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Slow crack growth in Si_3N_4 at room temperature

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Tests of Si_3N_4 hot pressed with various types and levels of oxide additives show evidence of room temperature slow crack growth in delayed failure tests (using natural flaws), but not in fracture mechanics (e.g. DCB or DT) tests consistent with more limited literature data for these two types of tests. Neither type of test showed slow crack growth in either CVD Si_3N_4 or RSSN. Further the fracture mode in the latter two materials was essentially all transgranular, while it was predominantly (e.g. 80%) intergranular in the hot-pressed materials. It was thus postulated that (1) the oxide grain boundary phase is responsible for slow crack growth and; (2) varying distribution of the oxide boundary phase and grain boundary character result in sufficient boundaries not susceptible to slow crack growth to pin cracks with macroscopic crack lengths (i.e. as in DCB and DT tests). Both the much smaller crack front lengths and the large number of small (natural, e.g. machining) flaws allows some of these small flaws to grow to critical size, thus leading to delayed failure in the hot-pressed materials.

1. Introduction

Understanding the microstructural dependence of slow crack growth in Si_3N_4 is essential from both an applied and a scientific standpoint. Determining the parameters which affect slow crack growth in Si_3N_4 is necessary from an applied standpoint for predicting the safe life in a wide variety of applications [1]. On the other hand, the issue of whether or not Si_3N_4 intrinsically exhibits slow crack growth or whether slow crack growth in this material is determined by oxide phases normally associated with the densification of the material is important from the standpoint of understanding the basic mechanisms of stress corrosion in ceramics. While static [2, 3] and cyclic [3] fatigue has been demonstrated only in limited studies of some Si_3N_4, slow crack growth (K–V) data via fracture mechanics, e.g. DCB tests is even more limited and erratic [4, 5]. The former, e.g. delayed failure, tests indicate slow crack growth while the latter fracture mechanics tests question it. Further, studies have been limited to Si_3N_4 with only one additive composition for each study, and limited comparison has been made with reaction sintered Si_3N_4 (RSSN), and apparently none with chemical vapour deposited (CVD) Si_3N_4. This paper reports both delayed failure and fracture mechanics K–V studies at room temperature in Si_3N_4 hot pressed with various amounts and types of additives as well as in Si_3N_4 without additives, such as RSSN and CVD Si_3N_4.

2. Experimental procedure

The materials used in this study, a subset of those in a previous study [6], are listed in Table I along with an outline of their characterization. Depending on material availability, specimens for double torsion (DT) tests were machined in the form of plates approximately $75 \times 25 \times 2$ mm^3. A 1 mm deep center grove was machined into each specimen along its length to guide the crack propagation direction. The DT test was emphasized because it has a long test zone, high deflection to crack-growth-rate ratio allowing investigation of a lower crack velocity for a given strain rate, and requires no arm bonding or clamping [7]. For the CVD material, applied moment double cantilever beam (AMDCB) specimens approximately $26 \times 6 \times 3$ mm^3 with a 1.5 mm centered groove located down the length [8], were used due to material quantity limitations. All CVD specimens were machined such that the plane of the specimen was perpendicular to the direction of deposition. Similarly, most hot-pressed specimens were machined such that the plane of the specimen was perpendicular to the hot pressing direction. Remnants of AMDCB and DT tested specimens were used to machine flexural test bars approximately $25 \times 1.5 \times 1.5$ mm^3. The tensile edges of all bars were rounded. They were subsequently tested for strength and delayed failure using four-point bending with spans of 7.4 mm (minor) and 22.5 mm (major). All delayed failure specimens were first tested at one standard deviation below the mean fast fracture failure stress. Beyond this, further tests at other stresses were conducted within the limits of material availability. Specimen fractures were examined in the scanning electron microscope (SEM) to identify fracture origins [9, 10] and details of the fracture mode.

