Fracture Toughness and Reliability in High-Temperature Structural Ceramics and Composites: Prospects and Challenges for the 21st Century

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Abstract

The importance of high fracture toughness and reliability in Si_3N_4, and SiC-based structural ceramics and ceramic matrix composites is reviewed. The potential of these ceramics and ceramic matrix composites for high temperature applications in defense and aerospace applications such as gas turbine engines, radomes, and other energy conversion hardware have been well recognized. Numerous investigations were pursued to improve fracture toughness and reliability by incorporating various reinforcements such as particulate-, whisker-, and continuous fiber into Si_3N_4 and SiC matrices. All toughening mechanisms, e.g. crack deflection, crack branching, crack bridging, etc., essentially redistribute stresses at the crack tip and increase the energy needed to propagate a crack through the composite material, thereby resulting in improved fracture toughness and reliability. Because of flaw insensitivity, continuous fiber reinforced ceramic composite (CFCC) was found to have the highest potential for higher operating temperature and longer service conditions. However, the ceramic fibers should display sufficient high temperature strength and creep resistance at service temperatures above 1000 °C. The greatest challenge to date is the development of high quality ceramic fibers with associate coatings able to maintain their high strength in oxidizing environment at high temperature. In the area of processing, critical issues are, preparation of optimum matrix precursors, precursor infiltration into fiber array, and matrix densification at a temperature, where grain crystallization and fiber degradation do not occur. A broad scope of effort is required for improved processing and properties with a better understanding of all candidate composite systems.

For the last two decades, significant progress has been made in improving fracture toughness and reliability in Si_3N_4- and SiC-based ceramics and composites for advanced propulsion systems, such as gas turbine engines where these materials are envisioned for the hot section components. However, these ceramics are brittle because of covalent and ionic bonding that is characteristic of this class of material. No or very little yield can occur as a result of strong bonding, which results in large stress concentrations to develop at a crack tip and cause the crack tip to propagate with little expended energy. This results in material with low fracture toughness (K_{IC}). For example, typical monolithic polycrystalline silicon nitride materials have fracture toughness in the range of 4–6 $MPa\sqrt{m}$[1], while silicon carbide (SiC) has fracture toughness in the range of 3–4 $MPa\sqrt{m}$. In contrast, metals have much greater toughness because plastic deformation occurs at the crack tip, which effectively blunts the crack and prevents large stress concentrations. Therefore, in order to improve the fracture toughness of these ceramics, numerous investigations were pursued around the world in the area of ceramic matrix composites (CMCs). The investigations include particulate-, nano-particulate-, whisker-, fiber reinforced-composites, including in-situ toughening. In most CMCs, the various mechanisms for toughening are crack deflection, microcracking, transformation toughening, crack branching, and crack bridging. All of these mechanisms essentially redistribute stress at the crack tip and increase the energy needed to propagate a crack through the composite material, thereby resulting in improved toughening. In general, particulate reinforced Si_3N_4 and SiC composites did not result in noticeable improvement in fracture toughness (K_{IC}). For example, typically the fracture toughness of SiC-particulate reinforced Si_3N_4 composites falls in the range of 3.5–5 $MPa\sqrt{m}$[1]. However, SiC-nano particulate reinforced Si_3N_4 composite higher K_{IC} values ranging between 5.3–7.0 $MPa\sqrt{m}$[2]. All composites were fabricated with varying amounts of yttria, or yttria/alumina as sintering aids. In the area of SiC-whisker reinforced Si_3N_4 composites, fracture toughness values ranging between 6–8 $MPa\sqrt{m}$ were routinely achieved[1]. The predominant toughening mechanisms in these particulate composites were crack deflection with intermittent crack branching, while in SiC-whiskers reinforced composites, whisker pullout was predominant. On the other hand, in-situ grown monolithic Si_3N_4 ceramics with yttria/alumina sintering additives, resulted in much improved fracture toughness values ranging from 8–11 $MPa\sqrt{m}$, due to the formation of elongated β-Si_3N_4 grains with high aspect ratios[3]. The toughening mechanisms in this engineered microstructure include a combination of crack deflection, bridging, and whisker-like grain pull out. (ref. 5).

