FRACTURE STRENGTH AND TOUGHNESS OF ENGINEERING NITROGEN CERAMICS

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ABSTRACT

The temperature dependence of elastic modulus, flexural strength and toughness of reaction bonded silicon nitride have been examined in air or in nitrogen. The high temperature mechanical behaviour is discussed in terms of oxidation. Up to 1200°C, all the properties increase in air with internal oxidation which reduces the open porosity and modifies the flaws geometry. Such an increase is not observed in nitrogen along the same temperature range. Above 1200° C, all the characteristics are decreasing in air and in nitrogen. The oxidation dependence of room temperature properties were also measured.

KEYWORDS

Nitrogen ceramics ; silicon nitride ; elastic modulus ; flexural strength ; toughness ; critical strain energy release rate ; high temperature ; oxidation.

INTRODUCTION

A comprehensive understanding of the mechanical properties of engineering ceramics is an essential requirement for the use and design of structural components, particularly those that are used in severe environment as in gas turbines. Among these materials, the silicon nitride ceramics have been extensively developped during last ten years (Edington, Rowcliffe and Henshall, 1975). Most attention has been paid to the mechanical behaviour of hot pressed varieties (HPSN) but the problems associated with their fabrication process yield to a difficult technological development. On the other hand, the mechanical properties of reaction bonded varieties (RBSN) are lower than the hot pressed ones (Davidge, 1976) but these varieties present the considerable advantage of easy fabrication of intricate components. The present work was undertaken to study a commercial variety of RBSN and specially the influence of oxidation on the fracture toughness and strength at temperatures up to 1400°C.

EXPERIMENTAL PROCEDURE AND MATERIALS

Material

The silicon nitride samples were obtained from Annawerk GmbH (Ceranox NR 115) in the form of plates 50x50x5 mm^3. The density was about equal to 2,6 $g.cm^{-3}$ and the α/β phase ratio measured by X-ray diffraction (Gazzara and Messier, 1977) was found to be 70/30.

Two type of specimens were machined from the commercial plates : one for the determination of flexural strength and Young's modulus (40 x 5 x 4 mm^3) and another one for the measurement of fracture toughness (40 x 5 x 2,5 mm^3).

Mechanical testing apparatus

We have designed and built a high temperature testing apparatus based upon a 100 kN Instron testing machine which can work either in flexion or in compression up to 1500°C. A muffle attached to the furnace allows to test the specimen in air or in controlled atmosphere. For flexural tests, the load is applied to the specimen by three or four rollers held in a jig made of alumina or silicon nitride (Orange and others, 1980). The measurement of actual deformation is made by a differential displacement transducer (5mV/µm) in the proximity of the specimen.

Experimental procedure

Prior to testing, the surface of samples were lapped (600 - grit) and then finished with submicronic diamond paste. For the bend strength measurements, we have used a four-point test rig with a major span of 32 mm and a minor span of 10 mm. The measurements of K_{IC} were achieved with S.E.N.B. samples tested in four point bending. The notch, of 100 µm width and about 80 µm tip radius, was machined with a diamond saw on a depth of 2 mm. Stress intensity factors were calculated from the following equation (Brown and Srawley, 1969) :

$$K_{IC} = \frac{3\,P\,L}{dw^2}\sqrt{a}\,y \quad \text{with} \quad y = F\left(\frac{a}{w}\right) \qquad \frac{a}{w} = 0{,}4 \qquad (1)$$

d, w, L are breath, depth and span respectively ; a is the notch depth and P the applied load. All tests were performed at a cross-head speed of 5.10^{-2} $mm.min^{-1}$, either in air or in nitrogen (N_2+5% H_2). In air the specimen were maintained during 4 hours at the temperature before testing to assure effective oxidation.

RESULTS

Elastic modulus

Values of Young's modulus, E, were deduced from the measurement of the applied load and of the actual deformation of the specimen. The precision (±7%) is sufficient to observe large variations. The temperature dependence of Young's modulus in air or in nitrogen up to 1400°C is given in fig. 1.

