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Some recent promising developments in industrial application of advanced technical ceramics

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High temperature ceramics have yet to reach the long-expected stage of broad market penetration in the transportation sector. However, as the cost-to-performance ratio is improving new key markets are being opened. Use is often made of the property combinations unique to ceramics which add improved or new functionality to engineered systems.

The development efforts have also had a significant impact on property improvement of more traditional technical ceramics and refractories. Some new products such as SiC whisker reinforced alumina cutting tool inserts have rapidly been commercialized.

The paper will give some background to this development and briefly review the significant property features of advanced technical ceramics. Consideration will be given to the interplay between design criteria and manufacturing techniques.

Selected production processes as well as applications on different commercialization levels will be described. They include the emerging techniques such as the Lanxide/RBAO and Sullivan process as well as product areas involving metal working, bearings, wear parts, ceramic armour and ceramic matrix composites for heat insulation in aircraft engines.

1. INTRODUCTION

The oil crisis in the early 70s created a considerable market pull in the transportation sector for rapid development of high temperature ceramics for advanced energy-efficient engines and other energy conservation applications. The major material candidates have been based on fully dense silicon nitride, carbide and partially stabilized zirconia. The attraction of these materials is due to the set of properties highly desirable in designing thermally efficient engines, as listed below:

* High room/high temperature strength
* Low volume mass (density)
* Low thermal expansion
* High thermal shock resistance
* High hardness/abrasion resistance
* Low friction coefficient
* (Thermally insulating)

Concurrently, however, these properties are followed by another set of less advantageous features which have been constraining attainment of the commercialization stage:

* Low fracture toughness/impact strength
* Difficult machining/shaping
* Broad/variable property (strength) distribution
* High cost

Thus, despite extensive development efforts and the promise of huge markets in the transportation sector, thermo-mechanically loaded ceramic parts exposed to hot engine environments which currently can be manufactured on a sound commercial basis are still not up to specifications. In addition, the long-term development objectives have appeared to be a moving target. During the last twenty years the energy prices have dropped significantly. The automotive technology has also been considerably refined. This has decreased the potential gain of utilizing the structural ceramic engine parts. Nonetheless, further promising development is going on particularly in the US and Japan [1] making the ceramic engine applications and other, such as stationary gas turbine plants for power co-generation, a realistic alternative in not too distant a future.

On the other hand, today's structural ceramics frequently exceed specification levels for a vast number of other applications. As an example, fully dense silicon nitride or carbide ceramics may not be strong enough but display excellent wear and/or high temperature resistance. These applications are in market areas which are insufficiently explored and developed. In several countries, this discrepant situation has currently led to a re-direction of efforts to these new application areas, prioritizing those of less long-range pay-off cycle. This is, unfortunately again, a time-consuming and resource-intensive effort which, though, is highly motivated by the enormous wealth of knowledge and valuable competence created through the advanced ceramic R&D efforts.

The modified strategies for further development have been different depending on the type of problem to be addressed:

The cost issue is met by development of low-cost processes and also, by transferring the knowledge to the traditional technical ceramics. The structural ceramics development in particular has had considerable impact on the property improvement/ increased market penetration of alumina ceramics and of advanced refractories. In the case of alumina the ceramic group at ICI, Runcorn, England achieved strength levels of 1 GPa by refined processing. Composite alumina ceramics with SiC whiskers or zirconia second phase show twice as high strength/ fracture toughness compared to pure alumina matrix materials.

Poor property reproducibility is being attacked by designing more rugged, process parameter-insensitive processing, completely new processes or, switching to the ceramic composites (CMCs) to achieve guaranteed reliability and/or desired property combination in one material.

The objective of this presentation is to give a selective overview of some promising recent and potentially growing applications (in the first place within other sectors than transportation) to illustrate the scope of the market and the significance to the society. Another aim is to review some emerging technologies which will be of significance to further qualified applications for advanced technical ceramics.

