Strength of Structural Ceramics after Exposure to Sodium Sulfate

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Abstract

A variety of advanced structural ceramics were treated in air at 1000°C for 500 h in the presence of various amounts of sodium sulfate. Room temperature flexure strength was determined before and after treatments. Results show that Ce-TZP and alumina are resistant to strength degradation after exposure to sodium sulfate, but Si_3N_4 (NC-132) and, to a lesser degree, Y-TZP are not.

The addition of sodium sulfate also has an adverse effect on the high temperature performance of the Y-TZP, by reducing its load carrying capabilities between 900 and 1000°C. For the Ce-TZP, alumina and even the Si_3N_4 there appears to be no change in the high temperature performance when sodium sulfate is present.

Mehrere verschiedene Hochleistungskeramiken wurden in Luft, in Anwesenheit unterschiedlicher Konzentrationen von Natriumsulfat 500 h bei 1000°C ausgelagert. Die Biegefestigkeit bei Raumtemperatur wurde vor und nach den Probenbehandlungen bestimmt. Die Ergebnisse zeigen, daß die Ce-TZP- und Aluminium-Oxidkeramiken keinen Festigkeitsverlust erleiden, nachdem sie der natriumsulfathaltigen Atmosphäre ausgesetzt waren, wohl aber Si_3N_4 (NC-132) und, weniger stark, das Y-TZP.

Natriumsulfat hat ebenfalls einen negativen Effekt auf die Hochtemperatureigenschaften von Y-TZP, indem die Belastbarkeit des Materials zwischen 900 und 1000°C reduziert wird. Dagegen scheint, daß die Hochtemperatureigenschaften des verwendeten Ce-TZP, Aluminiumoxid und Si_3N_4 unter diesen Bedingungen nicht beeinflußt werden.

Plusieurs céramiques structurales ont été traitées à 1000°C dans l'air pendant 500 h en présence de diverses quantités de sulfate de sodium. La résistance en flexion à température ambiante a été mesurée avant et après traitement. Les résultats montrent que le Ce-TZP et l'alumine ne présentent pas de dégradation de leur résistance après exposition au sulfate de sodium, au contraire du Si_3N_4 (NC-132) et, dans une moindre mesure, du Y-TZP.

L'addition de sulfate de sodium a également un effect néfaste sur les propriétés en flexion du Y-TZP à hautes températures (entre 900 et 1000°C). Il n'y a par contre aucun changement dans les propriétés à hautes températures du Ce-TZP, de l'alumine et même du Si_3N_4 en présence de sulfate de sodium.

Introduction

The service environments projected for structural ceramics are quite hostile. In the gas turbine engine some of the structural ceramics will face hot corrosion, i.e. the attack by molten Na_2SO_4 ($T_m = 884°C$) which condenses on engine parts when ingested NaCl reacts with sulfur impurities in the fuel. Marine propulsion gas turbine engines experience a similar sulfate-induced corrosion. How long-term exposure to these corrosive environments affects the mechanical properties of ceramics is of critical importance to their successful application in engines as high temperature structural components.

At the present time monolithic tetragonal zirconia polycrystal ceramics (TZPs) are not being considered for structural applications such as gas turbine blades and other components in the high temperature regions ($> 1000°C$) of gas turbine engines. However, this does not preclude the use of composites based on a TZP matrix from finding application in this environment. Moreover, the use of TZPs and other zirconia-based ceramics in non-structural applications in the high temperature region of gas turbines appears inevitable (e.g. thermal barrier coatings, etc.). Thus the effect of hot corrosion on the mechanical properties of TZPs may have important technological implications. On the other hand, Si_3N_4 ceramics are being considered and, in certain applications, incorporated as monolithic components in advanced engines.[1]

The actual mechanisms of hot corrosion in TZPs[2-5] and Si_3N_4[6-11] have been studied. However, there has been little work examining the interactions between hot corrosion and mechanical properties. Important properties that may be affected by hot corrosion are room temperature and elevated temperature strength, toughness and creep-rupture behavior.

This paper presents results on the effect of hot corrosion on the room temperature and elevated temperature time-dependent strength of two TZPs and a Si_3N_4. A high purity alumina ceramic has also been examined for comparison.

