Tailored microstructures of silicon nitride ceramics

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Abstract: The microstructural evolution in Si_3N_4 ceramics is analysed by studies of pressureless and gas pressure sintered materials. Parameters controlling the size and aspect ratio of elongated grains are discussed, based on the assumption that only pre-existing β-Si_3N_4 particles of the starting powder grow. Furthermore, it is shown that the grain morphology is also controlled by the sintering additives due to their influence on the surface energy of Si_3N_4 crystals. Microstructures are also related to strength as well as toughness measurements at room temperature. It is demonstrated that strength decreases with increasing grain size, but controlled grain growth could significantly improve fracture toughness, reliability and thermal shock behaviour.

Introduction

Structural ceramics based on the compound Si_3N_4 have been explored since more than three decades. They exhibit excellent mechanical properties, good oxidation resistance and thermal shock behaviour at both room and high temperatures. The high wear resistance and the mechanical properties of these ceramics are interesting for several applications such as cutting tools, valves for automotive engines or gas turbines. However, despite the exceptional properties and the demonstration of clear advantages, a wide range of applications is still not realized (1). The breakthrough in their use was not only inhibited by the high costs of the components for the automotive market; it is also inhibited by a large scatter of the property data such as strength, fracture toughness and reliability plus insufficient reproducibility (2). This can be attributed to the relatively complex microstructure and the difficulties to tailor it.

Because of the highly covalent bonding, Si_3N_4 has to be densified with sintering additives. Today it is a common practice to densify Si_3N_4 by pressureless sintering, gas pressure sintering, hot-pressing or hot isostatic pressing. The sintering aids are usally metal oxides such as MgO, Al_2O_3 and most of the rare earth oxides (3-5). The densification is described as a liquid phase sintering process (6). At higher temperatures, SiO_2, which is always present at the surface of the Si_3N_4 particles, react with the oxide additives to form an oxide melt and, with increasing temperature, an oxynitride melt by dissolving Si_3N_4. Depending on the composition of the sintering additives, the liquid phase can form an amorphous or a crystalline grain boundary phase during cooling, both of which degrade the mechanical properties of Si_3N_4 ceramics at temperatures > 1000°C because of the softening of the grain boundary regions (7). Most silicon nitride ceramics were prepared by using α-rich Si_3N_4 powders which transform during sintering into β-Si_3N_4. The β-modification forms elongated needle-like grains with aspect ratios comparable to whiskers if there is no pronounced steric hindrance of grain growth. Although this tendency has been known for a long time, few attempts have been made to apply the concept of an in-situ whisker reinforcement to Si_3N_4 ceramics. This is quite surprising since F.F. Lange (8) had already demonstrated in 1979 that the average aspect ratio of β-Si_3N_4 grains at the end of phase transformation can be influenced by using Si_3N_4 starting powders with different α/β-ratios. Nevertheless, most of the investigations had been focussed on the analysis of the influence of additives on grain growth (9,10). With the introduction of the gas pressure sintering technique in the last few years, more studies have been performed in order to analyse the possibilties of an in-situ reinforcement by controlled grain growth of β-Si_3N_4 (11).

A multi-phase microstructure, consisting of Si_3N_4 grains embedded in a grain boundary phase, also provides a great opportunity to optimized material properties for specific applications. Therefore, a detailed understanding of the microstructural development is necessary in order to achieve the demands of engineers.

The objective of this paper is to summarize recent studies regarding the influence of the Si_3N_4 starting powder, the sintering additives and the densification conditions on the growth behaviour of β-Si_3N_4 and a correlation is made between microstructural factors and mechanical properties.