The figure 2 shows the evolution of room temperature modulus versus time of oxidation for specimens held at 1000°C, 1200°C, 1400°C in still air.

Bend strength

Several flexural strength determinations have been made after treatments in air at high temperature. Figure 3 shows the variation of the mean flexural strength σ_f up to 1400°C in air and in nitrogen. The oxidation time dependence of the room temperature strength, σ_f, of specimens oxidized at 1000°C, 1200°C and 1400°C is given by the fig.4.

Fracture toughness

The effect of temperature on K_{IC} in air or in nitrogen measured with SENB specimens, is shown in Fig. 5. We have also determined the evolution of room temperature fracture toughness as a function of oxidation time, the notched specimens being oxidized at 1000°C, 1200°C and 1400°C before testing at ambiant temperature (Fig.6).

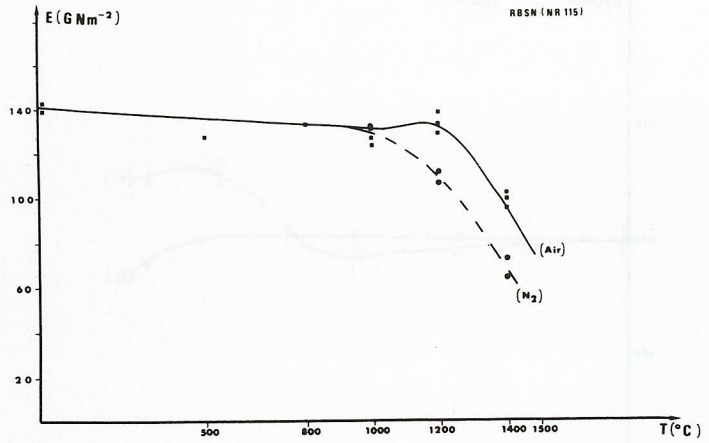

Fig. 1 Variation of Young's modulus versus temperature in air or in nitrogen

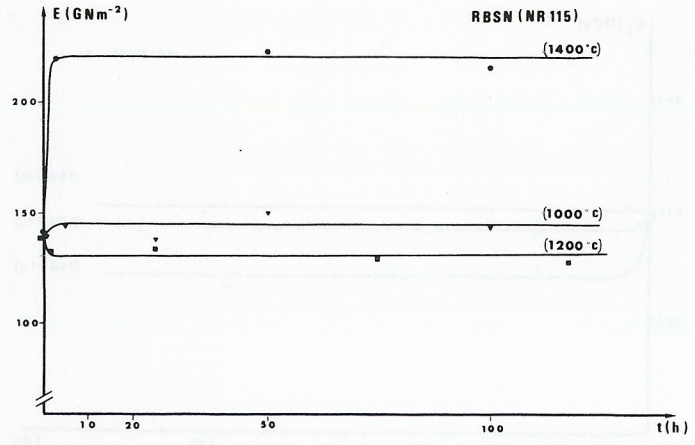

Fig.2 : Variation of room temperature modulus versus oxidation time

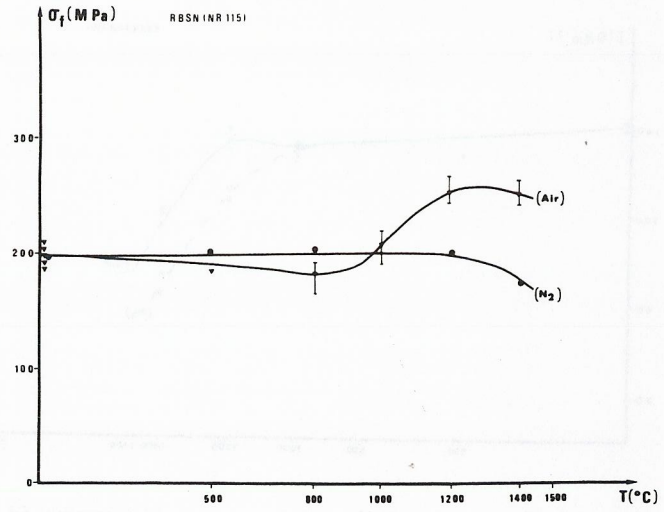

Fig. 3 : Flexural strength versus temperature in air or in nitrogen

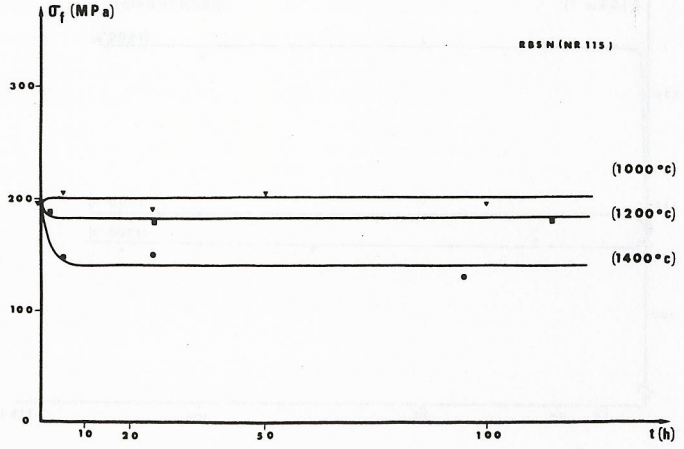

Fig. 4 : Evolution of the strength measured at room temperature as a function of oxidation time

DISCUSSION

Young's Modulus

The variation of Young's modulus as a function of temperature (Fig.1) shows a small decrease up to 1100°C ; the modulus decreases at a somewhat greater rate as the temperature is increased above 1200°C. The slight decrease observed up to 1100°C is similar to that observed by Lloyd (1968) but is high compared with that found by Jayatilaka and Leake (1975). We do not observe any modulus increase between 20°C and 1100°C, contrary to Noakes and Pratt (1972) and Larsen and others (1978) for RBSN with similar density. Also the change in modulus versus temperature up to 1100°C cannot be correlated with density. However, the precision of the modulus measurements is not sufficient to decide and it should be better to make measurements by resonance techniques.

