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Effects of heat treatments on the creep properties of a hot pressed silicon nitride ceramic

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Effects of heat treatment in an argon atmosphere at high temperatures for varying times on the creep properties of a Y_2O_3–Al_2O_3 (8–2 wt%) doped hot pressed silicon nitride (HPSN) ceramic were investigated. It was observed from the creep measurements that higher temperature, i.e. ≥1360 °C, and longer time, i.e. ≥8 h, heat treatment in an argon atmosphere improved the creep properties, (e.g. secondary creep rate) of this material. Heat treatment at a lower temperature of 1300 °C and for a shorter time of 4 h did not change the creep behaviour. Improvement of the creep properties was related to the crystallization of an amorphous grain boundary phase by heat treatment. Secondary creep rate parameters of the as-received material: stress exponent, n (2.95–3.08) and activation energy, Q (634–818 kJ mol^{-1}), were in the range of values found by other investigators for various hot pressed silicon nitride ceramics.

1. Introduction

The microstructure of hot pressed silicon nitride (HPSN) ceramics consists of three phases: Si_3N_4 grains (mostly in the β form $\approx$90–95%) are the major crystalline phase; a secondary crystalline phase; and an amorphous third phase, which develops from the liquid phase during the sintering process. This amorphous phase, which is located between the grains, behaves viscously during high temperature (e.g. ≥1000 °C) application of this material and is the controlling mechanism of creep, subcritical crack growth and oxidation. The viscosity of the grain boundary phase, which decreases above 1200 °C, controls the creep behaviour of hot pressed silicon nitrides by a mechanism of grain boundary sliding and formation of cavities between the grain junctions [1–9]. The formation of cavities as a result of creep, and linking them to form microcracks ahead of the main crack, is the mechanism of subcritical crack growth [10–13]. It is believed that high temperature strength degradation of hot pressed silicon nitrides is caused by subcritical crack growth to form critical size cracks for spontaneous failure [14–20].

In order to be able to use the hot pressed silicon nitride ceramics for high temperature structural applications, the negative effects of the viscous amorphous phase should be eliminated. Since the additives which form the amorphous phase are prerequisites for densification and sintering, they must be included for fabrication of hot pressed silicon nitrides.

Crystallization of the amorphous phase can be achieved by various heat treatments [6, 21–24] and these can help to improve the high temperature mechanical properties of these materials [6, 23]. In a previous paper [21], the state of crystallization of the amorphous phase of the same material studied in this investigation was thoroughly examined by electron microscopy and X-ray diffraction techniques. It was shown there that thigh temperature and lengthy heat treatment in an argon atmosphere converted the amorphous grain boundary phase to various crystalline phases up to about 80 vol % of the as-received state.

In previous studies, in order to analyse the effects of heat treatment on the high temperature mechanical properties of this material various experiments were performed: controlled crack growth measurements [25], elastic constant measurements and fracture toughness measurements [26]. Expected improvements of the various mechanical properties of this material due to crystallization of the amorphous phase were very small. The controlled crack growth experiments were relatively complex, which resulted in experimental uncertainties and also error was involved during numerical evaluation of the crack resistance curves. As for these, controlled crack growth experiments were not sensitive enough to evaluate the effects of heat treatment on the high temperature mechanical properties of this material. Similarly, fracture toughness measurements did not respond well to the expected improvements due to the nature of these measurements (i.e. since the fracture toughness was measured by fast fracture, the effect of the grain boundary phase was irrelevant when the crack velocity was so high; at fast fracture the fracture-path would be transgranular in polyphase polycrystalline ceramics).

