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Oxidation of sintered silicon nitride

Part II *Mechanical properties*

CHUAN HE*, LING WANG, JIANGUANG WU
Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

The influence of oxidation at 1200 °C in air for up to 1000 h on the mechanical properties of two Si_3N_4–Y_2O_3–Al_2O_3 materials with different Y_2O_3/Al_2O_3 ratios, Material A (Si_3N_4–13.9 wt% Y_2O_3–4.5 wt% Al_2O_3) and Material B (Si_3N_4–6.0 wt% Y_2O_3–12.4 wt% Al_2O_3), was investigated. The oxidation significantly improves the high-temperature strength and fracture toughness of both materials, but more for Material A. After oxidation, Material A at 1300 °C retains 93% of its room-temperature strength and 87 % higher than that before the oxidation. The oxidation has a different effect on the room-temperature K_{IC} for the two materials. The room-temperature Weibull modulus of Material A decreased by more than half while the 1200 °C Weibull modulus decreased slightly after oxidation. The annealing treatment prior to oxidation had no effect on the high-temperature strengths of the materials after oxidation. The effect of oxidation on mechanical properties is discussed in terms of the microstructure change of the materials.

1. Introduction

The oxidation resistance of Si_3N_4 material is an important factor in its application at high temperature in oxidizing environments. Si_3N_4 is thermodynamically unstable in an oxidizing atmosphere at high temperatures and will react with oxygen. The phase composition and microstructure of Si_3N_4 ceramics changes during oxidation, resulting in changes in the mechanical properties of the materials.

Maeda *et al.* [1] investigated the oxidation behaviour of hot-pressed Si_3N_4 with Al_2O_3–Y_2O_3 additives at 1200 °C in flowing air for up to 3000 h. They found that the room-temperature strength of Si_3N_4 decreased with oxidation time up to 750 h, as the surface roughness increased during the same period. Subsequently, the strength changed little, although the surface roughness decreased. Tomlinson and Stephen [2] also observed the room-temperature reduction for sintered Si_3N_4–5.5 wt % Al_2O_3–5.0 wt % Y_2O_3 after 24 h oxidation at 1200 °C in air. Furthermore, the Weibull modulus decreased by more than half, after oxidation. Meada *et al.* [3] reported that for hot-pressed and sintered Si_3N_4 materials with almost the same amount of Al_2O_3–Y_2O_3 additives, the room-temperature strengths decreased during the first few hundred hours of oxidation at 1300 °C in flowing air, while for another hot-pressed Si_3N_4 material with a lower amount of Al_2O_3–Y_2O_3 additives, the strength increased up to 360 h, and then decreased up to 1000 h.

In previous work [4], the influence of the oxidation at 1200 °C in static air for up to 1000 h on the phase composition and microstructure of two sintered Y_2O_3–Al_2O_3-doped Si_3N_4 materials with different Y_2O_3/Al_2O_3 ratios was investigated. It was found that the weight gain had a linear relation with oxidation time for the first 2 h, which indicates that the oxidation during the first 2 h is active. Then the oxidation became passive but deviated from the parabolic law. This deviation was also observed by Pomeroy and Hampshire [5]. There was no difference in weight gain between the two materials. Both the oxidation reactions on the surface and crystallization of grain-boundary glassy phase in the bulk of the specimens occurred during oxidation. It was also found that the annealing treatment prior to oxidation has no effect on the phase compositions either on the surface or in the bulk of the specimens after oxidation. In this paper the influence of oxidation on the mechanical properties of the two materials studied in the previous work [4] is presented and discussed through the change in microstructure of the materials during oxidation.

2. Experimental procedure

2.1. Starting materials

The materials used were two sintered Y_2O_3–Al_2O_3-doped Si_3N_4: Material A had a composition of Si_3N_4–13.9 wt % Y_2O_3–4.5 wt % Al_2O_3, and Material B was Si_3N_4–6.0 wt % Y_2O_3–12.4 wt % Al_2O_3. The processing and phase composition of the materials were described elsewhere [4]. The as-sintered specimens were ground and polished to 7 μm diamond paste finish. The dimensions of as-polished specimens were 3 mm × 4 mm × 36 mm for the strength test and

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* *Present address*: Ceramic Division, National Institute of Standards and Technology, Gaithersburg, MD20899, USA.

