

Development of the Microstructure of the Silicon Nitride Based Ceramics

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Received: August 15, 1998; Revised: March 30, 1999

Basic regularities of silicon nitride based materials microstructure formation and development in interrelation with processing conditions, type of sintering additives, and starting powders properties are discussed. Models of abnormal or exaggerated grain growth are critically reassessed. Results of several model experiments conducted in order to determine the most important factors directing the microstructure formation processes in RE-fluxed Si_3N_4 ceramics are reviewed. Existing data on the mechanisms governing the microstructure development of Si_3N_4 -based ceramics are analyzed and several principles of microstructure tailoring are formulated.

Keywords: silicon nitride, microstructure, phase transformation, liquid phase sintering

1. Introduction

Mechanical properties of the Si_3N_4 -based ceramics such as strength and fracture toughness as well as Weibull modulus are strongly dependent on the microstructure. Formation of the resulting microstructure is dictated by the densification mechanism, *i.e.*, reactive liquid phase sintering. The α - Si_3N_4 in the starting powder compact is transformed to β - Si_3N_4 via solution-reprecipitation in an oxynitride liquid-phase sintering medium. The final β - Si_3N_4 grain size and shape distribution in the material are controlled by the Si_3N_4 starting powder characteristics, the metal oxide sintering additives, and the processing conditions. Microstructural observations have shown that the β - Si_3N_4 grains grow as elongated hexagonal prisms in suitable liquid-phase environment¹.

It is generally agreed that for superior mechanical properties a fine microstructure with a high proportion of elongated β -grains, the so called high aspect ratio grains, or even more preferably fibrous β -phase grains is necessary. The aspect ratio characteristic means the ratio of length to width of the elongated hexagonal prismatic β - Si_3N_4 grains.

Detailed studies of the grain morphology on fracture toughness and strength of silicon nitride ceramics have been reviewed recently by Becher *et al.*². Briefly, the fracture toughness increases monotonically with the longitudinal directions of the elongated grains. Both grain size and the grain aspect ratio must be controlled to optimize

the Weibull modulus of the fracture strength of silicon nitride. A small transverse grain size was shown to give higher Weibull modulus than the coarse microstructures. The observed increase in fracture resistance was mainly attributed to crack deflection, and crack bridging mechanism³⁻⁶. In some cases crack branching was also observed. An important role in fracture resistance improvement is played also by the secondary phase. If on cooling or after post-sintering heat treatment tensile stress is induced in the material due to thermal expansion coefficient mismatch between Si_3N_4 and the secondary phase or due to volume changes upon phase transformation, the fracture toughness may be diminished. Under such conditions the crack is not deflected by elongated grains of β -phase and a transgranular crack development is characteristic. Considering the importance of the microstructure tailoring for the further improvement of the Si_3N_4 -based ceramics properties the present paper has the goal of systematizing and analyzing the existing data and concepts in this field.

2. Factors Governing Microstructure Formation in Si_3N_4 -based Ceramics

One of the main factors of elongated grains formation is the viscosity of the liquid phase formed during sintering which, in turn, depends on the type of the metal oxide(s) used as a sintering aid. Grain growth in Si_3N_4 -based materials is diffusion-controlled and can be considered in terms of Ostwald ripening⁷. Therefore, it is to be expected that

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the liquid phase with higher viscosity will yield β -grains with higher aspect ratios. The higher viscosity hinders both the heterogeneous nucleation and the material transport by means of diffusion during solution-precipitation, thus promoting preferential growth of the pre-existing intrinsic β -grains. This, in fact, was proved by observations in Y_2O_3 - and Yb_2O_3 -doped Si_3N_4 ceramics. In Yb_2O_3 -doped materials higher average aspect ratios were observed in comparison with the Y_2O_3 -doped ones. It is a well known fact that ytterbia as a sintering aid produces the liquid phase of the highest viscosity among all the other rare-earth (RE) oxides. Moreover, for the Y_2O_3 -doped ceramics a pronounced diminishing of the β -grains aspect ratios was observed with the increase of alumina addition. Alumina is known to diminish the viscosity of the liquid phase formed during sintering. It must be emphasized that in order to produce the favorable microstructure the presence of impurities, which decrease the viscosity of the molten liquid phase, *i.e.* iron, alkali and alkaline-earth metals, etc., must be avoided.