Microstructural Development

<u>Influence of the Si_3N_4 starting powder</u>

The microstructural development of Si_3N_4 ceramics is controlled by three parameters. The properties of the Si_3N_4 starting powder, the additive composition, and the sintering conditions. Model experiments with oxynitride glasses (12-13) had revealed that the growth of β-grains starts from inital β-particles, while the homogeneous and heterogeneous nucleation could be neglected in case of the Y_2O_3/Al_2O_3 additive system, used for the present investigations. This means that grain size and morphology of β-Si_3N_4 are strongly influenced by the number of initial β-Si_3N_4-particles. A low number results in a large interparticle distance between β-grains in the powder compact and the grains are able to grow during the first stage of densification without a significant impingement by other β-grains. On the other hand, in the extreme case of β-rich powders (> 95 vol.%), steric hindrance is already effective at the beginning of densification. The resulting microstructure is fine-grained, homogeneous and characterized by equiaxed grains. Figure 1 shows two Si_3N_4 microstructures densified under the same conditions and with the same sintering additives but different Si_3N_4 starting powders.

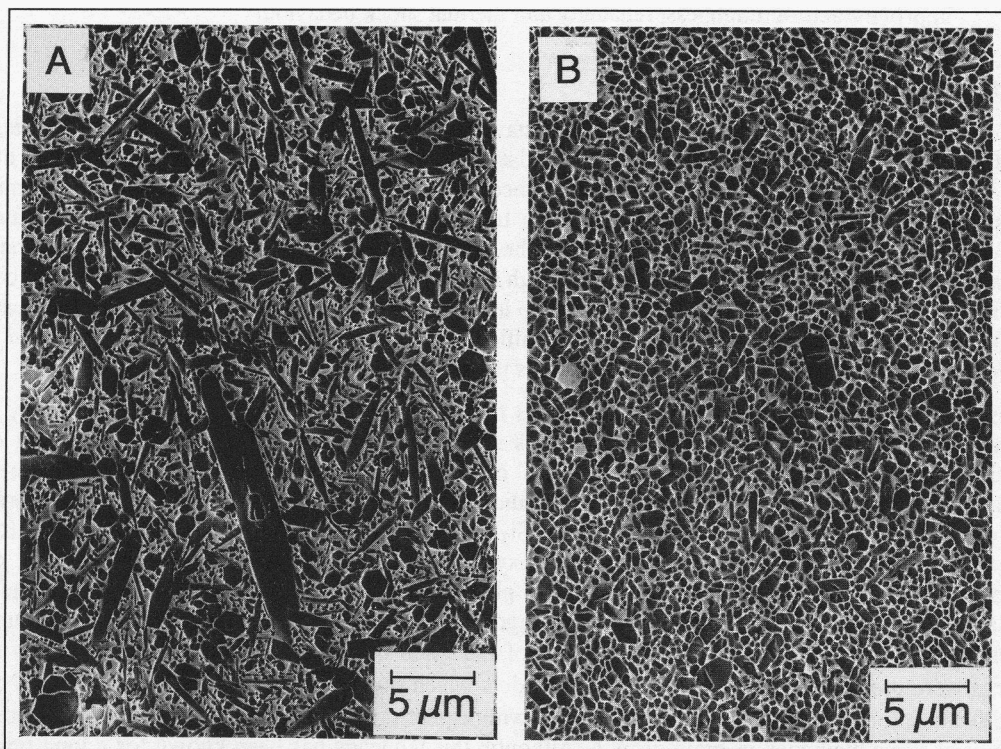Fig. 1   Plasma etched Si_3N_4 microstructure of an α-rich Si_3N_4 (A) and a β-rich (B) Si_3N_4 powder after pressureless sintering.