Experimental Procedure

Four commercially available ceramics, an yttria-TZP, a ceria-TZP, an alumina, and a Si_3N_4, see Table 1, were obtained and machined into two different-sized bend bars. The type 'B' bar was $3 \times 4 \times 50$ mm long and the type 'A' bar was $1·5 \times 2 \times 25$ mm long. Both were carefully ground by a surface grinder such that the surface striations were parallel to the long axis. All four long edges were chamfered $\sim 45°$ to a depth of $\sim 0·15$ mm; the bars were machined according to Ref. 12. A minimum of five type 'B' bars from each ceramic were

used to determine the as-received room temperature strength. They were broken in four-point flexure according to Army MIL STD 1942, with inner and outer spans of 20 and 40 mm respectively, and a cross-head speed of 0·5 mm/min.

Three other groups of five type 'B' bars from each ceramic were then subjected to one of the following heat treatments:

500 h at 1000°C with no Na_2SO_4, in air

500 h at 1000°C with 10–20 mg/cm² of Na_2SO_4, in air

500 h at 1000°C with 50–75 mg/cm² of Na_2SO_4, in air

Sodium sulfate was applied by mixing anhydrous sodium sulfate (Na_2SO_4) with distilled water then applying the solution to one 4×50 mm face of each bar. The application was limited to a centered 30 mm span of the face. The bars were then heated using a hot plate, driving off the water and leaving behind a layer of Na_2SO_4. The weight of each bar was measured before and after application of the Na_2SO_4 to ensure the amount was in the specified range. Tensile surfaces of each material from each condition were analyzed for phase changes by X-ray diffraction using $CuK\alpha$ radiation.

Heat treatments were done in air, at laboratory ambient humidity (40–60%), in an unstressed condition on silicon carbide knife edges to assure uniform heating. The knife edges supported the bar well outside the area to be tested during four-point flexure testing, assuring no effect on the subsequent strength determinations. The surface with Na_2SO_4 was placed face-up during the heat treatments to minimize any loss of the coating.

Once the strength was determined the fracture surface of each bar was examined optically at low magnification, and a scanning electron microscope (SEM) was employed for high magnification examination of selected fracture surfaces to determine cause of fracture.

Stepped-temperature stress-rupture (STSR) testing was done on the type 'A' bars following the procedure outlined by Quinn and Katz.[13] Tests were done on the as-received materials and on materials

Table 1. List of ceramics tested

Material	Manufacturer	Code	Process	Additives	Grain size (μm)	% Theoretical density
Y-TZP	NGK Insulators	Z-191	Sintered	Y_2O_3	0·2	97
Ce-TZP	Ceramatec	CZ203	Sintered	CeO_2/Al_2O_3	1·2	95
Al_2O_3	Coors Ceramics	AD999	Sintered	None	3–6	99
Si_3N_4	Norton Co.	NC-132	Hot pressed	MgO	3–6	99

with 10–20 mg/cm^2 of Na$_2$SO$_4$ but no previous treatments. STSR testing allows rapid screening of a material's stress-rupture behavior over a wide range of temperatures and stresses using a small number of bend bars. The procedure involves loading a bend bar into a furnace containing a four-point flexure fixture (inner and outer spans of 10 and 20 mm respectively) and heating the furnace to 800°C in 2 h, in air, with no load applied to the bar. Upon reaching temperature a dead-weight load is applied. Should the bar survive 24 h at this temperature, the furnace is then heated (in ~10 min) to 900°C and again the bar is allowed to soak for 24 h while under the same load. This cycle is repeated for 1000°, 1100° and 1200°C. If the bar fractures or excessive creep occurs, the power to the furnace is shut off by a microswitch. The time of fracture is then denoted on the STSR plot using an arrow, with the applied stress that caused fracture above the arrow. The symbols for the STSR plot are: (←) failure occurred upon loading at 800°C; (→) survived the full test cycle through 1200°C; and (↓) denotes time of failure between loading but before the full cycle is complete.

Type 'A' bars were used for STSR testing because the set-up for the 'A' bar allowed the tensile surface with the Na$_2$SO$_4$ to be placed face-up whereas the the tensile surface in the type 'B' bars were face-down. This reduced the potential loss of the Na$_2$SO$_4$ once it became molten.