The effect of such impurities on microstructure formation can be seen on Fig. 1, where microstructures of samples of silicon nitride doped with 5 wt.% of Al_2O_3 and 5 wt.% of Y_2O_3 with different amounts of model impurities (Si and $FeSi_x$) are presented⁸. It is clearly seen that with the increase of either one of the model impurities microstructure refinement and morphological homogenization occurs, the amount of large β - Si_3N_4 grains with high aspect ratios substantially diminishes. The effect is much more pronounced if $FeSi_x$ is added.

As it was mentioned before, there are other factors that control the microstructure development and may cause the so-called exaggerated or abnormal grain growth, that leads to the formation of extremely large β - Si_3N_4 grains, which may act as crack initiation sites⁹. Several factors are believed to contribute to such an occurrence: inhomogeneous distribution of crystalline secondary phases¹⁰, β - Si_3N_4 grain morphology, the β - Si_3N_4 nuclei density, and the β - Si_3N_4 grain size distribution within the starting powder mixtures¹¹.

3. Models of Exaggerated Grain Growth in Si_3N_4 -based Ceramics and Model Experiments

One of the models of exaggerated grain growth which is mostly attributed to reaction-bonded silicon nitride but is also fully applicable to all Si_3N_4 -based ceramics is based on the assumption of intermediate (transient) crystalline secondary phase formation on the early stages of nitridation and their inhomogeneous distribution in the volume of the material. The proposed mechanism of abnormal grain growth may be presented as follows (Fig. 2)¹⁰. In the proposed model it is assumed that metastable crystalline

secondary phases, revealing a high thermal stability field^{12,13}, are already formed on the early stage of densification. During subsequent sintering, these phases remain stable up to their melting point, while the eutectic liquid had already formed at a lower temperature and facilitates initial densification. The eutectic temperature in the Si_3N_4 - Y_2O_3 - SiO_2 ternary system lies at 1550 °C^{10,14}. However, the eutectic temperature is lower, owing to the Al_2O_3 content of the starting powder blend. With increasing temperature, dissolution-precipitation occurs simultaneously with the α to β silicon nitride phase transformation, which is complete at about 1650 °C for these materials. At 1630 °C the secondary H-phase (Fig. 3) is still crystalline. Even at 1730 °C this phase still lies outside the liquid phase field. It is thought that the crystalline secondary phase only melts at higher sintering temperatures, forming excess liquid. The latter is inhomogeneously distributed over entire sample, owing to inhomogeneous distribution of crystalline secondary phase at lower sintering temperatures, which is thought to initiate both increased densification and the onset of abnormal grain growth. A strong increase in densification rate at temperatures about 1800 °C was experimentally confirmed by dilatometry measurements during sintering. Moreover, the formation of large, elongated β - Si_3N_4 grains, randomly oriented in the sintered body, was also reported¹⁰. It is thought that some of the excess liquid will progress through the reaction bonded silicon nitride (RBSN) pore channels by capillary forces and simultaneously permit densification, but it is presumed in this model that excess liquid remains at the site containing the original metastable Y-Si oxynitride phase. This liquid would act as a flux for the rapid growth of highly elongated β - Si_3N_4 grains by a dissolution - reprecipitation process¹⁰.

This model is based on two requirements. Firstly, upon liquid formation the wetting liquid should not be drawn completely out of the central reservoir into the surrounding porous RBSN matrix. The situation could arise if the volume of liquid exceeds the porosity in the RBSN and also, if densification occurs simultaneously with capillary extrusion. Secondly, exaggerated β - Si_3N_4 grain growth and elongation is required to occur at the liquid reservoir, whereas normal coarsening should prevail in the surrounding matrix. To prove this requirements two model experiments were carried out by Dressler *et al.*¹¹.

