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Static fatigue and creep resistance of a commercial sialon

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The static fatigue and creep resistances of a commercial sialon material were evaluated by elevated temperature flexural stress rupture testing in air. The material is a ceramic alloy with a solid solution β' sialon phase, $Si_{6-z}Al_zO_zN_{8-z}$, with a substitution level z less than 1. The utilization of yttria sintering aids and post-sintering heat treatments leads to a fully crystalline grain-boundary phase. Creep and static fatigue resistances were excellent at temperatures up to 1200° C.

1. Introduction

Silicon nitride ceramics have considerable potential for utilization in heat engines. Progress in the field has been hampered by difficulties in fabricating sintered silicon nitride with the same level of strength, creep and static fatigue resistances of hot-pressed materials. The high-temperature stress rupture and creep resistances of many structural ceramics depend upon the amount and refractoriness of grain-boundary phases usually present. These grain-boundary phases are typically a consequence of the sintering aids and impurities in the starting powders. One processing approach is to use a fugitive additive that promotes sintering but forms a stable solid solution with silicon nitride leaving no residual glass phase at the boundaries. This approach has been demonstrated on a laboratory scale with 7 wt % of both $BeSiN_2$ and SiO_2 additives in silicon nitride with gas pressure sintering [1]. Creep and static fatigue resistances were excellent to 1200° C. At higher temperatures, the tiny amount of residual glass phase began to degrade the mechanical properties.

An alternative approach is to add alumina and silica sintering aids to form solid solution sialon materials. Unfortunately, these often have appreciable residual glass-boundary phases present which limit high-temperature mechanical properties.

Yttria sintering additions, often with some alumina, have been tried in attempts to form crystalline grain-boundary phases. Many studies in this area have been disappointing. Once again, glassy grain-boundary phases have limited elevated temperature mechanical properties. Indeed, in some instances, catastrophic phase instability has occured at intermediate temperatures in air.

One of the more promising materials in the sintered silicon nitride family is the sialon alloy series with yttria additives wherein the grain-boundary phase is completely crystallized by post-sintering heat treatments [2–5]. In this report, the mechanical properties of a commercially available form of this material are evaluated at room and elevated temperature. An assessment is made of the success of this fabrication approach and an upper use temperature is determined.

The present study was done as part of a ten year programme to evaluate new and promising heat engine grade ceramics [6, 7]. The test programme included room temperature flexure strength, flexural stress rupture and stepped temperature stress rupture experiments in air [6–8]. Eighteen commercial and research grade ceramics in the silicon nitride and carbide families have been evaluated in the programme. A list of the materials and a complete bibliography is given in Quinn and Slavin [6].

2. Material

The material evaluated is a commercial sialon, designated Syalon 201 (Lucas Cookson Syalon Ltd, Shirley, Solihul, UK), whose development has been reported previously [2–5]. Sialon is an acronym of the elements that compose it: silicon, aluminium, oxygen and nitrogen. The specific alloy of this study is termed Syalon since yttria is also incorporated. Syalon is processed with alpha-phase silicon nitride powder with an aluminium nitride polytype and yttria. The sintered product is a ceramic alloy with a solid solution sialon phase, $Si_{6-z}Al_zO_zN_{8-z}$ with z less than 1, and a matrix phase which is the residue of the liquid sintering aid. A post-fabrication heat treatment is given which crystallizes the boundary phase into yttrium aluminium garnet (YAG). A variety of such sialon materials is possible depending upon the initial compositions and post-sintering heat treatments. The Syalon 201 grade is tailored for high-temperature applications; up to 1350° C [3–5].

The sintered material was obtained in the form of three billets, nominally 100 g each, of approximate size 50 mm × 25 mm × 25 mm. They were fabricated in January 1985. Each billet had two faces ground flat and parallel, and point longitudinal and shear wave ultrasonic readings were taken to evaluate the consistency of the elastic modulus and Poisson's ratio at the ends, and the middle. The elastic modulus varied less than 0.5% and averaged 321 GPa. Poisson's ratio was 0.286 with no discernible variation. These