Nevertheless, the microstructure cannot be directly correlated to the initial β-content of the Si_3N_4 powder. The β-content by itself does not provide information concerning the number and size of the β-particles. A comparison of the calculated number of β-particles in the starting powder and the experimentally determined particle density in sintered samples indicate that only a part of the initial β-particles are able to grow (14). The number of growing β-particles depends on a critical particle diameter (d_{crit}). Particles with a size below d_{crit} will dissolve in the phase transformation stage (Fig. 6). The critical diameter is mainly

determined by three parameters. First, the size distribution of α- and β-Si$_3$N$_4$ particles due to a higher stability of large α-grains compared to small β-grains in the early stage of sintering (a high volume fraction of large α-grains causes an increase in d$_{crit}$). Second, the nitrogen solubility of the oxynitride melt which is determined by the additive composition (a higher nitrogen solubility shifts d$_{crit}$ to higher values). Third, the volume fraction of β-Si$_3$N$_4$; if the powder does not contain enough α-Si$_3$N$_4$ smaller β-particles will dissolve to supersaturate the oxynitride melt and d$_{crit}$ increases (in cases of β-rich powders).

Fig. 2 Schematic of β-particle size distribution of a Si$_3$N$_4$ powder.
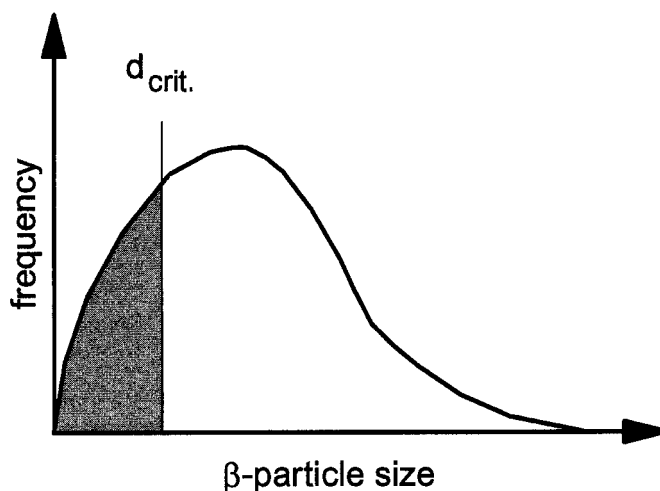
Detailed experimental studies showed furthermore, that the microstructural evolution is controlled by the effect of grain impingement. Theoretical considerations of the Si$_3$N$_4$ crystal structure revealed a higher stability of the prism planes of the hexagonal shaped grains compared to the basal planes. However, the growth rate of basal planes is much higher than the one of prism planes resulting in needle-like grain morphology. The difference in growth rates can be related to the Si$_3$N$_4$ crystal structure and is attributed to a energetically more favourable attachment of a surface nucleus on a basal plane (15). Based on the assumption of a higher stability of prism planes and a higher growth rate of the basal planes, three microstructure controlling cases of grain impingement can be derived (Fig. 3). The growth of a basal plane will be stopped, if it hits a more stable prism plane (A). The prism planes can cause a diameter reduction of a growing basal planes (B). If the diameter of a basal plane is large enough it will grow around smaller grains and dissolve them (C).
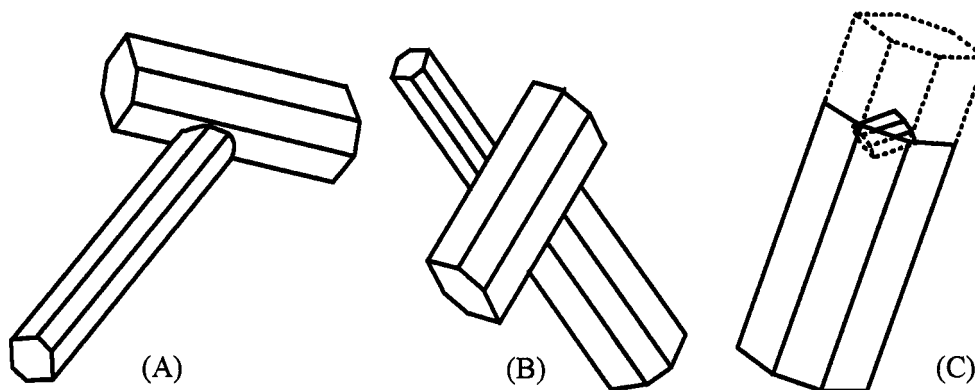

Fig. 3 Schematics of the steric hindrance of grain growth.