In the first one a large piece of pre-synthesized crystalline secondary phase (about 5 mm in diameter) was embedded in a silicon nitride powder compact and subsequently consolidated, as schematically depicted on Fig. 4.

It was expected that in the region around the embedded crystalline secondary phase, or at the secondary phase-matrix interface, a high amount of excess liquid was formed during sintering, which would strongly enhance abnormal grain growth. However, microscopic investigations gave

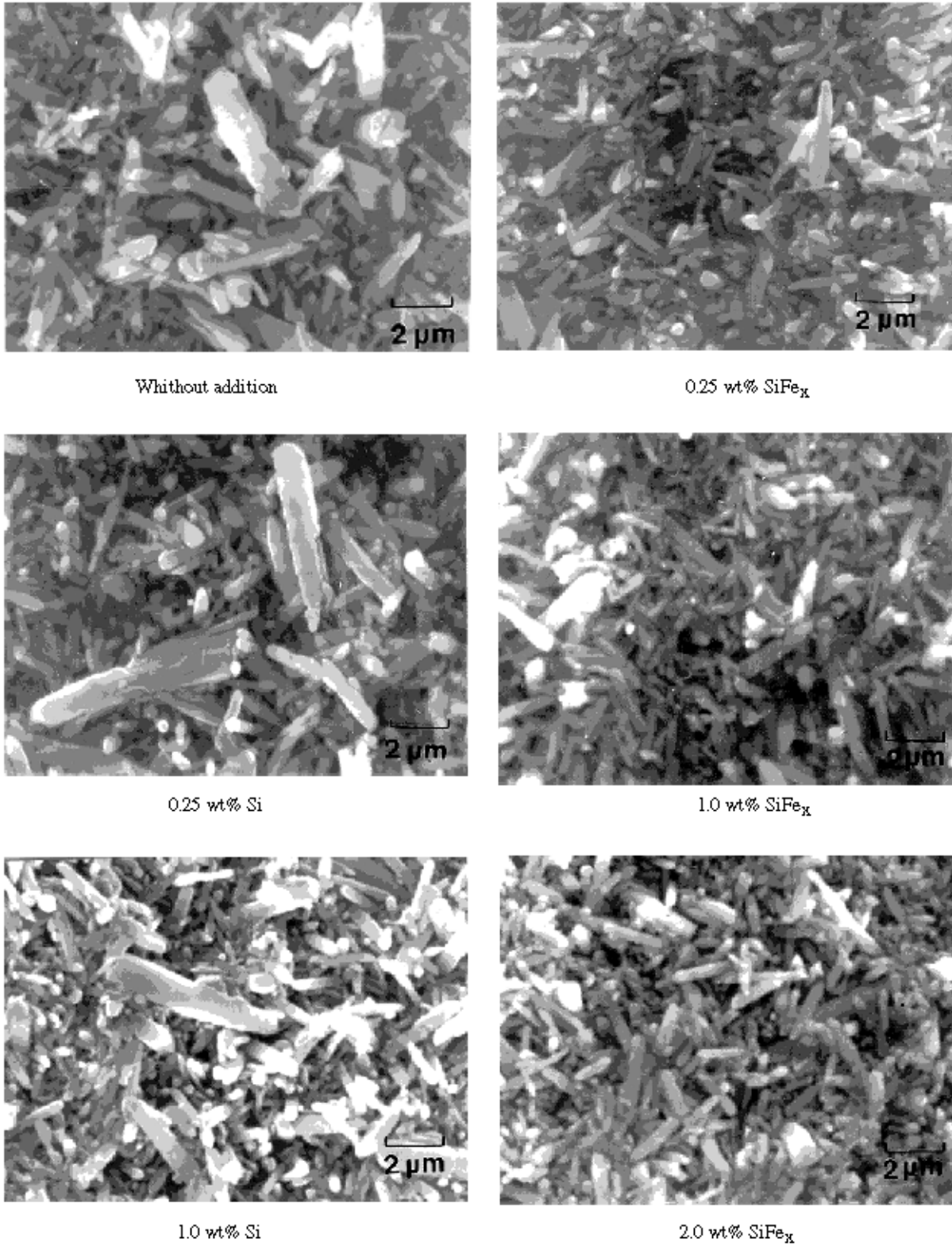


Figure 1. Microstructures of samples with Si and SiFe_x⁸.

