter decreases linearly with temperature to the matrix K_0 value. The realisation of the temperature sensitivity of transformation toughened ceramics has lead researchers to search for other less temperature sensitive toughening mechanisms to enable materials to have high toughness at temperature.

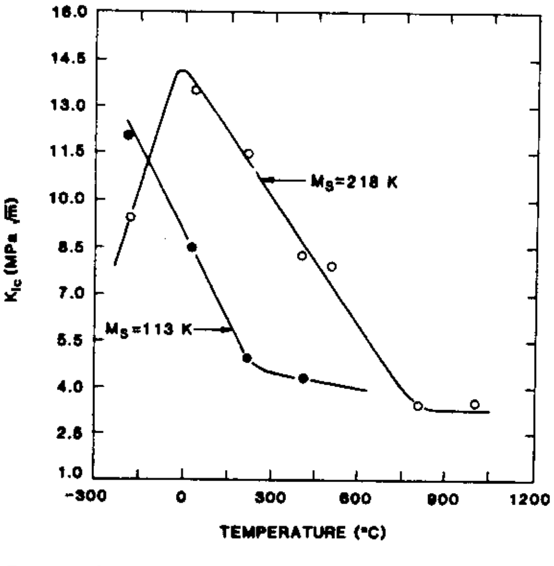

Figure 6. Temperature dependenace of the toughness of Mg-PSZ materials.

The basis of toughness of ceramics, particularly of engineering ceramics, has been that it is a constant. However, as observed and predicted theoretically transformation toughened materials exhibit R-curve behaviour [12, 20]. This occurs because the volume dilation provides closure forces behind the crack tip, the observed R-curves in PSZ materials are shown in Figure 7. The rise in toughness occurs over approximately 5 times the transformed zone height. This feature only becomes significant for materials with well developed transformed zones or materials with high K_c values. R-curves have been observed for Mg-PSZ and Ce-TZP materials directly with standard fracture mechanics tests, e.g. DCB and SENB, as well as optically on tensile surfaces of flexure bars [21,22]. An example of the growth of a crack on the surface of a polished Mg-PSZ specimen is shown in Figure 8. Associated with such cracks are surrounding zones of transformed zirconia which are readily observed using interference microscopy. A consequence of an R-curve is that the crack becomes unstable when the rate of change of strain energy G with crack length exceeds the rate of change of crack resistance.

$$\frac{dG}{da} > \frac{dR}{da} \qquad (3)$$

For transformation toughened ceramics where the toughness maybe modified by heat treatment the consequences of R-curve predict a maxima in a plot of the strength versus toughness (steady state) [21,22].

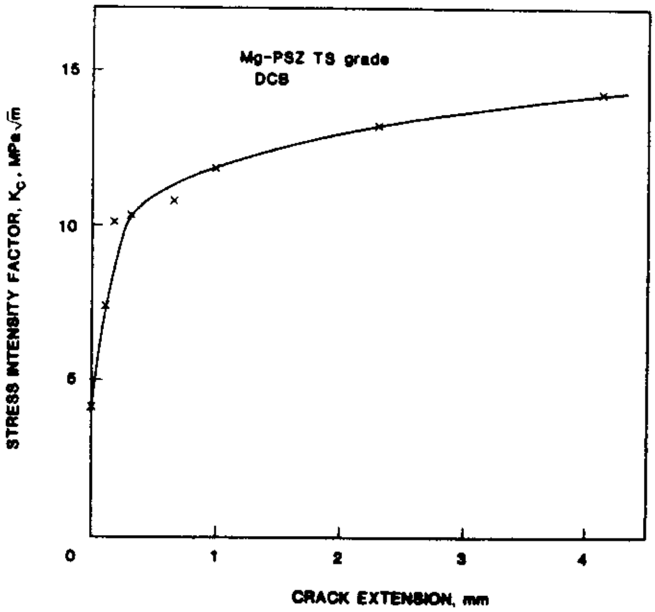

Figure 7. Observed R-curves in transformation toughened ceramics.

Another feature of transformation toughened materials is their observed non-linear stress-strain relationships in tension and compression [23]. This is shown in Figure 9 for Mg-PSZ and Ce-TZP materials. The onset of ductility occurs because of the metastability of the tetragonal phase and the dilation is associated with the transformation to monoclinic due to transformational plasticity. This is determined by the M_s temperature which maybe modified by heat treatment, composition and grain size. In the PSZ materials the ductility takes place by means of a collaborative transformation of tetragonal precipitates often leading to microcracking at grain boundaries [24]. In TZP materials luders like bands are observed which occurs because of monoclinic laths are formed within tetragonal grains initiating adjacent grains [25]. Examples of such bands within Ce-TZP and TEM observations of microstructure within grains are shown in Figure 10.