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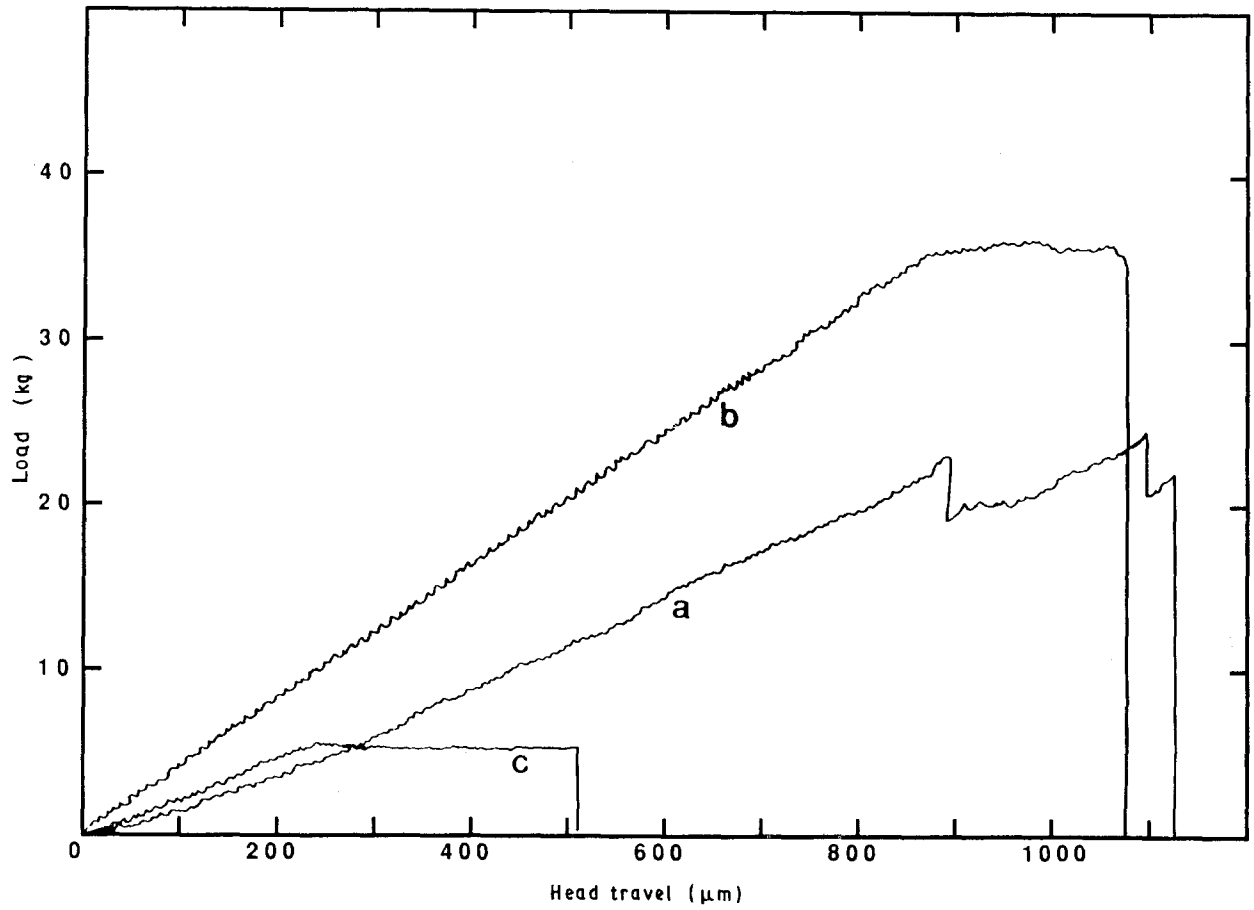

Figure 1 Plot of load against time for DT specimens loaded at a constant rate of 0.63 μm s^{-1} showing (a) NC 132 Si_3N_4, (b) AD 99 alumina and (c) soda-lime glass.