no evidence of the latter. Both for Yb-silicate (Yb₂Si₂O₇) and apatite (Yb₉Ca(SiO₄)₆ON) a large pore, containing a

small pocket of residual secondary phase, was formed at the site of the formerly embedded pre-synthesized crystal-

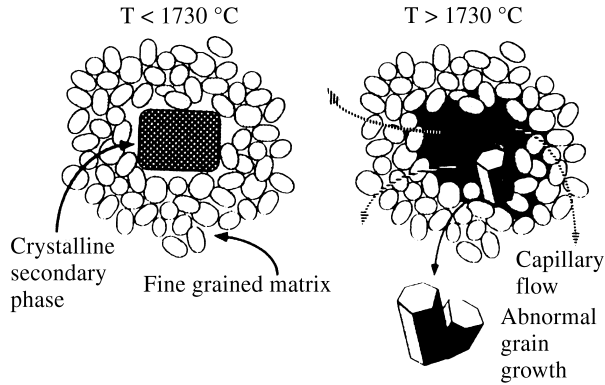


Figure 2. Mechanism of the abnormal grain growth for an inhomogeneous distribution of crystalline secondary phase¹⁰.

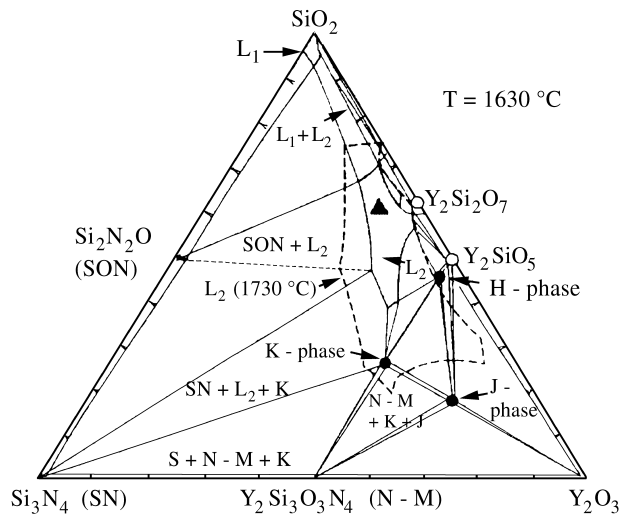


Figure 3. Phase diagram of the $Y_2O_3 - Si_3N_4 - SiO_2$ system indicating the H phase¹⁰.

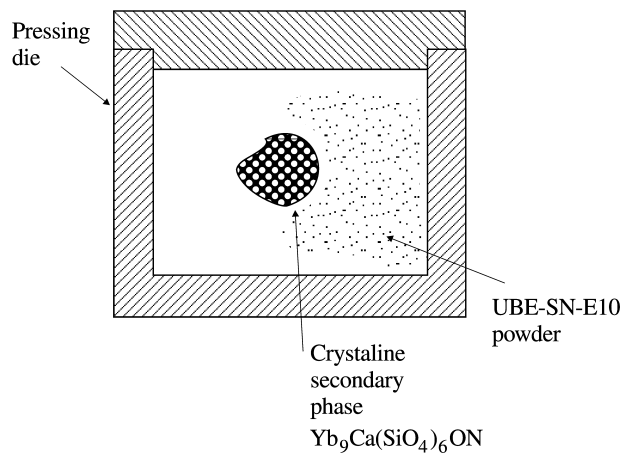


Figure 4. Schematic illustration of the cold-isostatic pressing set-up of Si_3N_4 green bodies with an embedded crystalline secondary phase¹⁶.