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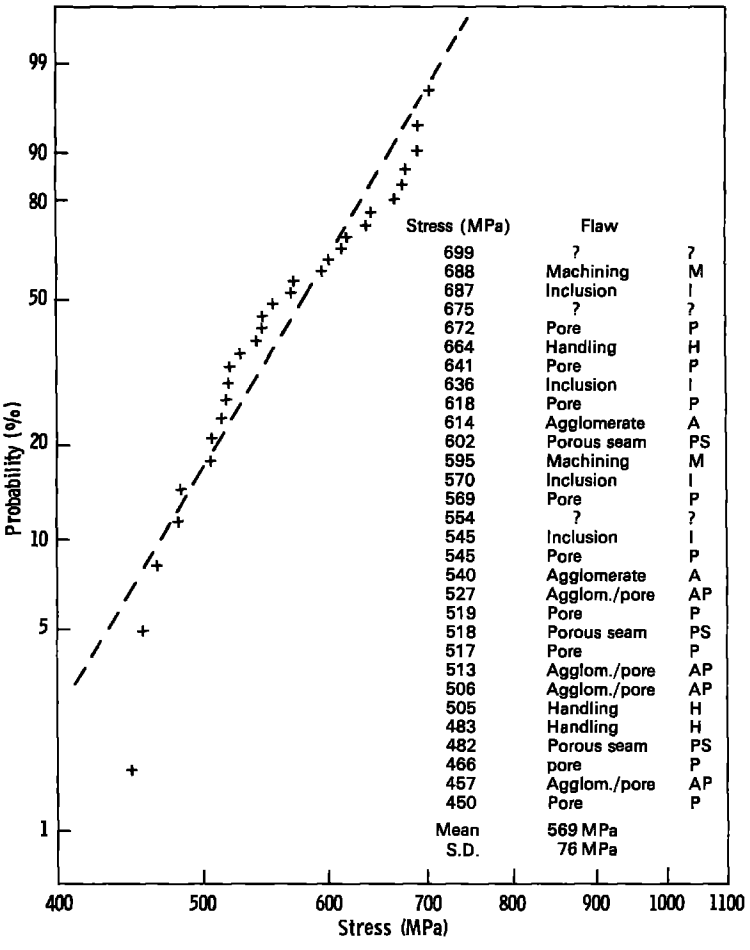


Figure 1 Room temperature flexure strength of Syalon 201. σ = 601 MPa, m = 9.0, 90.1%.

preliminary measurements indicated the billets were very uniform.

Metallic impurity or additive concentration was measured either by emission spectroscopy or atomic absorption. Table I shows the principal additives are aluminium and yttria. The iron content may, in part, reflect a pickup from a steel mortar and pestle used to crush specimens prior to analysis.

Phase analysis was by X-ray diffraction with copper $K\alpha$ radiation. Four crystalline phases were present in the as-received material: mostly β'-Si_3N_4, some α'-Si_3N_4, some YAG and some $YSiO_2N$.

A subtle and faint pattern of fine white lines was evident on the surface. These delineated zones of the order of 1 mm diameter. The YAG boundary phase forms long-range single-crystal skeletons. The fine white lines are where adjoining zones of single crystal YAG of different orientation meet [2]. In the present study, these lines had no effect upon mechanical properties.

Sixty flexural specimens, 3 mm × 4 mm × 45 mm in size, were prepared in accordance with MIL STD 1942(MR) size B [9]. The bulk density of these specimens was very consistent at 3.24 g cm^{-3} with only a 0.01 standard deviation.

3. Experimental procedure

Room temperature flexure strength, which served as a reference strength, was performed in four-point flexure in accordance with MIL STD 1942(MR) size B [9]. Fixture spans were 40 and 20 mm. Load application bearings were permitted to roll to eliminate friction error. The crosshead rate was 0.5 mm min^{-1}. All testing was in air at 27° C with 40 to 50% r.h.

Flexural stress rupture experiments were performed in air at 1200° C in ten small test furnaces. This temperature was chosen to permit direct comparison to a wide variety of ceramics previously tested [6, 7]. The firebrick furnaces use silicon carbide heating elements to achieve up to 1500° C in air [7, 10]. Four-point flexure fixtures with spans of 38.1 and 19.0 mm were made of hot-pressed silicon carbide. Load applications bearings were fixed in place. A deadweight lever assembly applied load into each furnace. The furnaces were allowed to stabilize for 5 min at temperature prior to load application. All applied stresses were computed on the basis of the elastic stress formulation. Further details of the test procedure are given in [7, 10, 11].