TABLE I Elastic properties of hot-pressed silicon nitride materials

Additives (wt %)	Density (g cm^{-3})	Young's modulus (GPa)	Poisson's ratio	Source
~1 MgO	3.224	318	0.273	Norton Co.
5 MgO	3.175	304	0.273	Ceradyne
5 Y_2O_3	3.258	312	0.285	Ceradyne
10 Y_2O_3	3.305	305	0.283	Ceradyne
15 Y_2O_3	3.165	302	0.270	Ceradyne

3. Results

None of the materials in this study exhibited continuous crack growth normally associated with slow crack growth processes in AMDCB and DT tests (Fig. 1). In the AMDCB tests (i.e. of CVD material) a crack would be observed to jump occasionally ahead erratically once to a few times before catastrophic failure. In other cases, specimens failed catastrophically without any evidence of preceding crack motion. The DT test (used to investigate lower velocities) exhibited similar erratic behaviour in hot-pressed Si_3N_4 and RSSN as described for the AMDCB tests of CVD Si_3N_4.

Results of the delayed failure test are given in Table II, where the materials are listed in the overall order of increasing slow crack growth susceptibility. The CVD specimens showed no delayed failure, and only limited, erratic delayed failure was observed in RSSN. All other materials clearly exhibited delayed failure. While there was some trend for greater delayed failure with increased additive level of a given oxide, the 5% Y_2O_3 samples violated this. Minimum delayed failure times were observed for the β-Si_3N_4 + 5% MgO even at three standard deviations below the mean fast fracture strength, which is in contrast to equivalent times at only 1.5 standard deviations below the mean fast fracture strength of α-Si_3N_4 + 5% MgO.

Figure 2 Fracture surface of CVD Si_3N_4 four-point bend test showing transgranular failure.

TABLE II Delayed failure times[a, b] of groups of Si_3N_4 specimens with various stress levels

σ_{1c}-0.5 σ^c	σ_{1c}-1 σ^c	σ_{1c}-1.5 σ^c	σ_{1c}-2 σ^c	σ_{1c}-2.5 σ^c	σ_{1c}-3σ^c
Chemical vapour deposited silicon nitride (19.7, 5.4)[d]					
	0.00[a]				
	0.00				
	> 139.00[b]				
	> 139.00				
	> 139.00				
NC 350 reaction bonded silicon nitride (38.7, 6.6)[d]					
0.00	0.00				
0.00	0.40				
0.05	14.10				
0.05	> 145.10				
0.40	> 145.10				
2.20	> 145.20				
> 42.80	> 145.20				
SIN-VH6-192 NRL silicon nitride (33.5, 4.1)[d]					
0.05	0.00	> 138.80			
16.70	0.05	> 138.90			
> 113.50	0.05	> 138.90			
> 113.50	> 139.20	> 138.90			
> 113.60	> 139.20	> 138.90			
> 113.60	> 139.30	> 138.90			
> 113.70	> 139.40	> 138.90			
Silicon nitride + 10% yttria (129.0, 22.7)[d]					
0.00	0.10	68.40			
0.05	0.20	> 144.80			
0.05	4.00	> 144.80			
0.10	47.60	> 144.80			
0.20	> 165.10	> 144.90			
0.30	> 165.20	> 144.90			
0.60	> 165.20	> 144.90			
NC 132 silicon nitride (111.6, 10.5)[d]					
	0.00	0.00	0.15		
	0.05	0.05	1.50		
	0.05	0.15	> 141.70		
	0.05	6.80	> 141.70		
	0.05	46.40	> 141.70		
	0.05	70.40	> 141.80		
	8.95	106.90	> 141.90		
α-Silicon nitride + 5% yttria (116.6, 15.3)[d]					
	0.00	0.00	0.05	0.00	
	0.05	0.05	0.50	2.40	
	0.05	0.05	2.10	4.40	
	0.05	0.05	2.80	> 140.90	
	0.05	0.10	5.30	> 140.90	
	0.05	0.20	36.90	> 140.00	
	0.05	1.90	> 115.60	> 140.00	
Silicon nitride + 5% yttria (123.0, 10.9)[d]					
	0.00	0.10	0.00	0.00	
	0.00	0.10	0.05	1.80	
	0.10	0.50	0.60	8.60	
	0.30	1.00	50.30	36.40	
	0.30	3.10	61.30	> 122.10	
	0.70	> 115.40	> 101.60	> 122.20	
	1.60	> 142.20	> 113.80	> 265.50	
α-Silicon nitride + 5% magnesia (104.3, 3.6)[d]					
	0.00	0.00			
	0.00	0.00			
	0.00	0.00			
	0.00	0.00			
	0.00	0.00			
	0.00	0.00			
	0.00	0.05			
β-Silicon nitride + 5% magnesia (76.6, 4.4)[d]					
	0.00	0.00	0.00	0.00	0.00
	0.00	0.00	0.00	0.00	0.00
	0.00	0.00	0.00	0.00	0.05
	0.00	0.00	0.05	0.00	0.05
	0.00	0.00	0.05	0.00	0.05
	0.00	0.00	0.05	0.05	0.05
	> 0.00	0.00	0.05	0.05	0.10