line secondary phase. Hence, it is concluded that high capillary forces were responsible for a homogeneous distribution of the excess liquid phase throughout the sample, which resulted in microstructures indistinguishable from those of the materials sintered without the incorporation of crystalline secondary phases. The main difference between the inhomogeneities (excess liquid) formed during post-sintering of reaction-bonded silicon nitride and the liquid generated in the above model specimens is that at the beginning of the sintering process the deliberately created inhomogeneities are surrounded by a highly porous silicon nitride powder compact. Therefore, a second model experiment was designed to minimize the porosity effect.

In order to suppress the influence of high capillary forces, a “sandwich” specimen was prepared using a dense Si_3N_4 slab with a pre-synthesized crystalline secondary phase and another dense Si_3N_4 slab on top, as schematically shown in Fig. 5. This “sandwich” was heated above the melting temperature of the crystalline secondary phase and a cross-section of the joined sample was prepared. No pronounced exaggerated grain growth was observed.

Diffusion process along the interface led to a uniform distribution of the secondary phase between the two Si_3N_4 slabs at the applied sintering temperatures, where all secondary phase present in the system is thought to be liquid. These results clearly exclude the initially proposed effect of inhomogeneously distributed crystalline secondary phases on abnormal grain growth in silicon nitride materials. Accordingly, the development of exceptionally large grains has to be due to intrinsic powder properties, such as the $\alpha-Si_3N_4$ $\beta-Si_3N_4$ content and grain size distribution as well as the β -nuclei morphology.

The influence of the intrinsic morphology of $\beta-Si_3N_4$ particles present in the starting powder on the microstructural development of gas-pressure sintered materials was studied. An α -rich silicon nitride powder (ESP) was therefore doped with 5 vol. % of $\beta-Si_3N_4$ whiskers (UBE-SN-WB). After sintering, the resulting microstructure studied on polished and plasma-etched surfaces by scanning electron microscopy. The plasma etching is a very sensitive technique regarding small chemical changes in the mate-

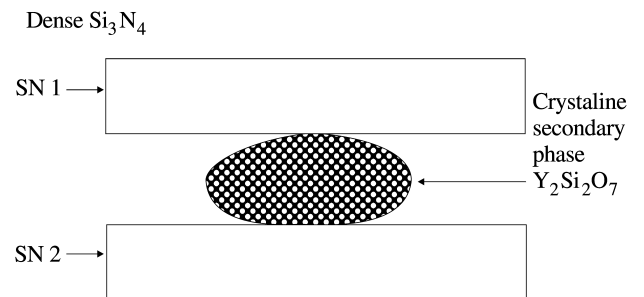


Figure 5. Schematic showing the “sandwich” specimen before sintering¹⁶.

rial. The etching rate strongly depends on the aluminum content of the Si_3N_4 grains. A higher aluminum concentration in the solid solution results in a lower plasma etching rate.

The resulting microstructure of the whisker-doped ceramics possessed a significant number of large elongated grains, which have a deeper etched core surrounded by a rim structure. According to the analytical transmission electron microscopy (TEM) investigations the core is aluminum-free while the rim structure contains, apart from the silicon and nitrogen, additional aluminum and oxygen. These findings and the fact that the observed cores are elongated and aligned parallel to the length direction of the abnormally grown β -grains suggest that the aluminum-containing outer region of the large elongated β - Si_3N_4 grains grew epitaxially on the starting aluminum-free β - Si_3N_4 whiskers. Owing to the kinetic growth advantage of the basal plane compared to the prismatic planes in silicon nitride crystals^{15,16}, the whiskers revealed a higher growth rate in length direction rather than in width upon sintering.

