Structural Ceramics: A Question of Fabrication Reliability

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Structural ceramics based on silicon nitride, silicon carbide, and transformation-toughened zirconium oxide are potential candidates for advanced heat engines. Flaw populations, introduced during processing, currently limit their reliability. Processing steps responsible for common flaw populations will be discussed. It will be shown that new processing steps, based on colloidal powder treatments, combined with second phase engineering can increase fabrication reliability.

INTRODUCTION

Ceramic heat engines have been under study and testing for more than 20 years. Earnest work in the United States on advanced gas turbines initiated in the late 60's at Ford with the use of reaction-bonded silicon nitride (Si_3N_4) for critical components such as combustion chambers and stator vanes, and at Westinghouse in 1968 with hot-pressed Si_3N_4, first commercialized in the U.S. by Norton, for the testing of stator vanes in huge powder generating turbines. This U.S. work reinitiated programs in Britain, where both reaction-bonded and hot-pressed Si_3N_4 were invented, and initiated heat engines and structural ceramic programs in Germany, Japan, Sweden, France, Italy, China, and more than likely, the Soviet Union. In the late 70's, emphasis was shifted from gas turbines to adiabatic diesels with less stringent requirements (lower temperatures, lower stresses, fewer components, etc.) and greater apparent payoff.

The cyclic temperature operation of heat engines and the nonductile (nonstress relieving) behavior of ceramics over a wide temperature range requires that candidate ceramics be chosen to best minimize thermal stresses, *viz* ceramics with low thermal expansion, low elastic modulus, high strength and high thermal conductivity. The size of the component and surface heat exchange rates, which are dictated by component design and operation, also govern thermal stresses. Today, candidates which best meet these property requirements at temperatures $\geqslant 800$ °C are ceramics based on either silicon nitride (Si_3N_4) or silicon carbide (SiC). Since both require second phase additions to fabricate dense shapes from powders, both are polyphase, polycrystalline materials.

Properties, particularly those of Si_3N_4, depend on the choice of the densification aid which, combined with impurities, govern the chemistry and content of the second phases. The attributes of each material class (Si_3N_4 *vs* SiC) depends on the application. Si_3N_4 has a smaller thermal expansion coeffieient ($\alpha_{Si_3N_4} = 3 \times 10^{-6}/°C$ *vs* $\alpha_{SiC} = 4.2 \times 10^{-6}/°C$), a smaller elastic modulus ($E_{Si_3N_4} = 300$ GPa *vs* $E_{SiC} = 420$ GPa) which better minimize thermal stress for extreme conditions, and a higher potential for strength due to its larger fracture toughness [($K_{c(Si_3N_4)} = 4$ to 6 Mpa • $m^{1/2}$ *vs* $K_{c(SiC)} = 3$ to 4 MPa • $m^{1/2}$)]. SiC, on the other hand, has a much higher thermal conductivity which can better minimize thermal stresses for less severe conditions (smaller or thin-walled components and low surface heat exchange rate coefficients), and does not exhibit significant property degradation until much higher ($\geqslant 1500$ °C) temperatures relative to Si_3N_4 ($\geqslant 1250$ °C). For these reasons, critical gas turbine components (vanes, rotors, combustors, etc.) used for testing are manufactured from either Si_3N_4 or SiC. Low expanding, glass-ceramic compositions are used for lower temperature components (flow path containment, heat exchangers, etc.)

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The need for low thermal conducting materials for current adiabatic diesel engines is in direct conflict with candidate materials which best minimize thermal stresses. The thermal conductivity of current Si_3N_4 and SiC materials is equal or greater than that for case iron. Here, zirconium dioxide (ZrO_2), which is an exceptionally poor thermal conductor, is emerging as a prime candidate, despite the fact that its thermal expansion is ~3 times that of Si_3N_4, and therefore develops greater thermal stresses. The ZrO_2 materials under investigation take advantage of a relatively new phenomenon called transformation toughening that results in high fracture toughness (K_C = 6 to 12 MPa • $m^{1/2}$ at room temperature) and therefore high potential strengths.