2. APPLICATION AREAS

Two major areas can be singled out - those related to wear and energy conservation/environmental control. The wear is often related to maintenance costs. An estimate for the U.K. industry [2] gives a figure of £500 million per annum (1966) as a wear-related cost. Use of ceramic parts is thus one obvious way to increase competitiveness for the companies. Advanced technical ceramics also have a strong position in the field of environmental restoration needs which are often coupled with energy-related issues. This type of application, such as filters, burners and catalysts is primarily legislation-driven but, once established, it creates the needed market pull which is necessary for the sustained growth.

Advanced technical ceramics are penetrating markets in many areas: machine wear parts in processing equipment, tooling and other applications in the engineering and transportation sectors, components in abrasive/erosive/corrosive environments at increased temperatures, bearing parts, defense materials, sports and leisure goods and environment-related applications. Selected application areas, which very often involve engineered systems of considerable degree of sophistication, are described in terms of properties and performance. **Most of these applications would never have been realized without the technology base created by the structural ceramic R&D efforts.**

2.1. Wear-related applications

Dense high alumina is well established as a chemically inert wear material and components such as sealing rings, nozzles, dies, crucibles, thread guides for textile machines, metal-forming tools, milling jars and milling media, valve components for abrasive slurries etc have been around for many years. A relatively novel interesting application is that of Morgan Matroc, Worcestershire, England - **ceramic coulter** for Hestair Farm Equipment, Ltd. sugar beet seeding machines. The corresponding metal coulters wear irregularly and suffer up to 3 times the wear of the alumina coulters over the same acreage. They are retailed for about £70 per pc and the market estimate for the U.K. only is about £1 million per annum (1984).

Tetragonal partially stabilized zirconia (TZP) of high toughness, however, outperforms alumina in terms of its combination of erosive wear resistance and impact resistance [3]. The same applies to zirconia toughened alumina (ZTA). These materials tend to replace alumina and increase performance in such applications like ball valves and seats. Zirconia has replaced both alumina and tungsten carbide in **sandblasting nozzles**. Although the unit cost is about 3 times that of alumina the effective life of the component is increased 20 times. Hence, the nozzles are 6 times more cost-effective, excluding reduced down-time and set-up costs.

Ceramic knives for industrial (paper, fish, food, sanitary ware) and medical use are a rapidly growing field. Deterioration of cutting performance affects yield, quality and productivity. Worn-out knives have to be sharpened/replaced which leads to maintenance costs. TZP zirconia blades display up to 20 times the edge retention of conventional steel blades without sacrificing sharpness. As an example, the knife performance for different edge geometries can be optimized using a cutting test through a card board [4]. Sharp edges in the surgical applications reduce tissue damage, the treatment time and cause less inconvenience to the patient. Less corrosion problems arise when sterilized, and ion release to open wounds is reduced considerably.

Metal machining/finishing operations require a combination of high hot hardness/fracture toughness, chemical stability and thermal shock resistance. Ceramics are an upcoming class of **cutting tool materials** with a growing potential for high production rate finishing as well as high removal rate cutting of difficult-to-machine materials as compared to traditional TC (tungsten carbide). According to a NIST estimate for the U.S. only, $120 million in 1990 and expected $530 million in 2000 will be saved in using ceramic cutting tools. This is mainly due to decreased flank wear of the tool tips.

The most common ceramic tool material until recently has been based on alumina. The major weakness of alumina is low strength/toughness/ thermoshock resistance. This is remedied by using so called mixed ceramics (i.e. Al_2O_3-TiC - "Black Alumina"). However, the most dramatic leap in performance has been achieved by designing an alumina composite with SiC whiskers. The strength and toughness have been doubled. The heat conductivity has been increased thus improving the thermal shock resistance. SiC whisker-reinforced alumina tool tips (WG-300) have rapidly been commercialized by the Greenleaf Corp. which sold licenses to major world manufacturers such as Sandvik Coromant, Sweden. The productivity increase in turning nickel-based superalloys is due to increased cutting rates by a factor up to 10 [5]. Zirconia toughened alumina which is being introduced [6] shows promise for cutting of low carbon steel and other ferrous metals.

