# Importance of chemistry in high-tech ceramics design*

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*Abstract*: This paper deals with the role of chemistry in the design of high-tech ceramic materials. Grain boundary composition of polycrystalline ceramics dictates the hardness fracture toughness and creep resistance of liquid-phase sintered silicon nitride and silicon carbide materials.

## INTRODUCTION

The role of chemistry in high-tech ceramics development is undisputable. A simple proof of this statement could be the proceedings series "Better Ceramics Through Chemistry" [1,2]. Until now, chemistry has been one of the most important backgrounds for the materials scientists dealing with the design of new synthetic materials for various applications. Recent activities concerning the role of chemistry in ceramic processing are focused on the development of ceramic powders and/or bulk materials from organometallic precursors, in this special issue [3]. For other literature, see refs. [4,5]. The advantage of this approach is the possibility of combining the proper constituents of a ceramic body on the atomic level. The main objection to this approach is an evolution of gases, which hinder the easy densification and cause a final inhomogeneity of bulk composites. A further detailed study of this approach is necessary. On the other hand, a "classical" approach (shown in Fig. 1), starting from the synthesis of ceramic powders, followed by the formation of the green body, and then by sintering to a dense ceramic
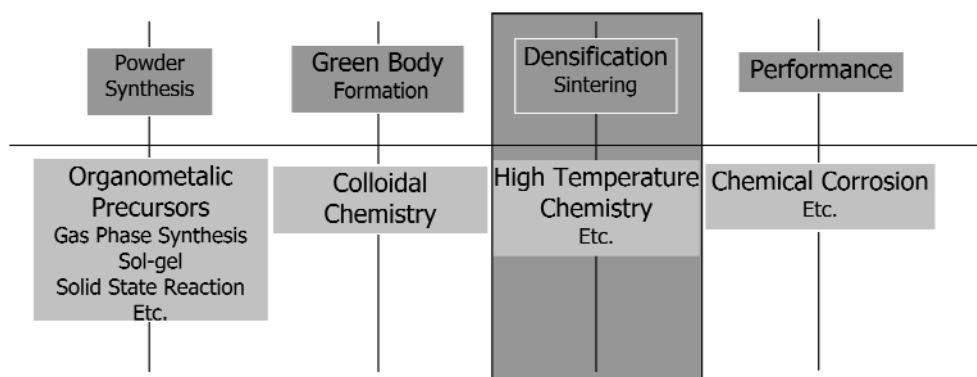


**Fig. 1** Schematic of "classical" ceramic processing.

body, seems to be well enough known. This is valid only on first sight. As Fig. 1 shows, different branches of chemistry are employed during particular steps of ceramic processing and performance.

These different areas of chemistry open the door to the endless variety of possible chemical reactions having an influence on the formation and, thus, properties of a solid ceramic body. This paper will be devoted to the chemical changes, proceeding during the densification/sintering step. The aim of this paper is to show a few examples of how high-temperature chemistry influences the microstructure, composition, and properties of a ceramics body.

## LIQUID-PHASE SINTERING OF $Si_3N_4$ AND SiC

Sintering is a method that allows fabrication of a solid/dense body from a porous "green powder body". In order to make the densification possible also for covalently bonded matter, the formation of a liquid, which speeds up the diffusion processes, is necessary. Silicon nitride is a typical example for this kind of matter. Figure 2 shows the schematic of constituents taking part at the liquid-phase sintering (LPS) of silicon nitride.
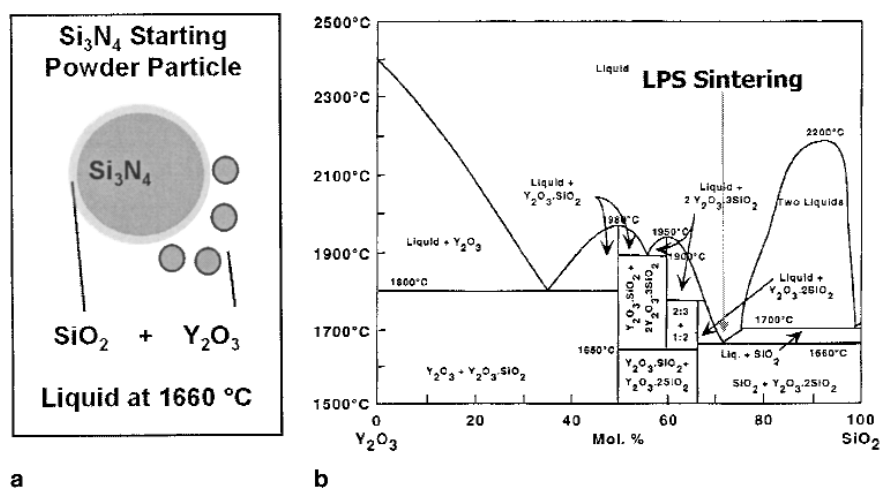


