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ADVANCES IN THE DEVELOPMENT OF SILICON NITRIDE AND OTHER CERAMICS

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ABSTRACT

The use of silicon nitride for high temperature components in gas turbine engine and other heat engine applications continues to be sought due to the potential for significant improvements in both efficiency and emissions. However, low impact resistance and inadequate resistance to environmental degradation of current materials reduce its reliability for rotating and stationary components. Material improvements are needed to overcome these limitations. Potential and demonstrated methods to achieve improved fracture toughness, strength, and high temperature environmental resistance are reviewed.

Key Words: silicon nitride, fracture toughness, self-reinforced, environmental resistance.

INTRODUCTION

Over the last 30 years, a number of programs in the United States, Japan, and countries of Western Europe and the former Soviet Union have sought to introduce monolithic and composite ceramic components into gas turbines with the goals of increasing thermal efficiency and output power, and lowering emissions. The superior high temperature strength and durability and acceptable physical properties make silicon-based monolithic ceramics (silicon carbide, silicon nitride) and continuous fiber-reinforced ceramic composites (CFCCs) attractive candidate materials for gas turbine hot section components.

In the U.S. and abroad, programs to develop and demonstrate the application of these silicon-based ceramics have not yet led to broad-based commercial application. Some

successes have been achieved in specific applications, such as silicon nitride turbochargers in cars, silicon nitride vanes in auxiliary power units (APUs), silicon nitride seal rings in small gas turbines, and SiC/SiC CFCC composites for combustor liners. However, long-term (20,000 – 30,000 hr) applications are not yet assured because of fundamental materials property deficiencies.

Three critical material property issues that limit the application of the silicon-based ceramics for gas turbine hot section applications include:

1. Fracture toughness and strength properties of silicon carbide, silicon nitride and CFCCs limit successful application. For example, in early field tests conducted under the Ceramics for Stationary Gas Turbine (CSGT) Program of Solar Turbines, Inc. silicon nitride first-stage blades failed after 948 hours most likely due to impact damage from a metallic locating-pin associated with the inner combustor liner [1]. Subsequent impact studies showed [2,3] that the low toughness values of the current silicon nitride ceramics are a major factor in limiting impact resistance. Further, studies reveal that both the Weibull modulus and strength can be greatly enhanced when the material has very high toughness associated with a rapidly rising R-curve response [4]. Although the tensile strengths of the monolithics are relatively high, ~700 MPa, their fracture toughness is typically in the 5-9 MPa*m^{0.5} range, which results in poor resistance to impact and slow crack growth. On the other hand, the CFCC composites have the characteristic of graceful rather than

catastrophic failure, but the mechanical strengths of CFCCs are quite limited (e.g., the stress required for the generation of matrix cracks is 150 MPa or less). This constrains the use of these materials to applications with relatively low stress such as combustor liners, transition pieces, seal rings, and shrouds, and excludes their use for stationary applications with significant temperature gradients (nozzle vanes) and rotating applications where stresses are typically in the 200-300 MPa range.

2. Elevated temperature oxidation results in surface and subsurface microstructural damage, including the formation of pits or voids, subcritical crack growth, or creep. After long exposures to high temperatures newly formed oxidation damage controls the performance and lifetime of the material [5-8]. In ambient air, these damage mechanisms are influenced by reactions of silicon nitride and its sintering additives with an oxidative atmosphere. Besides the formation of a surface oxide, alterations in composition and distribution of the grain boundary phases and the formation of gas can occur after long-term exposures [9].
3. Environmental degradation in combustion atmospheres generally leads to unacceptable degradation of both silicon-based monolithics and CFCCs after 500 to 1000 hours of service in gas turbines with pressure ratios over 8:1 for parts operating at 1000°C and above [10]. The latter problem is currently being addressed with environmental barrier coatings (EBCs), and some measure of success has been achieved for EBC coated SiC/SiC CFCCs in the CSGT program sponsored by the U.S. Dept. of Energy [11,12].

Notwithstanding the steady improvement in properties over the past few decades engine durability testing worldwide has shown that fundamental material limitations need to be addressed to assure that ceramics achieve their potential as enabling technologies for advanced gas turbine systems with improved performance compared to state-of-the-art all-metal engines. In addition to the research investigating refinements to further advance self-reinforced silicon nitride properties, a number of efforts around the world are investigating the tailoring of ceramic compositions and microstructures ranging from the nanoscale to the macroscale, and incorporating multiple levels of composition and structural design (hierarchical structures) to generate radically improved properties. There is now an opportunity to incorporate the variety of new material composition/microstructure and fabrication concepts that have been developed over the past ten years into a new generation of more sophisticated structural ceramics that overcome the limitations of current monolithics and CFCCs. This paper will review a number of technology

developments that are establishing the foundation for the needed improvements and technical areas that should be included in technology project planning.