[a] Time in unit of hours.
[b] > indicates run-out, i.e. specimens did not fail.
[c] Specimens loaded under stress relative to fast fracture strength σ_{1c}; σ. denotes standard deviation, see also note d below.
[d] Numbers in parenthesis are fast fracture strength σ_{1c}, and standard deviation, σ, in ksi.

SEM examination showed the CVD Si_3N_4 to have exclusively transgranular fracture (Fig. 2) and have relatively large grain size (> 10 μm). The fracture of the RSSN material was also predominantly transgranular (Fig. 3) even though its grain size is much finer (~ 0.2 μm). All other materials exhibit predominantly intergranular fracture regardless of grain size. As an example, for β-Si_3N_4 with 5% MgO, Fig. 4, the fracture surface showed about 80% intergranular fracture while the uniformity of the microstructure varied greatly from places with fair consistency of grain size (Fig. 4a), to places with grain structure overwhelmed by boundary phase rich in silicon and deficit in nitrogen (Fig. 4d). Fracture origins could generally be determined, and were found typically to be at the surface, Fig. 5. Examination of the fracture mode relative to the fracture origin showed no trend of fracture process with distance from the origin.

4. Discussion

As mentioned above, none of the materials in this study showed continuous macroscopic crack growth,

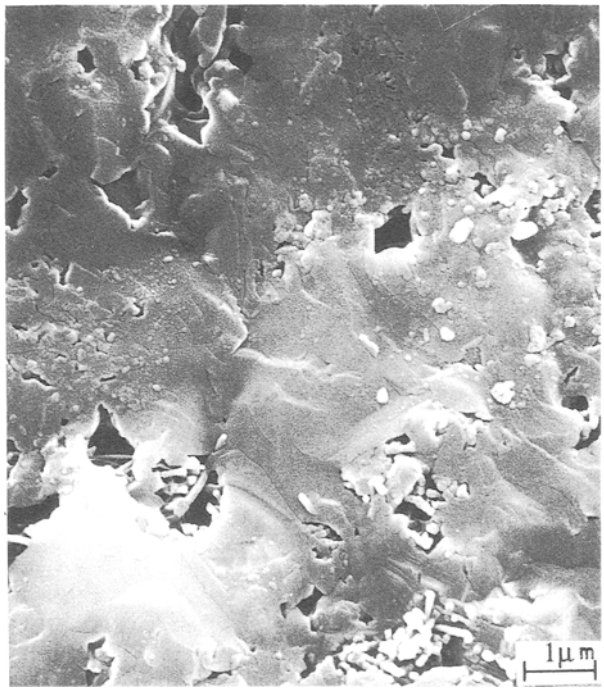

Figure 3 Fracture surface of RSSN four-point bend test showing predominantly transgranular failure.