**Fig. 2** Formation of liquid phase at 1660 °C. $SiO_2$ is an inherent impurity of all silicon nitride powders.

Silica and yttria mixed in the molar ratio 2.8:1 formed the liquid at 1660 °C. This liquid after densification remains at the grain boundaries (GBs) and triple points of the dense polycrystalline body, Fig. 3. The residual glassy phase dictates the room-, as well as high-temperature properties of the ceramic body. As Becher et al. [6] showed, the composition of the GB phase strongly influences the fracture toughness of silicon nitride-based ceramics. When $Y_2O_3$ and $Al_2O_3$ were used as sintering additives to the same starting powder, the fracture toughness increased with the increase of the $Al_2O_3/Y_2O_3$ ratio. The reason for such a behavior was lower bonding strength between silicon nitride grain and the GB phase with higher yttria content. Another example of the importance of GB chemistry on room-temperature (RT) properties is presented in Fig. 4. Fracture toughness and hardness of LPS silicon carbide strongly depend on the oxide additives used for LPS. This is valid even in the case when the microstructure of both tested samples is almost identical; see values marked by the open circle in Fig. 4. The abbreviations in Fig. 4 are as follows: SCα-Y means SiC sintered with the $Y_2O_3$ as the sintering additive and doped with α-SiC nuclei. The rest of the abbreviations have similar logistics, SCb-YYb means SiC sintered with $Y_2O_3$ and $Yb_2O_3$ as the sintering additive doped with β-SiC nuclei.
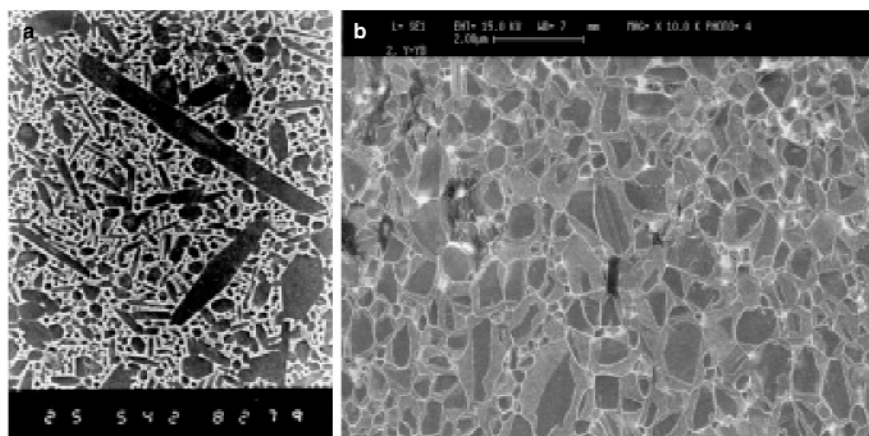
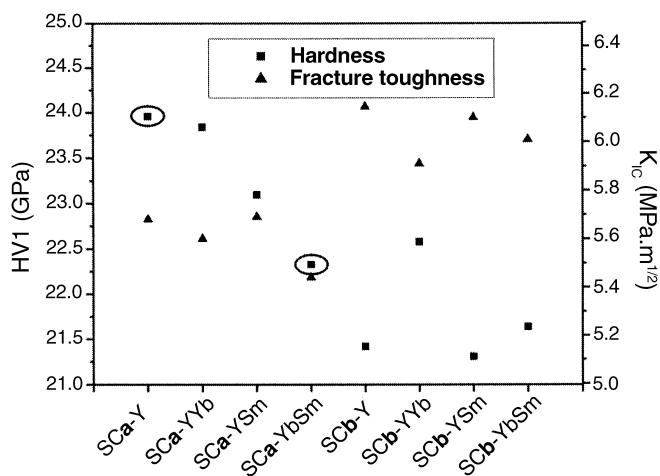**Fig. 3** Microstructure of LPS $Si_3N_4$ and SiC ceramics.