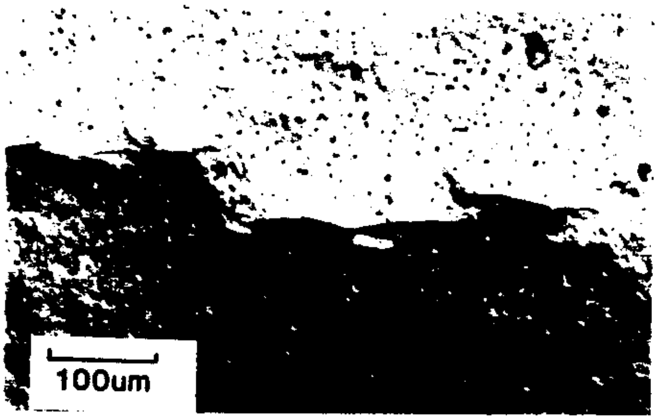

Figure 8. Stable microcrack development on the surface of flexure bars of a very tough Mg-PSZ material.

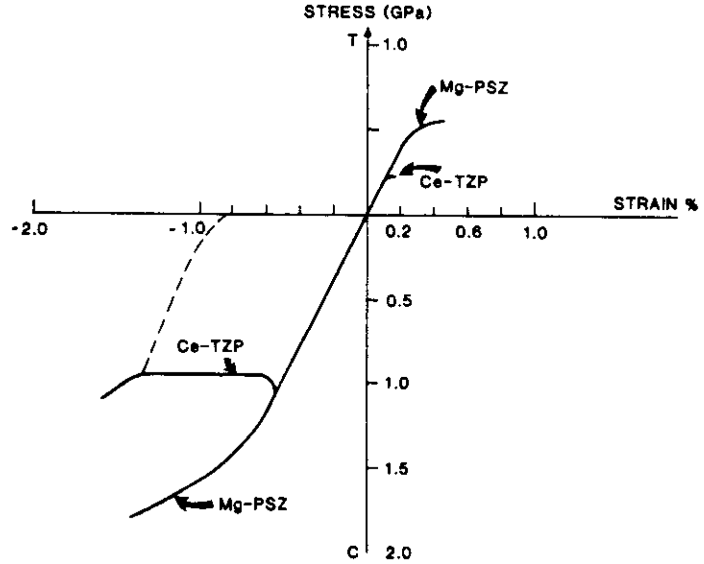

Figure 9. Stress-strain curves in tension and compression of Mg-PSZ and Ce-TZP.

A consequence of the ductility of PSZ and TZP materials lead the author to propose an inverse relationship between strength and toughness [23]. Tougher materials as seen for Ce-TZP in Figure 8 and also Mg-PSZ "yield" prior to fracture. Also Y-TZP materials increase in strength with decreasing toughness initially. The inverse relationship proposed is shown in Figure 11. The highest strengths of 2.4 GPa are observed in hot isostatically pressed (HIP) specimens of Y-TZP containing 20-40 vol% Al_2O_3. The slope of the line through the origin indicates the critical flaw size to achieve such high strengths at a specific K_c value. For instance damage of the very high strength materials with a 10N Vickers indentation introduces flaws of approx. 200μm and the strength plummets to only 200 MPa. Wheras for Mg-PSZ material with a K_c value of 15 MPa√m, indents with loads as high as 500N causes no reduction in strength. More complete reviews of the Science and Technology of Zirconia Ceramics are available in three recent conferences devoted to this topic [25].

Figure 10. Transmission electron micrographs of monoclinic laths within grains of Ce-TZP due to transformational plasticity.

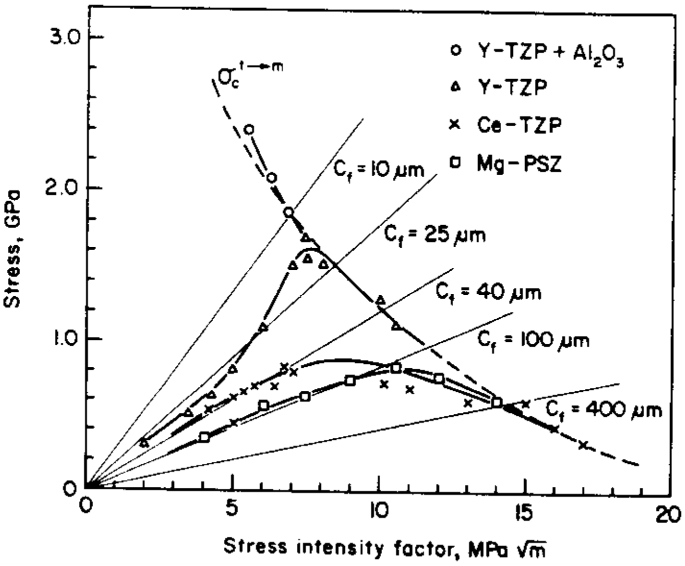

Figure 11. Strength-toughness relationships for several PSZ and TZP transformation toughened materials.

The most recent developments in the field of zirconia toughened ceramics include fabrication of composite zirconia - non oxide systems such as $TiB_2-ZrO_2(Y_2O_3)$ and similar type of materials [26]. These materials under specific atmospheres maybe sintered to near theoretical density and HIP'ed to achieve high strengths 1 to 1.5 GPa. Examples of the toughness hardness and strength dependence of such composites is shown in Figure 12. These materials are electrically conducting and maybe shaped using conventional electrical discharge machining (EDM) techniques. Two other interesting new developments in ZTC materials are the observation of superplasticity in TZP materials between 1100-1300°C enabling novel forming-forging techniques. This behaviour plus the observation of shape-memory behaviour in PSZ and TZP materials [28,29] confirms the original description of "ceramic steel" for these materials.