Ceramic heat engine programs have produced many positive results. Design engineers, who have been forced to work with materials engineers due to the lack of formal education in brittle material design, have discovered new design concepts to minimize stress concentration within components and contact stresses between components which have led to failure. Full ceramic engines have run for short periods at temperatures where metal engines would not survive. Individual components have survived for extended periods. Material scientists have developed relations between fabrication, composition, microstructure and properties which have led to improved materials and less costly fabrication methods. Although improved designs and materials are still needed for commercial realization of ceramic heat engines, the current major problem resides with the unpredictable strength of the ceramic itself, leading to the unpredictable failure of similar components tested under similar conditions.

It is widely acknowledged that the unreliable structured behavior of ceramic components and specimens is due to the large variation of pre-existing flaw types and sizes. Strength (σ) is proportional to the material's fracture toughness (resistance to crack extension) as measured by the critical stress factor, K_c, and the size (c) of the largest pre-existing crack (or flaw):

$$\sigma \alpha \frac{K_c}{\sqrt{c}}.$$

Experimental and analytical methods based on Weibull statistics have been developed in an attempt to treat the 'unpredictable' strength of ceramics.[1] These methods involve an analysis of fracture data to obtain statistical parameters which characterize the material's failure probability. These statistical parameters are used to design components under known loads, and thus stress distributions to obtain exceptable survival probabilities. Unfortunately, inconsistent fabrication procedures result in large variations in the 'charactertistic' statistical parameters, *viz* parameters obtained from one batch of material may not characterize the next batch.

Overload proof testing procedures and analysis that incorporate time dependent strength phenomena have also been developed to insure component survival.[2] These tests are not only costly, but may not mimic operating stress distributions with sufficient accuracy to insure survival under real, operating conditions. Programs aimed to develop nondestructive evaluation methods to identify the small, strength limiting flaws in ceramics have not made sufficient progress to be used in the foreseeable future for either accepting or rejecting ceramic components.

The ceramics community recognizes that flaw populations in virgin ceramic components are in some way related to inhomogeneities introduced during fabrication. All ceramics are fabricated by sintering preformed powder shapes by inducing mass transport at high temperatures to eliminate void space. Flaw populations must be related to inhomogeneities introduced during the different steps in this process, *viz* powder manufacture, powder processing, powder consolidation to shape, sintering, and subsequent machining. The average size, size distribution, and types of inhomogeneity introduced during each fabrication step will determine the average strength and strength distribution. It can be concluded that the poor reliability of current ceramics is primarily due to the unpredictable distribution of inhomogeneities introduced during fabrication. Namely, the structural reliability of ceramics is a problem of fabrication reliability.

Identification of the fabrication steps producing strength degrading inhomogeneities and the changes in fabrication, and/or microstructure required to eliminate the inhomogeneities (or reduce their size) is critical to improving the structural reliability of ceramics. Such a program has been initiated at Rockwell's Science Center. Different flaw populations, observed at fracture origins, have been related to inhomogeneities introduced by different processing steps. New fabrication procedures have been identified which either eliminate or reduce the size of the inhomogeneities, and therefore their corresponding flaw populations. These new fabrication procedures not only lead to higher strengths, but also uncover the next flaw population to be tackled by innovative fabrication procedures.

The following sections will summarize five common flaw populations (crack-like voids produced by agglomerates, voids left by organic matter, inclusions, large grains, and surface cracks), how they are introduced during fabrication, and new fabrication methods of minimizing their effect on potential strength.

Crack-like Voids Produced by Agglomerates[3]

Agglomerates are common to all powder processing routes. They can be classified as either soft, *i.e.*, particles held together by Van der Walls forces which can be broken apart with surfactants, or hard, *i.e.*, partially sintered groups of particles which require attrition to dismember. All dry powders contain soft agglomerates. Hard agglomerates are common to powder manufacturing routes that involve heating to decompose an oxide precursor. Some processing routes (spray drying) purposely form large agglomerates to produce a flowable 'powder' for dry pressing.

