

## Ceramic Microstructure - the Key to the High Performance Ceramics

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**Abstract**—The extending variety of applications and better control of processing methods have broadened the range of microstructures that are available for ceramics. Important features of ceramic microstructures which strongly influence the properties of ceramic products are (i) grain size and grain morphology and (ii) chemical and structural characteristics of grain boundaries.

The principles of microstructure evolution during sintering of ceramics are shortly reviewed, emphasizing the influence of additives and impurities forming solid solutions, inclusions and liquid phase on normal and abnormal grain growth.

As practical examples, microstructure development in ZnO voltage dependent resistors and SiC engineering ceramics are described.

### 1. INTRODUCTION

The demanding properties of contemporary technical ceramics may be achieved only by careful process control. Key attention is devoted to microstructure development during sintering. Structure should be dense, uniform and reproducible. The grain size depends on the application. Most applications demand fine grained microstructures; however, for some applications a coarse grain size is required, for example for low voltage varistors. Compositional homogeneity also depends on the application. Particularly in functional ceramics, controlled chemical heterogeneity is required. Even in such cases, reproducibility and uniformity is of prime importance.

In the present review, the basics of development of ceramic microstructures will be shortly described. Developments will be illustrated by examples from the field of functional ceramics (ZnO VDR) and engineering ceramics (SiC).

### 2. SOME PRINCIPLES OF MICROSTRUCTURE DEVELOPMENT DURING SINTERING OF CERAMICS

The basics are covered in textbooks and extensive reviews [1-4]. In analysing grain growth phenomena during sintering in ceramics, it is

assumed that the instantaneous rate of grain growth is directly proportional to the instantaneous average rate  $\bar{v}$  of grain boundary migration [5]. The average rate  $\bar{v}$  of grain boundary migration is usually represented in terms of a force-mobility product

$$\bar{v} = M \cdot F = M (-\Delta\mu/\lambda) \quad (1)$$

where  $M$  is mobility,  $F$  is the driving force,  $\Delta\mu$  is the chemical potential, and  $\lambda$  is the grain boundary thickness.

Microstructure development is usually distinguished as "normal" or "abnormal". Normal grain growth, which is striven for in ceramic processing because it is easily controlled, is defined as having two main attributes: (a) uniform appearance (a relatively narrow range of grain sizes and shapes), and (b) time invariant form of grain size distribution. Fig. 1 shows, as an example, the uniform microstructure of fully dense PLZT ceramic. In contrast in "abnormal" grain growth, a few large grains develop and consume a matrix of smaller ones, eventually impinging and reverting to normal growth. In practice, abnormal growth ends with a nonuniform structure. For example, see Fig. 2.

The importance of the driving force in grain growth kinetics is obvious, yet in describing grain growth phenomena it is frequently over-

looked. In a pure system, the chemical potential is due to the pressure difference across the boundary arising from its curvature. In a chemically heterogeneous system,  $\Delta\mu$  includes the chemical Gibbs energy. Chemical potential in heterogeneous systems greatly exceeds the potential due to the surface curvature and plays a decisive role, particularly in the first stage of densification and grain growth. In general, change of driving force is expected to influence migration mechanisms [6]. Since chemical reactions during sintering, caused by impurities and additives are specific, each particular system must be separately studied.

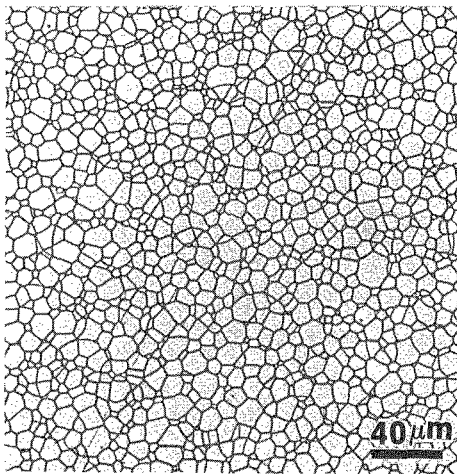


Figure 1. Microstructure of 9,5/65/35 PLZT ceramic sintered in oxygen at 1200°C and hot pressed at 1250°C for 24 hours. Courtesy M. Kosec.

The intrinsic grain boundary mobility, i.e. the grain boundary mobility in a pure system, is expected to be very high, since it involves rapid ionic motion across a grain boundary width of atomic dimensions. Therefore, the rate of grain growth in pure ceramics must be high.

