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Controlled surface-flaw-initiated fracture in reaction-bonded Si_3N_4

R. R. WILLS, M. G. MENDIRATTA
Systems Research Laboratories, Inc, 2800 Indian Ripple Road, Dayton, Ohio, USA
J. J. PETROVIC*
Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio, USA

Reproducible controlled surface flaws were introduced in reaction-bonded Si_3N_4 by Knoop microhardness indentation. Fracture was initiated at a single suitably oriented flaw on the tensile surface of a four-point bend specimen, and the stress required to propagate the controlled flaw catastrophically was used to calculate the critical stress intensity factor K_{IC} from standard fracture-mechanics formulae for semi-elliptical surface flaws in bending. K_{IC} was unchanged up to 1200° C, but values above this temperature together with those at room temperature after vacuum annealing were reduced approximately 25%. This reduction is thought to be due to reaction with oxygen concentrations present in the vacuum "atmosphere" rather than to a change in material properties. Although flaw "healing" was observed for annealing in air, it was accompanied by a decrease in fracture stress. It is suggested that this is due to volume mismatch between Si_3N_4 and the oxidation product, cristobalite, which introduces tensile stresses in the matrix material.

1. Introduction

Recently, a fracture-mechanics technique has been developed which employs a small semi-elliptical surface flaw produced by a Knoop micro-hardness indentation [1]. A single flaw introduced into the tensile surface of a conventional four-point bend specimen initiates fracture because it is the worst flaw in the specimen. The critical stress intensity factor K_{IC} can then be calculated from a knowledge of the flaw dimensions and fracture stress using fracture-mechanics analyses for semi-elliptical surface flaws in bending.

This technique has been applied previously in order to obtain both room and high-temperature K_{IC} values for hot-pressed Si_3N_4 [1] and hot-pressed SiC [2]. In the present investigation this technique has been extended to analyse the fracture behaviour of a fine-grained, porous ceramic – reaction-bonded Si_3N_4 (NC-350 grade, Norton Co, Worcester, Mass). Since Washburn and Baumgartner [3] have reported that the light-grey surface layer on this material in the as-fired condition affects its properties, this layer was removed on the tensile face of each specimen prior to the introduction of the flaw. The current investigation thus represents an evaluation of the matrix material itself.

2. Experimental procedure

The NC-350 reaction-bonded Si_3N_4 (density $2.52\,g\,cm^{-3}$) was obtained in the form of rectangular bars 5.080 cm x 0.6350 cm x 0.3175 cm. The grey as-fired surface layer on one side of each test bar was removed by diamond grinding, and the ground surface was then polished to a 600-grit finish. A single 2600 g Knoop microhardness indentation was placed in the centre of the tensile surface with a microhardness tester (Wilson Instrument Division of ACCO, Bridgeport, Conn). The long diagonal of the identation was aligned perpendicular to the tensile-stress direction. Bars were fractured in four-point bending at a cross-head speed of $5.08 \times 10^{-3}\,cm\,min^{-1}$ with the bend test-fixture described in [1]. High-temperature

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[*] Present address: University of California, Los Alamos Scientific Laboratories, Los Alamos, New Mexico 87545, USA.

tests were conducted in vacuum (1.3 to 6.5 x 10^{-7} atm) using a Brew furnace (Richard D. Brew Co, Concord, NH) mounted on an Instron testing machine (Instron Corp, Canton, MA). The high-temperature tests were carried out after each specimen had been at the test temperature for 5 min. The dimensions of the flaw were obtained from the fracture surface of specimens by light microscopy.

3. Calculation of the critical stress intensity factor K_{IC}

A flaw will grow catastrophically when the stress intensity K_I reaches a critical value K_{IC}. For a surface flaw in bending, K_I is given by [4]

$$K_I = \sigma M(\pi a/Q)^{1/2} \qquad (1)$$

where σ is the maximum outer-fibre tensile stress, a is the flaw depth, and M and Q are numerical factors related to flaw and specimen geometry. M is calculated from the ratio of flaw depth to specimen thickness [5] and

$$Q = \Phi^2 - 0.212\,(\sigma/\sigma_{ys})^2, \qquad (2)$$

where σ_{ys} is the tensile yield stress and $0.212\,(\sigma/\sigma_{ys})^2$ is a plastic-zone correction factor. This factor is considered to be insignificant in the present investigation, and thus $Q = \Phi^2$ where

$$\Phi = \int_0^{\pi/2} [\sin^2\phi + (a/c)^2\cos^2\phi]^{1/2} d\phi \qquad (3)$$

where $2c$ is the flaw length. This integral is tabulated in standard mathematical tables.