One of the first commercially successful spin-off applications for silicon nitride ceramics has been in another large niche area - cutting of cast grey iron [7]. Silicon nitride and Sialon tool tips have been commercialized by the early Lucas Cookson Co., Ltd., England (Cookson Zyalon, plc) and numerous licenses have been sold. Subsequent optimization has shown silicon nitride to be the most adequate for grey iron while Sialons are utilized for turning of Inconel-materials. Further development based on the pioneering work of Jack [8] indicates that an α/β-sialon composite may be the final choice. The elongated β-sialon grains cater for toughness while the equiaxed α-grains increase the hardness [9], resulting in considerable increase in the tool tip lifetime.

Apart from technical constraints an accelerated use is curbed by a human factor - the salesmen have to put down more work for less profit to convince new users than when selling conventional TC tools. The ceramic cutting tool tips are cost-competitive retailing at $5–50 per pc at the end user. Depending on application the current market share amounts to only 1–5 % but an enormous market expansion is ahead once a proper material for steel cutting will be designed.

One wear-related application from the automotive industry of significant volume potential [10], the need being 2.5 million parts per annum - only for Chrysler car engines - is silicon nitride for **cam shaft roller followers**. The ceramic part eliminates 18 small steel bearings. The benefit is in decreased wear/friction/weight. A certain cost reduction is required for the ceramic to make this application commercial.

The initially limited number of applications has in some instances created an oversupply. Silicon carbide sealing rings for engine water pumps have been commercialized by the US company Carborundum but other companies, such as the French Céramiques et Composites, also rapidly entered the market. This resulted in a retail price drop (to an amazing $0.5 per pc) below the profitability level.

2.2. Environment/energy-related applications

Diesel engines show promise over the Otto engines of improved energy efficiency but one of the major problems - particulate emissions - has to be solved as more stiff regulations are being imposed, not only in California but also in several European and Asian countries [11]. Ceramics are preferred for **particular filters/traps** because of their low density, chemical inertness, high temperature resistance and trapping efficiency. The ceramic traps must be capable of filtering diesel particulates of 1 μm or less and be regenerable.

The filter substrates manufactured by Corning, Inc. are based on cordierite with a honeycomb structure, with a high temperature capability to 1,400°C. Their diesel filters are of wall-flow type trapping the solid particulate matter at efficiencies ranging from 60 to 95 % and they have survived up to 1,000 regenerations. Development of testing methods is of crucial importance for performance optimization. NGK Insulators, Ltd. has developed a fatigue characterization method which has made it possible to reduce the critical circumferential stresses and thus extend the number of lifetime cycles.

Since 1974, 300 million cellular ceramic substrates have been produced for automotive catalytic converters and these same substrates are now used for the filter trap application. Cordierite is not the only material of choice. The Japanese company Ibiden Corp. has developed a SiC filter trap giving a lower pressure drop than a cordierite filter of a broad range of particulate accumulation. A corresponding type of filters ("Cerafil", developed by Cerel Ltd., Hinckley, England) has recently been tested at metal refinery and coal plants [12] accumulating over 2,000 hours of operation.

In addition to catalytic converters, several other ceramic components being introduced by the automotive industry are not directly involved in the engines but improve the features of their operation. The **exhaust port liners**, mass-produced [13] by the German Hoechst CeramTec Co., reduce the valve seat temperature, cater for faster heat-up of the catalytic converter and reduce the HC and NOx emission levels. Silicon nitride **valve** components, apart from reduced wear and improved performance, contribute significantly to lower noise level - another environmental effect which is expected to be subject to soon-to-come regulations.

The above three ceramic applications - catalytic converter, exhaust gas port liner and valve parts - illustrate the contribution of ceramics to the improvement of the existing engine technology. In so doing they, absurdly enough, decrease the gain potential for the gas turbine ceramic engine.

Another rapidly growing area is that of **heat exchangers** which can operate at temperatures up to 1,500°C in waste recovery applications. They can give fuel savings of up to 50 % compared to 20–30 % for metallic alternatives [14]. SiC is the most usual material since it is hard, corrosion/erosion resistant and, perhaps most important, has a high thermal conductivity of more than 100 W/mK. This property makes it possible to give the tube recuperators more compact design. The high hardness allows use of sandblasting to remove deposits from the surface. The Carborundum Co. nowadays gives up to two years guarantee for SiC tubes employed in erosive and corrosive environments. In particularly severe environments long-fiber CMCs will be utilized [15].