NEXT GENERATION SELF-REINFORCED SILICON NITRIDE CERAMICS: POTENTIAL FOR HIGHER TOUGHNESS AND STRENGTH

A real progression has taken place in silicon nitride and carbide ceramics with respect to strength and toughness, as seen in Fig. 1.

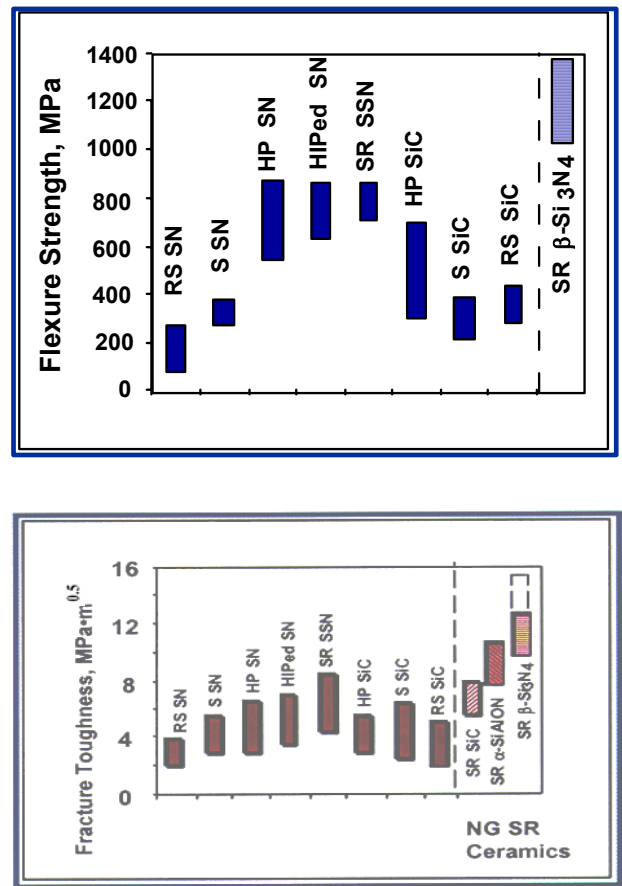


Figure 1. Progression in strength (top) and toughness (bottom) values versus time (x-axis) achieved in silicon-based ceramics including: reaction sintered Si₃N₄ (RS SN) and SiC (RS SiC), hot pressed Si₃N₄ (HPSN) and SiC (HPSiC), sintered Si₃N₄ (early vintages-S SN), HIPed Si₃N₄ (HIPed SN), sintered self-reinforced Si₃N₄ (SR SSN) and Next Generation (NG) (lined bars) ceramics including self-reinforced beta-Si₃N₄ (SR β-Si₃N₄) [13,14, 16,20,21], SiC (SR SiC) [23] and α-SiAlON (SR α-SiAlON) [22].

Both charts in the figure reflect progress with time in silicon nitride and silicon carbide, from left to right, with the self-reinforced and next generation ceramics representing the most recent results. In the case of the toughness for the next generation self-reinforced ceramics (NG SR β - Si_3N_4), the unfilled portion of this bar is representative of material with highly aligned elongated reinforcing grains [13,14] (e.g., similar to the effects of uniaxially aligned fiber-reinforced ceramics). The NG SR ceramics (e.g., beta-silicon nitrides, alpha-SiAlONs, SiC), properties exceed those of current commercial materials.

The fundamental understanding gained during the evolution of self-reinforced silicon nitride ceramics is now being utilized to develop the NGSN materials with higher toughness and strength to address the property requirements for a number of application areas, e.g. in advanced diesel and turbine engines, wear and friction applications, and heat exchangers (note that Si_3N_4 ceramics can have thermal conductivity that are now at the 150 W/m K level [15]).