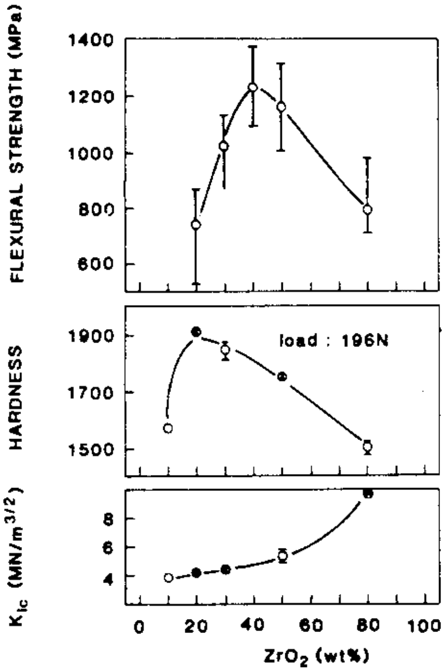

Figure 12. Dependence of strength and toughness of TiB_2-Y-TZP composites with composition.

Whisker Reinforced Ceramics

Almost two decades ago considerable interest was focussed on the preparation and properties of single crystal fibers or whiskers [29]. These materials are usually formed by vapour phase transport and preferential growth of certain crystal orientations. Because of their near perfect single crystal nature and fine diameters (μms) they exhibited in many instances near theoretical strength (> E/100). Interest in such materials as reinforcement for monolithic ceramics has resurged in the last three years. Most interest to date has centered on silicon carbide whiskers typically 0.5 - 1.0μm diameter and 100-200μm in length. Such materials are available from at least three suppliers although they tend to be very expensive ($200-500/kg).

A number of studies have shown that substantial improvements in strength, toughness and creep resistance maybe developed in polycrystalline ceramics by incorporating up to 20-30 volume % of whiskers [30,31,32]. The attractiveness of the types of materials is that they allow more conventional powder processing techniques to be used in fabrication. The initial approach was to fabricate by hot pressing of milled and blended compositions particularly alumina-silicon carbide. More recently emphasis has shifted towards being able to sinter/HIP such materials and obtain comparable mechanical properties [33].

Whisker reinforcement may involve a number of toughening mechanisms, such as, fibre pullout, crackbridging and crack deflection due to the high aspect ratio fibres. At this stage of the development and understanding of such materials it is difficult to quantify which mechanisms are most effective. To date more attention has been placed upon the critical role of silicous layers on the whiskers leading to glassy films at the whisker-matrix interface. Such layers degrade properties above 800°C and lower the fracture toughness. For many whisker composites large thermal expansion coefficient (TEC) differences exist between whisker and matrix material with usually the TEC of the whisker < matrix. This leads to a clamping of whisker by the matrix making pullout more likely at higher temperatures, such behaviour is particularly, evident in mullite - silicon carbide whisker composites [34].

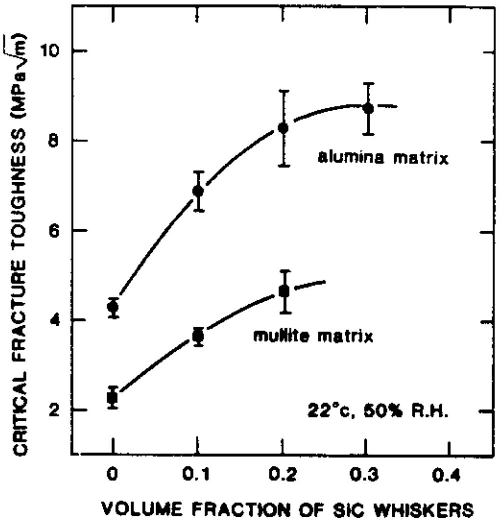

Figure 13. Variation of the toughness of alumina and mullite with volume fraction of SiC whiskers.

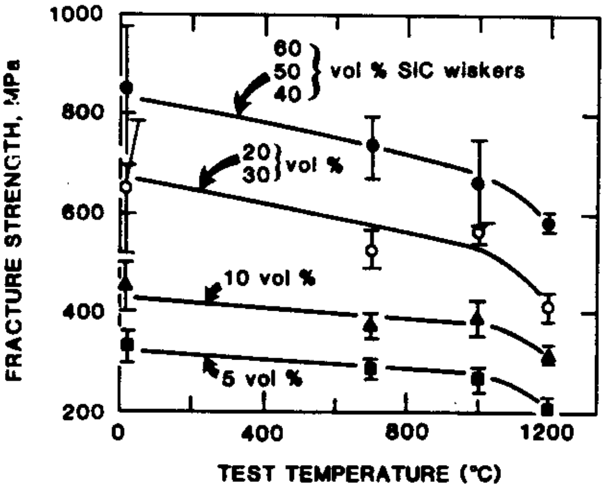

Figure 14. Influence of whisker content on the strength of alumina - silicon carbide whisker materials.