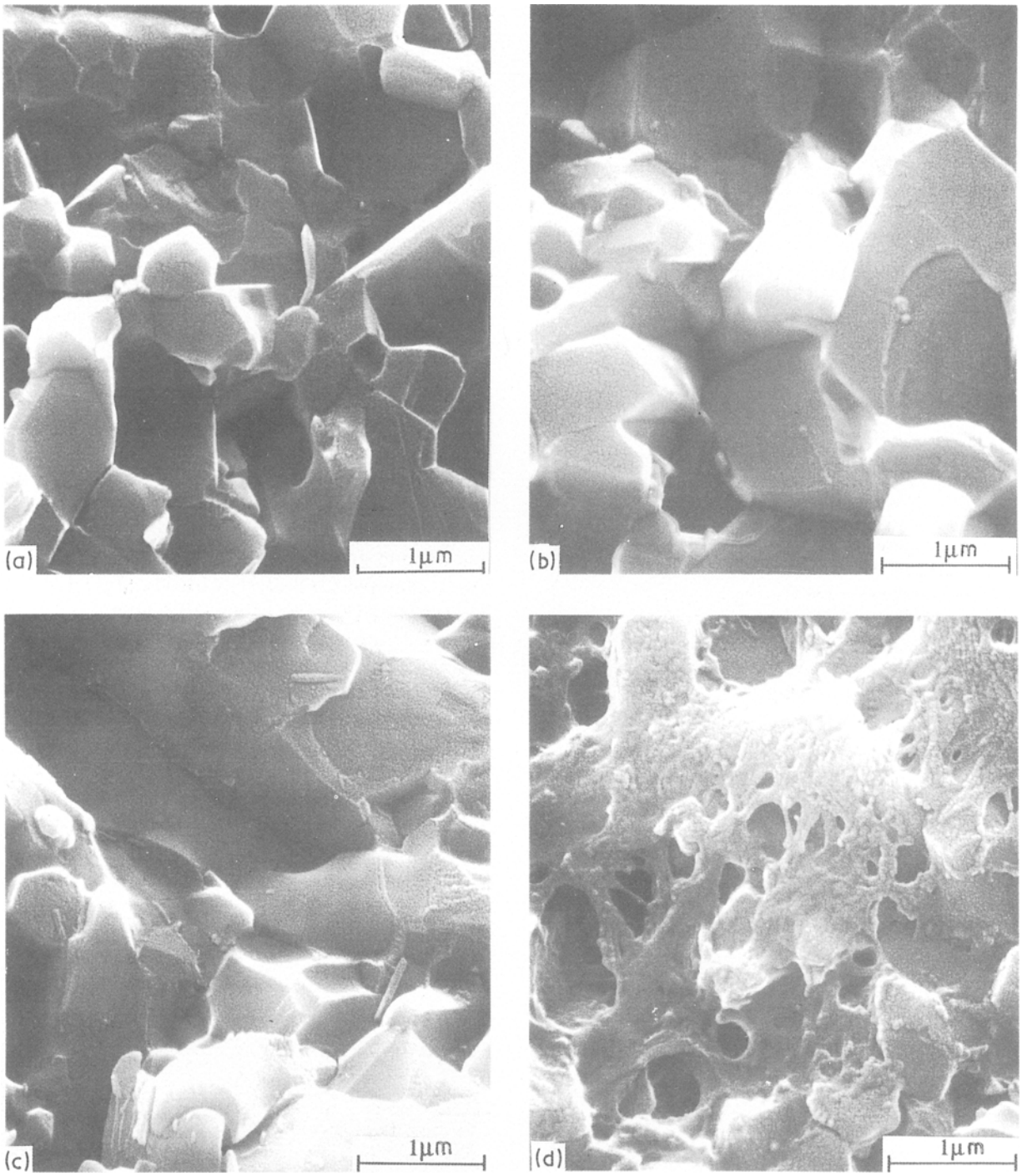

Figure 4 Fracture surface of ~1 μm grain size β-Si_3N_4 + 5% MgO four-point bend test showing ~80% intergranular failure. Note the inhomogeneity of both grain size and grain boundary phase increases from (a) to (d).