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TABLE I Manufacturer's data of the starting powder

Chemical analysis of the Si_3N_4 powder

Element	N_2	O_2	C	Ca	Al	Fe	Mg	Si
Wt %	37.9	1.9	0.3	0.25	0.22	0.2	0.08	59.15

Grain size

97% < 10.6μm, 50% < 1.6μm, 6% < 0.6μm

Specific surface area 6.1 $m^2 g^{-1}$

Modification

96% α-Si_3N_4, 4% β-Si_3N_4

Additives

8 wt % Y_2O_3, 2 wt % Al_2O_3

TABLE II Heat treatment in argon atmosphere

Sample	Temperature (°C)	Time (h)
A	1400	4
B	1400	8
C	1400 + 1300	10 + 10
D	1300	40
E	1360	30

It was observed that the effect of heat treatment on the elastic constants was also very low, (i.e. all the heat treated and as-received materials had similar elastic constant values).

In order to observe the effects of heat treatments on the high temperature mechanical properties in larger amounts, creep measurements were performed with all heat treated and as-received materials. The reason for performing creep measurements was that the creep data would be quite accurate due to constant loading at constant temperature for a long interval of time. Different materials would respond differently for the same constant load and constant temperature condition of creep, so that the effects of heat treatment could be observed in larger amounts.

2. Experimental procedure

2.1. Material

The material of this investigation was an Y_2O_3–Al_2O_3 doped hot pressed silicon nitride ceramic, which was produced by ESK, Kempten, Germany. Data on the starting powders before fabrication are presented in Table I. Strength was measured at room temperature by three-point bending. $\sigma_f = 923 \pm 51$ MPa, and the density was measured by immersion in CCl_4, $\rho = 3.28\ g\,cm^{-3}$. Other mechanical properties of this material, i.e. crack resistance curves, fracture toughness and elastic constant values, were previously determined [25, 26]. Heat treatments for the crystallization of the amorphous phase were performed in an argon atmosphere; details of the heat treatments are given in [25]. A complete list of all the heat treated materials for creep is presented in Table II with the assigned labels.

2.2. Creep measurements

Creep apparatus, experimental techniques and the evaluation of the creep parameters are discussed in detail in [27]; here some major points are summarized. Heating of the specimens to the desired measurement temperature was achieved in a well insulated resistance oven, and the temperature was measured with a PtRh30–PtRh6 thermoelement which was located close to the specimen. The measurements were controlled by a computer, which digitized the creep displacement data as a function of time at constant load and temperature. From these data a computer program plotted various creep curves: strain rate versus strain and strain versus time. Measurements were performed in a four-point bend system, with SiC ceramic rods as the load transferring points. For these measurements, upper and lower span lengths of the four-point bend system were 10 and 30 mm, respectively. Bending displacements were measured by an Al_2O_3 rod which was located at the centre of the bottom surface of the specimens. The dimensions of the specimens were $3 \times 4 \times 35\ mm^3$ with height W, thickness B, and length l, respectively. The edges of the tension sides of the specimens were first ground up to 50μm, and then these sides were polished up to 1 μm with diamond paste before measurements in order to avoid flaw or microcrack induced creep. The measurements were performed in air. A low heating rate of 5 °C min^{-1} for measurement temperature and cooling down to room temperature, was applied to the oven in order to avoid thermal shock effects on the test apparatus. Nearly constant stresses were achieved by loading the specimens statically by constant weights. In order to evaluate the stresses and strains at the mid point on the tension side of the specimens, linear–elastic formulations were used for four-point bending [27]. To characterize the creep behaviour of the as-received material, the secondary creep rate (steady state creep) formula

$$\dot{\varepsilon} = A\,\sigma^n \exp(-Q/RT)$$

was used to evaluate the creep parameters n and Q. In general the preexponential term, A, and the activation energy term for creep, Q, are functions of stress, temperature, structure and environment [1]. The structural term includes grain size, dislocation density and purity. In the above formula R is the universal gas constant and T is the absolute temperature. From this equation at constant temperature the stress exponent

$$n = \partial \ln \dot{\varepsilon} / \partial \ln \sigma$$

and similarly at constant stress the activation energy

$$Q = -R \partial \ln \dot{\varepsilon} / \partial (1/T)$$

are obtained, with the assumptions that A and Q are constants.

