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Influence of Si_3N_4 interface chemistry on both grain morphology and fracture resistance

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Abstract

Quantitative microstructural analysis was performed on Si_3N_4 materials doped with 5 wt% Y_2O_3 and 5 wt% Sc_2O_3 as sintering aids. Two different processing routes were utilized to achieve complete densification: (i) gas-pressure sintering of Si_3N_4 -starting powders (SSN) and (ii) post-sintering of reaction-bonded Si_3N_4 (SRBSN). Apart from quantitative evaluation of grain diameter and aspect ratio of the matrix grains, the fracture toughness was determined. While the two Y_2O_3 -doped materials (SSN, SRBSN) showed identical K_{IC} -values, a large discrepancy in fracture toughness was found for the Sc_2O_3 -doped Si_3N_4 ($\Delta K_{\text{IC}} = 5 \text{ MPa}\sqrt{\text{m}}$). SEM crack propagation studies and additional TEM interface characterization showed no significant difference between these materials. Quantitative microstructure analysis, however, revealed a pronounced variation in grain diameter and aspect ratio after thermal treatment. A correlation between interface chemistry and both resulting microstructure and fracture resistance is discussed.

1. Introduction

Owing to their given brittleness, e.g. low fracture toughness, most oxide- and non-oxide ceramics are strongly limited concerning their potential application in engineering. However, one of the recent and most interesting developments in Si_3N_4 -based ceramics is the possibility to grow large Si_3N_4 -grains, embedded in a fine grained Si_3N_4 -matrix, *in-situ*.¹⁻³ This can result in an improved fracture resistance up to a factor of 2-3x.⁴ Hence, a number of research activities focussed on the study of exaggerated grain growth in these in-situ reinforced ceramics. Different possible contributions to the observed increase in fracture toughness such as grain diameter, aspect ratio, and influence of crystalline secondary phases are still under discussion. It is thought that fracture toughness of monolithic ceramics is mainly governed by grain morphology. Both increased grain diameter and high aspect ratio can affect active toughening mechanisms such as (i) crack deflection and (ii) crack bridging.⁵⁻⁷ Moreover, interface structure and chemistry can affect crack propagation (transgranular or intergranular fracture mode).^{4,10}

In this study we report on quantitative microstructural analysis combined with in-situ dilatometry, scanning and transmission electron microscopy. This combined effort seemingly showed that the aspect ratio of the large Si_3N_4 -grains is the dominating morphological parameter and, in addition, that concerning microstructural development the interface chemistry has to be considered.

2. Experimental Procedure

The p,T,t conditions during densification were different for both material groups (SSN and SRBSN). The SSN materials underwent a two-step gas-pressure sintering cycle: 1875°C, 5 bar N₂-pressure and 1925°C, 100 bar N₂-pressure for 90 min total, followed by subsequent heat treatment at 1850°C for 8 hrs. The SRBSN materials were obtained by gas-pressure sintering of reaction-bonded Si₃N₄ at 1875°C, 90 min, 5 bar N₂-pressure and 1925°C, 60 min, 100 bar N₂-overpressure. It should be noted that the SSN materials were held at temperatures above 1800°C for a prolonged time (subsequent heat treatment) compared to the SRBSN grades. In-situ dilatometry was performed during densification of the SSN materials registering both linear shrinkage and densification rate. Quantitative microstructural analysis was performed by utilizing a Quantimet 500 image processing system on polished and subsequent CF₄-plasma-etched cross sections.⁸ The K_{IC}-values of the SSN materials were measured by Vickers hardness indentation method (10kg, 10s, 0.5mm/min), whereas the SRBSN materials were characterized by Chevron notch experiments. In addition, crack propagation mode was studied by SEM, and amorphous grain-boundary films were characterized by transmission (TEM) and analytical electron microscopy (AEM).

3. Results and Discussion

3.1 In-situ dilatometry

Influence of additive composition on densification behavior was monitored by in-situ dilatometry. In general, the addition of Y₂O₃ or Sc₂O₃ showed the same overall densification behaviour, as depicted in Figure 1. Both densification curves reveal two main maxima, with the first maximum having the highest densification rate. All materials showed nearly complete densification after sintering. However, two major differences concerning densification have to be emphasized: (i) the onset-temperature of densification is lower for Sc₂O₃ addition, while (ii) the densification rate (first maximum) is much higher compared to the Y₂O₃-doped material (compare Figure 1).

The observed onset-temperatures during densification can be correlated with the liquidus temperatures of the corresponding binary phase diagrams, in particular, with the eutectic temperatures of the systems. The large difference in densification-rate, however, is related to secondary phase composition. The Sc₂O₃ addition results in the formation of a liquid phase, which reveals lower viscosity compared to Y₂O₃ addition.⁹ Thus, densification proceeds much faster in the Sc₂O₃-doped system, although the resulting total volume fraction of residual glass is similar for all four materials (approximately 15 vol%), which was verified by quantitative image analysis. From dilatometry measurements it can be concluded that densification-rate is mainly governed by additive composition and interface chemistry (identical glass-volume fractions).

Fig. 1 ds/dt-curves monitored by in-situ dilatometry during densification of 5 wt% Sc₂O₃- and 5 wt% Y₂O₃-doped SSN.

3.2 Interface characterization by SEM and TEM

SEM observations of radial cracks, initiated by Vickers indents on polished surfaces, revealed no significant difference concerning fracture mode. All materials showed, independent of additive composition, intergranular fracture (see Figure 2), with the only exception of elongated Si_3N_4 -grains being perpendicular to the crack-propagation direction.