i.e. growth along a crack front having one macroscopic dimension (the specimen web thickness). In other words the loading curves exhibited erratic behaviour as opposed to leveling off and staying constant as is usual for materials subject to stress corrosion such as alumina or glass, Fig. 1. The results of the present study showing delayed failure in hot-pressed Si_3N_4 are, however, consistent with other studies of such failure in Si_3N_4 made with oxide additions [2–5]. The lack of any stable macroscopic slow crack growth (i.e. DT tests) in these hot-pressed and RSSN specimens is also consistent with results from other studies [4, 5]. While less delayed failure and less evidence of slow crack growth were seen in RSSN in this study than in other studies [2, 4, 5], the overall trend of limited delayed failure and no stable, reproducible macroscopic slow crack growth are self consistent. This work shows there is (1) no delayed failure or slow crack growth and exclusive transgranular failure in CVD Si_3N_4, and (2) predominantly transgranular fracture in RSSN in contrast to predominantly intergranular fracture found in hot-pressed Si_3N_4.

It is suggested here that the delayed failure–slow crack growth behaviour of various Si_3N_4 specimens can be attributed to oxide grain boundary phases as follows. Both the absence of oxide additions in CVD and RSSN and their failure by exclusively or predominantly transgranular fracture in contrast to clear delayed failure and predominantly intergranular failure in hot-pressed Si_3N_4 clearly point toward oxide

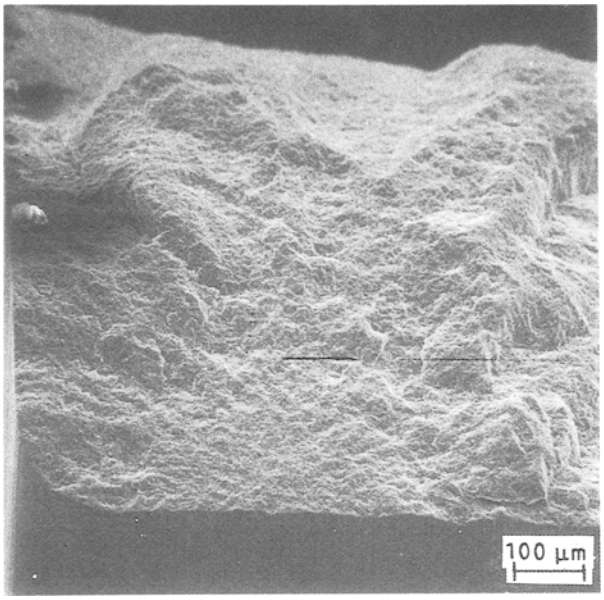

Figure 5 Lower magnification of Fig. 4 showing fracture origin.

grain boundary phases as the cause of these phenomena, as also suggested by other investigators [2–5]. The issue of intergranular as opposed to transgranular failure correlates respectively not only with the presence or absence of slow crack growth, but also with recent observations on such failure modes without the presence of non-oxides or grain boundary additives; thus, slow crack growth has been shown to preferentially follow intergranular routes in both oxides and non-oxides in materials otherwise showing extensive or exclusive transgranular failure whether or not additive grain boundary phases are present [9–11]. Variations in the resultant amount, character, and distribution of the oxide phase are seen as major factors in the variation of crack growth behaviour. Loss of oxide additions, and more commonly varying reaction of these with oxide (and other) impurities as well as the Si_3N_4 (to form oxynitrides) [12], are thus probable reasons why a clearer trend is not seen with the level or type of oxide addition. Variable amounts of limited oxygen contamination are seen as the major factors for erratic RSSN results. This is consistent with Gulden and Metcalfe [2] attributing greater delayed failure in as-sintered as opposed to machined RSSN to greater oxygen content in the surface of the former.