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4 mm × 8 mm × 36 mm for fracture toughness measurement. The as-polished specimens were cleaned in an ultrasonic bath and then put into a cool furnace. The temperature was then increased to 1200 °C and the oxidation time began. At different time intervals some of the specimens were pulled out and cooled in air. These specimens were then used to measure strength and fracture toughness without any surface treatment.

Three-point bending strength was measured at different temperatures in air. For the room-temperature test the crosshead speed was 0.4 mm min^{-1} and the span was 30 mm. The high-temperature strength of specimens was measured with an SiC fixture in an SiC furnace. Loading began 5 min after the specimen was put into the furnace. The loading speed for high-temperature strength test was 241 N min^{-1} and the span was 30 mm.

Fracture toughness, K_{IC}, was measured using the single-edge-notched beam (SENB) method. The specimens were notched to the half-depth of the specimen by a diamond saw of 0.25 mm width. The test was conducted using the same fixtures as in the strength test with different crosshead speeds or loading speeds. The crosshead speed for the room temperature test was 0.06 mm min^{-1} and the loading speed for the high-temperature test was 130 N min^{-1}. The span for the K_{IC} test was also 30 mm.

Annealing treatment is a useful technique to improve the high-temperature strength of Si_3N_4 materials, especially for sintered Si_3N_4 which has a relatively large amount of grain-boundary glassy phase. Because the glassy phase will crystallize during annealing, the phase composition of the material changes after treatment. For application of Si_3N_4 materials at high temperature in oxidizing environments, this treatment may not be necessary because the materials under such conditions are undergoing a kind of annealing. To study the effect of the annealing technique on the mechanical properties of the materials at high temperature in an oxidizing environment, some specimens of both materials were annealed at 1300 °C in a nitrogen atmosphere for 4 h prior to oxidation. The strength at 1200 °C of the annealed specimens as a function of oxidation time was measured. No room-temperature strength of the annealed samples was measured, because the annealing treatment affects only the high-temperature strength of the material.

3. Results

3.1. Strength

The strength data are illustrated in Figs 1–4. The room-temperature strength of Material A decreases drastically during the first 2 h oxidation (from 770 MPa to 546 MPa) and then levels off as the oxidation continues up to 1000 h (Fig. 1). The 1200 °C strength of Material A, however, increases significantly during the first 2 h oxidation (from 309 MPa to 473 MPa) and then also levels off up to 1000 h. For Material B, the room-temperature strength increases slightly during the first 2 h (Fig. 2). With increasing oxidation time, the strength of Material B decreases very slowly up to 1000 h. The 1200 °C strength of Material B is improved by oxidation for the first 15 h and then does not change up to 1000 h.

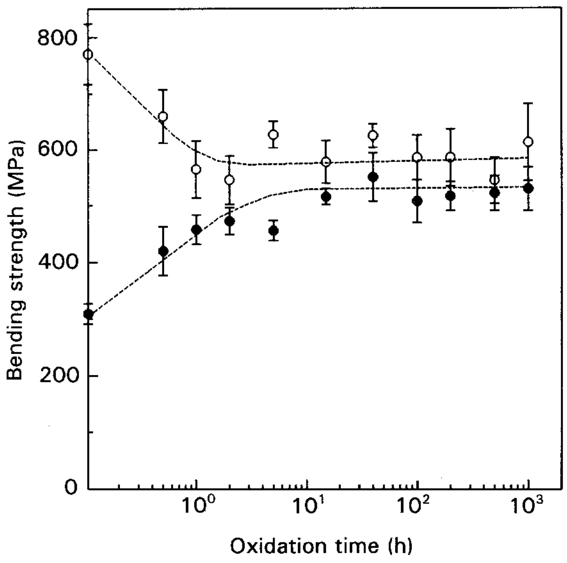

Figure 1 The strength of Material A as a function of oxidation time at (○) room-temperature, and (●) 1200 °C. The oxidation was carried out at 1200 °C in air.