In order to find the optimum conditions for creep, primary measurements were done with the as-received specimens at 100 MPa stress and at temperatures of 1400 and 1250 °C. At 1400 °C the creep rate was very high, measurement lasted only about 30 min, at 1250 °C the creep rate was relatively very low, measurement lasted more than a day up to the fracture of the specimens. After these results, in order to have all the creep regimes (i.e. primary, secondary and tertiary) and for practical reasons (i.e. to finish the measurement in an optimum time), it was decided to perform the measurements at 100 MPa constant stress and 1300 °C constant temperature for all the heat treated and as-received specimens to analyse the effects of heat treatment on the creep behaviour of this material. Also in order to characterize the material, stress–change measurements at 1300 °C and temperature–change measurements at 100 MPa were performed with the as-received specimens to obtain the stress exponent, n, and activation energy, Q, values respectively.

3. Results and discussion

Diffusional processes and dislocation motion are not observed in Si_3N_4 at temperatures below 1700 °C. The high temperature creep behaviour of HPSNs has generally been interpreted in terms of deformation processes depended on the presence of an intergranular silicate phase, i.e. amorphous phase, containing additives and impurity elements, Mg, Al, Y, Ca, Na, K [1, 2]. The viscous amorphous intergranular phase, of which the melting point is much influenced by alkaline (e.g. Li, K, Na, Ca) oxides, controls the creep behaviour of HPSNs. Addition of about 0.06–0.3 wt% CaO has the most important effect on the viscosity of the amorphous phase [1, 3]; the material of this investigation contains 0.25 wt % Ca in the starting powder, see Table I. The mechanism of creep in the hot pressed silicon nitrides is grain boundary sliding, accommodated by cavity and microcrack formation, with viscous amorphous phases affecting the ease of sliding and microcrack development [2].

The creep measurements were performed with heat treated and as-received specimens with the aim of further understanding (see also previous work [21, 25, 26]) the crystallization of the amorphous phase and its influence on the mechanical properties of this material. In Figs 1 and 2 the results of all the creep measurements are presented for strain rate versus strain and strain versus time, respectively. It is shown in Figs 1 and 2 that all the creep rate regimes: primary (state I), secondary (stage II = steady state) and tertiary (stage III) were observed from all the creep measurements performed with the heat treated and as-received specimens at 1300 °C and 100 MPa. At stage I, initial deformation was rapid, lasting about 30 min. The stage I regime was followed by a steady state, nearly constant, creep rate. In stage II the strain rate was relatively low, but the specimens deformed most in this stage; about 70% of the total deformation occurred. Finally, in stage III the creep rate increased rapidly up to the fracture point of the specimens. All of the specimens were deformed by about 2.8% strain. Pictures of a typical crept specimen (e.g. heat treated at 1400 °C for 10 h and 1300 °C for 10 h) and an original specimen are shown in Fig. 3. This specimen crept more than 3% strain. The colour of the specimens changed from dark grey to almost white after creep measurement. This colour change is typical of this material at high temperatures, e.g. ≥ 1200 °C for long heating times in an oxidizing atmosphere.

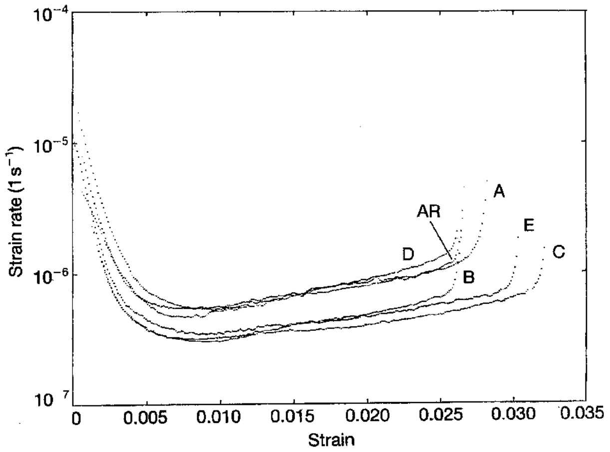

Figure 1 Creep curves (strain versus strain rate) for heat treated, A–E and as-received, AR specimens at 1573 K, 100 MPa.