It is further suggested that the difference in delayed failure from the AMDCB and DT behaviour can be explained based upon the oxide grain boundary phases being responsible for slow crack growth processes. The occurrence or rate of slow crack growth along any given grain boundary should depend on the amount of oxide along that boundary as well as possibly on the boundary structure (which also in turn may be affected by the amount and type of oxide layer there). It is thus reasonable to assume that some boundaries may be more resistant to, or not even allow, slow crack growth. They would clearly inhibit the propagation and possibly prevent the propagation of large cracks as used in the AMDCB and DT tests because the macroscopic scale of these crack fronts forces them to interact with a broad cross-section of the microstructure. On the other hand, in delayed failure tests, failure occurs due to slow crack growth of small cracks (e.g., in the range of 10 to 30 μm in depth) typically leading to one of many cracks growing to failure-causing size. Such small cracks need only change their size a few fold in order for failure to occur. There is, therefore, a good statistical chance, even with the significant number of boundaries that impede or are immune to slow crack growth, that such growth could occur for some cracks because of the variation in grain boundary paths along which any crack can grow, i.e., every time a crack hits a triple point it has a choice of two grain boundaries or grains along which it can proceed (e.g., Fig. 4). Further, it should be noted that slow crack growth around a few isolated boundaries immune to such growth is likely to provide a sufficiently high stress intensity on those individual boundaries or grains for them to be fractured due to the surrounding slow crack growth (e.g., Fig. 4). This would explain the erratic crack propagation seen in DT tests of hot-pressed material as well as the presence of limited amounts of transgranular fracture in hot-pressed Si_3N_4. Cracks could well reach a limit of slow crack growth when a sufficient number of pinning grain boundaries are encountered. This would also explain the fatigue limit indicated by Kawakubo and Komeya [3] since they used indent induced instead of natural (i.e. larger starting) flaws which could thus more rapidly reach the suggested limitation on growth than would (smaller) natural flaws.

Clearly, substantially more work is needed to verify the above hypothesis and in general to understand the micostructural dependence of these slow crack growth processes. The distinction between the macroscopic scale fracture mechanics, i.e., AMDCB and DT, tests and the delayed failure tests, however, clearly suggests a crack scale phenomena as proposed above. These observations as well as the above hypothesis have significant implications for applications of this material, i.e., they indicate that slow crack growth in Si_3N_4 may reach a fatigue limit, with this limit presumably having some dependence on the amount, type, and presumably homogeneity of the grain boundary phase and the grain size. They also have important implications for other materials, e.g. AlN with oxide additives, and SiC with oxide (e.g. Al_2O_3) as opposed to non-oxide (e.g. B_4C) additives.

5. Summary and conclusions

While hot-pressed Si_3N_4 shows clear evidence of slow crack growth in delayed failure tests, it shows little or no macroscopic slow crack growth in fracture mechanics, i.e., DCB or DT, tests. In contrast to this, CVD Si_3N_4 shows no, and RSSN shows limited, evidence of slow crack growth in either of these tests. These results, along with the observation of respectively exclusively or predominantly transgranular fracture in CVD Si_3N_4 and RSSN as opposed to predominantly intergranular failure in hot-pressed specimens show that the grain boundary phase in hot-pressed material is responsible for slow crack growth in hot-pressed

Si_3N_4. The differences between macroscopic slow crack growth (via DT or DCB) and microscopic growth via delayed failure tests is hypothesized to be due to some boundaries being sufficiently resistant or immune to slow crack growth (e.g. due to sufficiently limited oxide content) resulting in pinning of the crack when there is a sufficient number of such boundaries along a crack front. The distribution of such pinning boundaries could well be such that some typical strength-controlling flaws can grow sufficiently in size to cause failure in delayed tests while much larger crack fronts in DCB and DT tests typically intersect too many such pinning boundaries for general slow crack growth to occur.

Acknowledgements

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