It has been shown that agglomerates are retained when powders are consolidated to the desired shape prior to sintering. During sintering, the agglomerate can shrink differently from one another and/or their surrounding powder matrices. The differential shrinkage of the agglomerate relative to its surrounding matrix can produce a crack-like void. The crack-like void can either extend radially from the agglomerate for the case where the matrix undergoes a greater shrinkage, or extend circumferentially for the case where the agglomerate undergoes greater shrinkage. Figure 1 illustrates an example of a circumferential crack-like void produced by the greater phase, transformation-toughed Al_2O_3/ZrO_2 matrix.

The crack-like voids can be eliminated (or reduced in size) by two methods. First, the crack-like voids present in the near theoretically dense (>98 pct) bodies can be closed by hot gas isostatic pressing (HIPing). HIP treatment can significantly increase the strength of a Al_2O_3/ZrO_2 sintered body (500 MPa for sintered to 875 MPa for sintered and HIP'ed).

The second approach is more fundamental to processing science.[4] It involves dispersing the powder(s) in a liquid containing a surfactant which eliminates the soft agglomerates and consolidating the powder from the slurry state to form the desired engineering shape, which is dried and sintered. The colloidal route can also be used to obtain uniform dispersions of two or more phases. Hard agglomerates cannot be broken apart with surfactants. The colloidal route can still be used to eliminate hard agglomerates greater than a given size by sedimentation. Using the colloidal route, both single phase transformation-toughened (TT), tetragonal ZrO_2 (+2.2 m/o Y_2O_3), and two phase TT Al_2O_3 v/o ZrO_2 (+2.2 m/o Y_2O_3) have been sintered to $\geqslant 0.98\ \rho_t$ to result in a mean strength $\geqslant$1000 MPa (150,000 psi). Fracture origins in these stronger materials are no longer crack-like voids due to agglomerates, but voids produced by organic contaminants, such as lint.

Voids Produced by Organic Inclusions

Organic inclusions (lint, hair, etc.) are commonly found in powders; clean rooms are ineffective when powders are shipped from the manufacturer containing organic inclusions. Such inclusions pack with the powder during consolidation and leave irregular shaped voids when they burn out during sintering. These irregular shaped voids are found at fracture origins and are therefore a common flaw population. Figure 2 illustrates such an irregular void produced by a cellulose fiber which commonly leaves a residual skeletal ceramic backbond with the void.

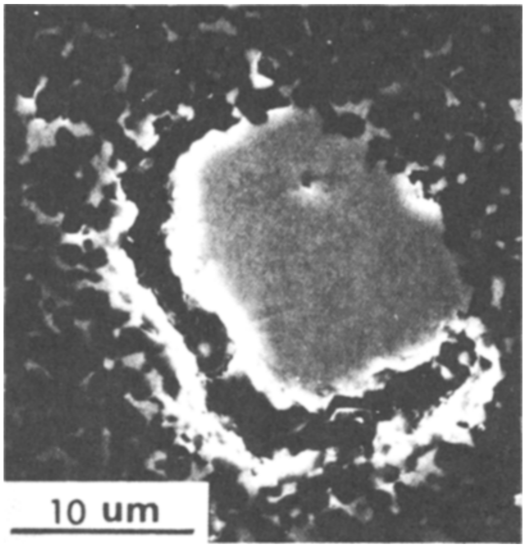

Fig. 1 — Circumferential crack-like void produced during sintering by a ZrO_2 hard agglomerate in a Al_2O_3/ZrO_2 composite.

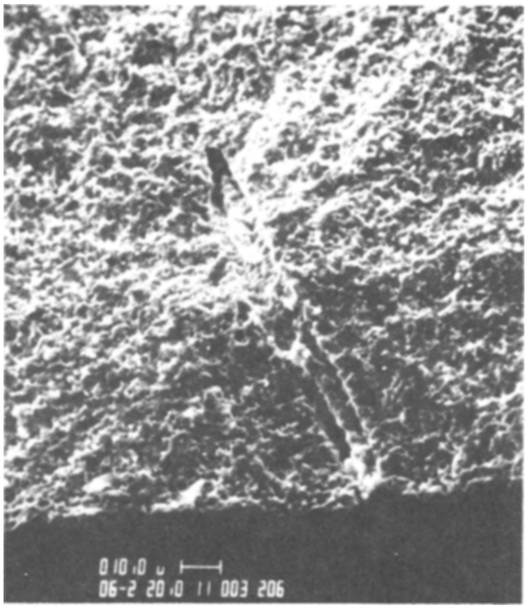

Fig. 2 — Long void located at a fracture origin in transformation-toughened Al_2O_3/ZrO_2 (30 v/o) produced by the burn-out of lint (organic matter).