Fig. 2 SEM micrograph of a propagated crack in SSN doped with 5 wt% Y_2O_3 .

This indicates that the 'weak link' during crack propagation are grain- and phase boundaries. Interface bonding must be relatively weak in order to support enhanced debonding along grain boundaries. Hence, it is thought that both interface structure and interface chemistry strongly affect crack propagation. High-resolution electron microscopy (HREM) studies on the interface structure in these materials showed a continuous grain-boundary film covering all Si_3N_4 -grains.¹⁰ The width of the amorphous intergranular films was about 1.0 - 1.5 nm for all materials investigated. In addition, analytical electron microscopy (AEM) studies revealed the presence of additive cations at the interface (for both dopants). Moreover, excess O and N was determined at all grain boundaries analysed. It is concluded, that crack propagation (interface debonding) is similar for all materials studied, although small variations in grain-boundary film thickness and interface chemistry were observed. Hence, the presence of a continuous amorphous interphase along phase- and grain boundaries gives no direct contribution to the resulting fracture toughness, however, it supports debonding to occur along grain boundaries and, therefore, indirectly determines fracture mode and effective toughening mechanism.⁴

3.3 Quantitative microstructure analysis

The distributions of grain diameter and aspect ratio were evaluated quantitatively for each material. Y_2O_3 containing materials (SSN and SRBSN) showed no significant difference concerning grain-diameter and aspect-ratio distribution. Moreover, identical fracture toughness data ($9 \text{ MPa}\sqrt{\text{m}}$) were evaluated for both materials. Microstructural development of the Sc_2O_3 -doped SRBSN material was also found to be nearly identical to the Y_2O_3 -doped materials (see Figure 3). This is consistent with the K_{IC} -value determined ($11 \text{ MPa}\sqrt{\text{m}}$), which is again similar to yttria-doping. The results presented thus far would seemingly suggest that microstructure development (and resulting fracture toughness) is independent of additive composition (Y_2O_3 or Sc_2O_3) and processing route (SSN or SRBSN).

However, it should be noted that the Sc_2O_3 -containing SSN material showed a completely different grain-diameter distribution and, in addition, a large difference in aspect-ratio distribution of the large grain fraction $>2\mu$ grain diameter (see Figures 3 and 4).

Fig. 3 Grain-diameter distributions of SSN and SRBSN doped with 5wt% Sc_2O_3 .

The addition of 5 wt% Sc_2O_3 (SSN) resulted in a microstructure characterized by a shift of the mean grain diameter to higher values (see Figure 3). Moreover, the distribution is, in general, broader compared to the other SSN and SRBSN materials. It is thought that globularization occurred during heat treatment and hence, resulted in the reduction of fracture resistance of about 50% (compared to the equivalent SRBSN material, $\Delta K_{IC} = 5 \text{ MPa}\sqrt{\text{m}}$). The results are consistent with dilatometry measurements which show that densification proceeds faster (due to lower viscosity of the liquid) in materials with Sc_2O_3 addition. This indicates that kinetic effects can strongly affect the grain-morphology development. In case of lower densification rates, as observed for Y_2O_3 addition, the diffusion controlled processes are significantly slower. Thus, retardation of material transport during heat treatment hinders major microstructural changes.

Fig. 4 Aspect-ratio distributions of SSN and SRBSN doped with 5wt% Sc_2O_3 . Note that only the large grain fraction $>2\mu$ grain diameter is shown.

The results presented show that kinetic and diffusion controlled processes strongly affect grain morphology. Moreover, interface chemistry in combination with residual glass viscosity (and diffusion path) influence the aspect-ratio and hence, resulting fracture toughness. It was shown that a high aspect ratio (in the large grain fraction) is necessary to support toughening mechanisms such as crack deflection and crack bridging. Furthermore, it should be born in mind that the presence of continuous amorphous films along grain boundaries is a prerequisite for debonding to occur (small changes in interface structure and interface chemistry seem to have no noticeable effect).

Conclusions

Four different Si_3N_4 -based ceramics (SSN and SRSBSN doped with 5 wt% Y_2O_3 and Sc_2O_3) were investigated by dilatometry, quantitative microstructural analysis and additional SEM and TEM observations. SEM studies showed intergranular fracture mode for all materials, independent of additive composition. HREM and AEM observations revealed only minor differences in interface structure and chemistry. A continuous amorphous grain-boundary film is present covering all grains. Additive cations, apart from excess O and N, were detected at the interface films. It is thought that debonding occurs along the interphase upon crack propagation. While the two yttria-containing materials as well as the Sc_2O_3 -doped SRBSN showed no significant difference in both overall microstructure (grain-diameter and aspect-ratio distribution) and fracture resistance, the Sc_2O_3 -doped SSN sample revealed a strong discrepancy in microstructure and fracture toughness (about 50% decrease). It could be shown that the observed deviations are mainly due to two effects: (i) change in grain morphology and (ii) influence of interface chemistry. A reduced aspect ratio of the large Si_3N_4 -grain fraction was found in Sc_2O_3 -doped SSN, which resulted in the observed reduction in fracture toughness. Moreover, the difference in interface chemistry (lower glass viscosity for Sc_2O_3 addition) in combination with a prolonged sintering time (heat treatment) strongly affects kinetic controlled processes such as grain-boundary diffusion, which in turn resulted in the change in grain morphology as well as fracture resistance.

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