The abnormal grain growth in this case schematically shown on Fig. 6. The exceptionally high growth rate in the c-direction is due to the large basal plane of the β - Si_3N_4 whiskers. This basal plane corresponds to a very low equilibrium concentration of silicon nitride in the surrounding liquid phase. Therefore, close to the abnormal growing particles the critical radius of dissolution is extraordinarily high. This enables the very fast dissolution of adjacent smaller particles and the observed exceptionally high aspect ratio of the rim structure grown during sintering.

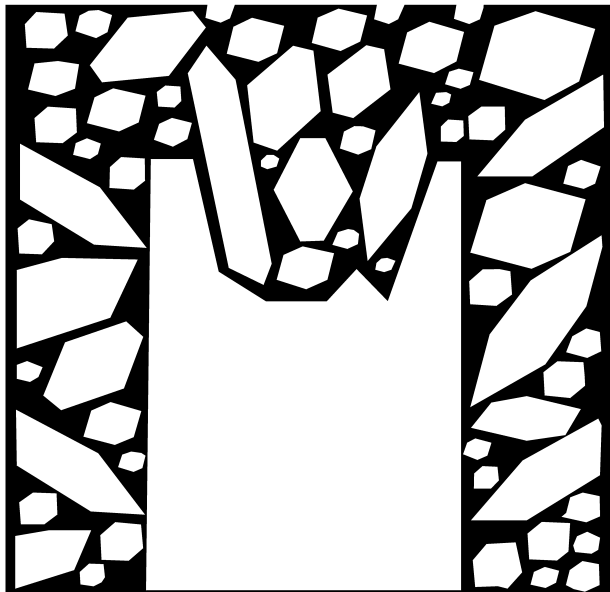


Figure 6. Model of abnormal grain growth in Si_3N_4 -ceramics. The larger particles reduce the Si_3N_4 -concentration in front of their basal plane and thus dissolve smaller particles in growth direction¹⁶.

It is important to note that the initially elongated shape of the whiskers remains during the α to β transformation and the following grain coarsening. The results seemingly suggest that it is possible to directly influence the resulting microstructure via the morphology of the pre-existing β - Si_3N_4 nuclei, as the morphology of whisker-like particles is preserved during consolidation.

Two α -rich silicon nitride powders (E10), doped with various amounts of equiaxed β - Si_3N_4 nuclei, using a Denka starting powder with a β - Si_3N_4 content of approximately 97%, were utilized to study the influence of initial β - Si_3N_4 content on the final microstructure. The β - Si_3N_4 doping of the α -rich silicon nitride powders on the one hand results in grain refinement if the dopant (Denka) possesses a comparable crystallite size to the α -rich matrix powder (ESP) and if the nuclei density is low. On the other hand, provided that the added β -nuclei (Denka) are larger than the β -particles in the α -rich matrix powder (E10) and that the nuclei density is high, grain coarsening is observed, since the β - Si_3N_4 / β - Si_3N_4 particle interaction is enhanced according to¹¹.

These results clearly reveal that, if the β - Si_3N_4 nuclei density reaches a certain value, depending on the grain size distribution of the starting powder, a dissolution of the smaller β - Si_3N_4 particles is observed, followed by a coarsening of the microstructure. These results can be explained using the model developed by Wagner¹⁷ for Ostwald ripening for spherical particles. According to this model equilibrium concentrations of α - and β -particles in a solvent, C_G^α and C_G^β respectively, are considered. These concentrations depend on the radius of the crystal (R), the surface energy (σ), the temperature T as well as the constants C_0 and K , as summarized by the relationship:

$$C_G = C_0 \exp\left(\frac{\sigma K}{RT}\right)$$

A deviation of the spherical morphology results in a different constant K , as calculated in Ref. 9. Since the transformation enthalpy of the reaction α - $\text{Si}_3\text{N}_4 \rightarrow \beta$ - Si_3N_4 is negative, the equilibrium concentration of the α -phase, C_G^α , must be higher in comparison to C_G^β . C_1 and C_2 are arbitrary Si_3N_4 concentrations in the liquid phase directly at the particle surface during the solution-reprecipitation process, which causes the α to β transformation as well as the grain coarsening. In the model of¹⁷ these concentrations depend on the particle dimensions and the mean concentration of the solute, because the crystals in this model are isolated from each other and thus the concentration gradients do not overlap. In contrast to that, the solid phase fraction in the above described experiments is so high that the Si_3N_4 concentrations at the particle surfaces are controlled by the surrounding crystals and their size distribution.

At a given Si_3N_4 concentration in the liquid the radii of α - and β -particles are critical grain sizes, which means that all particles being smaller dissolve, whereas larger crystals grow. This model predicts the dissolution of small β -crystals if they are located within the diffusion gradient of a larger β -particle, and therefore explains in full all the regularities observed.

The investigation unequivocally reveal that a broad β - Si_3N_4 grain size distribution in the starting powder causes exaggerated grain growth due to solution of α - as well as small β - Si_3N_4 particles and reprecipitation onto larger β - Si_3N_4 grains. Moreover, the morphology of the initially existing β - Si_3N_4 crystals also influences the resulting microstructure of the sintered ceramics. In addition, the effect of abnormal grain growth is enhanced by high sintering temperatures and long sintering times, as was shown in⁷.

Earlier studies confirm that an appreciable toughening effect can be monitored in silicon nitride based ceramics owing to the *in situ* development of elongated β - Si_3N_4 grains. However, in order to reach high fracture toughness accompanied by high strength, the abnormal grain growth has to be controlled. By using α - Si_3N_4 starting powders having a broad intrinsic β - Si_3N_4 grain-size distribution unfavorably large particles may grow, which can act as crack initiation sites. In order to optimize mechanical properties, initial silicon nitride powders should possess a narrow intrinsic β - Si_3N_4 grain-size distribution and have faceted, elongated β - Si_3N_4 crystals. Ceramics prepared from such starting powders should exhibit microstructures containing a large amount of elongated β - Si_3N_4 grains without exaggerated grain growth development, and therefore combines both high strength and high fracture toughness. This effect can be further enhanced by the use of appropriate sintering aids producing liquid phase of high viscosity during sintering.

These considerations show that tailoring of the final silicon nitride ceramics microstructures becomes possible by means of relatively simple methods.

4. Microstructure Tailoring in SIAIONS

SiAlONs represent a large family of so-called ceramic alloys based on silicon nitride, that provide a possibility to prepare fully dense polycrystalline ceramics by pressureless sintering techniques. There are two SiAlON phases that are of interest as engineering ceramics, β -SiAlON and α -SiAlON, which are solid solutions based on β - and α - Si_3N_4 structural modifications, respectively. β -SiAlON is formed by simultaneous equivalent substitution of Al-O for Si-N and has most commonly been described by the formula $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$. In this formula the z value can be varied continuously from zero to about 4.2^{18,20}. The homo-

geneity region of β -SiAlON extends along the Si_3N_4 - $(\text{Al}_2\text{O}_3/\text{AlN})$ line. The unit cell contains two Si_3N_4 units.

The α -SiAlON phase region has a fairly limited two-dimensional extension in the plane $\text{Si}_3\text{N}_4/3(\text{Al}_2\text{O}_3/\text{AlN})$ - MeN_3AlN of a Me-Si-Al-O-N, phase diagram presented in the form of a Jancke prism²¹. The β -SiAlON is thus falling on one border of this plane. Of special interest are the Me-Si-Al-O-N systems where α -SiAlON phase is stabilized by the added Me ion, where Me could be Li, Mg, Ca, Y, and the rare earth metals except La, Ce, Pr, and Eu²²⁻²⁴. The α -SiAlON unit cell content comprising four Si_3N_4 units, can be given in the general formula $\text{Me}_m\text{Si}_{12-(pm+n)}\text{Al}_{(pm+n)}\text{O}_n\text{N}_{16-n}$ for a metal ion Me^{p+} . Two substitution mechanisms may act. The first is similar to that of β -SiAlON with $n(\text{Si} + \text{N})$ being replaced by $n(\text{Al} + \text{O})$. The second mechanism supposes the further replacement of $pm\text{Si}^{4+}$ by $pm\text{Al}^{3+}$, the electron balance being retained by incorporation of $n\text{Me}^{p+}$ into the α -phase structure.