Studies have now established a basis for controlling both the development of microstructures containing larger elongated grains and the tailoring of the sintering additive composition to improve the fracture toughness [16,17]. The elongated grains serve as the reinforcing elements much like whiskers in whisker-reinforced ceramics [17,18], or fibers in fiber-reinforced ceramics [19]. Control of the microstructure is a key here as the toughening achieved by crack bridging processes is dependent upon the size and volume fraction of these larger elongated grains. In commercial self-reinforced ceramics, the elongated beta-phase grains are generated during the sintering of the ceramic, which greatly simplifies the processing and avoids the use of expensive ceramic fibers or whiskers. Such reinforcing grains form in silicon nitride ceramics and larger grains form due to the initial presence of some beta-phase in the alpha-phase silicon nitride powders typically used. Unfortunately, when sintering these powders it is difficult, if not impossible, to regulate the size of the larger reinforcing grains and to obtain a uniform spatial distribution of them. Both factors must be satisfied in order to achieve both high toughness and high strength. Control of the size and distribution of reinforcing grains is one of two major factors that have limited the achievement of high toughness, high strength self-reinforced silicon nitride ceramics. Studies have shown that control can be achieved by the incorporation of a small fraction of rice-like beta seeds into the silicon nitride powder. The “beta-rice” seeds used to date are typically 3 to 4 μm long by $\sim 1 \mu\text{m}$ in diameter; however, the optimum size and shape of such seeds has not been determined as yet. These “beta-rice seeds” serve as the nuclei for generating well dispersed elongated reinforcing grains with controlled size(s) [16,20,21]. Recent studies suggest that toughening by self-reinforcing grains can be also developed in alpha-SiAlON ceramics using a similar seeding approach [22]. Results using

these principles show that next generation self-reinforced silicon nitride (NGSRSN) ceramics can have high strengths (1 to 1.4 GPa) combined with high fracture resistance, which yield plateau values (i.e. toughness values) of up to 11 $\text{MPa m}^{0.5}$ (Fig. 2).

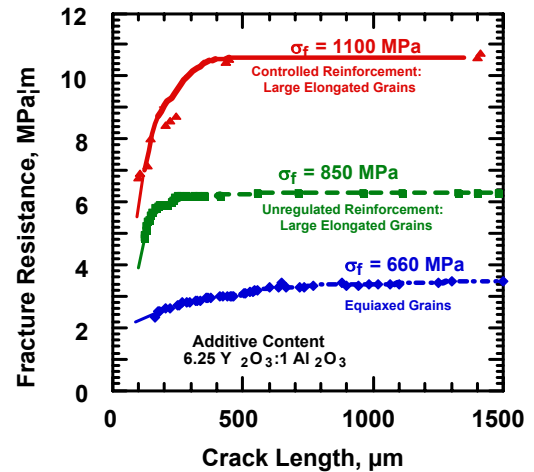


Figure 2. Very high strength and toughness values are achieved by controlled generation of large elongated β - Si_3N_4 reinforcing grains into a fine-grained β - Si_3N_4 matrix (e.g., see ref. [16]).

Control of the sintering additive compositions, which dictate the intergranular films typically formed in the sintering step, is the second important factor in the development of self-reinforced silicon nitride ceramics. The additive composition is important because both the growth of the reinforcing grains and their subsequent ability to act as reinforcements, are controlled by the intergranular material typical found in silicon nitride ceramics. (They are also a major factor in the intermediate and elevated temperature oxidation, strength, and creep properties). These intergranular films (typically $< 2 \text{ nm}$ thick) are a result of the reaction between the native oxygen in silicon nitride powders and the specific chemical additives used to promote sintering. This reaction results in the formation of a viscous glass that allows liquid phase sintering to occur and acts as a media for the growth of the elongated reinforced beta grains. The resultant intergranular films (IGFs) also control the debonding of the reinforcing grains from the matrix material in the crack tip region [24,25]. This debonding process prevents the crack from cutting through the reinforcing grains and allows them to bridge across the crack. This is similar to the steps that occur in fiber-reinforced ceramics. Recent studies show that the composition of the sintering additives and, hence, the IGF can be tailored to optimize the toughening effects of the elongated reinforcing grains in silicon nitride ceramics. As an example, the fracture toughness of SRSN ceramics with $\sim 7 \text{ wt. } \%$ additives of yttria

plus alumina was raised by ~ 50 % simply by increasing the yttria to alumina ratio in the additives [26,27]. Tailoring of the additive composition plus the microstructure is now recognized as the critical factor in obtaining both high fracture toughness and high fracture strength.

Similar, controlled and elongated grain microstructure approaches apply to oxide ceramics as well. A $\text{LaAlO}_3\text{-Al}_2\text{O}_3$ composition with strength over 600 MPa and high fracture toughness of $6 \text{ MPa}\cdot\text{m}^{0.5}$ was achieved by a combination of elongated Al_2O_3 grains and $\text{LaAl}_{11}\text{O}_{18}$ platelets. The increase in toughness is achieved by the crack bridging effect of anisotropically grown alumina grains, while the lanthanum aluminate platelets play a role in hindering the alumina growth [14]. Compared with silicon-based materials these results are not impressive but they are for oxides where insufficient toughness is problematic.