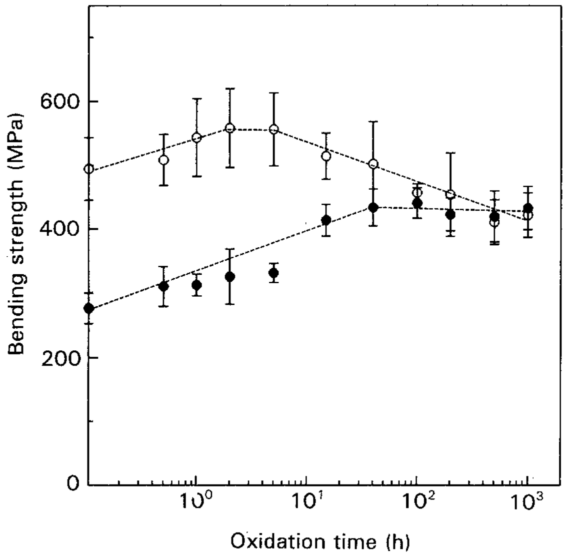

Figure 2 The strength of Material B as a function of oxidation time at (○) room-temperature, and (●) 1200 °C. The oxidation was carried out at 1200 °C in air.

Figs 3 and 4 show the strengths of both materials as a function of temperature before and after oxidation. Before oxidation the strength of Material A degraded even below 1000 °C (Fig. 3). When the temperature was above 1100 °C the strength decreased rapidly but stopped dropping between 1200 and 1300 °C. After oxidation, the strength of Material A, which at room temperature is a little lower than that before oxidation, did not change up to 1100 °C and retained 93 % of its room-temperature value at 1300 °C. After oxidation, the strength of Material A was 570 MPa at 1300°C, which is 87 % higher than that before oxidation. For Material B (Fig. 4) the strength before oxidation deteriorated drastically from 1100–1200 °C and then did not change between 1200 and 1300 °C. However, after oxidation, the strength of Material B

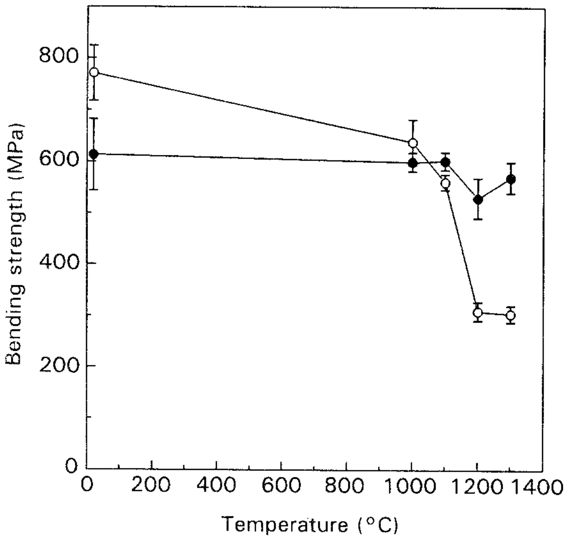

Figure 3 Bending strength of Material A versus temperature (○) before and (●) after oxidation at 1200 °C in air for 1000 h.

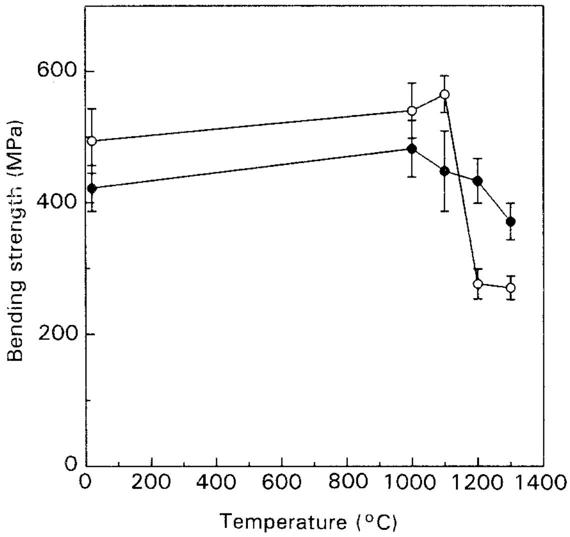

Figure 4 Bending Strength of Material B versus temperature (○) before and (●) after oxidation at 1200 °C in air for 1000 h.

decreased much more slowly than it did before oxidation. The room-temperature strength of Material B was also lower than that before oxidation.