α -SiAlON was most extensively studied in the Y-Si-Al-O-N system^{23,25-28}. It was shown for Y-SiAlONs that by changing the overall composition of initial mixtures (α/β)-SiAlON ceramics can be prepared with the varying α -SiAlON : β -SiAlON phase ratio^{29,30}. In the microstructure of these materials α -SiAlON always appears as equiaxed grains, while β -SiAlON forms elongated grains with an aspect ratio typically in the range of 4 to 7. Hardness increases markedly with increasing α -SiAlON phase content, whereas the fracture toughness decreases. High α -SiAlON content also improves oxidation resistance of the material as well as the thermal shock resistance. It is also evident from its chemical composition that α -SiAlON offers possibility of reducing the amount of residual glassy grain-boundary phase by incorporating constituents of sintering aids into the crystal structure, which otherwise will be present as substantial amounts of residual glassy phase and deteriorate the high-temperature performance of the material.

The possibility of varying α -SiAlON : β -SiAlON phase ratio by slightly changing the overall composition was shown to open many possibilities to prepare Y-SiAlON ceramics with desired properties. Other ways of changing properties of SiAlON ceramics by means of replacing Y_2O_3 by other RE-oxide additives were also investigated³¹. Precisely this direction of research led to the discovery of the full reversibility of the α -SiAlON to β -SiAlON transformation for certain phase assemblies under conditions of post-sintering heat treatment³²⁻³⁴. It has been observed that the α -SiAlON phase is less stable at low temperatures and decomposes into rare-earth-rich intergranular phase(s) and β -SiAlON with a remarkably elongated crystal morphology. The extent of the transformation was observed to be more pronounced with increased heat treatment tempera-

ture. The mechanism of the fully reversible α -SiAlON to β -SiAlON transformation was thoroughly investigated and described in³⁵.

This transformation provides an excellent possibility for optimizing phase content and microstructure without further additions of oxides and nitrides merely by heat treatment at appropriately chosen temperatures. In this way premeditated values of hardness, strength and toughness can be achieved from a single starting composition, which opens new perspectives for SiAlON ceramics successful application.

5. Conclusions

According to contemporary concepts several factors are of crucial importance in Si₃N₄-based ceramics microstructure formation and tailoring. The formation of high aspect ratio β -Si₃N₄ grains, which are considered to sufficiently enhance the most important mechanical properties of the materials, was shown to depend on the amount, grain size distribution, and morphology of β -Si₃N₄ nuclei in the starting powder mixtures. Additionally, grain morphology may be influenced by impurities that diminish the liquid phase viscosity thus altering the diffusion process during solution-precipitation stage of densification.

Two reasons are believed to be responsible for the so-called abnormal grain growth: inhomogeneous distribution of crystalline secondary phases, formed on early stages of sintering, and the presence of abnormally large β -Si₃N₄ particles with exaggerated aspect ratios in the starting powder. The first factor, although somewhat arguable, can not be totally discarded from consideration during silicon nitride processing.

The group of ($\alpha\beta$)-SiAlON composites offers the possibility of premeditated microstructure modification by means of post-sintering heat-treatment using the full reversibility of the α -SiAlON to β -SiAlON transformation recently discovered.

Acknowledgments

The authors acknowledge the PADCT/FINEP and CNPq for the financial support.

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