The fall off in modulus above 1200°C can be attributed to intergranular sliding, due to the presence of an amorphous phase in grain boundary (Noakes and Pratt 1972 ; Grathwohl and Thümler, 1978). However, the observed modulus decrease is smaller than that found by Noakes and Pratt (1972) ; this difference can arise from a smaller oxygen content or a better behaviour during oxidation, our material being characterized by a narrow distribution of the pore size, 50 % of the pore volume having a size smaller than 0,04 µm. The evolution of room temperature Young's modulus with oxidation (Fig. 4) shows that the modulus is nearly constant up to 1200°C and increase quickly at 1400°C. This increase with oxidation above 1200°C can be linked to a microstructural change and to a decrease of the porosity in surface ; this last point is confirmed by microporosity measurement : the mean size of the pores varies from 0.04 to 0.01 µm. Davidge and others (1972) have shown that above 1200°C a continuous film is formed on the specimen surface, whereas under 1200°C the oxidation is mainly internal. This variation of porosity with oxidation gives a measured modulus at high temperature which is higher in air than in nitrogen (Fig.1).

Bend strength and Fracture toughness

The variation of the flexural strength σ_f as a function of temperature (Fig. 3) shows in air a small decrease up to 800°C, a marked increase up to 1200°C and a slight decrease above this temperature. In nitrogen, there is no increase of strength between 800°C and 1200°C. We don't observe any plasticity during flexural tests up to 1400°C ; on the other hand there is no strain-rate dependence of strength at 1400°C and for a variation of strain rate from $\dot{\varepsilon}_1 = 1{,}7.10^{-4}$ to $\dot{\varepsilon}_3 = 1{,}7.10^{-6}$ s^{-1}. Also at, this temperature, the sub-critical crack growth must not be very important; nevertheless this point must be confirmed by systematic tests at different temperatures or by double torsion test. Our results are similar to some published data but differ from those of other authors (Thompson and Pratt, 1966 ; Evans and Davidge, 1970 ; Noakes and Pratt, 1972 ; Mangels, 1977).