Long fiber CMCs appear to be the only material type of choice for airborne applications where the design strength limit is set below the crack formation strength level. In order to increase thermal efficiency of jet engines and simultaneously reduce the NOx emission there is actually no alternative to ceramics in terms of high temperature resistance, strength and low weight. One currently promising concept is **burning chamber insulating tiles,** being developed, among others, by Volvo Aircraft Engine AB, Sweden in cooperation with other partners. The metallic walls of the currently used burning chambers contain lots of channels for inner wall cooling. The operation temperature is about 1,000°C at the wall surface and about 2,000°C in the middle burning zone, leading to a high level of NOx emissions. Approximately 20 % of air is consumed for cooling rather than propulsion. With the CMC tiles, wall cooling is eliminated, a uniform temperature distribution of 1,500–1,600°C can be sustained over the entire burning zone and the NOx level is pushed down by up to 80 %. A full-scale engine, based on this principle, has been constructed and the concept has been demonstrated in on-ground runs.

The CMC material used is NICALON SiC/CVI-SiC matrix from SEP, France but it is anticipated that the future belongs to oxide-based composites, given the expected temperature/corrosion conditions.

Accordingly, another CMC material under investigation is based on an oxidic matrix/ALMAX alumina long fiber from Mitsui Mining Co., Ltd., Japan.

2.3. Defense applications

These include armour ceramics which are hard, of relatively low density, with high sonic velocities, low Poisson's ratio and transgranular fracture mode [16]. The materials are based on various aluminas, SiC, AlN and the more expensive B_4C, TiB_2 and whisker/fiber CMCs. No single material property can be selected as the most important one since the impact damage is highly variable depending on the ballistic limits. Their use is based on superior ballistic performance/light weight in tanks, submarines and for personal protection. One example is helicopter seat protection shield of sintered SiC against small fire arms, another one is in protective vests. These are built up of three layers: the outer one is for camouflage/handling protection, the middle one for splitting of incoming projectiles (i.e. small alumina tiles) and the inner one containing aramide fibers for energy dissipation of the fragmented projectile over a large body area. The tank protection armor is more sophisticated in that it is frequently composed of layered ceramics.

2.4. Multiple function applications

Structural ceramic materials display a broad range of property combinations going beyond the needs for engine-related applications. Once strength/strength consistency and toughness are raised beyond a certain minimum design level they out-perform any other material. The commercial success is then dependent on the possibility of setting up quality-assured manufacturing lines at a competitive cost.

One of the more impressive growth areas is that of **ceramic bearings**. Fully dense silicon nitride has become a given choice due to its non-catastrophic failure mode - steel-like spalling. Most expanding products are so called hybrid bearings - steel rings with ceramic balls or rollers [17]. The current world production of silicon nitride balls is estimated at 600,000 per annum and is expected to increase to several millions within the next five years.

There is a considerable number of advantageous property features resulting in improved system functionality, Table 1.

Table 1

LOW DENSITY	Higher operating speed due to lower centrifugal force.
INCREASED E-MODULUS	Better dynamic bearing stiffness
HIGH STRENGTH	High compressive strength is important for the ability to withstand the high contact stresses in rolling bearings
LOW THERMAL EXPANSION	Enables operation within a broad temperature range
HIGH HARDNESS	Better surface finish; resistance against scratching
LOW FRICTION COEFFICIENT	Less demanding lubrication conditions
TEMPERATURE STABILITY	Ability to retain mechanical properties up to 800°C
CORROSION RESISTANCE	Stability in oxidizing/corrosive environments

The above features provide a much higher freedom for design selection. In tool machines these advantages bring higher productivity, better machining accuracy and better product quality. Conventional bearings are often lubricated with an oil/air mix system. The hybrid systems can be lubricated with grease which leads to substantial cost reduction for the machine maker. Hybrid bearings with light silicon nitride balls in jet engines give the engines higher efficiency, apart from considerable weight reduction. In order to identify critical material defects effective control methods have been developed by companies like SKF. Most present applications are in high precision/high rpm machines but as the price keeps on dropping ceramic balls are considered for everyday uses such as central axis pedal bearings of bicycles.