However, despite this improved fracture toughness (K_{1C}) in Si-based ceramics, it was understood later, that flaws can develop at any stage during service condition and lifetime of a ceramic component, i.e. during processing, machining, or service, etc. (ref. 4). Therefore, production of flaw-free structural or engineering ceramics was seen as an impractical route for fabrication of high strength ceramics. Also, it was felt that the high initial strength is not a solution if the material is readily degraded as a result of service conditions. Further, eliminating flaws did marginal to enhance the reliability or toughness of the ceramic throughout the duration of its operational lifetime. Subsequently, the research focus expanded to develop continuous fiber reinforced ceramic matrix composites (CFCC) because of much greater flaw insensitivity and potential for delayed failure, as compared to particulate-, whisker-reinforced, chopped fibers, and in-situ grown composites. The advantages of continuous fiber reinforced ceramic composites (CFCC) are, improved toughness by crack deflection and crack bridging, and increased modulus and stress to strain in failure. Figure 1 shows the tensile stress-strain behavior considered desirable for a structurally reliable CFCC[4]. There are generally three regions in the stress-strain curve: (1) a region of linear stress-strain behavior before matrix cracking; (2) a nonlinear region after matrix cracking where multiple matrix cracking occurs without fiber fracture; and (3) a region of decreasing stress where fiber fracture and pullout occurring. Figure 2 shows a typical fracture pattern of a chemically vapor infiltrated (CVI) ceramic grade (CG)-Nicalon SiC_f/C/SiC composite material indicating gradual fiber fracture and fiber pull outs. For high-temperature applications requiring long term durability,

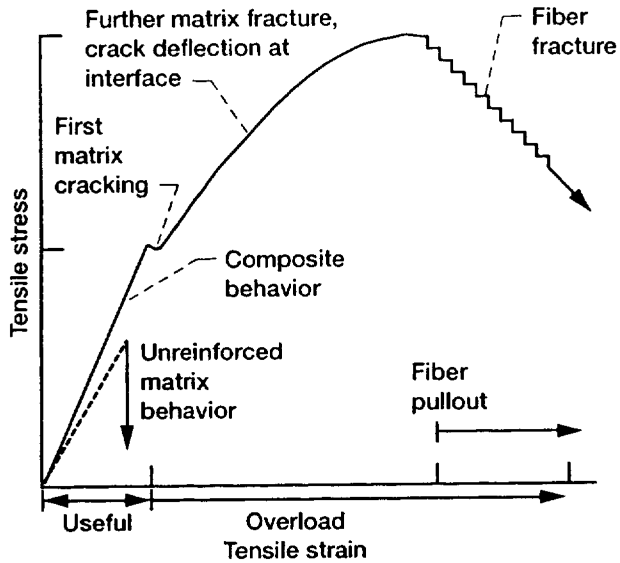

Figure 1.—Idealized stress-strain behavior of continuous fiber-reinforced ceramic matrix composites.

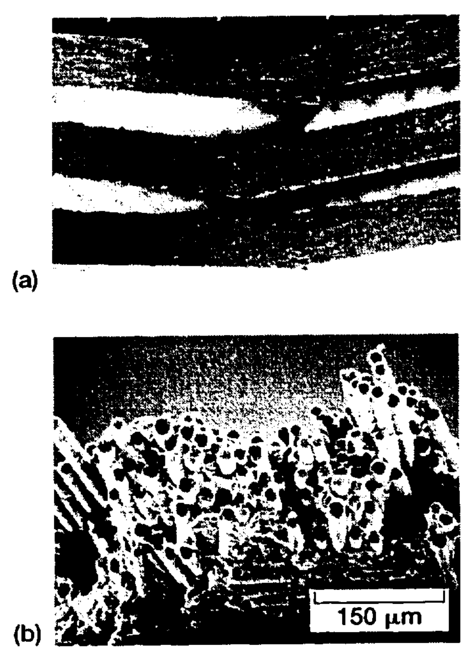

Figure 2.—Bend test fracture appearance of SiC reinforced SiC composite showing a) delayed fracture and b) fiber pull outs.

design below the point of first matrix cracking is preferable because it avoids degradation in composite stiffness, oxidation resistance, fatigue resistance, and thermal conductivity. Composite theories indicate that the matrix cracking point can be enhanced by increasing the fiber volume fraction in the composite and by selecting fibers with the smallest diameter, highest modulus, and greatest creep resistance at the service temperature. It is also very important that the fiber and matrix have nearly equivalent thermal expansion characteristics in order to avoid detrimental expansion-induced residual stresses within the CFCC. When these guidelines are followed, the matrix cracking point occurs at stress and strain levels that are generally higher and more reproducible than those for the unreinforced matrix itself. In addition, due to significantly higher fracture toughness (K_{IC}) and flaw insensitivity of the ceramic composite, the point of first matrix cracking degrades less with time than that for unreinforced matrix under the same service conditions[4]. Since CFCC will probably have their greatest challenge in long-term high temperature applications under oxidizing conditions, the ceramic fibers should be able to maintain high fracture strengths at high temperatures for long times, even when exposed to oxygen containing environments.