Stepped temperature stress rupture (STSR) testing [7, 8] evaluated static fatigue and creep resistance over a broader range: 1000 to 1400° C. STSR testing is a simple variation on isothermal stress rupture tests except that a range of temperatures are used on each specimen. A sequence of 24 h each at 1000, 1100, 1200, 1300, and 72 h at 1400° C was used. The specimen is

TABLE I Impurity or additive content of Syalon 201 (wt %). ND = not detected (< 0.01%)

Al	B	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V	W	Y	Zr
4.8	0.06	0.06	ND	0.02	ND	0.4	0.03	ND	ND	0.02	ND	0.34	4.5	0.01

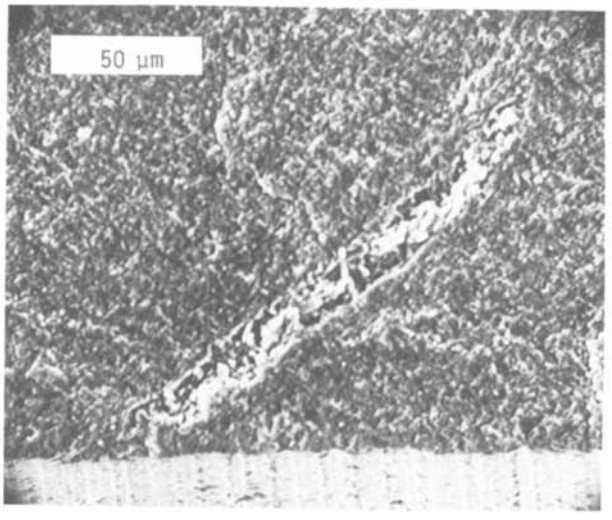


Figure 2 A pore which was strength limiting at room temperature (517 MPa).

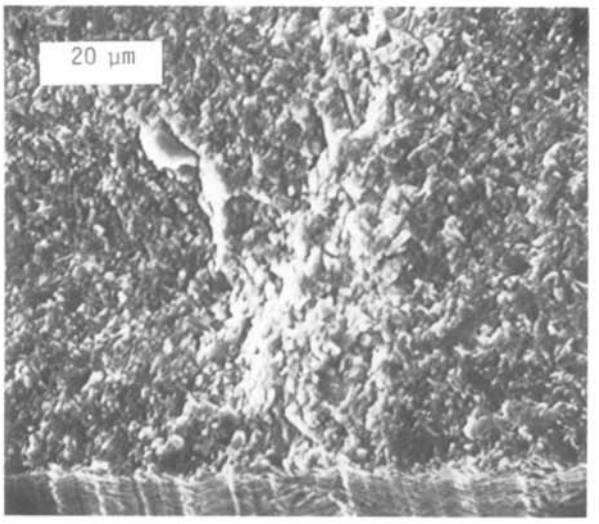


Figure 4 An iron and chromium-rich inclusion which caused fracture at 545 MPa.

deadweight loaded at 1000° C and if it survived intact for 24 h, the furnace was stepped to the next temperature. Once again, this specific sequence was used to permit ready comparison to previously evaluated ceramics [6, 7].

Specimens which survived stress rupture or STSR testing were measured for weight gain, final creep strain, and retained strength at room temperature. Creep strain was determined by photographically enlarging the inner span curvature and measuring the midspan deflection relative to the inner load points. (Strain = 4 × specimen thickness × midspan deflection/inner span^2.) Retained strength was measured with the MIL STD fixtures with the tensile face from high temperature loading, again orientated in tension.

4. Results

The fast fracture strengths at room temperature are shown in Fig. 1 along with a detailed fractographic characterization. All specimens were examined optically with a stereo binocular microscope up to × 80.

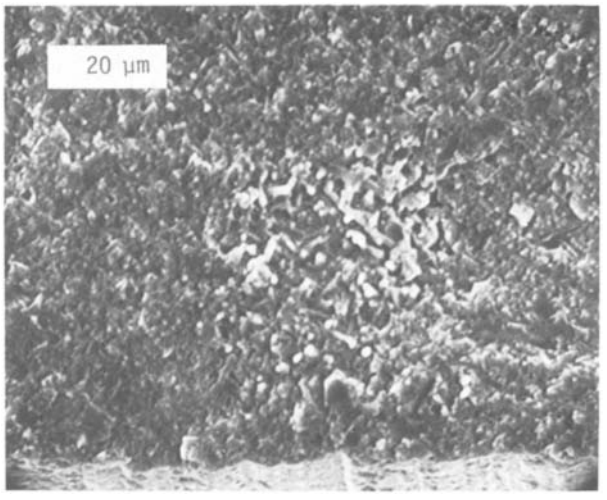


Figure 3 A porous zone which limited the room-temperature strength to 519 MPa. Surface machining damage may have interacted with the flaw.