Sialons [18] which are more easy to densify than silicon nitride are reaching an increased market acceptance in the field of refractory applications (19). They are replacing zirconia and graphite in handling molten non-ferrous metals such as aluminum alloys as well as steel.

Owing to the combination of high strength/low expansion coefficient the β-sialons possess an excellent thermal shock resistance up to 900°C, they are not wetted by the non-ferrous metals and have a good oxidation resistance to 1,400°C. The field of use includes pumping and metering parts, crucibles for investment casting and thermocouple sheaths. One excellent illustration of the functionality of these materials is the use of **break ring** exposed to molten steel in a horizontal caster. The requirements are: corrosion/erosion resistance, thermoshock resistance and dimensional stability. Since the β-sialon is wetted by steel a boron nitride-β-sialon composite has been designed and is manufactured in sizes up to 300 mm in diameter. The break ring is an important component since it influences the surface quality of the finished product. It is one of numerous components penetrating the fairly conservative refractories market. This market is of particular interest to the ceramic makers because of its potential for large volume.

Ceramic coating/finish grinding of rolls for typesetting machines and other applications for surface wear protection is a widely practised technique. Structural ceramics technology has made it possible to fabricate fully **ceramic rolls**. The attractive properties are strength, thermal shock resistance, high stiffness (E-modulus), wear/corrosion resistance and, product final surface finish. The environmental concerns may also favour the selection of ceramics. In aluminum sheet rolling machines the processing additive fluids are increasingly water-based which leads to corrosion problems. In type-setting machines the use of isopropyl alcohol may be banned which will affect the lubrication between the rolls and the sheet paper feed. In steel plants feeding of strip steel bands with the aid of ceramic rolls with high thermal shock resistance, low heat conductivity and chemical inertness can improve productivity.

Hitachi Ltd. [20] can manufacture Sialon ceramic rolls which are claimed to provide thin, smooth and bright metal strips. Thanks to the high E-modulus of Sialon cost effectiveness can be achieved also in producing very thin strips.

Due to the above multiple property advantages, ceramics are also being utilized instead of metals/polymers in high speed paper machines as suction boxes, forming boards and sheet-cleaning devices. Alumina, having been used initially, is replaced by zirconia (TZP) due to its higher fracture toughness and thermal shock resistance, despite a higher cost.

3. EMERGING TECHNOLOGIES

Fabrication of structural ceramic components usually involves a number of processing steps starting with submicron powder raw materials. These are processed and formed to shape, often by component-specific techniques, the major ones being slip casting, injection moulding and pressing. The green parts which typically attain a density of 50–70 % of the theoretical, are consolidated to the final shape at temperatures up to 2,000°C. Some machining is almost always required to control the tolerances/surface finish.

The large number of processing steps makes the fabrication costly and less amenable to an effective quality control. The step from the green to the sintered part (involving considerable shrinkage) is critical because the quality variation of the starting powder/shaping-related defects will strongly influence the quality of the product. Very often, Hot Isostatic Pressing (HIP) is required to achieve a satisfactory shape/density consistency. Current technological development has led to new methods which avoid the powder starting materials completely or are improvements/upgrading of existing technologies. One important feature is that the densification shrinkage is minimized or eliminated. Those which will be mentioned can be seen in Table II.

Table 2

Technology	Principle	Features/Benefits
LANXIDE (Dimox)	Liquid phase reaction sintering	No shrinkage, net shape, CMC fabrication capability
RBAO	Ceramic/metal powder reaction sintering	Low shrinkage; near net shape
SULLIVAN process	Reaction/supercritical fluid extraction	Potentially low cost; CMC fabrication capability
CVD SILICON CARBIDE (Morton International)	CVD deposition	No shrinkage, net shape, high heat conductivity, high polishability

The Lanxide (DIMOX) process presented already 1986 [21] is based on **oxidative conversion of a molten metal**, enclosed in a pre-shaped container, to a ceramic body. Initially designed to make alumina shapes, it has been developed to make all types of ceramics including CMCs with reinforcing phases (particles, whiskers, fiber preforms).