Thus the key to high temperature and commercially viable CFCC is the judicious selection and incorporation of continuous ceramic fibers which display the qualitative property needs summarized in table 1[4]. Two most critical fiber needs in table 1 are thermomechanical stability (strength retention and creep resistance) and oxidative stability at temperatures above 1000 °C. Although many commercial carbon and graphite fibers can satisfy most of the table 1 property needs, including thermomechanical stability, they are not considered for long term CFCC applications because of their rapid oxidation above 400 °C. Over the last two decades, this carbon oxidation problem has led to a strong focus on the development and production of continuous ceramic fibers with compositions based on SiC, Si_3N_4, and alumina compounds.

Table 1.—Key Property Needs for Continuous Fibers as Reinforcement for High Temperature CFCC.

Fiber Property Need	CFCC Benefit
• High Modulus	• Improves CFCC stiffness and reduces matrix stresses
• High As-Produced Strength	• Improves CFCC toughness and ultimate strength
• High Thermo-mechanical Stability	• Improves CFCC as-fabricated strength and CFCC strength retention and creep resistance during service
• High Oxidative Stability	• Improves CFCC service life in oxidizing environments
• Small Diameter	• Improves matrix strength and facilitates fabrication of thin and complex-shaped CFCC
• Low Density	• Improves CFCC specific properties for weight-sensitive applications and reduces stresses in CFCC rotating components
• Low Cost	• Reduces CFCC cost and improves CFCC commercial viability

Although significant progress has been made in producing current commercial high strength SiC fibers such as Nicalon, Hi-Nicalon, and Hi-Nicalon Type S, it is seen that due to process-related factors, these fibers cannot retain their as-produced strengths for composite fabrications conditions above 1200 °C (2192 °F) (fig. 3), or for composite service conditions above 800 °C (1472 °F) (fig. 4)[4]. Because these issues severely limit composite fabrication and use temperatures and thus their technical and commercial viability, fiber manufacturers are examining new and improved processing approaches, which attempt to eliminate or minimize the microstructural sources for fiber strength degradation. For example, the new CVD monofilament SiC fibers from Textron are being produced with slightly carbon-rich rather than silicon-rich compositions[5,6], the polymer-derived Hi-Nicalon SiC fibers are being processed to minimize the unstable and creep-prone oxygen-containing phases[7], and the sintered SiC fibers from Dow Corning and Carborundum and the chemically converted SiC fibers from MER Corporation are using processes which inherently eliminate second phases that enhance creep and creep related flaw growth. For short time exposures at high temperatures, these newer fibers are showing better strength retention

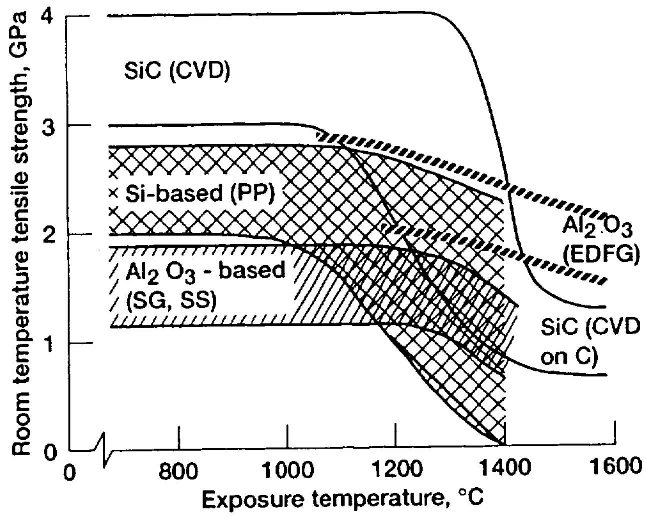

Figure 3.—Room temperature strength retention after short-time thermal exposure (1 to 10 hours) for commercial fibers based on silicon compounds and alumina.