Alternate or combinatorial approaches have also demonstrated to improve strength and toughness:

- Hitachi, Ltd. has developed nanocomposite silicon nitrides with high strength (1400 MPa) and K_{Ic} ($10.5 \text{ MPa}\cdot\text{m}^{0.5}$) [28].
- Low elastic modulus materials developed by IHI have given high strength (1030 MPa) combined with high K_{Ic} ($15 \text{ MPa}\cdot\text{m}^{0.5}$). IHI has made high strength and toughness components using tape casting and a technique based on alternating dense and porous layers [29].
- When research emphasis was on reducing the elastic modulus of silicon nitride to improve its strain to failure, a 14% porous silicon nitride with aligned fibrous grains was evaluated. Using a chevron-notched beam technique a K_{Ic} ranging from ~ 11 to ~20 $\text{MPa}\cdot\text{m}^{0.5}$ was achieved for crack sizes from ~0 to 2.6 mm, respectively, in material with a flexural strength of 1081 MPa, and an elastic modulus of 246 GPa. The fracture energy was determined to be about 490 J/m^2 , about 7 times larger than that of the dense silicon nitride reference material [30].

What can we expect out of such toughened ceramics? The object must be to generate more robust materials that exhibit improved mechanical properties and resistance to damage during handling or in-service. As an example, the fracture strength should not be altered by surface damage. The resistance to damage of toughened silicon nitride ceramics has been evaluated by examining how the fracture strength is influenced by more severe (i.e., coarser diamond grit size) surface grinding [31]. A very significant benefit of the toughened self-reinforced silicon nitrides can be seen in Fig. 3 where the high strengths are unaffected by the severity of the surface damage. In this figure, the x-axis represents the size, in microns, of the diamond particles used in the grinding wheel used to finish the tensile surface of four point flexure bars. In this case, the depth of the residual grinding grooves and

associated damage zone as well as the size of the surface cracks generated all increase as the size of the diamond particles in the grinding wheel increases. These results suggest that such self-reinforced silicon nitride ceramics should have both greater resistance to local impact damage and less flaw size dependent strengths (e.g., narrow strength distributions). Indeed, the self-reinforced silicon nitride ceramics typically exhibit a substantial narrowing of the fracture strength distributions with Weibull moduli of up to 40 as compared to ~ 10 in the absence of toughening effects [4].

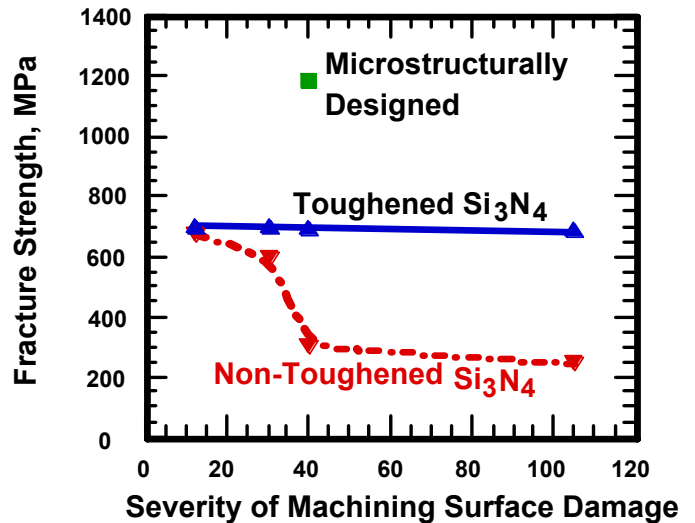


Figure 3. The self-reinforced silicon nitride ceramics exhibit fracture strengths that are not degraded by increasingly severe surface damage while the unreinforced silicon nitrides undergo substantial strength loss. Data for toughened and non-toughened silicon nitride are taken from ref. [31].

POTENTIAL FOR IMPROVED OXIDATION AND CREEP RESISTANCE

The mechanical reliability of silicon nitride ceramics at intermediate and elevated temperatures is also dominated by the intergranular phases present. Amorphous and or crystalline intergranular films control the temperature and stress for the onset of crack growth at intermediate temperatures and creep deformation at elevated temperatures. Recent work reveals that substitution of smaller rare earth (RE) ions into Si-RE-Al oxynitride glasses can be used to increase the softening point of such glasses and, hence, raise the glass viscosity at elevated temperatures [32-34]. The diffusion of oxygen along intergranular films typically increases as the glass viscosity at a given temperature is lowered. This increases the susceptibility of ceramics to degradation by oxidation processes. The results of these glass studies provide directions for tailoring the sintering additives for silicon nitride