4. Results and Discussion

4.1. Flaw dimensions and room-temperature fracture stress

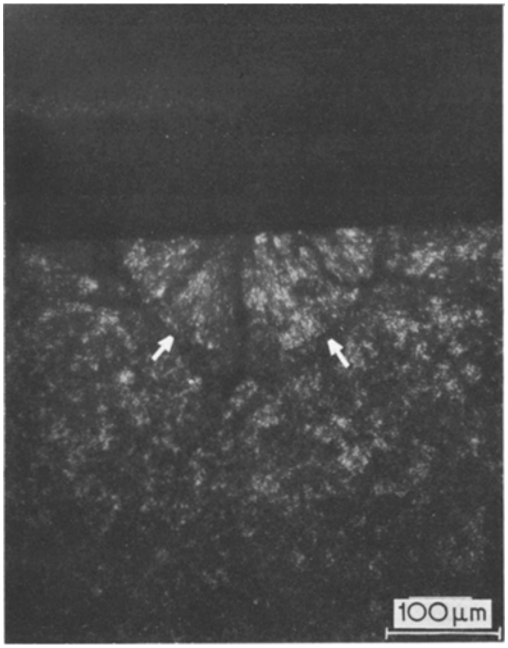

Figure 1 Profile of 2600 g Knoop flaw in NC-350 Si_3N_4.

TABLE I Flaw dimensions

$2c$ (length at surface) (mm)	Coefficient of variation	a (depth) (mm)	Coefficient of variation
0.252	2.47%	0.127	6.6%

TABLE II Room temperature fracture stresses

	Fracture stress ($MN\,m^{-2}$)	Coefficient of variation
As-received	252.4	13.26%
With surface layer removed	235.8	9.1%
Flawed	89.1	4.4%

The profile of a 2600 g Knoop flaw on the fracture surface of a bend specimen is shown in Fig. 1. The flaw is semicircular in shape and has the dimensions given in Table I. In general, the flaws in the NC-350 were more difficult to observe than those in the hot-pressed Si_3N_4 [1]. The results of room-temperature fracture strengths for the as-received and indented specimens are shown in Table II. Considerable scatter in room-temperature strengths was observed for the as-recieved specimens as well as for specimens with the surface layer removed. However, upon introduction of a controlled surface flaw, an appreciable decrease in scatter was observed. This attainment of better reproducibility in fracture-length values makes this technique particularly advantageous in the study of the effects of fabrication procedure and environment on the strength of structural ceramics [1, 2, 6].

4.2. Variation of K_{IC} with temperature and effect of residual stress

The effect of temperature and residual stress on K_{IC} is shown in Fig. 2. The lower values labeled K_{IN} refer to the residual-stress effect which will be discussed later in this section. K_{IC} (average value 1.87 $MN\,m^{-3/2}$ at room temperature) was unchanged at 1200° C but at 1400 and 1500° C was approximately 20% lower. K_{IC} values found by this technique for HS-130 Si_3N_4 [1] and