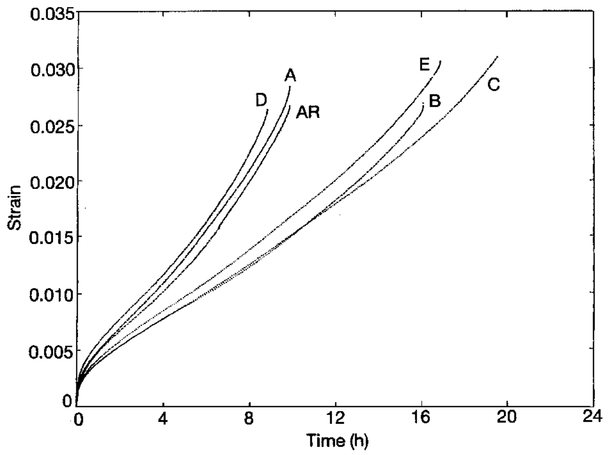

Figure 2 Creep curves (time versus strain) for heat treated, A–E and as-received, AR specimens at 1573 K, 100 MPa.

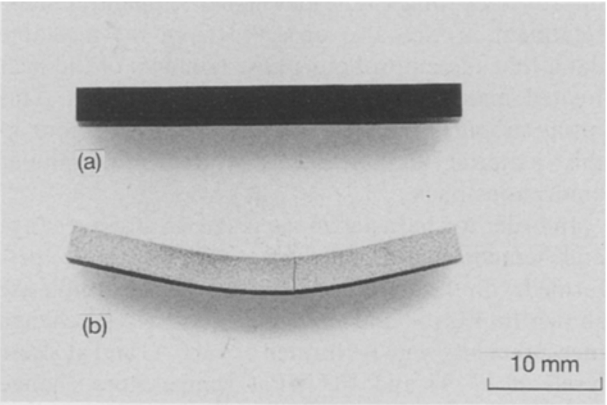

Figure 3 An original specimen (a) and a crept specimen (b) of heat treatment C (1400 °C, 10 h + 1300 °C, 10 h).

The important result of the creep measurements was improvement of the steady state creep rate after heat tratment. Most of the heat treatments B (1400 °C, 8 h), C (1400 °C, 10 h + 1300 °C, 10 h) and E (1360 °C, 30 h) resulted in better creep properties (i.e. lower creep rate in the steady state regime) than the as-received material (Figs 1 and 2). This was due to

TABLE III Secondary (stationary) creep rate and amorphous phase contents of the as-received (AR) and heat treated samples

Sample	Secondary creep rate ($\times 10^{-7} s^{-1}$)	Amorphous phase content (vol %)
AR	6.9	10.93 ± 2.10
A	6.8	–
B	5.4	–
C	5.1	2.70 ± 1.21
D	6.6	–
E	4.8	2.59 ± 1.45

crystallization of the amorphous grain boundary phase after heat treatment [21]. Transmission electron microscopy and energy dispersive X-ray microanalysis determined that the grain boundary phase in the as-received material was mostly amorphous, and after heat treatment it became predominantly crystalline [21]. Some of the heat treated specimens, did not show any improvement in the creep properties. Heat treatment specimens A (1400 °C, 4 h) and D (1300 °C, 40 h) showed similar creep behaviour to that of the as-received material. The reasons for this could be relatively short heat treatment time (4 h) in the case of A, and for D, relatively low heat treatment temperature (1300 °C); probably, reflecting insufficient crystallization of the amorphous grain boundary phase in comparison to that of the other heat treatment samples (i.e. B, C and E).

A summary of the secondary creep rates of the as-received and each of the heat treated specimens is given in Table III. In that table amorphous phase contents are also shown from [21] for some of the specimens, to correlate creep behaviour with amorphous phase contents. It is observed from the table that the creep behaviour (e.g. secondary creep rate) was improved by longer time and higher temperature heat treatment. It was also observed from the available data, that the amorphous phase contents of the heat treated materials decreased in large amounts. This result supports the idea that the creep behaviour of this material is controlled, by the intergranular amorphous phase.