to improve the mechanical reliability and reducing the transport of oxygen through the grain boundaries of these ceramics at intermediate and high temperatures. In addition, studies at Oak Ridge National Laboratory (ORNL) reveal that the reinforcing microstructure with the larger elongated grains can be used to gain additional increases in creep resistance [35]. In fact, the creep resistance of commercial silicon nitrides has been improved by taking advantage of these approaches while eliminating deleterious additives like alumina, which tend to lower glass viscosity. The highest reported tensile creep resistance has been obtained in a self-reinforced silicon nitride that utilizes Lu_2O_3 as a sintering additive [36].

An additional aspect of oxidation resistance has included the evaluation of SiC or MoSi_2 particles in a Si_3N_4 matrix [9]. With the addition of 10% SiC or MoSi_2 in a Y_2O_3 doped Si_3N_4 , after 1000 hours of oxidation testing from 1400 to 1500°C the composites had a residual strength of 650 to 700 MPa versus a level of ~450 MPa for the unreinforced material. The improvement is attributed to the increased formation of a layer of crystalline Si_2ON_2 caused by a modified oxidation mechanism. The layer, formed below the upper surface of the material, prevents both the diffusion of oxygen into the bulk material, and the formation of typical oxidation defects such as cracks, pores, or glassy-rich regions. The formation of the Si_2ON_2 rather than SiO_2 also reduces the driving force for grain boundary cations to diffuse into the silica rich glass at the surface of the material. With the formation of the Si_2ON_2 during oxidation, the degradation of the composite materials was reduced. Further, hot pressed $\text{Si}_3\text{N}_4/\text{MoSi}_2$ composite materials were exposed for 10,000 hours at 1500°C with only minimal alterations in the microstructure while maintaining ~65% of their baseline room temperature strength [37].

SPIN-OFF BENEFITS

While it is critical to improve the room and elevated temperature properties of silicon nitride ceramics, it is also important to understand and control other properties that will make them more reliable. Studies have indicated that the presence of oriented large elongated grains, the substitution of rare earth ions, or elimination of alumina in the sintering aids can greatly increase, or alter the thermal conductivity of silicon nitride ceramics (e.g., up to 120 W/m K, which approaches that for AlN) [15, 38-41]. Nissan Motor Co., Ltd. is developing silicon nitride with exceptionally high thermal conductivities. In a 2-D structure a value of 128 W/mK has been achieved, while in a 1-D structure values in the range of 140-160 W/mK have been measured [28]. The strategy is to combine the high thermal conductivity with low friction characteristics. It will continue to be important to exploit the understanding that is being developed on how composition and microstructure can be utilized to achieve a combination of optimum properties.

IMPROVED ENVIRONMENTAL RESISTANCE

With the advent of more extensive silicon nitride and silicon carbide component testing in industrial gas turbines in the late 1990s, it became obvious that the combination of significant amounts of water vapor with high temperature, high pressure and high velocity air resulted in excessive surface recession [10] due to rapid volatilization of the surface protective SiO_2 layer. Recently, coatings such as mullite and celsian have been applied to silicon nitride monolithic materials and silicon carbide matrix composites to inhibit water vapor and oxygen penetration to the silicon nitride or carbide beneath. The coatings have been selected to closely match the coefficient of thermal expansion (CTE) of the ceramic substrate to prevent spalling, and for the ability to be applied by conventional methods on dense parts (e.g. plasma flame spraying, chemical vapor deposition - CVD, electron beam-physical vapor deposition - EB-PVD). The coatings show some improvements in protection but they still have significant oxygen permeability and contain silicon, which makes them susceptible to the water vapor induced volatilization mechanism. There are obvious concerns about coating integrity, adherence, and performance over the thousands of hours of life needed for these components to be accepted for commercial implementation. In addition, engine manufacturers have identified applications, which require higher temperatures (1450 – 1500°C) than the current coatings being evaluated can handle. It is also likely that effective surface EBCs will need to be multi-component, because many materials being considered for their resistance to water vapor attack have significant oxygen permeability.