It is important to point out that cases (A) and (B) will stabilise the microstructure against grain growth. However, at higher temperatures and long sintering times exaggerated grain growth of particles with a large initial diameter occur by the mechanism schematically shown in Fig. 3 (C).

Influence of the sintering additives

The influence of rare earth oxides on the microstructure development was studied by using an additive combination of Al$_2$O$_3$ and Ln$_2$O$_3$ (Ln = La, Nd, Gd, and Yb). The additive compositions were calculated in consideration of the different nitrogen solubilities in order to keep the volume fraction (V$_{liq.}$ = 0.15) of

liquid forming additives constant (16). Specimens were densified by pressureless sintering at 1780°C until the end of phase transformation has been reached and subsequently heat treated for further 2 h. The microstructures were characterized by a quantitative analysis taken into account the 3-dimensional random distribution of elongated, hexagonal Si_3N_4 prisms (17). The results of the four examined systems are shown in Figure 4. The plots indicate a finer-grained microstructure with high aspect ratios grains for the La-containing sample compared to the material densified with Yb_2O_3 which required a 30 min shorter sintering time due to the faster phase transformation rate. Observations of the microstructural development after phase transformation revealed a nearly one-dimensional growth for the La-containing Si_3N_4 in contrast to a predominantly diameter growth for the Yb-containing Si_3N_4 (16). In general, the diameter distribution broadened with a decrease in rare earth element cation radius (from La to Yb). The pronounced growth of the prism planes (grain thickness direction) in samples with smaller rare earth cations is attributed to an influence of the sintering additives on the Si_3N_4 surface energy (15) causing a change of the ratio of basal and prism plane growth rates.
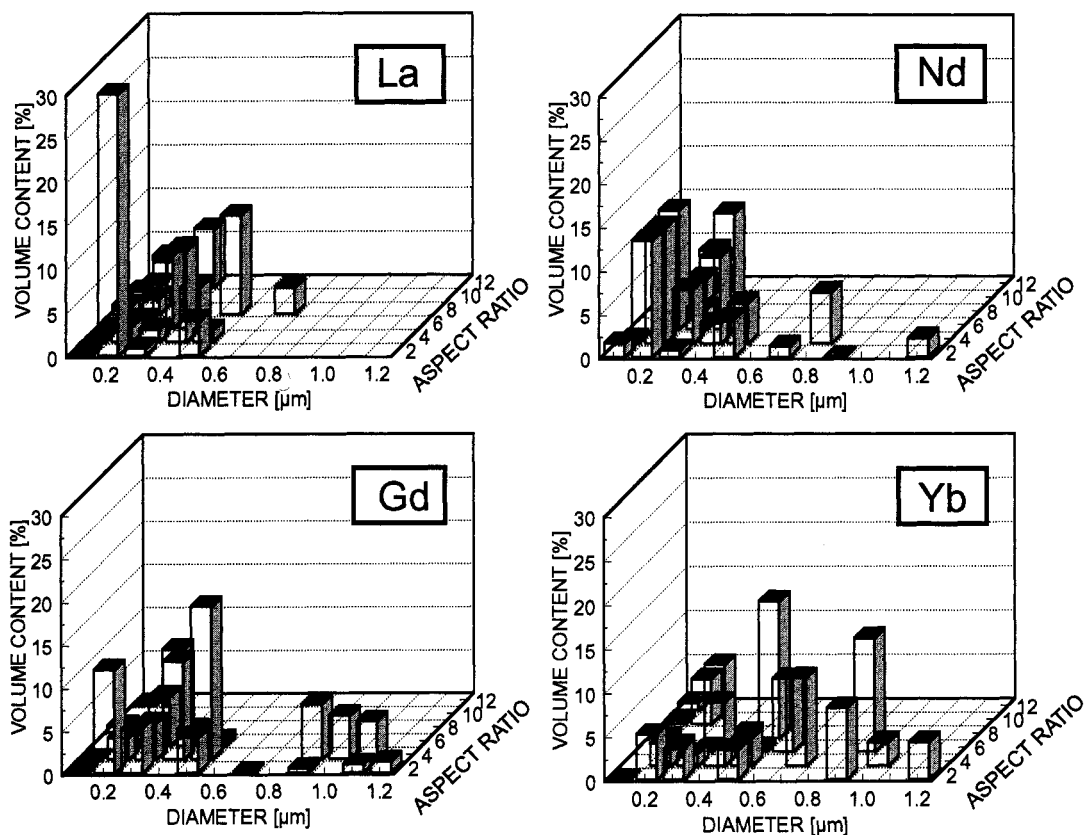