One method for eliminating such voids is simply to burn out the organic matter at a low temperature, cool to room temperature, iso-press the powder compact, and then sinter. Iso-pressing after burn-out and before sintering can eliminate the void produced by the organic inclusions and further increase the average strength of transformation-toughened ZrO_2 from 1050 MPa (152,000 psi) to 1300 MPa (185,000 psi).

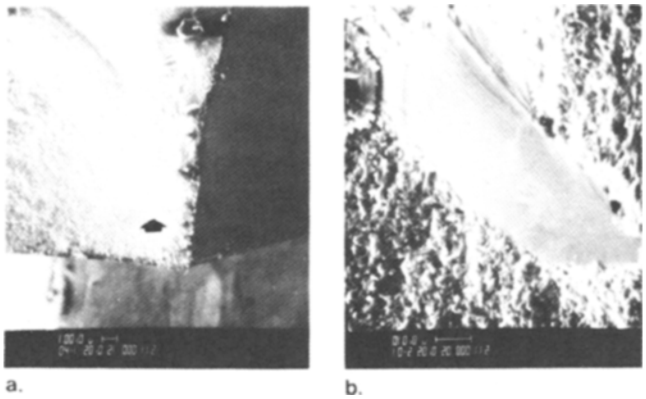

Fig. 3—Fracture surface of Si_3N_4 (Norton, NC132) showing fracture origin (*a*) and SiC inclusion (*b*) at fracture origin.

Inclusions[5]

Large second phase inclusions are commonly observed at fracture origins, as shown in Figure 3, for the case of a SiC inclusion in dense Si_3N_4. Such inclusions are usually contaminates introduced during powder manufacture and processing. Since the thermal expansion and/or elastic properties of the inclusion are different than the matrix phase, localized stresses develop within and around the inclusion during cooling from the fabrication temperature and/or during subsequent stressing. The distribution of these stresses is well known for simple inclusion shapes, *viz* spheres and ellipsoids. The largest tensile stress arises at the inclusion/matrix interface. For the case of differential thermal contraction, the magnitude of the largest tensile stress depends on the elastic properties of the two phases, the change in temperature, and which of the two phases contracts more during cooling.

When certain conditions are met, a small preexisting flaw at the inclusion/matrix interface can extend into a large microcrack, either during cooling or subsequent stressing. Similar to the agglomerate problem discussed above, the type of microcrack developed depends on whether the inclusion contracts more than the matrix (circumferential) or less than the matrix (radial). Although analyses of this problem have produced many subtle and interesting conclusions, the major conclusion is that the conditions for microcrack formation not only depend on the magnitude of the maximum tensile stress and the size of the preexisting flaw, but also on the size of the inclusion. That is, for a given maximum residual tensile stress (σ_r) microcracks will *not* form during cooling if the inclusion is less than a critical size, R_c^o.

Analyses concerning the effect of an added, applied tensile stress are more recent. Again, the principal conclusion is that the inclusion size also governs the formation of a microcrack under residual and applied tensile stresses. That is, if the inclusion is too small to produce a microcrack during cooling ($R < R_c^o$), then a microcrack can be produced at an applied stress (σ_a) dependent on the inclusion size:

$$R > R_c = R_c^o F\left(\frac{\sigma_a}{\sigma_r}\right)$$

where the function $F(\sigma_a/\sigma_r)$ is ≤ 1 and depends on the type of crack (*e.g.*, circumferential or radial).

These results are important to the fabricator who must guard against strength degrading inclusions. The results tell the fabricator that despite the possibility of large residual stresses, inclusions will not produce any strength degradation at a given applied stress if their size is $<R_c$. Here again, colloidal dispersion and sedimentation can be used to eliminate inclusions greater than a given size.