Examples of the mechanical properties of such whisker reinforced materials are shown in Figures 13, 14. The toughness values appear to show a parabolic increase with volume fraction of whiskers. Whereas the strength increases with increasing volume fraction of whiskers and displays a modest decrease with temperature to 1000°C before dropping significantly. The increase in strength with volume fraction of whiskers is partially due to a reduction in grain size. The creep properties of alumina-silicon carbide whisker materials are much improved over pure alumina as shown in Figure 15 [32]. Further work in this areas is proceeding along the direction of the importance of aspect ratio and diameter of the whisker plus the use of other whiskers apart from silicon carbide.

One of the problems of whisker reinforcement of ceramics has been to obtain homogeneous distributions of the whiskers throughout the material. As fabricated whiskers usually are highly matted materials with clumps sometimes difficult to disperse. Such regions usually result in subsequent failure origins and may have remnant porosity about them. Alternate approaches for achievement of whisker like microstructural reinforcement has been developed by other workers. For instance Tani et al [35] have found by sintering silicon nitride with small additions of alumina and yttria or ceria at up to 2000°C and an overpressure of nitrogen that large high aspect ratio β-silicon nitride grains develop. Such materials have K_c values double that of conventional equi-axed silicon nitride materials.

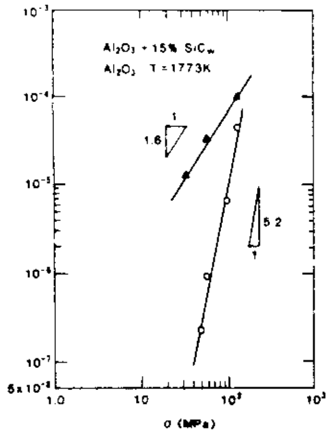

Figure 15. Creep behaviour of alumina-silicon carbide whisker reinforced material.

Fibre Reinforcement

The recent availability of strong high quality fibres of various ceramics has lead to a renewed interest in fibre reinforced ceramics. Again this area achieved considerable attention well over a decade ago [36] however at that time only good quality carbon and glass fibres were available. Such materials were not suitable for high temperature composites in oxidising atmospheres. A major breakthrough occured about 10 years ago when Yajima [37] fabricated continuous silicon carbide fibres with diameters 15-20μms . These materials begin to degrade at temperatures above 1000°C. A list of currently available fibres and their properties is shown in Table 1. A detailed discussion of the properties and oxidation behaviour at elevated temperature is given by Mah et al [38]. These authors point out that behaviour of isolated fibers in various atmospheres does not necessarily determine their behaviour in a composite material. The important parameters tend to be, refractoriness, compatability between fibre and matrix and composite fabricability.

A range of potential matrix materials includes various glasses and glass ceramics, crystalline oxides, carbides, borides nitrides etc. The most widely used matrices have been glass and glass ceramics because of the relative ease of composite fabrication generally by low pressure hot pressing techniques. Attempts to fabricate ceramic matrix - continuous fibres have usually been unsuccessful because of the difficulties of densification about the fibres. Such problems also exaggerate thermal expansion mismatch cracking between matrix and fibre. More recently, following procedures developed for carbon-carbon fibre composites, infiltration by chemical vapour techniques as well as by polymer precursors have been used for carbide, nitride and oxycarbonitride matrices [39,40]. Chemical vapour infiltration can take place above 1000°C leading to dense composites with closed porosity and typically 80-85% theoretical density. A key parameter that maybe taken advantage of in such a processing route is that a thin interface coating maybe deposited on the woven structure prior to deposition of the matrix. In this manner the interface properties of the matrix to fibre maybe controlled and so determine whether genuine reinforcement occurs resulting in stable fracture fibre fracture and pullout or catastrophic fracture through the composite. Crack stability requires that the interface is strong enough to transfer load from the matrix to the fibres yet weak enough to fail preferentially prior to fibre failure.

The mechanical properties of fibre reinforced composites are impressive. The stress - strain behaviour of these materials has a closer resemblance to a metal than a ceramic. An more detailed example of a flexural stress-strain curve in a composite of SiC fibres in a matrix of barium osumilite are shown in Figure 16. The changes in the stress-strain behaviour indicate processes taking place in the material namely matrix microcracking followed by compression buckling just prior to fibre failure and reduction in load bearing capacity. Examples of the temperature dependence of strength and toughness of glass - ceramic - SiC fibres composite are shown in Figure 17. These materials are critically dependent upon the atmosphere and strain rate dependence at temperatures above 600°C, this is because of oxidation of thin layers of NbC at the interface changes the interface bonding between matrix and fibre [38].

More extreme values of toughness have been measured for SiC-SiC fibre composites fabricated by chemical vapour infiltration. Values of K_c as high as 39-40 MPa√m have been measured which are temperature insensitive to 1200°C [42]. An extremely steep R-curve has also been found. A consequence of such extreme toughness is that the material exhibits no reduction in strength upon thermal shock testing into water from temperatures as high as 1300°C. These materials response to crack extension are being addressed in a manner similar to that of tough metals which exhibit initial crack tip blunting prior to crack advance [43]. Work on such materials is currently limited by the high temperature degradation of fibres and the oxidation or creep response of the matrix. Attempts are underway to raise the operating temperature of such composites to 2000°C in air.