The isothermal rate of normal grain growth during sintering can be expressed by the phenomenological kinetic grain growth equation:

$$G^n = K \cdot t \exp(-Q/RT) \quad (2)$$

where  $G$  is the average grain size at time  $t$ , the  $n$  value is the kinetic grain growth exponent,  $K$  is a constant,  $Q$  is the apparent activation energy,  $R$  is the gas constant and  $T$  is absolute temperature.

Theoretically, for pure, dense systems  $n=2$ . In most experimental studies, higher  $n$  values were found, the most commonly observed value being 3 [3]. Large grain growth exponents are indicative of slowly coarsening microstructures, for the rate of grain growth  $dG/dt$  decreases with increasing value of  $n$ .

A slower rate of grain growth is usually ascribed to decrease of the grain boundary mobility term in Eq. (1). Boundary mobility and hence grain growth is hindered by pores, foreign atoms or inclusions.

The higher grain growth exponents frequently found in the early stages of sintering are generally ascribed to large porosity. Inclusions and impurities also significantly lower the value of constant  $K$ . For example, 250 ppm of MgO lowered  $K$  for  $Al_2O_3$  by a factor of 50 at 1600°C [7]. In  $Al_2O_3$ - $ZrO_2$  composite ceramics,  $K$  values for  $Al_2O_3$  and  $ZrO_2$  were reduced by factors of 160 and 3500, respectively, at 1650°C [8].

The homogeneous distribution of porosity and second phases is of prime importance for reproducible preparation of ceramics with well-defined properties.

When pores, additives or inclusions are not distributed uniformly, unhindered boundaries may move faster and some grains grow larger relative to their neighbours. The boundaries of larger grains with neighbouring smaller grains become more strongly curved, and will be able to migrate past pores or inclusions and trap them inside the grains. The result will be still larger grains with even more strongly curved boundaries which should easily grow further in the fine grained matrix. At this point it seems worthwhile to mention that growth of larger grains in a fine matrix may be promoted by other factors, not the size alone. Srolowitz et al [9] have recently reported the results of computer simulations which show that the inhibition of normal growth and the introduction of abnormally large grains is not a sufficient

condition for abnormal growth. However, the anisotropy of interfacial energy or a small amount of liquid phase greatly accelerate the growth of large grains, once present. The difference in driving force for growth between large and fine grains becomes so great, that the growth of matrix grains can be neglected. The grain growth exponent becomes 1, i.e. the abnormal grains increase in size linearly with time, as demonstrated by Hennings in the case of BaTiO<sub>3</sub> [10].

The trapped pores inside grains shrink so slowly that for all practical purposes densification ceases. The consequence is porous, coarse grained ceramics with inferior properties. Abnormal grain growth (also called "discontinuous" growth) may be avoided by avoiding heterogeneities [11] and/or, as is common practice, by additives, which may act in various ways [3]:

- (a) as foreign particles, which pin the grain boundaries ("second phase model"),
- (b) as a segregated layer at the grain boundary, slowing down the grain growth by a solute drag mechanism ("solute segregation theory"),
- (c) by enhancing the sintering rate relative to the grain growth rate ("solid solution mechanism").

The use of second phase particles for grain growth control can be limited by particle mobility, particle-boundary unpinning and coarsening by Ostwald ripening [12]. The use of solid solution additives is limited in that they are system specific [13].

The presence of liquid phase generally enhances the grain growth. When the solid grains are wetted by the liquid phase and are also soluble within it, the accepted mechanism is dissolution of smaller grains in the liquid phase and precipitation on the surfaces of the larger grains. The apparent activation energy for grain growth is usually reduced relative to that in the solid state.

The kinetics of grain growth is controlled by phase boundary reaction or by the diffusion through the liquid phase. In the latter case,

the rate of grain growth should be dependent on the grain boundary liquid phase thickness.

Again, the homogeneous distribution of liquid phase is of prime importance, particularly when the amount of liquid is small and/or the wetting is incomplete. Grains in contact with liquid growing faster than the grains in regions without liquid push the liquid layer and frequently develop an anisotropic shape due to the difference in surface energy of various planes or preferential segregation of impurities. The result is a heterogeneous microstructure, with grain size increasing with decreasing amount of liquid phase. The liquid phase may be transient in nature and may remain undetected.