Fig 4. Grain diameter and aspect ratio distribution for Si_3N_4 ceramics densified with various additive systems.

The preliminary results indicate a strong influence of the additive on the Si_3N_4 grain morphology. Nevertheless, further investigations with well defined boundary conditions have to be conducted to obtain a more complete understanding of the grain growth phenomena.

Influence of the sintering conditions

Another important parameter for the microstructural development is the sintering temperature and time. After complete phase transformation grain growth starts by dissolution of smaller β-grains, as concluded from Fig. 5. Mitomo et al. (18) observed an increasing aspect ratio with increasing sintering temperatures

up to 1950°C and a decrease with further temperature increase. Comparing α- and β-rich Si_3N_4 powders he found only small differences in the mean aspect ratio after sintering at 2000°C for 1 h compared to the microstructures shown in Fig.1 after pressureless sintering for 40 min at 1800°C. The observed development of a needle-like microstructure, also in cases of β-rich powders, is determined by the particle size distribution at the beginning of the grain growth stage. Broad particle size distributions lead to a faster grain growth than very narrower ones. As explained earlier, some grains with a large initial diameter can grow in length direction with a minor steric hindrance more minor than the smaller ones (Fig. 3 / (C)). Their maximum length could reach 100-200 μm and they could reduce the bending strength of the material.

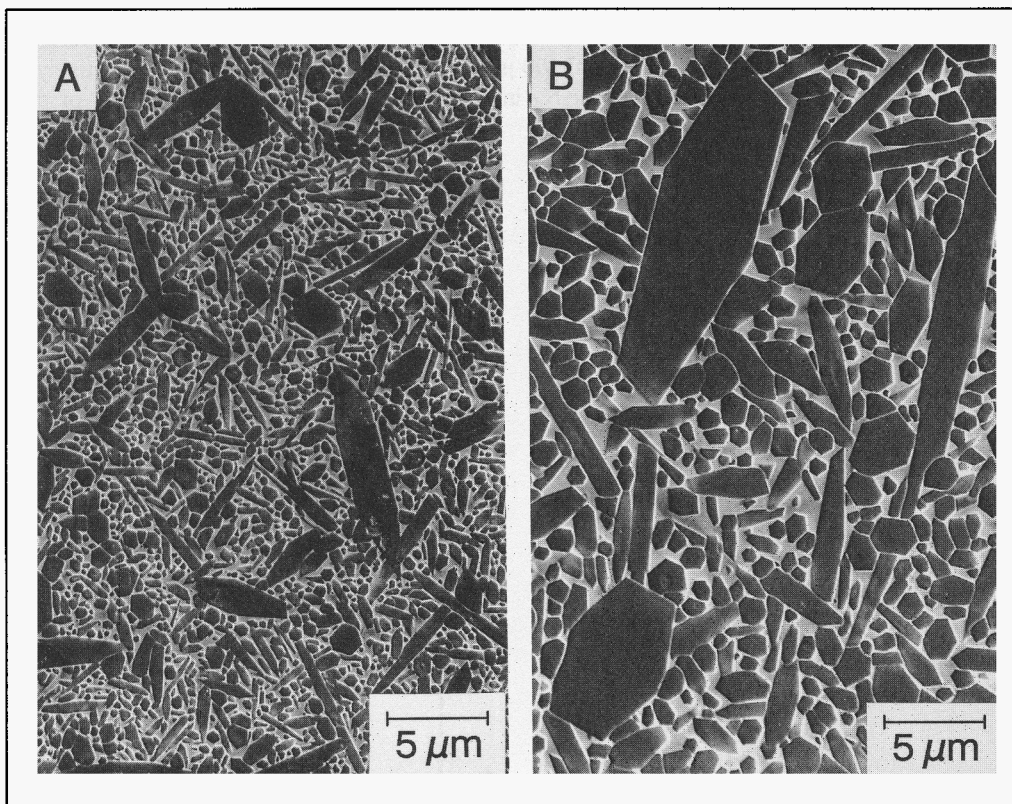Fig. 5 Microstructure of gas pressure sintered Si_3N_4 after 35 mins at 1835°C (A) and 360 mins at 1900°C (B), respectively.