3.2. Fracture toughness

Fig. 5 shows the room-temperature fracture toughness, K_{IC}, as a function of oxidation time. For Material A the toughness decreased from 6.5 MPa $m^{1/2}$ at the beginning of oxidation to 3.8 MPa $m^{1/2}$ after 15 h oxidation and then continued to increase up to 1000 h. The fracture toughness of Material B rose slightly from the beginning to 100 h and then decreased very slowly up to 1000 h.

Fig. 6 shows the fracture toughness of Material A as function of temperature. Before oxidation the toughness degradation began at 1200 °C. After oxidation, the toughness did not deteriorate up to 1200 °C.

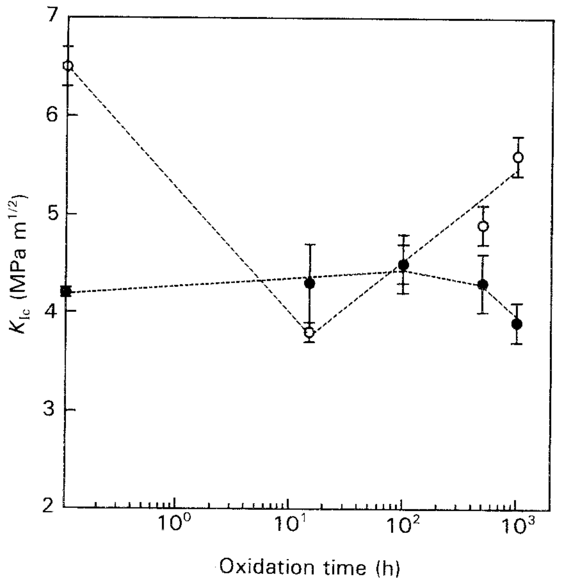

Figure 5 Room-temperature fracture toughness as a function of oxidation time. The oxidation was carried out at 1200 °C in air. (○) Material A, (●) Material B.

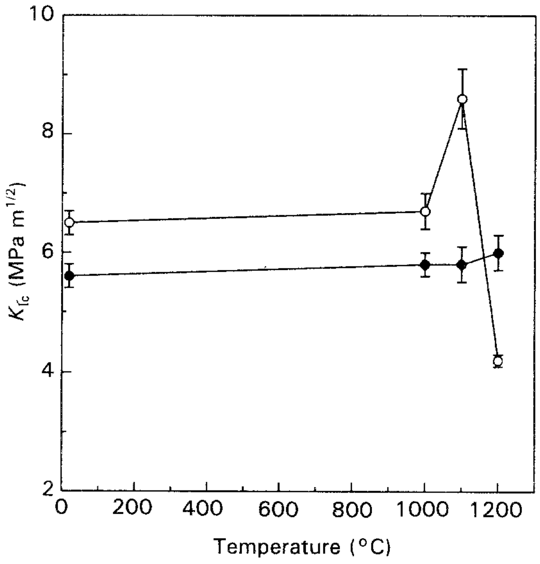

Figure 6 Fracture toughness of Material A as a function of temperature (○) before and (●) after oxidation. The oxidation was carried out at 1200 °C in air for 1000 h.

3.3. Weibull modulus

Fig. 7 shows the effect of the oxidation on the Weibull modulus of Material A at room-temperature and 1200 °C. The Weibull modulus is calculated from the equation [6]

$$P = 1 - \exp[-(\sigma - \sigma_u)/\sigma_o]^m \quad (1)$$

where P is the probability of failure, σ the applied stress (strength), σ_u the threshold stress, and σ_0 the characteristic stress. σ_u is assumed to be 0. The total number of strength data for each calculation of m is 18. Before oxidation, the Weibull modulus was 15.1 at room temperature and 16.7 at 1200 °C. After oxidation, the room-temperature Weibull modulus decreased to 7.3, while the 1200 °C Weibull modulus decreased slightly to 14.3.