The variation of K_{IC} as a function of temperature (Fig. 5) shows in air an increase of K_{IC} from 20°C up to 1200°C and a small decrease above ; in nitrogen we observe a constant value up to 1200°C and a slight increase at high temperature. In no case the load versus displacement curves show any departure from linearity and failure always occurred catastrophically. The determination of toughness, with the S.E.N.B. technique, requires the measurement of the real crack length and thus, a correct K_{IC} value is not obtained when a subcritical crack propagation occurs (Munz, Himsolt and Eschweiler, 1980). In the case of RBSN, a small or no slow crack growth is observed up to 1400°C (Davidge, 1977 ; Mangels, 1977). However, the influence of environment is not well known and we must consider the K_{IC} results with caution Nevertheless, the fracture toughness data, we can determine the effective surface energy γ_i with the following equation :

$$\gamma_i = \frac{K_{IC}^2 (1 - \nu^2)}{2E} \qquad (2)$$

where ν is the Poisson coefficient.

The temperature dependence of γ_i, in air or in nitrogen, is shown by Fig. 7 ; in air, γ_i increases clearly between 800°C and 1200°C whereas in nitrogen γ_i increases only above 1200°C.

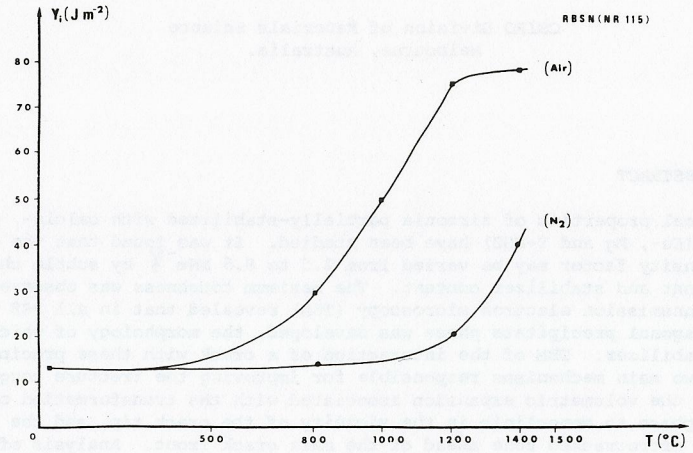

Fig. 7 : Variation of γ_i versus temperature in air or in nitrogen

These results can be interpreted in terms of microstructural variations. The increase of γ_i and thus of σ_f, in air, is certainly linked to a variation of the pore size distribution with oxidation.

$$\sigma_f = \frac{1}{\sqrt{\Pi}} \frac{K_{IC}}{\sqrt{a}} = \frac{1}{\sqrt{\Pi}} \left(\frac{2E\gamma_i}{a}\right)^{1/2} \qquad (3)$$

Between 800°C and 1200°C, the oxidation is mainly internal (Davidge and others, 1972 ; Grathwoll and Thummler, 1978), the oxide layer being formed on the surface of internal pores. The oxide (silica) has a volume larger than Si_3N_4 and thus the oxidation leads to a reduction of the porosity, and on the other hand to a rounding of the flaws. This last process gives an effective increase of the effective surface energy, the geometry of the flaw dependence of γ_i being given by a relation (Davidge and Evans, 1970):

$$\gamma_i = F^2\left(\frac{\Pi}{8} \nu_o \frac{\rho}{b}\right) \qquad (4)$$

F = factor including the plastic flow effects
ν_o = thermodynamic surface energy
b = lattice spacing ; ρ = radius of curvature of the crack tip

The increase of γ_i can be also associated with the decreasing porosity (Dalgleish and Pratt, 1975) . The rounding of the flaws being not effective without oxidation we don't observe any increase of γ_i, and therefore of K_{IC} and σ_f between 800°C and 1200°C in nitrogen atmosphere.