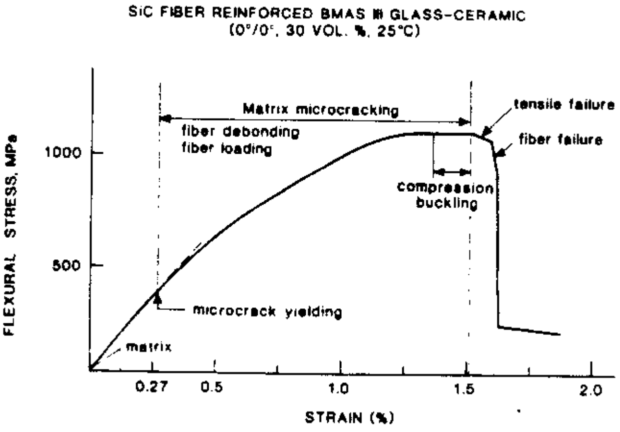

Figure 16. Flexural stress - strain behaviour of a SiC fibre reinforced glass ceramic indicating deformation mechanisms that lead to changes in slope of the curve.

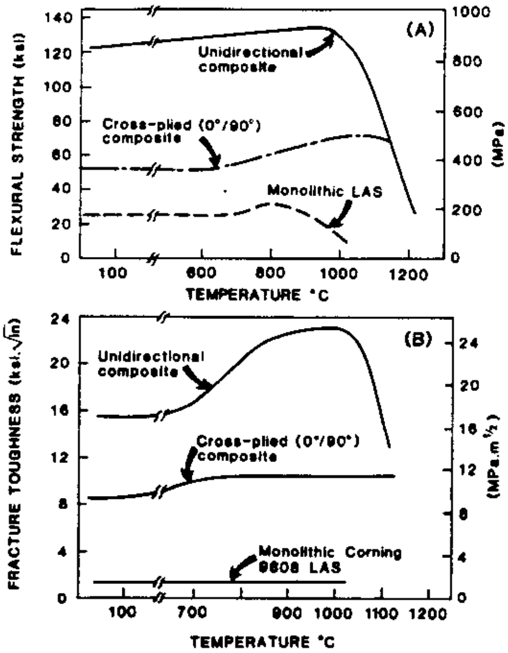

Figure 17. Temperature dependence of strength and toughness of SiC reinforced glass ceramic.

Strength

The maintenance of strength, or understanding of factors controlling its degradation in service, is one of the major considerations of current ceramic materials research. Considerable attention over the last decade has been given to the parameters that are important for the nucleation of cracks through contact with sharp or blunt indenters and in abrasion and machining operations [44,45]. This has entailed a detailed understanding of deformation and contact fracture mechanics and has lead to simple indentation techniques being routinely used to characterise K_c values of materials. Other studies have explored the influence of defect shape, modulus and thermal expansion mismatch of inclusions on the resultant strength. The other key issue has been the influence of environment on slow crack growth resulting in failure of a component sometime after loading. These areas are reasonably well understood and procedures exist to enable design of ceramic structures within well defined safety limits or probabilities [46].

A number of key areas in the field of mechanical behaviour of ceramics still require considerable attention. They include the influence of cyclic loading on the lifetime of a structure and measurement of simple S-N curves. This becomes particularly important for toughened materials or those that exhibit non-linear stress-strain behaviour prior to fracture. For instance in Mg-PSZ materials the lifetime predictions based upon static loading greatly overestimate the observations of lifetime under cyclic loading [47]. This is shown in Figure 18. The reason for this difference has recently been shown to be due to a genuine fatigue crack growth behaviour in PSZ materials with a slope much less than seen for static fatigue loading [48], Figure 19. Similar behaviour might be anticipated for fibre composite materials for stresses exceeding the onset of matrix-microcracking [6].

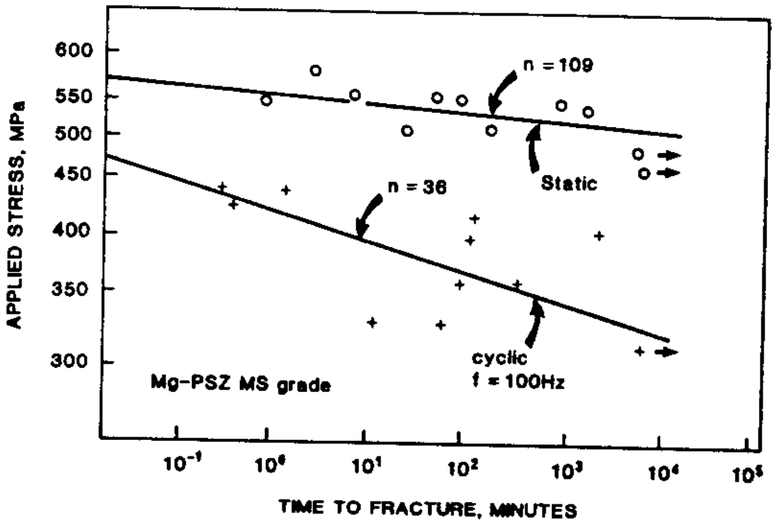

Figure 18. Comparison of lifetimes of Mg-PSZ tested under static and rotational cyclic flexural loading with applied stress.