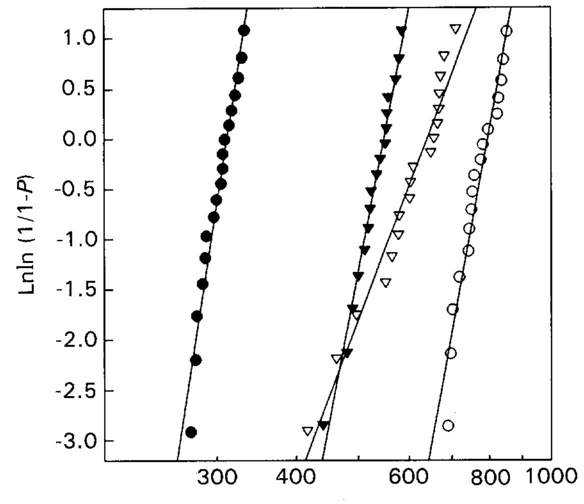

Figure 7 Effect of the oxidation on Weibull moduli of Material A. The oxidation was carried out at 1200 °C in air for 1000 h. (○) Before oxidation, room-temperature strength, $m = 15.1$, $\sigma = 771 \pm 53$ MPa; (●) before oxidation, 1200 °C strength, $m = 16.7$, $\sigma = 309 \pm 18$ MPa; (▽) after oxidation, 1200 °C in air for 1000 h, room-temperature strength, $m = 7.3$, $\sigma = 613 \pm 69$ MPa; (▼) after the oxidation, 1200 °C strength, $m = 14.3$, $\sigma = 530 \pm 39$ MPa.

3.4. Effect of heat treatment

Some specimens of both materials were annealed prior to oxidation. The 1200 °C strengths of these annealed specimens as a function of oxidation time are shown in Fig. 8. The strength of annealed Material A increased in the first few hours and then did not change up to 1000 h. The increase in the strength of annealed Material A is less than that of Material A. The 1200 °C strengths of both annealed Material A and unannealed Material A are on the same level after oxidation. For annealed Material B, only the strengths before and after oxidation were measured. The annealed Material B had a slightly higher 1200 °C strength than unannealed Material B before oxidation, but both were the same after oxidation.

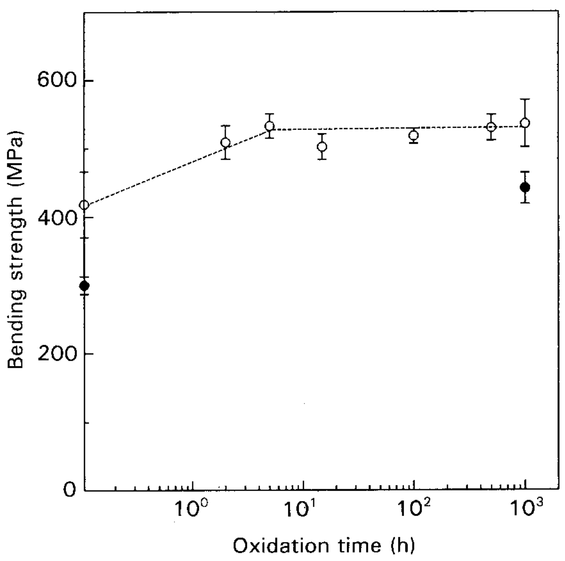

Figure 8 The 1200 °C strength of annealed Materials A and B as a function of oxidation time. The oxidation was carried out at 1200 °C in air. (○) Material A, (●) Material B.