About half were subsequently studied with a scanning electron microscope. The mean strength was 569 MPa; the standard deviation was 76 MPa. A Weibull two parameter function, with a least squares fitted modulus of 9.0, was not an especially good fit as shown in Fig. 1. The correlation coefficient was only 90.1%. The characteristic strength of the bend specimen was 601 MPa. The poor fit is probably the consequence of the multiple flaw populations which are typical of sintered silicon nitride ceramics. The most common defects were discrete pores (Fig. 2), porous zones or seams (Fig. 3) and powder agglomerates with associated porosity. Iron-rich inclusions, occasionally with chromium, were strength limiting in at least four instances (Fig. 4). Several specimens had machining damage or handling scratches that limited strength. The final tally was 66% sintering or powder defects, 17% machining or handling, and 17% uncertain.

The 1200° C flexural stress rupture results are shown in Fig. 5. Most failures (either on loading or in a time-dependent manner) occurred for specimens loaded to stresses within the reference room temperature strength scatter. Time-dependent failures only occurred at stresses 80% or more of the mean reference strength. The fracture surfaces of the time-dependent failures were very similar to the reference strength fractures. Small mirrors were centred on the same flaws that were strength limiting at room temperature: pores, porous zones and inclusions. No slow crack growth markings were evident. Fracture was predominantly intergranular as with the room-temperature specimens. Creep strains were negligible ($< 0.05\%$). A thin coherent oxide formed on the surface and had slight colour variations as shown in Fig. 6. These colour variations did not correlate with any failure. Failure origins of two of the longer time experiments are shown in Figs 7 and 8. The three specimens which survived 1000 h at stresses of 450, 400 and 400 MPa had permanent strains of 0.14, 0.08 and 0.15%, respectively. The retained strengths were 650, 681 and 689 MPa. These are very high values, at the limit of the range of the reference strength values (Fig. 1). In each case, a small internal fracture mirror

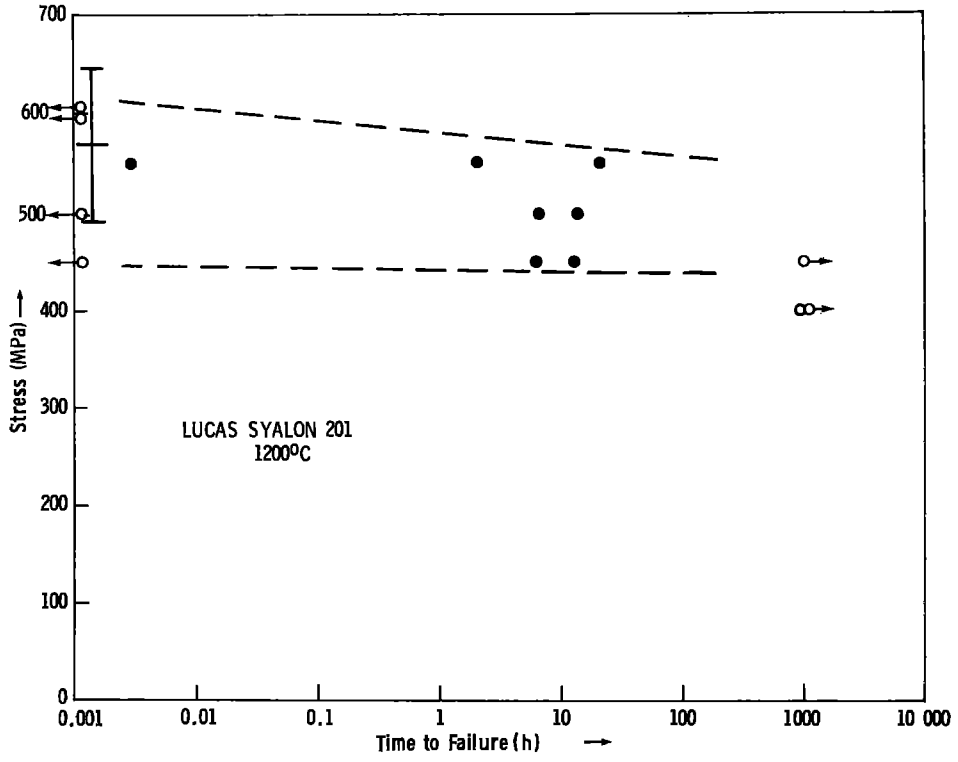


Figure 5 Flexural stress rupture at 1200° C in air. Hollow points arrowed left are failures on loading; arrowed right are specimens which survived intact. The mean room-temperature strength (569 MPa) is superimposed with standard deviation brackets.