The other area where serious problems arise is in the area of high temperature application. At elevated temperatures ceramic materials are no longer chemically or physically stable. Chemical reactions between ceramics and the environment lead to the formation of new populations of flaws and or result in chemical or physical modification of the ceramic microstructure. All these processes may result in strength degradation in service. Transport processes such as bulk diffusion or viscous flow of a grain boundary phase are highly temperature dependent. Hence crack nucleation and growth are observed to occur at elevated temperatures in oxide and non-oxide ceramics as a result of creep. In this manner flaw populations are generated in the material with time, leading to mechanical failure of a component [49].

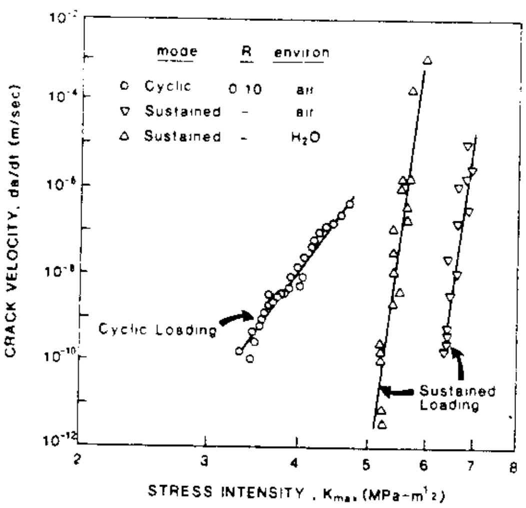

Figure 19. Comparison of the crack propogation rates with applied stress intensity factor for Mg-PSZ under static and cyclic testing conditions.

Attempts to understand behaviour of materials at elevated temperatures are still very much at the experimental stage. Quinn [50] has generated a fracture map for silicon nitride at elevated temperatures, this is shown in Figure 20. These observations are for the lifetime of static loaded silicon nitride (MgO doped) that been given a 16N Knoop indentation prior to testing in order to reduce scatter of the results. These observations and others in alumina [51], silicon carbide [52], suggest that, for short periods of time, failure occurs by crack growth from pre-existing flaws.

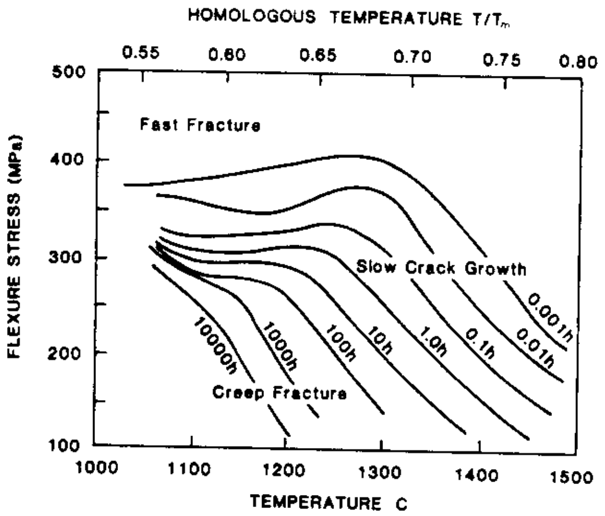

Figure 20. Fracture - mechanism - lifetime map of silicon nitride at temperatures where creep becomes significant.

At lower stresses and higher temperatures failure is controlled by creep fracture processes. These results have been found to fit empirically derived creep fracture relationships for metals, the Monkman-Grant equation (namely $t_f \varepsilon^{\alpha} = \beta$, where ε is the minimum creep rate, β and α constants), or modified such relationships. Hence for a particular material data must be obtained to determine the mechansims of failure. Parametric relationships may then be obtained which provide the basis for structural design.

3. FABRICATION DEVELOPMENTS

Associated with recent advances in the toughening mechanisms available to ceramics has been associated developments in the area of ceramic powder production and consolidation. Many of the processes are not novel but equipment and techniques are readily available or sufficiently well understood to be utilized on semi-production/commerical basis.

Until recently most ceramic processing consisted of familiar milling of powders to achieve particle sizes that may be sintered with or without the assistance of sintering aids. Such processing even with the advent of more rapid attrition milling systems was time consuming and introduced many steps where contamination was inadvertantly introduced into powder. A number of processes are now available that completely eliminate such milling/mixing procedures and result in greatly improved purity of powders and performance of products. A listing of such processes (not meant to be exhaustive) includes,

Sol-gel (aero-gel)
Polymer precursors
Melt processing - rapid quenching
Chemicl reaction deposition (plasma, laser)
Chemical vapour deposition.

Extensive reviews of the progress possible in these areas may be found in two recent MRS conference proceedings and elsewhere [53,54]. The usual problem with many of these techniques is that the cost of powders produced is much greater than by current production methods, and as mentioned this factor limits penetration of ceramics in the highly cost competitive automotive engine market. Where these alternate processes are making a significant impact is in the area of highly refractory materials such as carbides and borides. Plasma chemical reaction techniques have been used to fabricate highly sinter active powders of titanium diboride with incorporated sintering aid and grain growth inhibition (carbon) into powders typically 0.1 - 0.4µm diameter. These materials may then be sintered to near theoretical density at temperatures as low as 1700°C - a feat not possible by traditional techniques [55]. Other advantages of such an approach to powder fabrication is that it enables homogenous solid solutions of various species and so develop complex precipitate laden highly refractory materials.