4. Discussion

As discussed in the previous paper [4] the oxidation of the materials in the present work is active in the first 2 h. During this period, the Si_3N_4 grains on the surface react with oxygen in air and the resultant SiO_2 reacts with grain-boundary glass to form needle-like $Y_2Si_2O_7$ grains [4]. The morphology and stress on the surface of the samples change drastically due to the above reactions and the volume change associated with the reactions. Room-temperature strength is dominated by surface condition. During the active period of the oxidation, the amount of oxidation product, SiO_2, is insufficient to cover the whole surface to form a protective layer. The surface of the specimens becomes rough due to the oxidation, and the strength decreases rapidly. When the SiO_2 covers the whole surface of the specimens the oxidation become passive and the surface becomes smooth due to the protective layer. Although the surface roughness was not measured in the present work, Maeda *et al.* [1] reported that the surface roughness of hot-pressed Si_3N_4 with Al_2O_3–Y_2O_3 additives increased at the beginning of oxidation under similar conditions and then decreased with increasing oxidation time. With increasing oxidation time the surface condition changes little and the strength does not change any more. The high-temperature strength of the materials is controlled by the grain boundary and is not sensitive to the surface condition. The 1200 °C strengths of both materials increase during the beginning of the oxidation. Crystallization of intergranular glassy phase at the oxidation temperature makes a contribution to most of the improvement in the 1200 °C strength. When the crystallization is completed the 1200 °C strengths of both materials stop increasing. This strength can be maintained up to 1000 h. Therefore, as long as the protective layer on the surface is not removed during oxidation, the microstructure in the bulk of the materials will change little. Heat treatment of Material A prior to oxidation improves the 1200 °C strength, indicative of the importance of the crystallization. During oxidation, the strength of annealed Material A still increases but to a lesser extent than the strength of unannealed Material A, reflecting the continuation of the crystallization and the relaxation of the internal stress resulting from the crystallization. Another possible contribution to the improvement of high-temperature strength during the oxidation comes from the decrease in impurities level inside the materials. It has been suggested that the diffusion of impurities outward from the bulk of samples to the surface occurs during oxidation [7, 8]. This process reduces the concentration of impurities in the bulk of the materials and improves the thermal resistance of the grain boundary, and hence the high-temperature strength of the materials [8]. It is noted, however, that in the present work, the 1200 °C strength of Material A does not change after 15 h oxidation and 100 h for Material B. This suggests that the outward diffusion of impurities is a very slow process.

From Figs 3 and 4, it can be seen that before oxidation the strength decreases before 1000 °C for Material A and after 1100 °C for Material B. The strength of Material B degrades more slowly than Material A. Material B, which has lower Y_2O_3/Al_2O_3 ratio than Material A, retains 55 % of its room-temperature strength at 1300 °C, while Material A only retains 39 % of its room-temperature strength. It is believed that aluminium in the material facilitates liquid-phase sintering by lowering the viscosity of the intergranular glassy phase at elevated temperature [9, 10]. However, in present work, the density of Material A is higher than that of Material B, although both have the same amount of additives [4]. The phase diagram of Y_2O_3–Al_2O_3–SiO_2 [11] shows that when the ratio of Al_2O_3/Y_2O_3 is small, increase of Al_2O_3 will bring the composition closer to the eutectic point, making it easier to sinter. When the Al_2O_3/Y_2O_3 ratio is larger than a certain value (eutectic composition), however, the increase of Al_2O_3 will produce a composition further from the eutectic point. The Al_2O_3/Y_2O_3 ratio in Material B is much higher than in similar materials from other works [10, 12, 13], probably the reason why the higher ratio of Al_2O_3/Y_2O_3 in Material B results in a lower density. Although both materials have the same amount intergranular glassy phase (if the solution of Al^{3+} in Si_3N_4 is not taken into account), the viscosity of the intergranular glassy phase of Material A will decrease more rapidly than that of Material B. This is justified by the strength deterioration with temperature before oxidation (Figs 3 and 4). The slowing down of the deterioration of the strength from 1200–1300 °C may contribute to the crystallization of the grain-boundary glassy phase during the 5 min heating before loading in the high-temperature strength test.

After oxidation, the strength of Material A decreases slightly up to 1300 °C, while the strength of Material B decreases after 1000 °C, but much more slowly than it does before the oxidation. In a previous work [14] it was found that a high concentration of Al^{3+} in Si_3N_4–Y_2O_3–Al_2O_3 materials retards the crystallization of the intergranular glassy phase, consistent with Ahn and Thomas's work [12]. This is partly due to the higher viscosity of the grain-boundary glassy phase with higher Al^{3+} concentration [14]. The intergranular glassy phase crystallizes more in Material A than in Material B during oxidation [4], indicating that less glassy phase is left in Material A than in Material B after oxidation. This is responsible for the higher high-temperature strength of Material A after oxidation.

As shown in Figs 1, 2 and 8, the 1200 °C strengths of both unannealed and annealed Material A are the same after 10 h oxidation, although the strength of the annealed Material A is higher than that of the unannealed Material A before oxidation. In addition, there is no difference in 1200 °C strength between the annealed and unannealed Material B after oxidation. A question arises: is the heat treatment necessary for Si_3N_4 materials for high-temperature application? Heat treatment can improve the high-temperature strength of Si_3N_4 materials [9]. The present study suggests that, as far as the mechanical properties are concerned, it is not necessary to anneal Si_3N_4 materials before they are used at high temperature in an oxidizing environment. It is required, however, that the temperature be high enough for the intergranular glassy phase to crystallize.