The above results are also important to those who want to design new materials for new properties by producing composites of two (or more) compatible phases (*e.g.*, to achieve a desired thermal expansion, etc.). That is, despite large differences in thermal and mechanical properties, two-phase composites can have mechanical integrity if the size of the second phase is less than a critical value.

Control of Grain Size

Bimodel and large grain size microstructures must be avoided to obtain high strengths. Large single grains within a fine grain matrix are common fracture origins. It is also well known that average strength is inversely proportional to the average grain size. Similar to the case of inclusions discussed above, localized stresses arise within and around grains due to thermal expansion and elastic anisotropy. The conditions for microcracking in single phase polycrystalline ceramics are similar to those of inclusions. That is, a critical grain size exists for spontaneous microcracking during cooling. Spontaneous microcracking occurs in single phase, polycrystalline Al_2O_3 with an average grain size ≥ 80 μm. For materials exhibiting a much greater thermal expansion anisotropy, *e.g.*, $MgTi_2O_5$[6] and Nb_2O_3,[7] the critical grain size is ≤ 5 μm. Similar to the inclusion case, an applied stress will reduce the critical grain size required for spontaneous microcracking. Control of grain growth is therefore required for mechanical integrity.

It is well known that control of grain growth can be achieved with the addition of a chemically compatible second phase. As discussed in the previous section, two phase composites can be designed to avoid microcracking. Figure 4 illustrates the strengthening that can be achieved for Al_2O_3 with additions of SiC with an average particle size of 4 μm.[8] Despite the large differential thermal expansion ($\alpha_{Al_2O_3} \simeq 8 \times 10^{-6}$/°C, $\alpha_{SiC} = 4.2 \times 10^{-6}$/°C, small additions (1 v/o to 8 v/o) of the 4 μm SiC can decrease the average grain size from ~30 μm to ~5 μm to increase the average strength by a factor of 1.6.

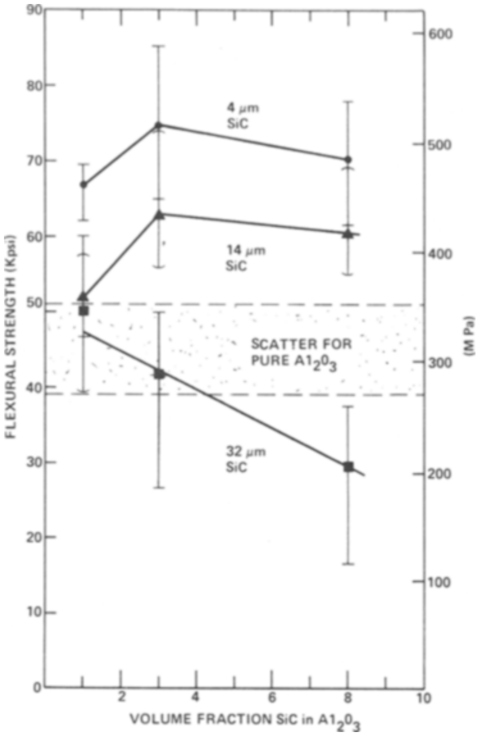

Fig. 4 — Flexural strength of Al_2O_3/SiC composites *vs* volume fraction and size of SiC particulates.

Recent results[9] indicate that the second phase is most effective when located at four-grain junctions *viz* it costs more energy to relocate the inclusion within a grain from a four-grain junction than a two-grain junction. Grain growth of the major phase will therefore be controlled by the number of four-grain junctions filled by the second phase. Thus the second phase size distribution, volume fraction and uniformity of distribution are critical parameters. Figure 5 illustrates the average Al_2O_3 grain size and the largest to average size ratio in various Al_2O_3/ZrO_2 composites as a function of temperature. At higher temperatures, grain growth control required ZrO_2 volume fractions $\geqslant 0.075$ for the given sizes distribution of starting powders. Note that 1 v/o ZrO_2 produces a much larger grain sizes relative to pure Al_2O_3. This result is caused by the nonuniformity of the ZrO_2 distribution, *i.e.*, some portions of the material contained a higher concentration of ZrO_2 than others.