**Fig. 4** Hardness and fracture toughness of LPS SiC with different glassy-phase composition.

        LPS samples were annealed after hot pressing for 10 h at 1850 °C in mixed $N_2$+Ar atmosphere. Substantial grain growth was not observed for the samples doped with α-SiC seeds. On the other hand, the average grain size of β-doped samples increased from 0.7 to 2–7 µm after annealing for 10 h. The annealing of SiC samples was accompanied by a decrease of density in the range 0.9–5.5 %. The energy-dispersive spectrometry (EDS) analysis of the SCα-Y sample showed the transport of $Y^{3+}$ ions toward the surface, Fig. 5, most probably due to the concentration/temperature gradient across the sample. The sample surface was free of yttrium up to the depth of 150 µm. On the other hand, the hardness of this particular sample, measured in the bulk, changes from 21 to 25 GPa after annealing.

        These results should serve as the examples that confirm the importance of GB chemistry with respect to selected RT properties. The proper chemical composition of sintering additives, later on, the GB phase, is always connected with the other requirements, which result from the limits of processing and high-temperature application.

        Sintering additives/GB chemical composition should fulfill two contradictory requirements; the first one requires the formation of liquid at a reasonable "low" temperature because of the "easy" den-
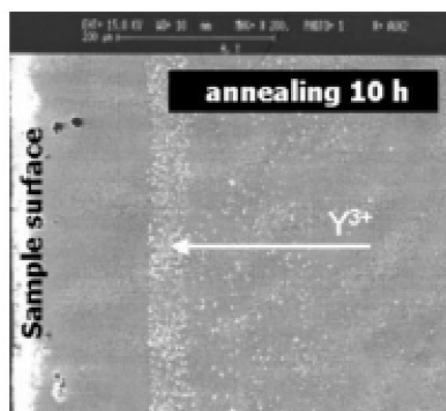
**Fig. 5** EDS analysis of yttrium in the LPS SiC ceramics after annealing at 1800 °C for 10 h.

sification of the ceramic body, the second one requires a reasonably "high" temperature of GB softening because of the high-temperature applications. The optimization of the GB and triple-points chemical composition is principally possible. Generally, three ways could be used: (a) crystallization of triple points/GBs after densification; (b) in situ formation of inclusions of other phase/chemical compounds; and (c) change of chemical composition of the triple-points/GB phase by reduction of oxides after the densification. All these three ways have only aimed to increase the softening temperature of the triple-point/GB phase and thus decrease the creep rate of these polycrystalline ceramic materials at high-temperature stress.

## CRYSTALLIZATION OF TRIPLE-POINTS/GRAIN BOUNDARY PHASE IN SILICON NITRIDE CERAMICS

The crystallization of the triple-points/GB phase is often mentioned as a good method for improvement of the high-temperature behavior of silicon nitride-based ceramics. Interestingly, there exist only limited results confirming this statement [7]. The present example shows one of the reasons why this approach could fail due to the local changes in chemistry.