was centred on a sintering defect. The flaws were well into the interior, implying a flaw healing or blunting phenomenon had affected defects near the surface. The oxide layer on the three survivors was uniformly clear, glossy and coherent (Fig. 6). Weight gains were very slight, averaging 0.0012 g over an average initial mass of 1.839 g. A final experiment at 1200° C and 400 MPa is ongoing and will be allowed to run 10 000 h.

The STSR results are illustrated in Fig. 9. Several highly stressed specimens either failed on loading or within 2 h at 1000° C. Fracture was from the same flaws that were strength limiting at room temperature. Crack growth markings were not evident. Fast crack growth was again intergranular. The surface appearance of these specimens was unchanged. Permanent strains were negligible. Lower stressed specimens (< 400 MPa) survived the 1000, 1100 and 1200° C exposures, but failed in the 1300° C step. These specimens had white surfaces. The fracture surfaces were very glassy as shown in Fig. 10, very much unlike the lower temperature fractures. Although the furnaces shut down immediately upon specimen fracture, some of the fracture surface oxide may have formed on cooldown. A gradient in a bubble concentration was evident with higher amounts in the interior (Fig. 10b). These are presumably nitrogen bubbles reported previously [4]. Permanent strains were negligible (< 0.1%). The single specimen which survived into the 1400° C step had a severe surface reaction and crept a gross amount (1.6%) such that the test was suspended (Fig. 11).

Several additional experiments were done to address

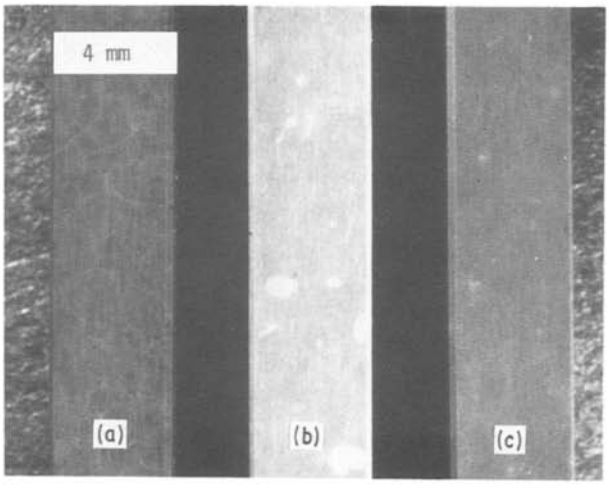


Figure 6 Surface appearance of three specimens: (a) as-machined, (b) 14.7 h at 1200° C, and (c) 1000 h at 1200° C.

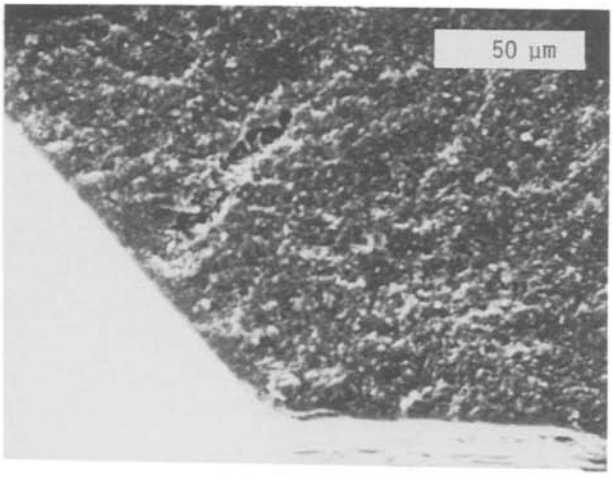


Figure 7 Fracture origin of a specimen which failed in flexural stress rupture at 1200° C at 22.2 h with 550 MPa stress.