Ideally, a self-healing protection system would be designed into the material itself. This system would function much the same way the Si does in silicon nitride when it forms a protective SiO_2 coating in an oxidizing atmosphere. The protective species could be uniformly distributed throughout the ceramic or localized near the surface. The challenge to this self-healing approach would be to maintain the integrity of both the protection system, and the grain boundary phase so that the material properties are not degraded. The benefit of such an approach is that the protection system would be an integral part of the component, would not add dimensionally to critical gas path surfaces, and would not require additional expensive processing steps. Studies in the $\text{Si}_3\text{N}_4/\text{MoSi}_2$ composite systems using an Yb_2O_3 sintering additive have been shown to behave in such a manner [42]. After hot pressing the composite, an Yb_2O_3 coating was applied, and the material was exposed in a natural gas combustion atmosphere at 50 m/s, 1400°C, 5 bar pressure, with steam introduction. Although EBC adhesion was poor, the functionality of the EBC was demonstrated, and below the EBC a stable layer of amorphous SiO_2 , cristobalite and $\text{Yb}_2\text{Si}_2\text{O}_7$ was observed, which prevented substrate oxidation.

Many potential EBC materials being considered as oxygen/water vapor protectors have significantly higher CTE than silicon nitride or silicon carbide, which currently prevents their use. Two potential methods being investigated to allow application of new candidate surface oxygen/water vapor protective coatings are:

- Post-densification displacement or diffusion reactions, where the densified component is processed in a gas, liquid metal, or powder bed to generate a near-surface composition gradient of the desired surface protection composition. The graded composition would have the potential to minimize CTE mismatch stresses and maximize adherence to prevent spalling.
- Generation of graded compositions on part surfaces during fabrication using solid freeform processes such as Direct Photo Shaping (DPS) or Fused Deposition. The surface compositions would obviously need to be compatible with the ceramic densification conditions. This type of technology has already been demonstrated with DPS on silicon nitride turbine nozzles where a CeO₂ doped surface layer was applied as part of the net-shape forming step, and then co-sintered and oxidized to form a compressive surface stress [43], taking advantage of the volume change expansion of the CeO₂-doped layer.

Ideally, surface EBC protection mechanisms should be combined with damage resistant surface coatings/mechanisms to create a holistic approach to surface protection – addressing both environmental and impact resistance.

THE SYNERGY CERAMICS PROJECT: A MODEL FOR MATERIAL DEVELOPMENT

Recently, in Japan materials development programs have been conducted which focus on routes to solve the inadequacies of current silicon based ceramic materials. Specifically, the Synergy Ceramics project has been ongoing at the National Industrial Research Institute of Nagoya (NIRIN) (now known as National Institute of Advanced Industrial Science and Technology, Synergy Materials Research Center) and other organizations in Japan. By focusing on the micro- and macro-scale aspects of processing new materials many of the improvements reported in this review have been achieved.

The Synergy Ceramics project was inaugurated in 1994 as a collaborative effort among national research laboratories under the Industrial Science and Technology Frontier Program of the Japanese Agency of Industrial Science and Technology (AIST) of the Ministry of International Trade and Industry (MITI) currently renamed as the Ministry of Economy, Trade and Industry (METI). A part of the program is being conducted under the sponsorship of New Energy and Industrial Technology Development Organization (NEDO) through entrustment to the Fine Ceramics Research Association

(FCRA). The project is being conducted in two phases. Phase I, conducted between 1994 and 1998, emphasized basic research in materials structure control and supportive analysis and evaluation method development. The mode of operation during Phase I was free-flow, open ended R&D without focus on specific applications. Phase II, which started in 1998 and will be conducted through 2003, is much more focused on taking the successful areas of Phase I research to the applications stage. At this stage collaborations with industry are an important aspect of the program. Participants in the Synergy Ceramics project are currently national research laboratories, universities, industries, and overseas research institutes. Of the Japanese gas turbine Original Equipment Manufacturers (OEMs) Hitachi, Ltd., Toshiba Corp. and Ishikawajima-Harima Heavy Industries (IHI) are involved. NGK Insulators, Ltd., Kyocera Corporation, and Asahi Glass Co. are supplier participants. Toyota Motor Corp. and Nissan Motor Co. represent the automotive industry. Dow Chemical Co. is also a participant. Collaboration is also occurring between some Synergy Ceramics Project and ORNL researchers.

The basic premise of the Synergy Ceramics project is to develop materials that have multi-functionality and multi-capability, combining properties that are currently only present in different classes of materials, often with antagonistic properties. An example is the development of materials that combine high mechanical strength with high fracture toughness, as presented in this report, or materials that have good strength and good thermal conductivity. The objective of synergistic properties is being achieved by a strategy broadly termed “Hyper-Organized Structure Control”. In the Phase I core research area the four predominant themes were: precursor design, structure development simulation design, nano-structure processing, and in-situ structure controlling process. One objective of the Project is to produce ceramics with excellent mechanical strength (1000 MPa flexure strength) and superior fracture toughness (15 MPa*m^{0.5}) [44].