Dense silicon nitride ceramics sintered with $Al_2O_3$ and $Y_2O_3$ sintering additives were crystallized at 1400 °C for 50 h. This crystallization should lead to the enhancement of the creep resistance of these materials. In contrary, the creep behavior of crystallized material was worse compared to those as sintered. The crystallized phases were mainly the $Y_2Si_2O_7$ and $Y_2SiO_5$ phases. Transmission electron microscopy (TEM) analysis, shown in Fig. 6, revealed the presence of spherical objects containing Fe, Ti, and Cr. These elements were not detected in the original glassy-phase triple points of density as a sintered body. These were created during crystallization. The majority of elements detected within the spherical objects were analyses as impurities in the $\beta$-$Si_3N_4$ whiskers added to the starting powder mixture. Where these impurities were probably uniformly dissolved in the glassy pockets (triple points) with concentration below the detection limit of energy-dispersive X-ray spectrometry (EDXS), after crystallization of the yttrium silicate phases their segregation occurs. The schematic of their possible distribution is shown in Fig. 7a. These results help to understand the high-temperature behavior of the composite. Figure 7b shows cavity formation on the whisker matrix interface of the composite after the creep test at 1200 °C. The impurity enhanced the intergranular cavity formation and, thus, destroyed the properties of the carefully designed composite.
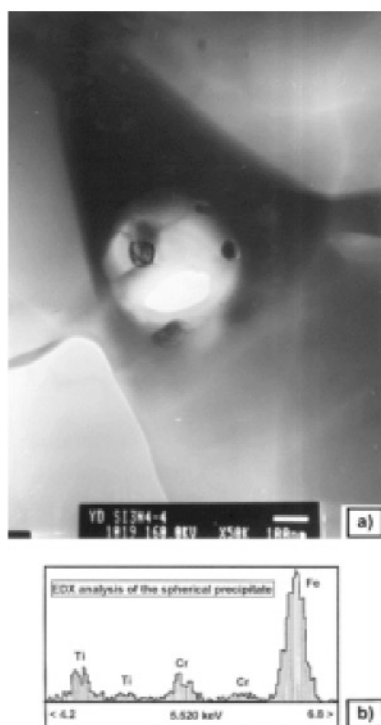
**Fig. 6** TEM analysis of the triple point: (a) bright-field TEM image of crystallized triple point; (b) EDX analysis of the spherical object.
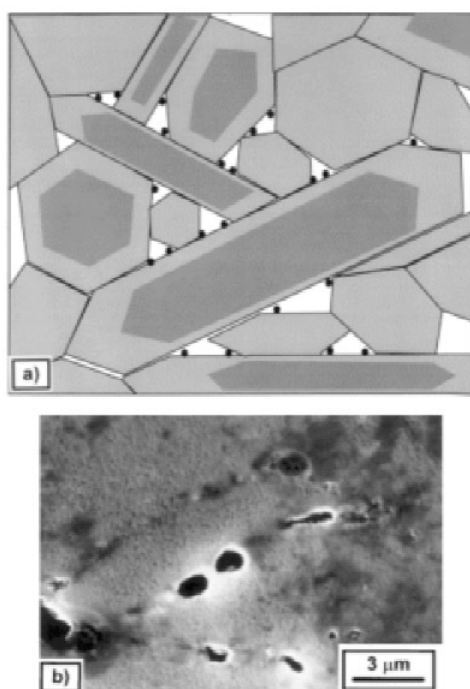


**Fig. 7** Distribution of segregated impurities/cavities: (a) schematic of possible distribution of segregated impurities (black spots); (b) cavity formation at the whisker-matrix interface.

## IN SITU SYNTHESIS OF SiC INCLUSIONS WITHIN THE GRAIN BOUNDARY OF Si$_3$N$_4$-BASED CERAMICS

Another effective way of modifying the glassy phase of triple points/GB is the in situ synthesis of new compounds. The presence of silica in silicon nitride-based composites offers a chance to apply this approach to this kind of ceramics.

Model experiments of SiO$_2$ + Y$_2$O$_3$ glasses doped by carbon black showed the possibility of reducing SiO$_2$ content within the composition and simultaneously forming SiC particles at the temperatures similar to those used for sintering of silicon nitride-based ceramics [8]. The same approach was used for the preparation of the SiC/Si$_3$N$_4$ nanocomposite. The sintering additives used were Y$_2$O$_3$ + SiO + C. A special hot-pressing regime allowed us to densify this composition and create SiC inclusions within the dense silicon nitride matrix. The microstructure of such a composite is shown in Fig. 8.
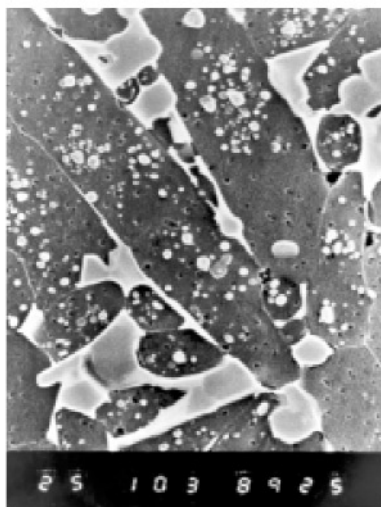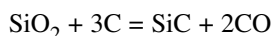