It should be noted here that when colloid routes are employed to achieve a uniform phase distribution, the fabricator must guard against sedimentation. Figure 6 illustrates bottom and top regions of a slip cast$^{\beta}$-Al_2O_3/15 v/o ZrO_2 composite. The large ZrO_2 agglomerates and large β''-Al_2O_3 grains sedimented to the bottom. This problem can be avoided by pre-sedimentation as discussed above and/or by flocking the colloid prior to consolidation.

It can be concluded that the mechanical reliability of a ceramic can be increased by controlling grain growth with a dispersed second phase. This approach can be optimized with strict controls on phase distribution.

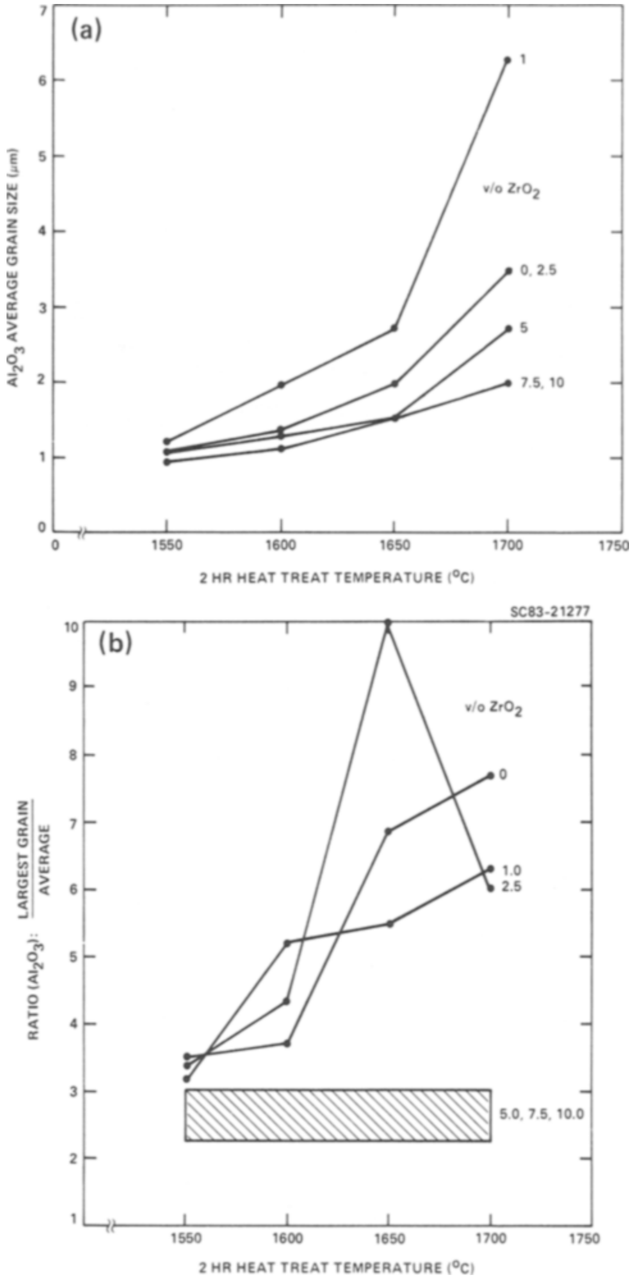

Fig. 5 — Al_2O_3 average grain size (*a*) and ratio of largest to average size (*b*) for a series of Al_2O_3/ZrO_2 composites *vs* heat treatment temperatures (2 hr).

Surface Cracks

Final shaping of ceramic components is performed by diamond grinding, a process that unavoidably introduces surface cracks. Rice *et al.*[10] have shown that two types of radial cracks exist within the groove made by the plowing abrasive grain: 1) closely spaced cracks that traverse the groove produced by slip-stick, and 2) longitudinal cracks which overlap one another along the length of the groove. The overlapping, longitudinal cracks produce the greatest strength degradation and result in a strength anisotropy when tensile strength is measured parallel and perpendicular to the grinding direction.