Results and Discussion

Room temperature flexure testing

The results of the room temperature flexure strength testing, Fig. 1, show the Ce-TZP to be the most resistant to strength degradation after exposure to molten sodium sulfate at 1000°C, followed by the alumina and the Y-TZP. The Si$_3$N$_4$ shows the largest strength loss after exposure.
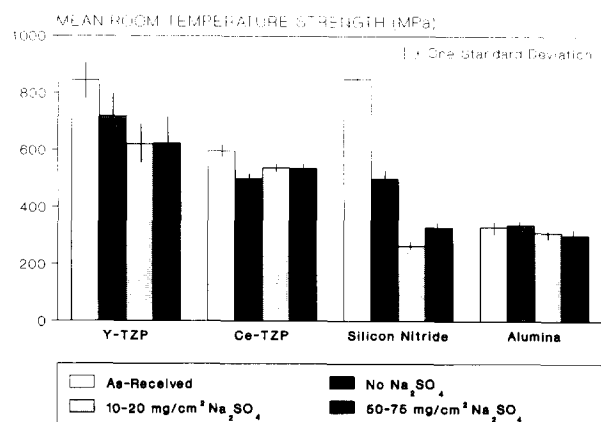

Fig. 1. Mean strength after exposure with and without sodium sulfate. Treated for 500 h at 1000°C.

Long-term exposure without sodium sulfate

The slight strength reduction of the Ce- and Y-TZP after 500 h at 1000°C with no Na$_2$SO$_4$ can be attributed to the fact that these materials are transformation toughened ceramics and are susceptible to overaging when exposed to elevated temperatures for a prolonged time. The addition of a small amount of a rare earth oxide, such as CeO$_2$ or Y$_2$O$_3$, along with an appropriate processing technique, allows for the retention of metastable tetragonal zirconia at room temperature. However, when overaging occurs the tetragonal zirconia transforms to the stable monoclinic phase, resulting in a reduction in strength.[14–17]

The Si$_3$N$_4$ has a significantly large reduction in strength (~40%) when exposed to the same treatment conditions. This strength reduction is due to the oxidation of the Si$_3$N$_4$. During oxidation a layer of SiO$_2$ forms, and the Mg in the glassy intergranular phase diffuses to the surface in an attempt to equilibrate the glassy phase with the SiO$_2$.[18] This results in the formation of oxidation pits (Fig. 2(b)) which become the new strength limiting flaw. Other investigators[19,20] have seen similar strength reductions with oxidation pits as the failure origin. Alumina does not undergo these phenomena. Thus, there is no reduction in strength as a result of this exposure.