**Fig. 8** Microstructure of SiC/Si$_3$N$_4$ nano/microcomposite; large gray grains: Si$_3$N$_4$; white spots: SiC.

The SiC inclusions are located on the GB and also within the Si$_3$N$_4$ grains, as shown in Fig. 8. The formation of the inclusions, according to the reaction:

$$SiO_2 + 3C = SiC + 2CO$$

has two important consequences. The first one is connected with the formation of SiC nanoparticles, which hinder the formation of the cavities during the creep test at high temperature. Figure 9 compares the behavior of Si$_3$N$_4$-based ceramics without the SiC inclusions on the GBs. The exaggerated cavitation as a consequence of GB sliding was observed for the silicon nitride-based material, Fig. 9a. On the other hand, the presence of SiC inclusions on the GBs hindered the GB sliding, Fig. 9b, by interlocking of Si$_3$N$_4$ grains by SiC inclusions. This change of creep mechanisms is reflected also in the substantial lower creep rate of the SiC/Si$_3$N$_4$ composite, Fig. 10. The other important consequence is a lowering of SiO$_2$ content in the original mixture, which should lead to an increase of the melting temperature of the GB glassy phase, as can be seen from the phase diagram shown in Fig. 2.
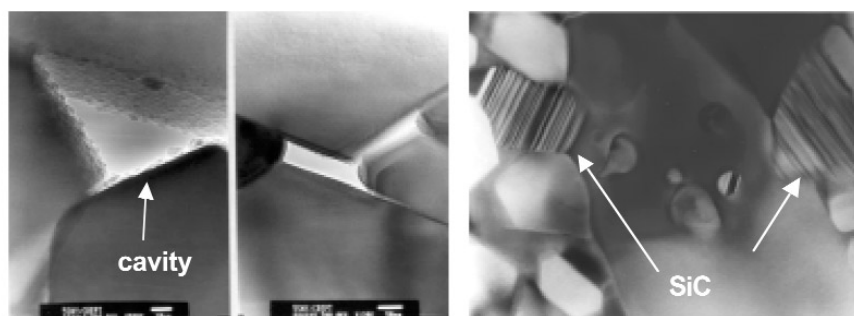
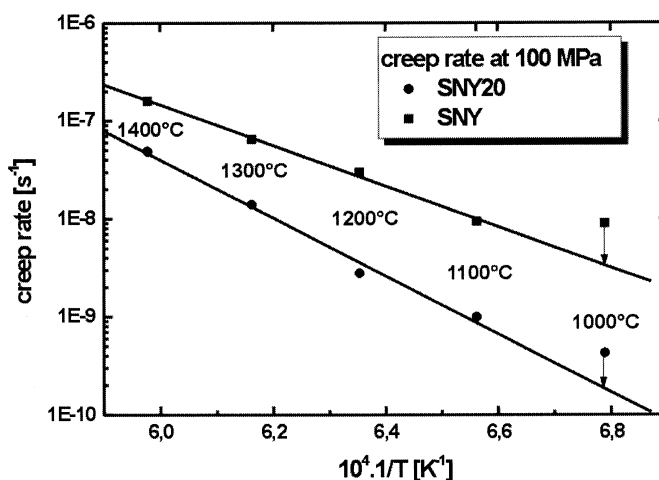**Fig. 9** (a) Exaggerated cavitation in $Si_3N_4$ ceramics; (b) interlocked $Si_3N_4$ grain by SiC inclusions.



**Fig. 10** Creep resistance of $Si_3N_4$ ceramics and $Si_3N_4$/SiC nanocomposite sintered with the identical amount of $Y_2O_3$.

## CONCLUSIONS

The present paper showed enormous sensitivity of ceramic polycrystalline materials on the composition of phase located at the triple points and/or GB. The fracture toughness and hardness of silicon nitride/silicon carbide are usually dictated by the composition of the GB. A slight change of used oxides has a large response in properties. Local changes in chemistry at high temperatures either as a consequence of crystallization or in situ reactions dictates the properties of these materials dramatically. Creep resistance strongly depends on the GB softening temperature and on the other crystals present at the triple points and GBs.

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