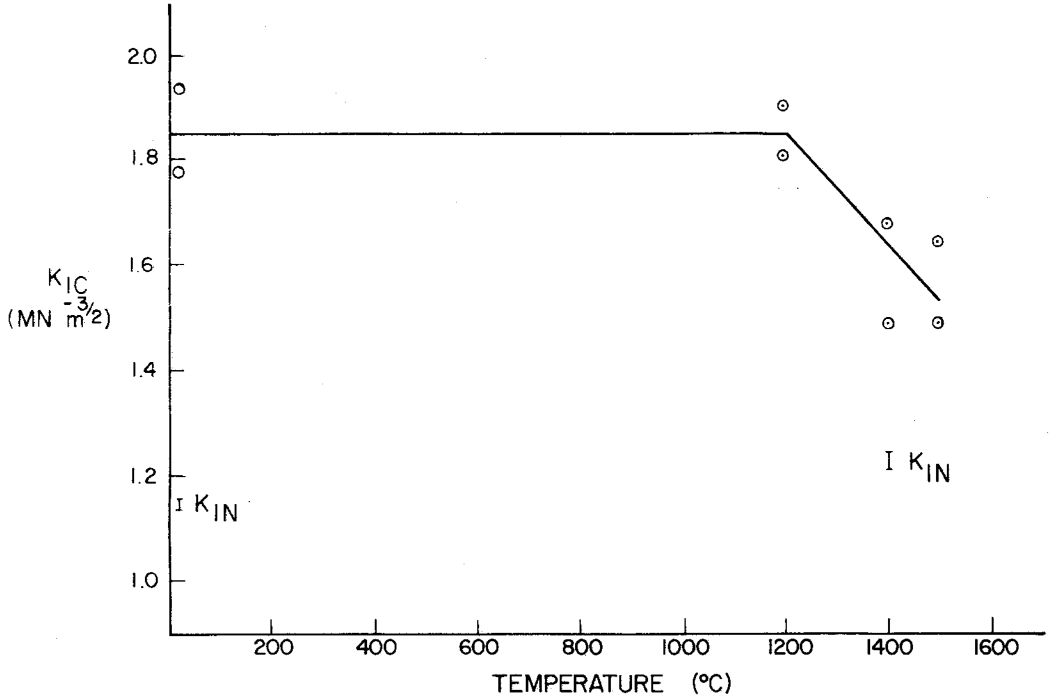

Figure 2 Effect of temperature and residual stress upon K_{IC}.

NC-203 SiC [2] were somewhat higher, 4.65 and 3.90 MN m$^{-3/2}$, respectively. The variation in K_{IC} values for these three materials can be analysed in terms of the plane-strain expression for K_{IC} for surface flaws in bending [4, 7]

$$K_{\mathrm{IC}} = \left[\frac{2\gamma E}{1-\nu^2}\right]^{1/2}, \qquad (4)$$

where γ = fracture-surface energy, E = elastic modulus, and ν = Poisson's ratio. The γ values calculated using this equation are shown in Table III. The difference in K_{IC} values of NC-350 Si_3N_4 and NC-203 SiC is due mainly to the much higher elastic modulus of SiC, whereas the considerably higher value of K_{IC} for HS-130 Si_3N_4 is due largely to the three-fold increase in γ.

Room-temperature values of K_{IC} for hot-pressed Si_3N_4 [1] and hot-pressed SiC [2] determined by this technique were originally found to be significantly lower than those obtained by the double torsion method. The reason for this was shown to be the presence of residual tensile stress produced in the vicinity of the flaw tip during the identation process. Vacuum annealing at elevated temperature or removal of ~ 0.020 mm of material from the tensile face of bend bars prior to four-point bending yielded values of K_{IC} that were in good agreement with double-torsion values. A similar effect is evident for reaction-bonded Si_3N_4 (see Fig. 2); the lower values labelled K_{IN} being calculated from the fracture stress required to break the specimen at the flaw after indentation but without any surface grinding. In order to obtain correct K_{IC} values, the surface-layer-removal method was used to relieve the residual stress introduced by the indenter, the thin surface layer being removed by diamond grinding followed by hand polishing using a range of abrasive papers down to 600 grit. Since there is an appreciable difference between K_{IN} and K_{IC}, it is useful to calculate the magnitude of the residual stress.

TABLE III Fracture mechanics data for Si_3N_4 and SiC

	HS-130	NC-203	NC-350
E (GN m^{-2})	313*	452*	160*
K_{IC} (MN m$^{-3/2}$)	4.65	3.90	1.87
ν	0.29*	0.168*	0.26*
γ(J m^{-2})	31.64	16.35	10.20

* From [8]

For the "as-indented" specimen

$$K_{\mathrm{IN}} = M(\pi a/Q)^{1/2}\sigma_{\mathrm{M}}, \qquad (5)$$

where σ_{M} is the measured fracture stress. Assuming the residual stress acting upon the flaw tip to be additive to the applied stress,

$$K_{IC} = M(\pi a/Q)^{1/2}(\sigma_M + \sigma_R). \qquad (6)$$

Combining Equations 5 and 6 yields

$$\sigma_R = (K_{IC} - K_{IN})/M(\pi a/Q)^{1/2}. \qquad (7)$$

Using Equation 7, the residual stress introduced as a result of the indentation process is calculated to be 51.9 MN m^{-2} which is of similar magnitude to values for HS-130 Si_3N_4 (107 MN m^{-2}) and NC-203 SiC (35.4 MN m^{-2}). The significance of these values is not known at this time, but they presumably reflect the different amounts of complex deformation which each material has undergone during the indentation process.