In order to characterize the material, stress–change and temperature–change measurements were performed with the as-received specimens. The results are shown in Figs 4 and 5, respectively. Stress–change measurements were performed at 1300 °C and at stress levels of 77, 94 and 103 MPa. Temperature–change measurements were at 100 MPa stress and at temperature levels of 1250, 1300 and 1275 °C. From the stress–change measurements, the value of the stress exponent, $n = 2.95$–3.08, and from the temperature–change measurements, the value of the activation energy, $Q = 634$–818 kJ mol^{-1}, were calculated. These values support the creep mechanism of this material, which is controlled by the amorphous grain boundary phase. Similar values for the stress exponent, n[1–5, 8, 9, 28, 29], and for the activation energy, Q [1–3, 8, 9, 28, 29], were reported by others for various hot pressed silicon nitrides.

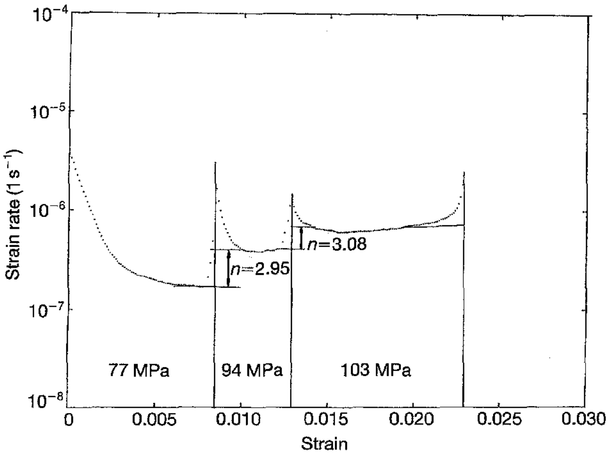

Figure 4 Strain rate versus strain measurement at 1300 °C for an as-received material.

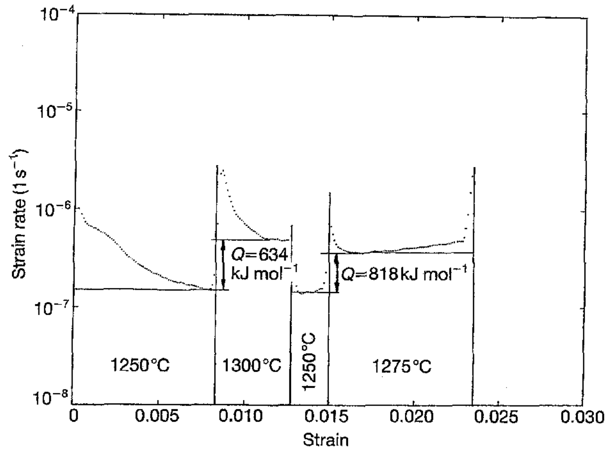

Figure 5 Strain rate versus strain measurement at 100 MPa for an as-received material.

4. Summary

The effects of argon atmosphere heat treatment on the four-point bend creep behaviour of an 8 wt % Y_2O_3 + 2 wt % Al_2O_3 doped hot pressed silicon nitride (HPSN) ceramic were investigated.

Positive effects of heat treatment on the creep behaviour of this material have been observed following longer time and higher temperature heat treatment. These heat treatment specimens had better creep resistance, i.e. lower secondary creep rate, than that of the as-received material. This improvement of the creep behaviour was due to crystallization of an amorphous phase by heat treatment [21].

It was observed in [21] that heat treatment achieved the formation of crystalline grain boundary phases in most of the large intergranular pockets, but an amorphous phase still remained in the small intergranular pockets and in thin intergranular regions. The degree of crystallization was dependent on the time and temperature of the heat treatment. As a result, lower temperature and shorter time heat treated specimens did not show any improvement in the creep behaviour of this material.

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