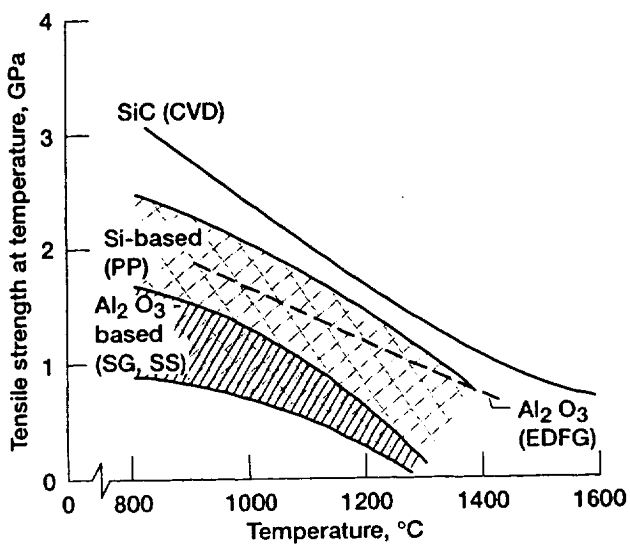

Figure 4.—Fast-fracture strength at room temperature for commercial fibers based on silicon compounds and alumina.

and better fast fracture strength than the commercial SiC fibers. The improved strength retention follows from the fact that many of these fibers employ maximum processing temperatures well above 1200 °C (2192 °F), some to 1800 °C (3272 °F) and above. Thus fiber strength degradation under zero stress conditions should no longer be a significant issue in limiting CFCC fabrication temperatures. However, the issue remains whether these new fibers under structural loading can also improve CFCC long-time service temperatures.

In light of the above CFCC material needs, it follows that the ceramic fibers for high payoff, high temperature applications should qualitatively display all of the table 1 property needs. In terms of quantitative goals, the biggest challenge is, that the fibers should display sufficient *high temperature strength* and *creep resistance* to yield CFCC with performance at least equivalent to the best superalloys, but at service temperatures above 1000 °C (1832 °F). Since mechanical performance for many applications is evaluated on specific basis, the fibers should also have a sufficiently *low density* to provide the CFCC with high toughness and the capability to be fabricated into complex shapes and thin sections. Finally, the fibers should have sufficiently *low cost* so as not to adversely affect the overall CFCC fabrication cost.

In the area of processing, critical issues are, preparation of optimum matrix precursors, uniform precursor infiltration into fiber array, and matrix densification to high final density. Slurry infiltration technique was successfully used in fabricating SiC-glass matrix composites, which are typically hot-pressed at temperatures near or above the softening point of the glass, such that densification readily occurs with viscous flow of the matrix[11]. On the other hand, the slurry infiltration and mixing technique has been less effective because of the need for higher processing temperatures necessary to densify Si_3N_4/SiC-based matrices. Also, fiber degradation and grain crystallization occur at higher processing temperatures including fiber-matrix chemical reactions. In addition, anisotropic behavior resulting from preferred orientations induced by uniaxial hot pressing is a crucial factor which should be considered. Polymer pyrolysis technique offers lower processing temperatures around 1400 °C (2552 °F), compared to 1800–2000 °C (3272–3632 °F) required for hot pressing/sintering. However, the key issues in polymer pyrolysis process are the choice of proper precursors, high shrinkage, low yield and microcracking at the matrix. Further, development is necessary in order improve the merits of the polymer pyrolysis technique to produce CFCC.

Chemical vapor deposition (CVD) and chemical vapor infiltration (CVI) techniques produce uniform coatings of tailored compositions, including multiple layers of different compositions. Currently CVI technique has demonstrated the greatest commercial success to form complex shapes CFCCs, including single continuous deposition step rather than multiple infiltration. However, a key issue is to achieve highly dense matrices. Surface reaction must remain rate controlling to progressively deposit a matrix to high density.

Concluding Remarks

The present paper described the importance of improved fracture toughness in producing high strength and reliable ceramics matrix composites for high-temperature structural applications in aerospace, military, and industrial applications. However, the greatest challenge to date is the development of high quality continuous ceramic fibers with associate coatings able to maintain their high strength in oxidizing environment at high temperature. Emphasis here has been placed on seven key properties (table 1), important for achieving structurally reliable CFCC at high temperatures. Application of CFCC is feasible and probably inevitable, although the exact time phasing is difficult to predict. However, the challenges to toughened-CFCCs will require broad scope of effort such as improved processing and properties composites, better understanding of all candidate composite systems, and further development of design/material interrelationship.

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