Furthermore the size of the critical flaw responsible for the failure (equ.3) increases during the oxidation process, unless the γ_i values deduced from the K_{IC} and E measurements are high in comparison with the true values because of the occurence of crack branching or secondary fractures. The increase of the flaw size (in air, $a_c \simeq 30$ µm at 20°C, $a_c \simeq 80$ µm at 1000°C) could be explained in terms of linking of sub-surface pores at sub-critical stress to form a critical flaw. This process has been established in alumina by Meredith and Pratt (1975). This pore linking could be enhanced by internal oxidation at relatively low temperature (about 800°C) along the grain boundaries. Such an increase of the flaw size is not observed when testing in nitrogen because the oxide layer formation does not take place ($a_c \simeq 30$ µm up to 1200°C). This hypothesis should be verified by further micrographic observations.

Above 1200°C γ_i increases no more in air ; the oxidation is mainly superficial and the flaw rounding is less important. The slight σ_f and K_{IC} decrease which probably results from a localised plasticity at grain boundaries. This flaw process is responsible for the increase of γ_i observed in nitrogen in the same temperature range, as suggested by Coppola and others (1972).

The increase of K_{IC} during oxidation (fig. 6) can be related to the variation of γ_i previously mentioned; this variation is higher at 1000°C than at 1400°C. This is due to the different behaviour during oxidation : at 1000°C most of the oxidation is internal whereas at 1400°C there is formation of a continuous film of silica, which impedes the internal diffusion of oxygen, and which is severely cracked after cooling at room temperature (Davidge and others, 1972). This cracking is responsible for the lowest increase of K_{IC} after oxidation at 1400°C. Furthermore, the variation of σ_f observed during oxidation (fig. 4) (no or little decrease at 1000°C and 1200°C) is consistent with the increase of critical flaw size. The fall off of room temperature flexural strength observed after oxidation at 1400°C is induced by the cracking of oxide layer.

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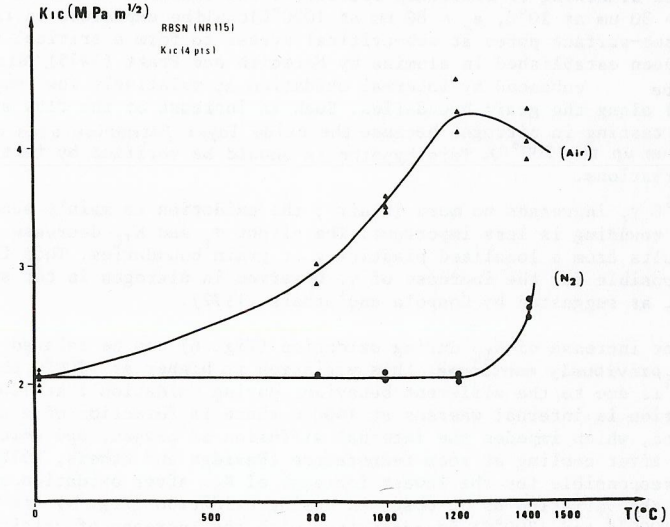

Fig. 5 : Fracture thoughness versus temperature in air or in nitrogen

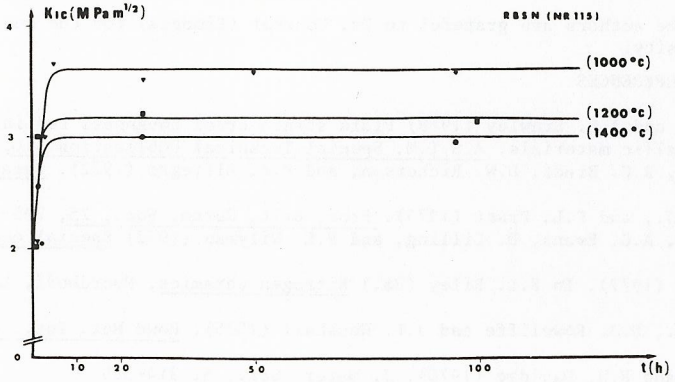

Fig. 6 : Variation of K_{IC} versus oxidation time