Long-term exposure with sodium sulfate

The addition of Na$_2$SO$_4$ to the long-term, high temperature exposures does not cause any further strength reduction in the Ce-TZP and only minimal reduction in the alumina. However, the Y-TZP and to a greater extent the Si$_3$N$_4$ experience significant reductions in strength. Hamilton and Nagelberg[2] have reported that molten vanadates 'leach' Y$_2$O$_3$ from a ceramic, causing degradation of the material. Others[3,4] have shown that SO$_3$ is highly reactive with Y$_2$O$_3$ and that the combined action of Na$_2$SO$_4$ and SO$_3$, under SO$_3$ partial pressures as low as 70 Pa at 700°C, caused degradation of the ceramic through Y$_2$O$_3$ depletion. This is similar to the hypotheses proposed by Lange *et al.*[21] to account for the catastrophic degradation of Y-TZP that can occur when it is treated between 150 and 400°C in the presence of water vapor. They have found that the Y$_2$O$_3$ reacts with the water vapor to form α-Y(OH)$_3$. The formation of this hydroxide depletes the Y$_2$O$_3$ from the tetragonal grains, creating monoclinic nuclei which can grow spontaneously to transform the tetragonal grains to monoclinic. If the monoclinic grains become large enough microcracks will develop, allowing further leaching that leads to
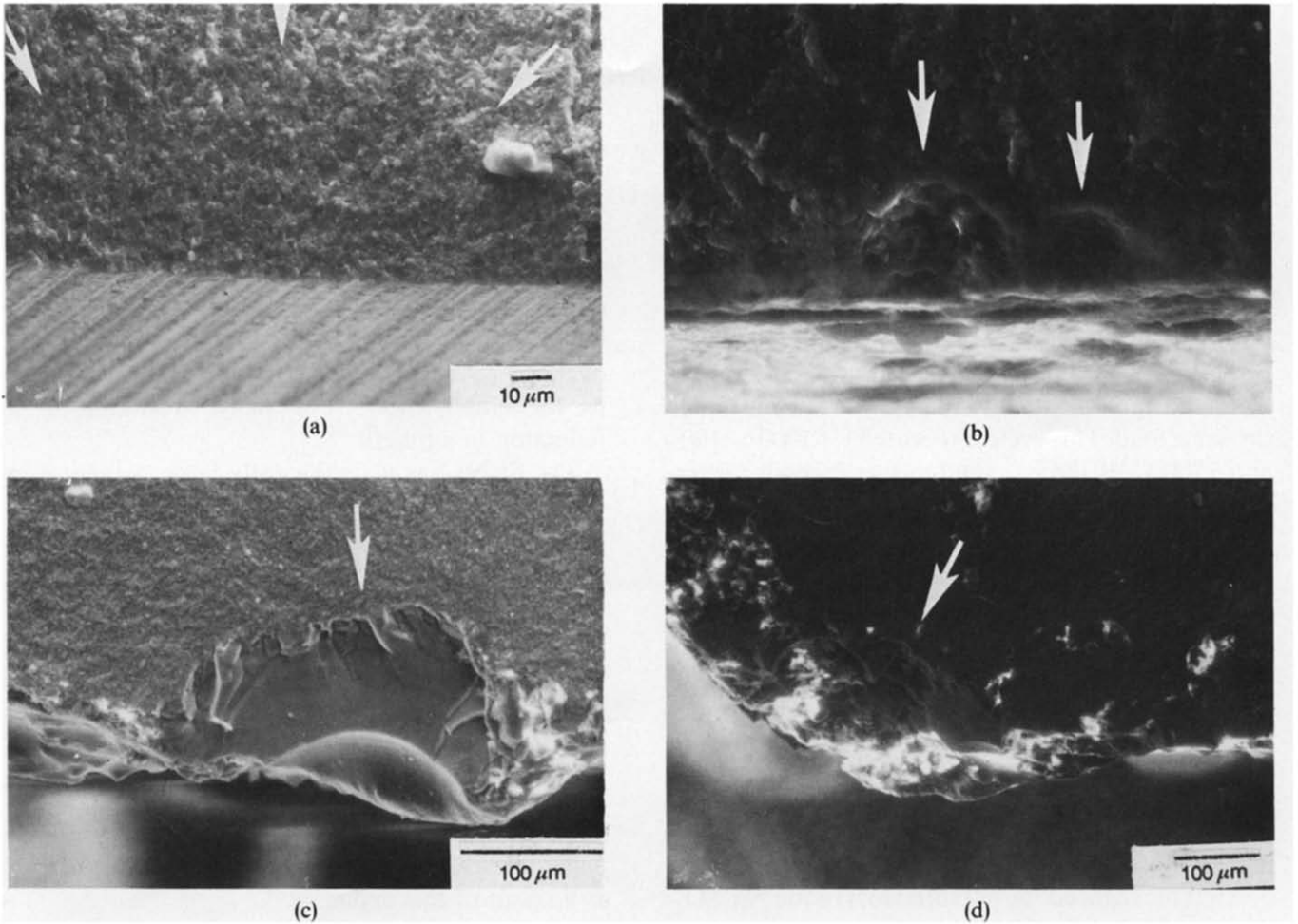
Fig. 2. Fracture origins of silicon nitride: (a) as-received, machining damage; (b) after 500 h at 1000°C without sodium sulfate, oxidation pits; (c) after 500 h at 1000°C with 10–20 mg/cm² sodium sulfate, corrosion pits; (d) after 500 h at 1000°C with 50–75 mg/cm² sodium sulfate, corrosion pits.

strength degradation. Thus 'surface corrosion' of Y-TZP could be due to Y_2O_3 depletion, resulting in the spontaneous tetragonal-to-monoclinic transformation of the zirconia and a reduction in strength beyond what can be attributed to overaging alone.

Figure 3 shows the phase stability of the TZPs. The high amount of monoclinic ZrO_2 in the as-received TZPs can be attributed to the stresses
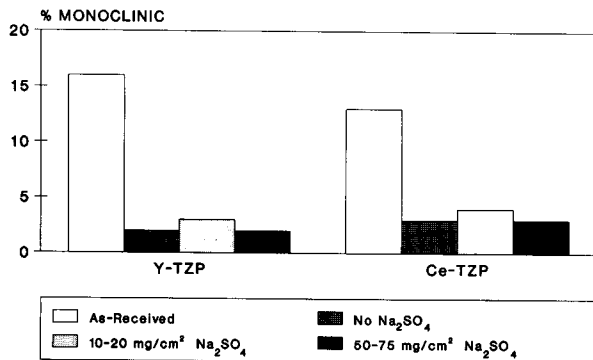

Fig. 3. Surface phase stability of Y-TZP and Ce-TZP after exposure with and without sodium sulfate. Treated for 500 h at 1000°C.

placed on the surface of the bar during machining. These stresses transform the surface ZrO_2 from tetragonal to monoclinic. Subsequent treatment at 1000°C relieves the stresses, allowing most of the monoclinic grains to revert to tetragonal grains.