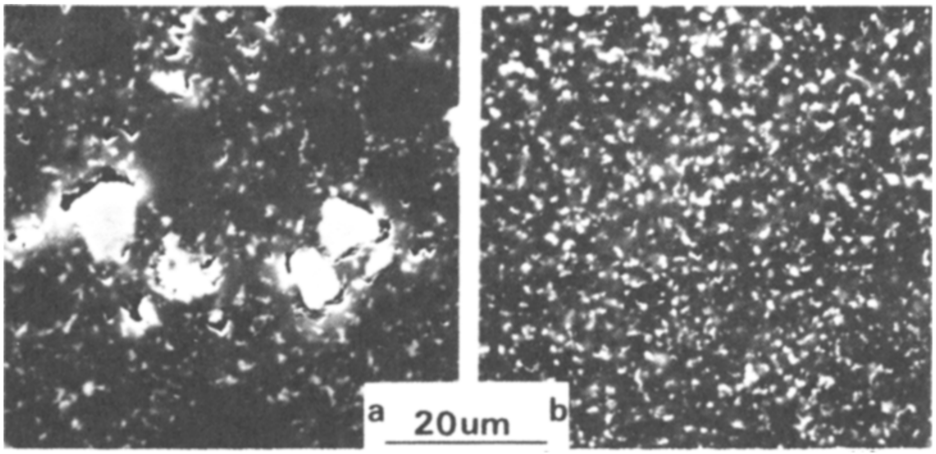

Fig. 6—Bottom (*a*) and top (*b*) regions of a slipcast β''-Al_2O_3/ZrO_2 composite powder compact after sintering. Note large single phase areas on bottom due to sedimentation (courtesy of D. J. Green).

It has been demonstrated that the effect of surface cracks on strength degradation can be minimized by the introduction of residual surface compressive stresses. The most effective means of introducing residual surface compressive stresses is by inducing a molar volume increase at the surface through either a stress induced phase transformation or a chemical reaction.

Abrasive machining or particle impact of transformation toughened ZrO_2 materials induces the tetragonal to monoclinic ZrO_2 transformation at the surface. The molar volume increase (~3 pct) that accompanies this transformation can produce compressive surface stresses as high as 1000 MPa (150,000 psi).[11] Contrary to other classes of ceramics, the strength of transformation toughened ceramics is significantly increased *after* abrasive grinding.

Molar volume increases can also be induced at the surface by a chemical reaction with the environment, *e.g.*, oxidation.[12] Here, a two-phase ceramic is engineered such that the second phase increases its volume through a surface reaction. As demonstrated, for the Si_3N_4/Zr-oxynitride system, the magnitude of the surface compressive stresses depends on the volume fraction of the second phase Zr-oxynitride, the molar volume increase produced by the Zr-oxynitride + $O_2 \rightarrow ZrO_2 + N_2$ reaction, and the depth of the reaction layer which is governed by oxidation kinetics (temperature and time). If the volume fraction of the Zr-oxynitride phase is >0.10, the compressive surface stresses can be too severe and will eventually produce surface spalling.

Concluding Remarks

It has been demonstrated that strength limiting flaw population, inherent to conventional ceramic fabrication procedures, can be eliminated or minimized using new fabrication methods and by engineering two phase materials. Voids produced by the differential shrinkage of agglomerates and/or organic inclusions can be eliminated by post-sintering HIP (hot gas iso-pressing) treatments, a process that the ceramic manufacturers are beginning to implement. A more cost effective approach is the use of colloidal methods for powder treatment and consolidation.

Colloidal methods (powder dispersion, sedimentation, and slurry consolidation) effectively reduce the size of agglomerates and inclusions. They also uniformly distribute second phases needed to control abnormal grain growth and/or to produce residual surface compressive stresses through environmental reactions. Effort to further develop these colloidal methods will certainly increase the fabrication and structural reliability of ceramics.

ACKNOWLEDGMENTS

Work at the Science Center uncovering processing related flaws in ceramics is supported by the Air Force Office or Scientific Research under Contract No. F49620-81-C-0036.

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