In conclusion it may be stated that the microstructure development in each particular system must be studied thoroughly. The measurements of grain growth parameters, such as grain growth exponent  $n$ , activation energy for grain growth  $Q$ , and constant  $K$  are not sufficient to explain the mechanism of microstructure development in specific system. Other microstructural and compositional parameters must be observed and analysed: pore size, pore distribution, extent of solid second phase, level of dopants, and nonstoichiometry [3]. The intermittent stages of microstructure development must be also recorded. A complex analysis of data, the identification of the rate controlling process and of the influence of process variables can provide a path to reproducible manufacture of ceramic devices with optimal properties.

### 3. MICROSTRUCTURE OF VOLTAGE DEPENDENT RESISTORS

ZnO varistors, first developed by Matsuoka and his research groups in Japan in the late sixties [14] are ceramic semiconductive devices which exhibit highly nonlinear current-voltage characteristics. They are widely used as valve elements of lightning arresters for protecting electric power lines or as surge absorbers to protect electronic components against voltage surges.

ZnO VDR or varistors are complex multi-component ceramics, produced by sintering of ZnO powder with small amounts (0.5 - 1%) of additives such as  $\text{Bi}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  and others. Sintering and densification take place in the presence of  $\text{Bi}_2\text{O}_3$  based liquid phase.

The nonlinearity in the ZnO varistor is a grain boundary phenomenon and the performance of ZnO varistors depends on precise control of composition, impurities, mixing methods, particle sizes and sintering conditions. Extensive reviews have been published in recent years which delineate the conduction mechanisms and fabrication details [15-17].

The break-down voltage of the varistor depends on the number of grain boundaries between the electrodes. For high voltage applications, grain size is kept small, primarily with addition of  $\text{Sb}_2\text{O}_3$ , whereas for low voltage applications the microstructure has to be fairly coarse-grained, which is achieved by addition of  $\text{TiO}_2$ .

In recent years, extensive investigations have been carried out to clarify the mechanisms by which various additives influence the densification and grain growth in ZnO ceramics.

Early studies of  $\text{Sb}_2\text{O}_3$  containing varistors lead to the conclusion that  $\text{Sb}_2\text{O}_3$  forms a spinel phase ( $\text{Zn}_2\text{Sb}_2\text{O}_{12}$ ) which acts as a grain growth moderator by pinning grain boundaries during sintering. It was also observed that  $\text{Sb}_2\text{O}_3$  retards densification of ZnO [18]. More recent studies performed on the binary ZnO- $\text{Sb}_2\text{O}_3$  system revealed several details of the process.

Trontelj and Kraševc [19] showed that during heating at lower temperatures (below  $1100^\circ\text{C}$ ) a small addition of  $\text{Sb}_2\text{O}_3$  forms a continuous layer of Sb-rich film on the surface of ZnO particles which retards onset of densification and grain growth up to  $1100^\circ\text{C}$ . Kim et al [20] proposed that  $\text{Sb}_2\text{O}_3$  distributes on ZnO grains by an evaporation/condensation process at about  $500^\circ\text{C}$ , forming a non-crystalline phase. Densification does not start until the antimony oxide film on ZnO particle surfaces is eliminated through the formation of crystalline  $\alpha$ - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$  at about  $900^\circ\text{C}$  and subsequent

growth to fine inclusion particles at higher temperatures. Kraševc et al [21] confirmed formation of the films, and observed an oriented overgrowth of the crystalline spinel  $\text{Zn}_7\text{Sb}_2\text{O}_{12}$  on the prismatic as well as on the basal planes of ZnO crystallites. It was shown that these coherently overgrown spinel films are responsible for the inhibition of grain growth at high temperatures.

The densification and microstructure development of high voltage varistor compositions reflect the influence of both main additives used with ZnO, i.e.  $\text{Bi}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$ . Phenomena depend on the  $\text{Sb}_2\text{O}_3/\text{Bi}_2\text{O}_3$  ratio and temperature, as recently demonstrated by Kim et al [22].  $\text{Sb}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_3$  react below  $700^\circ\text{C}$  to form the pyrochlore phase  $\text{Bi}_{3/2}\text{ZnSb}_{3/2}\text{O}_7$  [23]. In compositions with excess  $\text{Sb}_2\text{O}_3$  ( $\text{Sb}_2\text{O}_3/\text{Bi}_2\text{O}_3 > 1$ ), the ZnO- $\text{Bi}_2\text{O}_3$  eutectic at  $750^\circ\text{C}$  does not form and densification and grain growth is hindered by the pyrochlore second phase. In compositions with excess  $\text{Bi}_2\text{O}_3$  ( $\text{Sb}_2\text{O}_3/\text{Bi}_2\text{O}_3 < 1$ ) the eutectic at  $750^\circ\text{C}$  accelerates densification and grain growth. The second phase moderates grain growth and keeps it uniform.