Although chemical vapour deposition (CVD) may appear as an expensive route to fabricate monolithic components it does offer some unique advantages. Materials maybe fabricated over a range of compositions at reasonably rapid deposition rates and variable crystallinity. Hirai and colleagues [56] have shown that CVD materials have exceptionally clean grain boundaries that improves the oxidation resistance of silicon nitride materials by at least 200°C over that of sintered materials. Other modifications in processing enable fibre like microstructures to be developed and the density of stacking faults to be modified, both means of increasing the fracture toughness [37].

The recent widescale availability of hot isostatic pressing (HIP) facilities with operating conditions exceeding 2000°C and 200 MPa has been another great means for improvement of the strength of ceramics. The most spectacular examples of this have been in the area of zirconia toughened ceramics where strengths up to two times that achievable by conventional sintering are possible [58]. This is shown in Figure 21. However as discussed in another paper at this meeting HIP'ing may lead to the undesirable introduction of carbon into the ceramic. This is observed in zirconia ceramics when HIP'ed in argon atmospheres with carbon heating elements. This aspect is discussed elsewhere and at this conference [59,60]. The most recent vintage HIP facilities provide for oxygen containing atmosphere up to 1500-1600°C. Another advantage of such an approach is that a range of oxides may now be fabricated to near transparency.

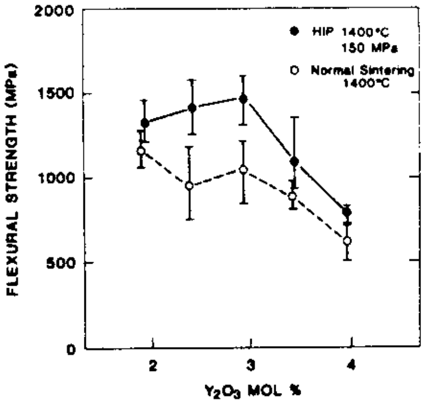

Figure 21. Comparison of the strength of zirconia ceramics before and after hot isostatic pressing (HIP).

With the appreciation that superplasticity is possible in fine grained ceramic materials the opportunity for a range of shaping techniques more usual considered for metallic materials such as forging becomes possible [27].

The future direction in processing and fabrication of ceramics is likely to follow in some instances along similar directions to metals processing. That is, greater emphasis placed upon solid solution/melt processing followed by heat-treatment precipitation processing as currently applied to PSZ materials. Already the literature on TTT curves for the development of various phases and the role of dopants in PSZ ceramic is available [61,62]. The other direction will be the greater emphasis placed upon coating technology to assist in overcoming the problems of high temperature oxidation/erosion/corrosion currently experienced by all non oxide materials. Already such approaches are being utilized in the fabrication of continuous fibre composite structures.

4. APPLICATIONS

In the last two decades there have been two major thrusts that have helped to stimulate research and development in ceramics. In the early to mid-seventies the OPEC oil cartel and its effect on energy prices lifted the interest in research particularly in the field of high temperature gas turbine systems based almost exclusively on silicon nitride and silicon carbide. Despite massive efforts this effort ran into the age old stumbling block of the fragility of ceramics coupled with often in-appropriate design procedures. Towards the end of the 70° a new concept to improve automotive engine efficiency, namely adiabatic or insulated diesel engine was concieved [63]. PSZ materials which were developing during this period appeared to offer just the right combination of properties [64,65]. Examples of some of the materials fabricated for research projects during that period are shown in Figure 22. They include cylinder liners, hot plates for pistons, valves and seats - valve guides etc. However 5-6 years later the general consensus is that the gains from the hot diesel engine approach are much less than the 10-30% improvements deemed possible [66].

Figure 22. Examples of PSZ materials developed for the adiabatic diesel engine research program.

Instead during the last few years the emphasis in the automotive industry has swung back to high temperature gas turbine systems. Already automotives are being fitted with silicon nitride turbocharges, although the environmental and temperature conditions these turbines experience are modest (<800°C) compared with intended applications (1500°C coal ash laden fuel). The advantages of ceramic turbo chargers over metallic ones are their lower mass and inertia and are reputedly cheaper than metallic systems.

Although the automotive applications with their large volumes have attracted many companies into "high tech" ceramics, most are looking for markets for their products elsewhere. Brochures from a range of companies often show similar products with reputed better performance than their competitors. In some instances, particularly Japanese companies have headed directly into the household consumer market with such mundane products, but brilliantly designed and presented, as scissors - knives, etc. Other companies have attempted to seek markets in the high value added microelectronics area.

(a computer magnetic disk readheads) An example of one such device with a ceramic core of PSZ is shown in Figure 23.

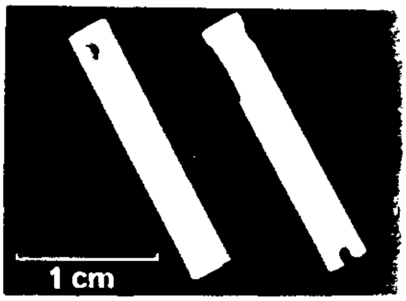

Figure 23. PSZ component for the read head of a magnetic disk device.