Mechanical Properties

Experimental studies revealed that the fracture toughness of Si_3N_4-ceramics increases with an increase in volume fraction of elongated grains and scales with the square root of their diameter (19). The toughening is mainly attributed to crack wake mechanisms such as crack bridging, grain rotation, and grain pull-out (20). However, the grain morphology itself is not the only requirement to obtain a high toughness. A second important parameter is the grain boundary phase. Tajima (21) observed a significant decrease in fracture toughness in a MgO/ZrO_2-doped silicon nitride with the addition of small amounts of the sintering additive Al_2O_3, although the Si_3N_4 grain size and morphology were not changed. The decrease in fracture toughness was attributed to a transition from a predominantly intergranular to a more transgranular fracture mode due to a higher interfacial bonding force of the grain boundary. More detailed studies of Becher et al. (22) with β-Si_3N_4 whiskers dispersed in oxynitride glasses with various compositions showed a similar trend. The interfacial bonding increases with a decreasing Y_2O_3:Al_2O_3 ratio and increasing nitrogen content.

Coarse grained microstructures with a weaker interface are favored to achieve high toughness. However, experimental results reveal a strength decrease with increasing grain size. Figure 6 shows a comparison of the strength distribution of two Si_3N_4 ceramics densified with the same additives, but different Si_3N_4 starting powders. The powder compacts were sintered under two different conditions to obtain a fine

grained (1835°C/35 min) and coarse grained (1900°C/360 min) microstructure (Fig. 5). Fracture toughness measurements showed no significant difference between powder (A) and (B). The fine grained ceramics with a toughness of 7.2 and 7.4 MPam$^{1/2}$ had a mean strength ($\overline{\sigma}$) of 1134 and 1105 MPa, respectively. However, the strength distribution (Weibull modulus, m) is quite different after an extensive grain growth, despite the same fracture toughness of 8.4 MPam$^{1/2}$ for both materials. The material with powder (A) reveals a strength decrease to 902 MPa, but a remarkable improvement in reliability as indicated by an increase of the Weibull modulus from 13.5 to 46. The material prepared with powder (B) shows a higher strength decrease after grain coarsening and no change in Weibull modulus. Powder (B) is characterized by a broad inital β-particle size distribution which leads to an exaggerated grain growth of the large diameter particles due to their minor grain impingement, as discussed above. The analysis of the fracture origin indicates indeed large elongated grains of several 100 μm length as fracture origin. This is relatively easy to understand if debonding occurs at the weak Si$_3$N$_4$ interface causing cracks with flaw sizes of the grain length.