A summary of the project to-date is illustrated in Figs. 4 and 5 [14]. Figure 4 classifies material structures based on the scale (atomic-molecular-, nano-, micro-, macro-scale). To attain compatibility of antagonistic properties and a synergistic effect of functions, it is necessary to select the elements conforming at each level, and exert simultaneous control of different structural elements, such as shape and size, at plural scale levels. Fig. 5 illustrates how two antagonistic properties, strength and toughness can be combined in the same material. Strength benefits from a homogeneous microstructure while toughness is favored by a heterogeneous microstructure; both of these are characteristics at the micro-scale level. It is rather difficult to achieve simultaneous improvement of both properties with traditional techniques of structural control operating at a single scale level. The solution proposed by the Synergy Ceramics project is to perform structural control at

two different scale levels. For example, combining an intra-granular dispersion of nano particles (supplying strength) with orientation control of anisotropic grains (providing toughness) will have the synergistic result of a hybrid material with both properties.

BIOMIMETIC AND HIERARCHICAL CERAMIC MATERIALS DEVELOPMENT IN THE UNITED STATES

The U.S. does not have an analogous coordinated synergy ceramics program but a small number of individual research efforts are investigating similar aspects of nanoscale structural ceramic composition and structure. Additionally, two other specific areas of ceramic composition/structure research hold the potential to significantly improve structural ceramic properties – biomimetics and hierarchical structured materials.

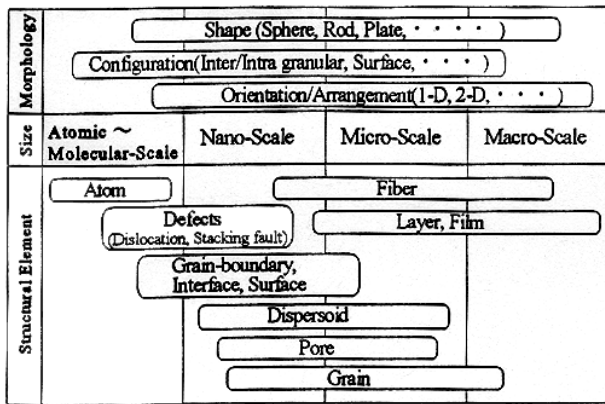
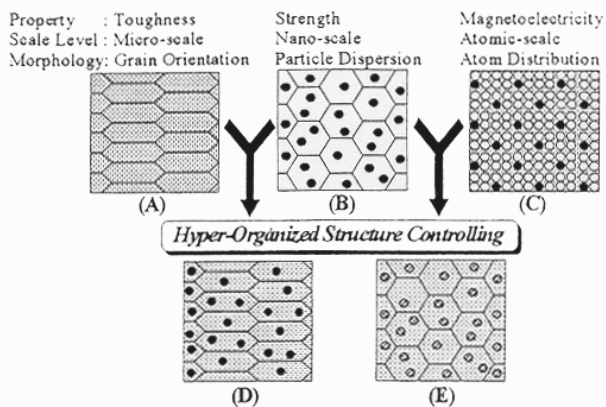


Figure 4. Classification of Material Structures. Reprinted with permission from ref. [14]



(D): Compatibility of strength and toughness.
(E): Compatibility of mechanical properties and a magnetic function.

Figure 5. Conceptual Diagram of Hyper-Organized Structure Control. Reprinted with permission from ref. [14]

One potential path to improving structural ceramic material properties is to simulate structures in nature – referred to as biomimetics [45]. A number of examples exist in nature of strong structures being generated from weak starting materials due to ingenious nanoscale and hierarchical structures (e.g. seashells being made from calcium carbonate). One of the key tools used in nature is to “self-assemble” inorganic nanoscale structures using biological (organic) processes [46]. Researchers now are able to generate a myriad of nanoscale structures with materials such as SiO₂. The self-assembled SiO₂ structures have been shown to demonstrate unique elastic modulus properties in bulk material, compared to SiO₂ fabricated from traditional processes such as melting and sintering [47]. This is a very nascent field, but one that holds promise for providing tools to allow generation of desired nanoscale structures in structural ceramics.

At the other end of the size scale, since the mid-1980s a number of U.S. researchers have been developing structural ceramic materials technologies that generate “macrostructures” in monolithic materials to provide improved toughness, an example being fibrous monoliths [48]. The scale of structure is one to two orders of magnitude greater (e.g. 200-500 μm) than the ceramic grain size. With careful tailoring of interface properties between these macroscopic structures, effective debonding can be generated and toughnesses of 15-20 MPa*m^{0.5} can be demonstrated. Although current fibrous monolith materials exhibit some significant limitations, such as temperature limited interfaces (e.g. BN) and relatively low strengths (150-300 MPa), there is obvious potential for improvement in temperature and strength capability.