One would expect an increase in the monoclinic ZrO_2 as the Y_2O_3 was being leached from the surface. However, since this potential phenomenon only occurs in the first few layers of this fine grained material $(\sim 0 \cdot 2 \, \mu m)^{14}$ due to the small amount of Na_2SO_4, the resolution of the X-ray diffraction equipment probably is not sensitive enough to pick up these changes. In addition, flexure testing is sensitive to surface flaws rather than volume flaws. Thus during high temperature corrosion the corrosive medium may penetrate in and around these flaws, causing several layers of grains to transform. This transformation can be accompanied by microcracking[21] which would enhance the severity of the flaws. This potential flaw enhancement may not be discernible in routine examinations. Chemical analysis of the residual
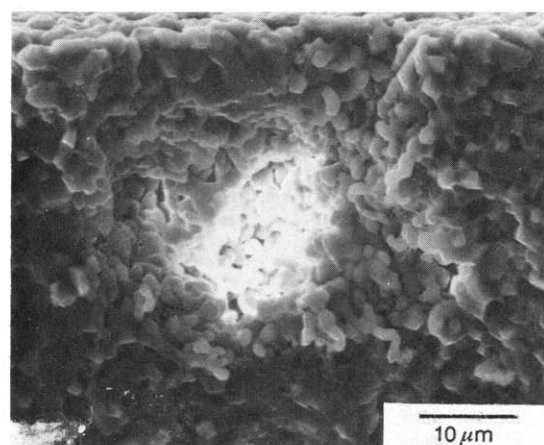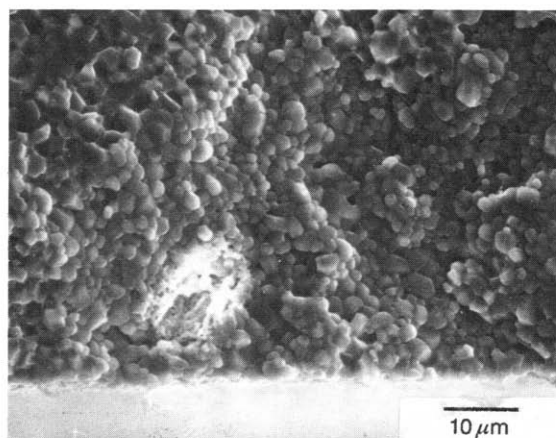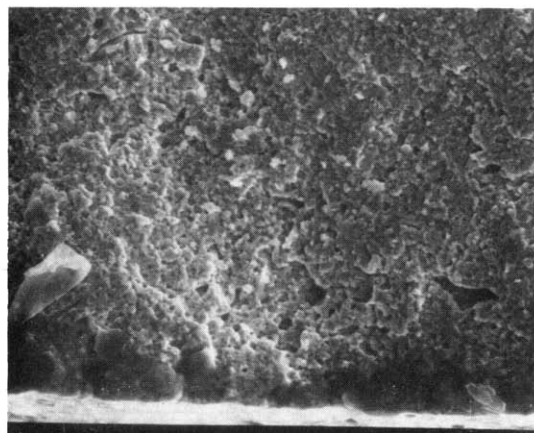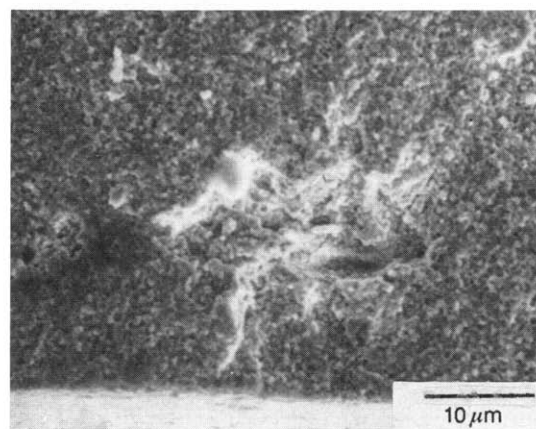
Fig. 4. Fracture origins of alumina: (a) as-received; (b) after 500 h at 1000°C with sodium sulfate.