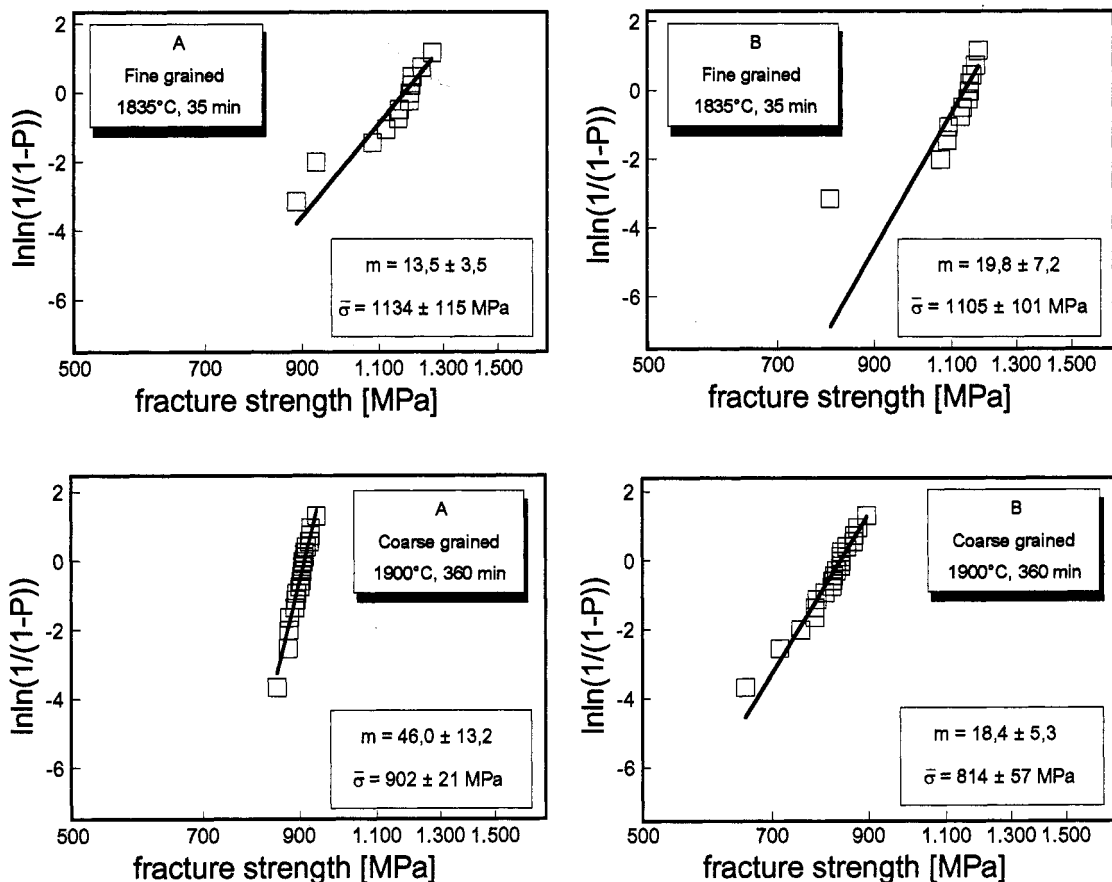Fig. 6 Influence of the powder properties on strength distribution of fine and coarse grained Si$_3$N$_4$.

Narrow strength distributions, as in the case of material (A) may be attributed to a narrow flaw size distribution, if homogeneously distributed large elongated grains are considered as fracture origin. On the other hand, a narrow strength distribution can also be explained by a rising fracture resistance with the extension of a crack (R-curve behaviour), as pointed out in a previous paper (14). The existence of an R-curve behaviour in Si$_3$N$_4$ ceramics seem to be evident (22, 23), but there is still little information concerning the relationship between microstructure and the shape of the fracture resistance curves. It is assumed that the fine grained silicon nitrides exhibit very steep R-curves with lower plateau values in contrast to coarse grained materials with a smaller steepness, but a higher base toughness.