Previous work [4] showed that the weight gains of Materials A and B are the same in spite of their composition difference. From Figs 1 and 2 it can be seen that the changes in both room- and high-temperature strengths of Material A are different from those of Material B during oxidation. This suggests that the weight gain may not be an appropriate parameter by which to judge the oxidation resistance of Si_3N_4 materials.

The room-temperature toughness of both materials in the present work should not be affected by the surface condition of the specimen because a notch was used to simulate a crack in the specimens after the specimens were pulled out of the furnace. Lee and Hilmas [15] found that the dislocation density in Si_3N_4 grains increased during the crystallization of the grain-boundary glassy phase due to the stress induced by the volume change during crystallization and then decreased as further annealing released the stress. This internal stress change may be one of the reasons for the change in K_{IC} with oxidation time. For the first 15 h the stress resulting from the volume change during crystallization causes a decrease in the fracture toughness. When the crystallization is complete, the stress is released with increasing time and the fracture toughness increases. Other possible factors are the thermal mismatch stress between matrix and grain-boundary phase, the strain energy associated with the crystallization of the grain-boundary glassy phase [9], and the effect of the composition of the grain-boundary phase on the fracture energy of the materials. The improvement in the high-temperature K_{IC} of Material A after oxidation (Fig. 6), however, is an obvious result of the crystallization of intergranular glassy phase during oxidation.

The decrease of the room-temperature Weibull modulus during oxidation contributes to the change of the surface condition of the specimens due to the oxidation reactions. The room-temperature Weibull modulus of Material A is 15.1 before oxidation, but reduces by more than half to 7.3 after oxidation. The percentage of the reduction in the room-temperature Weibull modulus is almost the same as in Tomlison and Stephen's work [2]. The pores left by the escape of nitrogen on the surface [4] and the thermal mismatch stress between the oxidation products and the matrix are believed to be responsible for the decrease. The Weibull modulus is higher at high temperature than at room temperature, because the strength is less sensitive to the surface condition at high temperature. This is more obvious for the Weibull moduli after oxidation. Oxidation, therefore, has a greater effect on the room-temperature Weibull modulus than on the high-temperature Weibull modulus.

5. Conclusion

The effect of oxidation in air at 1200 °C on the mechanical properties of two Si_3N_4 materials with different Y_2O_3/Al_2O_3 additive ratio was studied. For Material

A, which has a higher Y_2O_3/Al_2O_3 ratio, the room-temperature strength decreases drastically in the first 2 h oxidation while the 1200 °C strength increases in this period. The change of surface condition of the specimens due to oxidation is responsible for the decrease of room-temperature strength, and the crystallization of intergranular glassy phase makes a contribution to the improvement of high-temperature strength. With increasing oxidation time, the surface condition changes little and the crystallization is completed and therefore, both strengths change little up to 1000 h. For Material B, which has a lower Y_2O_3/Al_2O_3 ratio, the room-temperature strength increases at the beginning of oxidation and then decreases very slowly with oxidation time. The 1200 °C strength increases in the first 40 h and then changes little with oxidation time up to 1000 h. The fracture toughness of Material A decreases in the first 15 h oxidation and then increases slowly with oxidation time. However, the fracture toughness of Material B remains constant up to 100 h and then decreases with oxidation time. The oxidation reduces the room-temperature strength but improves significantly the high-temperature strength and fracture toughness of both materials, though more for Material A. After oxidation, Material A retains 93 % of the room-temperature strength at 1300 °C and is 83 % higher than that before oxidation. The fracture toughness of Material A does not change up to 1200 °C after oxidation. The annealing treatment prior to oxidation, which increases the high-temperature strength of Material A before oxidation, has no effect on the high-temperature strength after oxidation, implying that for applications at high temperature in an oxidizing environment, it is not necessary to use the annealing technique for these materials. The oxidation reduces the Weibull moduli of Material A, more for the modulus at room temperature than for the modulus at 1200 °C.

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