4.3. Effect of vacuum annealing on room-temperature K_{IC}

The indented test bars were annealed in vacuum (1.3 × 10^{-9} atm) at 1200° C for 1 h prior to fracturing in four-point bending at room temperature. In each instance the sample broke at the flaw. K_{IC} was calculated from the fracture stress and flaw dimensions as described earlier. For three samples K_{IC} was found to be 1.369, 1.508 and 1.590 MN m$^{-3/2}$. These values are lower than for unannealed specimens (Fig. 2). Again no change in flaw dimensions was observed, indicating that the reduction in K_{IC} is due to a decrease in strength of the as-flawed material resulting from annealing.

4.4. Effect of annealing in air on room-temperature strength

The effect of air annealing on the room-temperature strength of 2600 g indented samples is tabulated in Table IV for three annealing conditions. In all cases fracture did not occur at the flaw, which can consequently be considered to have healed as a result of oxidiation. Similar behaviour has been observed in hot-pressed SiC [2]. More importantly, in all cases the fracture stress did not return to the initial value of 252.4 MN m^{-2} as would be expected upon healing of the flaw, but remained substantially reduced, ranging from 90.8 to 169.7 MN m^{-2}.

TABLE IV Effect of air annealing on room temperature strength

Oxidation conditions	Room-temperature fracture stress (MN m^{-2})
air, 1200° C for 1 h	112.6
air, 1200° C for 1 h	118.5
air, 1200° C for 1 h	169.7
air, 1200° C for 1 h	165.1
air, 1200° C for 1 h	144.3
air, 1200° C for 1 h	166.8
air, 1400° C for 1 h	146.8
air, 1200° C for 100 h	90.8

Washburn and Baumgartner [3] measured the effect of oxidation upon the room-temperature strength of both ground and as-fired surfaces of NC-350 Si_3N_4. After oxidation at 1200° C for 100 h the strength dropped 51% for the as-fired material; however, when 0.038 mm of material was removed after oxidation, the strength returned to its original value. In contrast, the ground specimens exhibited only a 4% decrease in strength. Under these oxidation conditions they found internal oxidation to be occurring rather than extensive oxide-scale formation on the surface of the material. The as-fired material gained 1.9% weight and the oxide layer was found to consist mainly of crystobalite. The ground specimens gained only 0.9%, and no cristobalite was found in the oxide layer. In the present investigation the oxidation also occurred mainly internally, the oxide scale being only 2 μm thick for oxidation at 1200° C for 100 h or at 1400° C for 1 h. However, in contrast to the findings of Washburn and Baumgartner [3], cristobalite was found on the ground surface of all air-annealed specimens, which suggests that the decrease in fracture stress is associated with the formation of cristobalite. Attempts to regain the initial strength by grinding 0.051, 0.254 and 0.381 mm thick surface layers from the tensile surface after oxidation were unsuccessful. The fracture-stress values did not increase to the initial value of 235 MN m^{-2} but were in the range 158 to 169 MN m^{-2}. Therefore, the internal oxidation must have occurred at greater depths, and in view of the porous nature of this material probably extended completely through the test bars.

Calculations based upon the chemical reaction ($Si_3N_4 + 3O_2 = 3SiO_2 + 2N_2$) and the densities of Si_3N_4 and SiO_2 show that the formation of cristobalite at high temperatures on the surface of Si_3N_4 grains will leave them under a tensile stress due to the volume mismatch between matrix and oxide (the densities being Si_3N_4 = 3.2 g cm^{-3} and cristobalite = 2.27 g cm^{-3} for the high-temperature form and 2.32 g cm^{-3} for the low-temperature form). Upon cooling through the cristobalite allotropic transformation at ~ 250° C, some slight reduction in these stresses would be expected, but probably not enough to alleviate them altogether. Thus, the presence of a thin oxide layer around the individual grains of the matrix material acts in much the same way as the residual stress induced by the Knoop indentation in lowering the necessary applied fracture stress to break the material at the critical flaw.

In view of the extreme sensitivity of the strength of reaction-bonded Si_3N_4 to oxidation, it seems possible that the decrease in strength of indented samples tested in vacuum at 1400 and 1500° C, as well as those tested at room temperature after vacuum annealing at 1200° C is due to low but finite oxygen concentration present in the vacuum "atmosphere" rather than to changes in material properties.

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