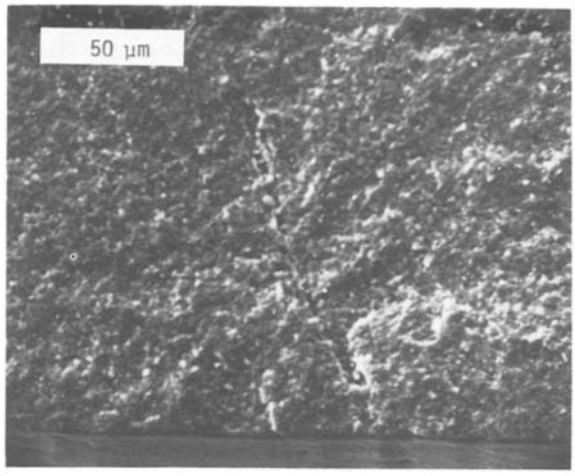


Figure 8 Failure origin of a specimen which failed at 13.5 h at 1200° C with 450 MPa stress.

specific questions. Silicon nitrides with yttria sintering aids are sometimes susceptible to intermediate temperature, oxidation related instability. A single specimen with 400 MPa stress was exposed to a modified STSR sequence, starting at 700° C and increasing at 24 h intervals to 800, 900 1000° C and finally 72 h at 1100° C. The specimen survived this sequence intact, had negligible strain (< 0.05%), and had a very high retained strength (632 MPa). Weight gain was negligible (0.0005 g) and the dark grey surface had a thin coherent oxide layer. A second specimen was loaded in stress rupture at a constant 1000° C with 450 MPa. It survived 1000 h and had negligible strain, very high retained strength (622 MPa), and negligible oxidation (0.0008 g). The surface was dark grey with a uniform coherent oxide layer. These two experiments indicate there is no intermediate temperature instability in this material.

A pretreatment of 200 h in air at 1300° C was applied to three specimens in the hope this would create a silica-rich surface to which metallic cations would congregate. This would presumably improve the refractoriness and creep resistance of the matrix [4]. Weight gains were significant, averaging 0.012 g, and the surfaces were a discoloured white glassy phase. Two of these specimens, with the surface layer intact, were then loaded in stress rupture at 1200° C at 500 and 550 MPa. Both failed on loading. The third specimen was exposed to the STSR 1000 to 1400° C sequence with 200 MPa. It failed at 26 h in the 1400° C step. The surface was severely blistered and discoloured. The fracture surface was glassy. These three experiments indicate the pretreatment was not effective in improving high-temperature stress rupture performance. This finding is similar to results obtained on hot-pressed silicon nitride with magnesia additive [12].

5. Discussion

The principal objective in the fabrication of this material was to use sintering aids that would go into solid solution with the silicon nitride, and to fully crystallize any residual grain-boundary phases. Residual glassy phases tend to degrade creep and static fatigue resistances. Detailed microscopy can be used to discern trace amounts of residual glass phase, such as demonstrated by Lewis *et al.* [2]. Ultimately, however, mechanical testing is necessary to assess the success in achieving the above goals. The results of the present study demonstrate excellent creep and static fatigue resistances up to 1200° C in air and indeed do substantiate the basic premises of the fabrication of this commercial material. It can be inferred that any residual glass phase, if present, is either dimensionally small or is isolated.

The original phase composition was principally β'-silicon nitride, a minor amount of α'-silicon nitride, some yttrium aluminium garnet (YAG) and some yttrium silicon oxide nitride ($YSiO_2N$). Elevated temperature exposure changed the composition as follows. Distinction will be made between analysis on powdered specimens, which reflects bulk composition, and surface analysis. The stress rupture specimen which survived 1000 h at 1000° C had appreciable surface cristobalite in addition to the original phases. The 1000 h at 1200° C survivors had identical bulk composition to the original phases, but the surface was significantly altered to β' and α'-silicon nitride with α-cristobalite, significant β-yttrium silicate ($Y_2Si_2O_7$), and one unaccounted peak (d = 0.1793 nm). YAG and $YSiO_2N$ phases were no longer present. The STSR specimen which failed at 2.2 h at 1300° C again had a bulk composition identical to the as-received material (even though the fracture surface appeared glassy). The surface was heavily oxidized and showed β' and α'-silicon nitride, appreciable cristobalite, yttrium