Fig. 5. Fracture origins of Ce-TZP: (a) as-received; (b) after 500 h at 1000°C with sodium sulfate.

sodium sulfate after treatment would be a more significant measure of the leaching phenomenon and resultant phase transformation.

Ceria also undergoes a sulfation reaction,[5] but the equilibrium SO_3 partial pressure at 850°C is ~1200 Pa whereas for Y_2O_3 it is only ~1·5 Pa.[4] Thus the thermodynamics of the sulfation reaction are much more favorable in the case of Y_2O_3. Therefore, all things being equal, a CeO_2 stabilized zirconia should be superior to a Y_2O_3 stabilized zirconia in resistance to hot corrosion by sodium sulfate.

The high purity alumina exhibited only a minor degree of strength degradation when exposed to Na_2SO_4. Gannon *et al.*[22] found that the hot corrosion resistance of alumina refractories to molten K_2SO_4 increased with decreasing open porosity. The increased resistance was due to a reduction in the surface area available for corrosion. They also showed that control of the grain boundary chemistry played an important role in corrosion resistance. The effect of Na_2SO_4 on a glassy grain boundary phase should be similar to that of K_2SO_4

since alkali elements tend to behave similarly in silicate-based glasses. Since the strength limiting defect did not change appreciably in character after exposure to Na_2SO_4, (Fig. 4) it suggests that the minimal strength degradation may be due to corrosion of a trace grain boundary phase which may be present.

Examination of the fracture surfaces of each of the TZPs and the alumina showed that the type of strength limiting flaw did not change after exposure to molten sodium sulfate (Figs 4–6). This was not the case for the Si_3N_4. It experienced an additional strength loss of ~25% when Na_2SO_4 was added, due to a change in the flaw type and size. The typical flaw for the as-received material was machining damage, Fig. 2(a), and that for the bars treated without Na_2SO_4 was oxidation pits, Fig. 2(b). For bars exposed to sodium sulfate the flaw was also a pit, but this time a corrosion pit, Fig. 2(c) and (d), which was on the order of 10 times larger than the oxidation pits. Analysis of the pit contents showed the presence of a small amount of Na in addition to Si and Mg. The presence of Na as well as the glassy-
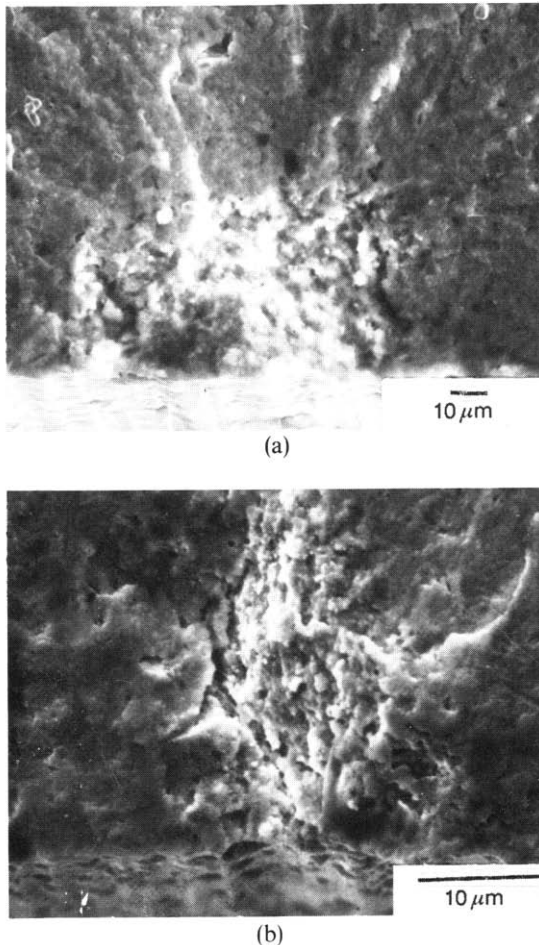
(a)

(b)

Fig. 6. Fracture origins of Y-TZP: (a) as-received; (b) after 500 h at 1000°C with sodium sulfate.

like appearance of the contents of the corrosion pit, indicate that a sodium-silicate glass may have been formed. The Mg is due to the addition of MgO as a hot-pressing aid.