The R-curve behaviour also has a significant contribution with respect to the thermal shock behaviour. High strength ceramics such as silicon nitride show in general a catastrophic failure at a certain quench temperature during water quench tests (Fig. 7a). Nevertheless, in coarse grained Si_3N_4 a continuous strength degradation, which is generally observed for low strength materials that exhibit R-curve behaviour, can be obtained (Fig. 7b).
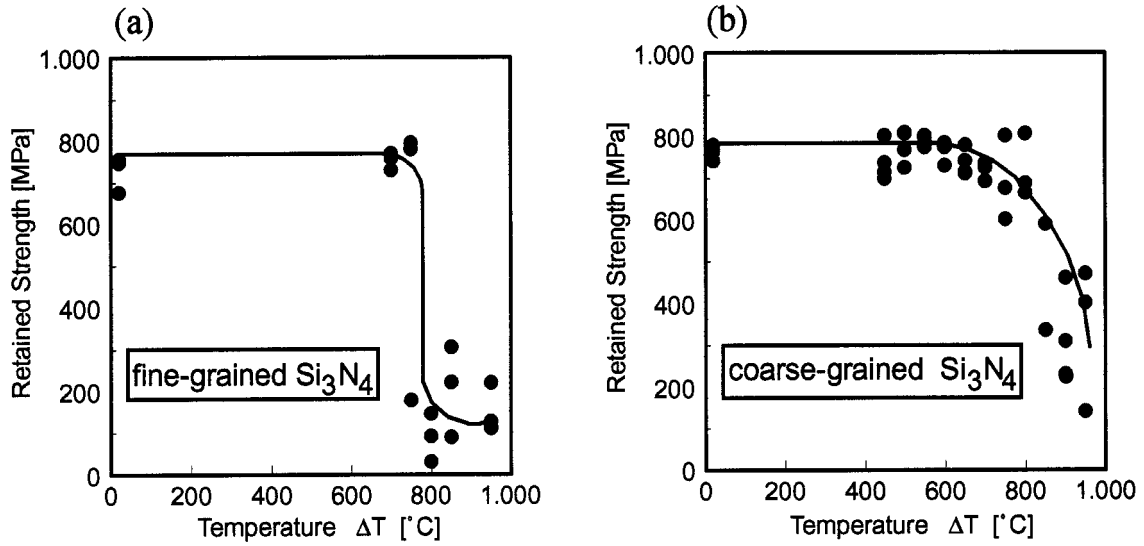

Fig. 7 Strength response of Si_3N_4 after thermal shock by water quench.

Since both materials were sintered with the same additives, the difference in thermal shock behaviour has to be attributed to the size and morphology of the Si_3N_4 grains which was varied by using different sintering times. The catastrophic failure of the fine-grained material is due to very small defects and a very steep inital portion of the R-curve causing instantaneously an unstable crack propagation during thermal shock above a certain temperature. A continuous strength degradation could be observed if the base toughness and steepness of the R-curve is high enough to produce stable crack growth during thermal loading (24).

Summary

Microstructural development of Si_3N_4 ceramics has been discussed regarding the importance of the initial β-particle size distribution of the starting powder and the effect of grain impingement under the assumption that only initial β-particles grow. After complete phase transformation and densification grain growth occurs and β-particles with an initially larger diameter grow in length direction due to their minor steric hindrance. When the maximum grain length exceeds 100-200 µm, the grain size becomes strength determining. Furthermore it has been shown that the sintering additives influence the grain morphology by changing the ratio of growth rates of prism and basal planes. A significant growth in thickness direction, which results in a lower aspect ratio, has been observed for rare earth elements with a small cation radius. The effect was explained by an influence of the additives on the Si_3N_4 surface energy.

Microstructures effects on mechanical properties demonstrate that high strength materials could be obtained with fine grained materials. High toughness and narrow strength distributions were observed in coarse grained materials, as long as exaggerated grain growth could be avoided. For coarse-grained microstructures an increase in fracture resistance with increasing crack extension (R-curve) is expected. The R-curve behaviour can be tailored by grain growth and it causes an improvement in reliability as well as thermal shock behaviour. In conclusion, it has to be pointed out that the properties of silicon nitride ceramics have to be optimized for each specific application.

Acknowledgement

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