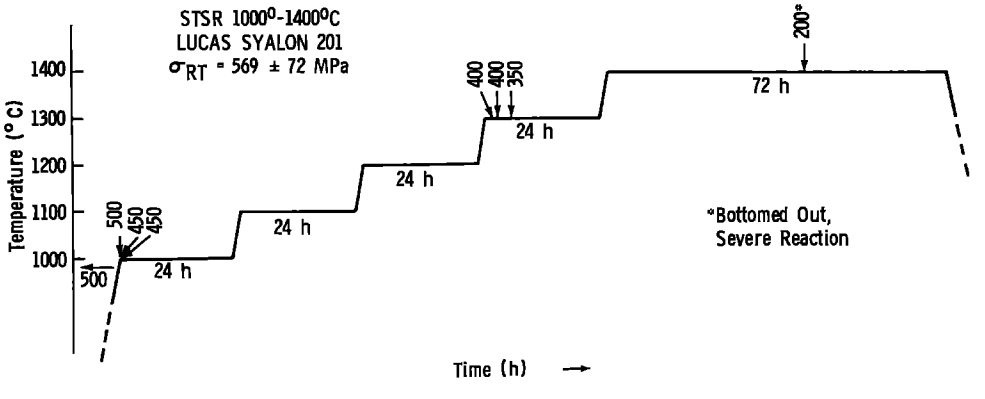
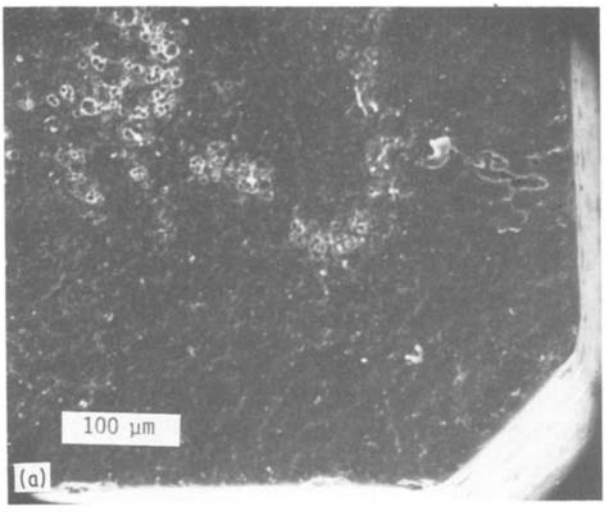
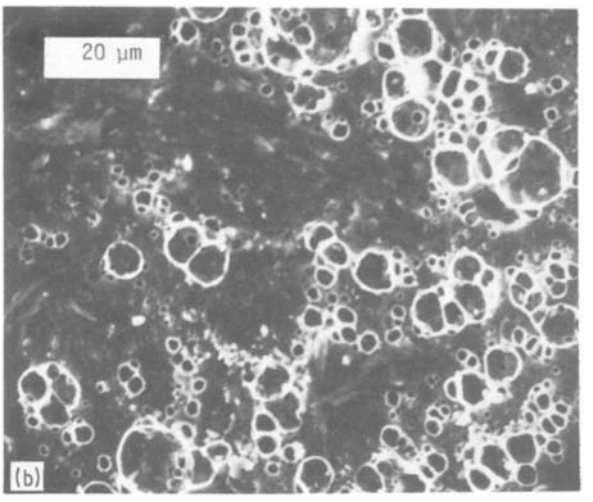


Figure 9 The STSR test sequence 11000–1400° C. Arrows left denote specimens which failed on loading at 1000° C. The remaining arrows show failure times of individual specimens. Arrow labels are the applied stress. σ_{RT} = 569 ± 72 MPa.





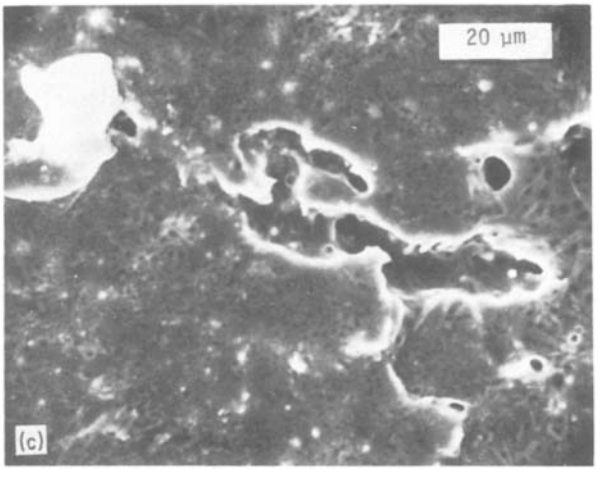


Figure 10 (a) Fracture surface of a STSR specimen which failed at 2.2 h in the 1300° C step. Applied stress was 400 MPa. (b) Closeup of the bubbles in the interior. (c) Closeup of the large pore in (a).

silicate and also the unidentified peak at 0.1793 nm. Once again, no trace of YAG or $YSiO_2N$ or Si_2N_2O were evident on the surface.