A key need for optimization of these synergy/hierarchical materials concepts is the ability to model and predict material properties from composition and structure designs. The National Institute of Science and Technologies’ (NIST) Object Oriented Finite Element Analysis of Real Material Microstructures (OOF) program [49] is a useful first generation tool. While currently limited to 2-D, one can input virtual or actual microstructures to establish the grid. Although its strength is in solving elasticity and thermal diffusion problems, one can gain some useful insights about microstructural effects [50].

Ideally, a tool is needed that allows plug-in of material properties (e.g. for silicon nitride – silicon nitride grain properties, second phase properties, and grain boundary interface properties) and predicts resulting properties for a given nano/micro/macrostructure based on applied external conditions – mechanical load, environment, temperature, etc. Even more desirable, given a set of material properties and microstructural constraints, is a model that would predict

optimum nano/micro/macrostructure and compositions for a
CONCLUSIONS AND RECOMMENDATIONS

A great deal of understanding of the material behavior of silicon nitride as a function of its composition, processing and microstructure has been developed during the past decade, particularly in the areas of strength, fracture toughness, and oxidation. In regards to toughness and strength, it has been demonstrated that these two “antagonistic” properties can be improved together. Further, the surface and subsurface oxidation damage observed at high temperatures appears also be largely preventable. Although less is understood about improving the protective systems used for resistance to degradation in combustion environments, progress is being made. However, with the exception of room temperature strength and fracture toughness, these improvements continue to be researched in a fragmented manner, without a full regard to the needs of these materials in a gas turbine environment. For example, many of the compositions or processes used to demonstrate a combination of strength and toughness are not suitable for long-term use at elevated temperatures. This could be due to the incorporation of porosity, which will increase oxidation, or the use of additives that do not provide the refractory and oxidation resistance required.

The challenge of ceramic materials is often viewed as a dilemma, in that parameters that increase flaw tolerance and fracture toughness at room temperature are the same ones that promote degradation at elevated temperature. However, the demonstrations of simultaneous improvements in both strength and toughness should stimulate a new attitude and focus. A holistic or system approach to improved structural ceramic material development is required. The approach must consider all of the material requirements together: Improved room and elevated temperature strength, fracture toughness, phase stability, oxidation resistance (that influences creep) and resistance to environmental degradation. Unless these are achieved simultaneously, ceramics will always fall short of the demands of gas turbine engines. Further, the desired material characteristics must be cost competitive and achievable in complex shapes, with thick and thin cross sections.

It is recommended that efforts be directed towards developing ceramic materials in the U.S. based in principle on the Japanese Synergy Ceramics program to achieve simultaneous improvements in antagonistic properties, but the vision should be expanded to address all of the gas turbine material requirements. A suggested multiphase approach is offered:

Phase I: Fundamental Studies. The objective is to create U.S. expertise and capabilities in high strength/high toughness ceramics processing and materials property characterization to achieve the desired goals. These fundamental studies would best be performed at Universities, National or Private Laboratories, or at suppliers with a very strong research

desired set of properties and component geometries. orientation. Goals need to be defined for materials performance and properties. Even at the fundamental level attention will need to be paid to cost issues, recognizing that cost can be reduced through economies of scale as well as materials issues. Short term and long term plans are needed to take advantage of the understanding that is being developed on how composition and microstructure can be utilized to achieve these goals. The focus of such studies, at a minimum should include identifying and characterizing (1) the performance of EBC candidate oxides, silicates, or other materials, (2) optimizing the size and shape and quantity of the “beta-rice” seeds, (3) optimizing the intergranular film for debonding, and (4) tailoring of the additive composition plus the microstructure in order to obtain both high fracture toughness, high fracture strength and low oxidation reaction and permeability.

Phase II: Component Fabrication Development. Once promising basic process technologies have been established, efforts must be directed towards fabricating actual and simulated components. Technology transfer to ceramic suppliers will need to be an integral aspect of the work in this phase. Component performance and cost targets need to be defined.

Phase III: Component and Engine Testing. In the final phase of the development program full-scale components need to be tested in representative rigs and engines. Proof test conditions need to be selected that rigorously evaluate the component performance. Engine testing needs to be of sufficient duration to establish component durability under typical industrial gas turbine conditions. Engine testing must be conducted for 4,000 hrs or more. Work at this level would require supplier and OEM participation in collaboration with laboratories conducting materials property support work.

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