Several studies have seen similar strength reductions[8-10] and changes in the strength limiting flaws.[8,9] Tressler *et al.*[6] reported that corrosive etching occurs at 1000°C involving the oxidation of hot pressed Si_3N_4, in the presence of Na_2SO_4, to SiO_2 and the dissolution of the SiO_2 layer as silicates. Further work[7] suggests that corrosion occurs due to attack of the oxide grain boundary phase, which creates the pits. X-ray analysis of the surface of the Si_3N_4 bars, with and without sodium sulfate, showed an increase in cristobalite with heat treatment time, while the addition of the Na_2SO_4 caused peak broadening, indicating the formation of an amorphous layer, possibly a sodium-silicate glass.

For all materials, increasing the amount of Na_2SO_4 present does not cause further reduction in strength. For the Y-TZP this indicates that once a certain level of Y_2O_3 has been removed from the surface further corrosion via this mechanism does not occur in the time frame of these tests. In the case

of alumina and Si_3N_4 the grain boundary phase in each is resistant to corrosion beyond a certain level.

Stepped-temperature stress-rupture (STSR) tests

STSR tests were conducted on as-received materials and materials with sodium sulfate but no previous treatments. Tests on the Y-TZP material, Fig. 7, show that the addition of Na_2SO_4 has an adverse effect on the material's high temperature load carrying capabilities. This effect is pronounced at 900° and 1000°C under stresses of 200 to 300 MPa. The material can no longer sustain stresses greater than 200 MPa through the 900° and 1000°C steps of this test. This shift is probably due to the previously mentioned Y_2O_3 depletion from the surface which allows for the tetragonal-to-monoclinic transformation of the zirconia.

Sodium sulfate melts at $\sim 884°C$,[23] thus one would expect little, if any, change in the high temperature performance at 800°C and indeed none is encountered. Since tetragonal zirconia is stable at $\sim 1170°C$ the depletion of Y_2O_3 from the surface, at or near this temperature, will not initiate the
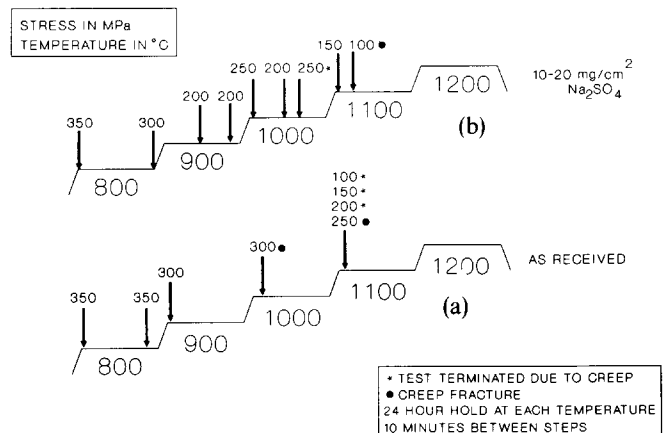

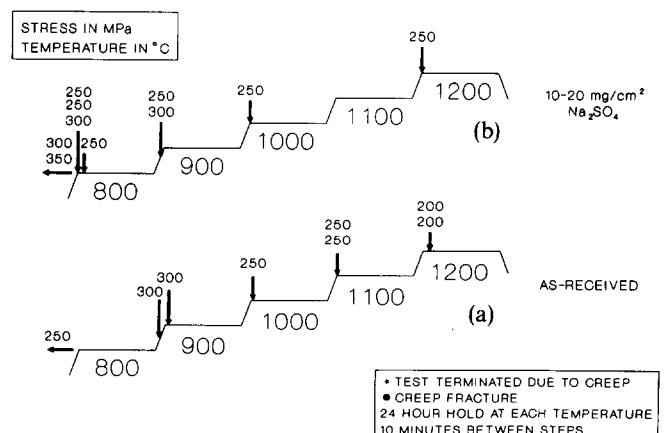**Fig. 7.** STSR results on Y-TZP material: (a) as-received; (b) with 10-20 mg/cm² of Na_2SO_4.