Finally, the specimens heat treated at 1300° C for 200 h had surface phases of β' and α'-silicon nitride, cristobalite, yttrium silicate but nine unidentified peaks (0.1793, 0.1806, 0.1733, 0.2245, 0.1682, 0.1584, 0.1574, 0.1493 and 0.1409 nm in order of intensity). Some of these peaks may be due to the yttrium silicate, but only if a severe preferred orientation existed. Some are probably due to an unclassified yttrium aluminium silicate. No silicon oxynitride was detected.

In summary, the interior remains essentially unchanged with exposure up to 1300° C in air. Surface compositions change considerably, initially forming cristobalite at 1000° C. At 1200° C the YAG and $YSiO_2N$ phases oxidize to yttrium silicate. Exposure at 1300° C leads to the same surface oxide products, as well as appreciable amorphous glass. An unidentified crystalline phase (possibly a yttrium aluminium silicate) forms with increased duration exposure at 1300° C. No silicon oxynitride was detected.

The formation of surface glassy and yttrium silicate phases at 1300° C and above in air is a critical issue since mechanical properties will begin to degrade as slow crack growth and creep phenomena commence. The glass formation is not surprising since a lowest melting point eutectic in the yttria–alumina–silica system occurs around 1350° C [4]. The sudden drop in load carrying capacity at 1300° C as shown by the STSR results, and the sudden change in fracture surface morphology from crystalline intergranular to a glassy appearance are consistent with this interpretation. The surprising aspect of the results is the high static fatigue and creep resistances of the material at 1200° C, which is very close to the 1350° C eutectic temperature in the yttria–alumina–silica system. Thus a safe upper use temperature for this material for long exposure under load is of the order of 1250° C. These findings are consistent with previous observations on the creep and oxidation resistances [2, 4].

Although mechanical properties are excellent at 1200° C, it is disappointing that even with a fully crystallized grain-boundary phase, that potential for rapid glass formation in oxidizing environments exists at 1300° C and above. This may prove an inherent limit to the creep and static fatigue resistances of materials in the sintered silicon nitride family with yttria and alumina additives. Silicon oxynitride, which is reported [4] to form a protective oxide surface layer that could permit higher temperature utilization, was not observed in the present study.

6. Conclusions

1. Syalon 201 retains high strength to 1200° C in air.
2. Oxidation, creep and static fatigue resistances are excellent to 1200° C in air, with no evidence of phase instability at intermediate temperatures.
3. The fully crystalline grain-boundary phases in the material oxidize at 1300° C and above, forming products which can become glassy. The maximum service temperature is thus about 1250° C. This may be generic to materials in the silicon family with yttria and alumina additives.

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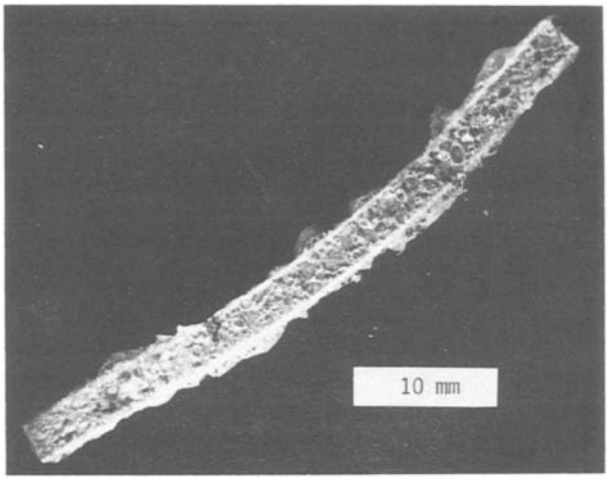

Figure 11 STSR specimen which survived to the 1400° C step. Creep strain is excessive and a severe surface reaction has occurred.

ations. The assistance of Mr M. Slavin in the test programme is appreciated. Dr A. Szweda contributed with helpful discussions.

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