The residual metal phase caters for an increased level of toughness. A composite of exceptional material properties [22] has been made starting from molten Zr/B_4C. The resulting ceramic composed of zirconium carbide/residual Zr metal matrix with ZrB_2 platelets is reported to have a strength of up to 1 GPa/toughness of 11–23 $MPam^{1/2}$ and a Weibull modulus of 20–68. This property combination makes it comparable to high strength steels thus opening a wide range of demanding applications.

RBAO (Reaction Bonded Aluminum Oxide) represents a family of ceramic materials made from **balanced metal/ceramic powder mixtures** to minimize the shrinkage [23]. Usual powder fabrication route is utilized to make the green shapes. The metal is than oxidized filling up the pore space, thus resulting in a dense ceramic. This technology is of interest, i.e. for making long fiber CMCs from fiber preforms.

The unique **Sullivan liquid process** [24] has originally been developed for light weight CMCs for space structures. The materials produced are silicon nitride and other difficult-to-sinter ceramics. The process includes two key stages:

1. reaction of the organometallic reactants in an autoclave to a liquid ceramic precursor,
2. supercritical extraction of non-ceramic reactants and formation of an amorphous ceramic shape in a mould.

The present applications include cam roller follower for the reciprocating engines and tools for tabs of beverage cans. Cemented carbide punches used at Continental Can Co., Olympia, Wash. are replaced after 20–25 million stampings. Corresponding silicon nitride punches made by the Sullivan process survived 200–400 million cycles. The process is claimed to be amenable to mass production and potentially capable of making complex shapes at about a tenth of the cost compared to the ordinary powder route.

The gas phase-based CVD SILICON CARBIDE (CVD: Chemical Vapor Deposition) technology has been developed by Morton International [25] to meet market needs within optics, wear parts, information storage and electronic packaging. The material, which is highly pure β-SiC, is said to be superior to the powder-based qualities in terms of hardness, E-modulus, strength, thermal conductivity (250 W/mK), polishability and oxidation resistance. The CVD technique permits build-up of a fully dense ceramic microstructure directly from a gas phase mixture on a hot substrate wall. The walls of the CVD-reactor can be of almost any geometry thus permitting fabrication of net shape parts. This reduces machining time and cost. Seals, wear components and automotive parts are envisioned as future applications, in addition to the optics.

The existing technologies are also amenable to considerable improvements as indicated by the following two examples.

Dow Chemical Co. has developed [26] the **ROC-TEC process (Rapid Omnidirectional Compaction)** based on uniaxial pressing, the pressure being applied isometrically to the compacted part via a fluid die as an auxiliary pressure-transmitting vehicle. The method thus resembles HIP but is said to involve very short processing time at lower temperatures than the conventional methods. Composite carbide parts of very high hardness (Rockwell A: 96.6/extremely fine microstructure (0.25 μm average grain size) - hence a superior wear resistance - are fabricated. Further features are high hot hardness and high stability in acid environments. The major fields of application include sliding wear and particulate flow wear.

The Norton Co. has considerably refined the fabrication process for silicon-infiltrated SiC [27] based on the so called REFEL SiC. Their **NT 230 SiSiC** has the strength/toughness level which is equivalent to the high temperature sintered SiC but has the key advantages of excellent net shape dimensional control due to shrinkage-free processing/lower cost. Complex shapes can be made by pressure slip casting. Applications are numerous including static structural components in gas turbine engines.

4. CONCLUDING REMARKS

The rate of market penetration is strongly and perhaps exclusively affected by the level of technological achievement versus cost. The classification of the commercial improvement can be done according to the following sequence:

1st/2nd/3rd class improvement ⇒ better performance at lower/equal/ higher cost, respectively.

There is hardly any doubt still where many of today's advanced structural ceramics will end up. The best illustration of the cost factor is the fact that there is an enormous latent market demand for ceramic components of complex geometry/reproducible quality/narrow dimension tolerances and, relatively small production volumes, which are of unmatched performance compared to other material choices but - too expensive to make. As the development proceeds the price can gradually be pushed down. This will cater for not a dramatic but still a very healthy market growth rate compared to other segments. Thus one cannot but agree with the words of G Marsh, Aerospace Composites & Materials, (28):

... Ceramics will yield to engineers eventually because they are too good to miss ...

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