Fig. 8. STSR results on Ce-TZP material: (a) as-received; (b) with 10-20 mg/cm² of Na_2SO_4.
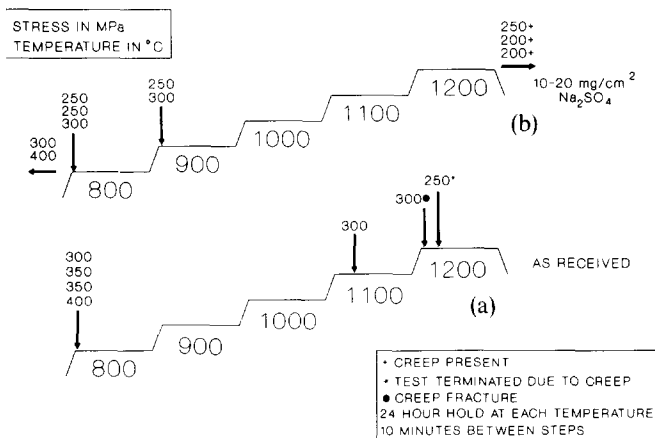
Fig. 9. STSR results on alumina: (a) as-received; (b) with 10–20 mg/cm² of Na₂SO₄.

transformation to monoclinic zirconia. Thus, at stresses below 200 MPa the high temperature performance appears unaffected.

The results of the STSR tests of the Ce-TZP and alumina, Figs 8 and 9 indicate that the high temperature performance of these materials is unaffected by the addition of Na₂SO₄. Based on the room temperature data presented here and in the case of the Ce-TZP, the thermodynamic data, these results are not surprising. However, the retention of the high temperature performance of the Si₃N₄ with Na₂SO₄, Fig. 10, was not expected based on the room temperature strength degradation seen after thermal exposure in the presence of Na₂SO₄. There are several possible explanations for this behavior: (1) the short duration of the tests does not allow sufficient time for the effects of the corrosion to be seen; (2) during the first step of the STSR test there is sufficient time for a protective layer to form, possibly through oxidation or the formation of a sodium-silicate glass, which prevents corrosion; or (3) the addition of the Na₂SO₄ does not effect the time-to-failure in this temperature range. In support of (3) Rowcliffe and Huber[24] examined the effect of hot
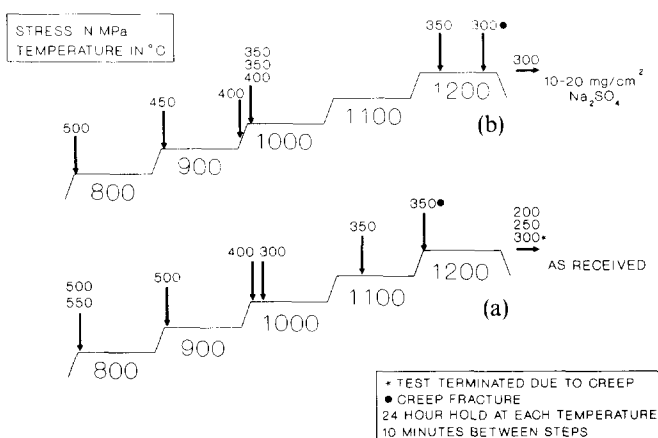

Fig. 10. STSR results on silicon nitride: (a) as-received; (b) with 10–20 mg/cm² of Na₂SO₄.

gas corrosion on silicon nitride by combusting and passing a fuel containing sulfur and sodium over notched specimens at 900° and 950°C. They found that the sodium addition to the fuel did not noticeably effect the failure time at these temperatures. However, our room temperature results lead us to believe that a combination of explanations (1) and (2) is more likely.

Conclusions

It was found that commercially available Ce-TZP has excellent resistance to strength degradation by molten sodium sulfate when compared to a Y-TZP or a Si₃N₄. A possible mechanism of strength degradation in the Y-TZP is the Y₂O₃ depletion of the Y-TZP surface which would allow the tetragonal-to-monoclinic transformation of the zirconia to occur spontaneously, resulting in a reduction in strength above that seen due to overaging alone. Strength degradation in the Si₃N₄ occurs due to the formation of large corrosion pits which occur when the sodium sulfate reacts with the protective SiO₂ layer, allowing attack of the oxide grain boundary phase. High purity, fully dense alumina is also very resistant to corrosion. However, it does exhibit a slight strength reduction which may be attributed to corrosion of a trace glassy grain boundary phase.

Stepped-temperature stress-rupture (STSR) results indicate that Na₂SO₄ additions have an adverse effect on the high temperature load carrying capabilities of a Y-TZP. This is noticeable at 900–1000°C under stresses of 200–300 MPa. However, Ce-TZP, alumina and even the Si₃N₄ subjected to the same test conditions appear to be unaffected. The unexpected results of the Si₃N₄ (NC-132) during STSR tests indicate the importance of the superposition of environmental parameters such as temperature, chemistry and stress, in determining the behavior of a material.

Acknowledgement

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