Another major market area is in the field of metal forming. For many years ceramic cutting tools based upon alumina have been used for high speed machining of metals. However the fragility of alumina limits its applications for rough duty cutting. Since then a range of zirconia toughened alumina cutting tools for this application as well as sialon cutters for various superalloys have appeared. More recently whisker reinforced alumina cutting tools are replacing hardmetals (WC-Co-TiC) for extremely demanding applications. Other applications in the metal forming area include a range of wire and extrusion dies - generally as replacement for hardmetals. Examples of various such dies made of Mg-PSZ for copper and aluminium extrusion are shown in Figure 24. A range of other applications in the metal forming area include guides for high temperature rolling, rolling mills of silicon carbide, metal powder compacting dies etc. Ceramic filters capable of removing particulate inclusions from molten metals prior to ingotting, casting, etc, are another rapidly growing area of application.

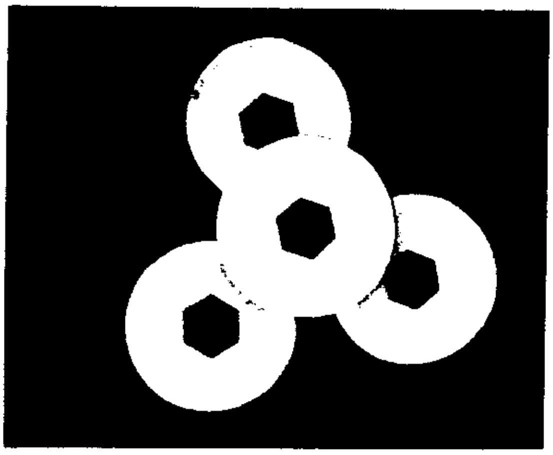

Figure 24. Examples of various extrusion dies of PSZ material for the copper, brass and aluminium industry.

The petroleum, chemical and mineral processing area also provides a range of applications where metallic materials have limited lifetimes because of severe wear, corrosion or combination of these factors. With increasing size, capital outlays and throughput of these industries all efforts to minimise costly maintenance of component replacement due to wear are being sought. Examples in the petroleum industry include down hole pumps and large valves on offshore oil drilling platforms. Ceramic components outperform existing hardmetal components by factors as large as 10 and in many instances at comparable costs. Other areas include flow monitoring of corrosive fluids such as caustic or acids. Until the recent availability of thermal shock resistant ceramics these components were of metal often necessitating weekly replacement and shut down of production systems. The food industry is another field where acidic solutions often cause severe corrosive wear and contamination. Mechanical seals in slurry pumps are a continued source of wear problems in the mining industry. Great improvements in this area are resulting from a combination of better seal design and availability of wear resistant ceramics such as silicon carbide.

Large quantities of ceramic wear resistant tiles - not generally "high-tech" materials - are finding application in the mining and bulk handling of many commodities from wheat to coal to iron ore. These materials often provide sufficient wear resistance to last the lifetime of the handling facility with minimal maintenance. Protection of another type, namely military or defence equipment is also becoming more widespread for ceramic application. In this field cost is not deemed as critical and more exotic materials such as boron carbide, titanium diboride and silicon carbide - all materials having high elastic modulus and hardness - are being used. Other more exotic markets for ceramics in the field of nuclear applications and aerospace also exist but these tend to be speciality areas linked in with national programs of specific countries with highly advanced technologies in these areas.

Apart from the growing interest in ceramics for structural or engineering applications greater interest in ceramic materials is taking place in the electronics - sensor - opto-electronic areas and more recently in the exciting new developments of hot superconductors. All these interests in ceramics will ensure that this previously neglected area, particularly in Australasia, will be to our mutual detriment if we continue to ignore it.

Table 1

Currently Available Ceramic Fibres

Manufacturer	Designation	Composition	Tensile Strength GPa	Tensile Mod GPa	Density gcm^3	Diameter (µm)
Nippon Carbon	Nicalon	Si(60),C(30),O(10)	2.5-3.3	182-210	2.55	10-20
Avco	SCS-6	SiC(C core)	3.9	406	3.0	140
3M	Nextel 312	Al_2O_3(62),B_2O_3(14) SiO_2(24)	1.7	154	2.7	11
DuPont	FP	-Al_2O_3(99)	1.4	385	3.9	20
Sumitomo	-	Al_2O_3(85),SiO_2(15)	1.8-2.6	210-250	3.2	9-17
		More recently available fibres				
Ube	Tyranno	Si, Ti, C, O	3.0	>200	2.4	8-10
Avco		Si, C	2.8	280-315	-	6-10
Dow Corning	MPDZ	Si, C, N, O	1.75-2.1	175-210	2.3	10
Celanese	HPZ	Si, C, O, N	2.1-2.4	140-175	2.35	10-15
"	MPS	SiC, O	1.0-1.4	175-210	2.65	10
3M	Nextel 440	Al_2O_3,SiO_2,B_2O_3	2.1	189	3.05	10-12
"	Nextel 480	Al_2O_3,SiO_2,B_2O_3	2.3	224	3.05	10-12
DuPont	PRD-166	Al_2O_3-ZrO_2	2.1-2.4	385	4.2	20

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