The pyrochlore phase reacts at about  $1000^\circ\text{C}$  with the ZnO matrix forming the  $\text{Zn}_7\text{Sb}_2\text{O}_{12}$  spinel phase, liberating  $\text{Bi}_2\text{O}_3$  which at this temperature is in the molten state. Eutectic liquid in compositions with excess  $\text{Sb}_2\text{O}_3$  accelerates densification and grain growth by a dissolution/precipitation mechanism. Accelerated grain growth is rapid at high temperature, causing nonuniform microstructure development with spinel inclusions in the ZnO grains.

Addition of  $\text{TiO}_2$  to varistor compositions causes development of a coarse grained structure, suitable for low clamping voltage devices [24-26]. The microstructure presented in Fig. 2 is typical of discontinuous grain growth in the presence of liquid phase. Large ZnO grains with other additive oxides in solid solution, contain spinel ( $\text{Zn}_2\text{TiO}_4$ ) inclusions. Spinel is located in the solidified melt among the grains, where  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  was also identified.

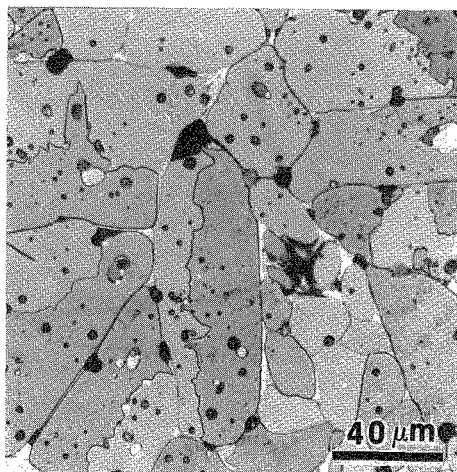


Figure 2. Microstructure of a low-voltage ZnO varistor ceramic, sintered for 1 hour at 1200°C [28].

Promoted grain growth in the ZnO-Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> system was ascribed to the increased reactivity of the Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> phase with ZnO, as compared with the reactivity of Bi<sub>2</sub>O<sub>3</sub> alone [27]. Discontinuous growth results from impeded growth at lower temperatures and accelerated growth in the presence of small amounts of liquid phase at higher temperatures. It was recently demonstrated that Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> rapidly diffuse on surfaces of ZnO grains even at 760°C. It was suggested that the thin Bi/Ti (Fig. 3) oxide layer effectively hinders densification and grain growth [28]. With increasing temperature slow grain growth takes place, impeded by Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>. Reaction of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> with ZnO at about 1040°C produces Zn<sub>2</sub>TiO<sub>4</sub> spinel and sets free Bi<sub>2</sub>O<sub>3</sub>, liquid at this temperature [29]. Reactive liquid together with a diminishing number of inclusions trigger exaggerated grain growth. A broader initial ZnO particle distribution produces a coarser microstructure, as expected [24]. The anisotropic growth of ZnO grains was interpreted as epitaxial growth of ZnO hexagonal prism planes [30]. It was argued that those planes offer a favourable atomic arrangement as compared with other planes.

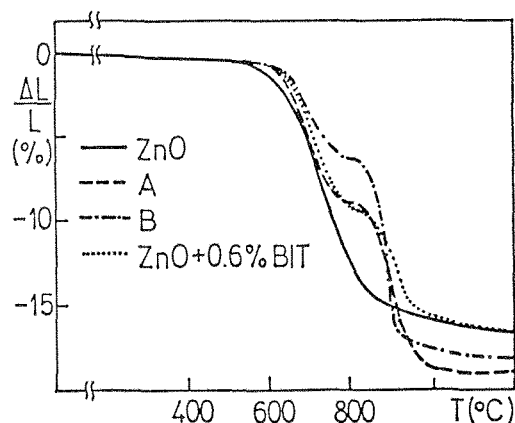


Figure 3. Constant heating rate dilatometric curves for ZnO ceramics [28]

ZnO without additives

ZnO + 0,6 wt% BiT (Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>)

A: ZnO + 6 wt% BiT

B: ZnO + 6 wt% BiT, 1 wt% Co<sub>3</sub>O<sub>4</sub> and 0,45 wt% Mn<sub>2</sub>O<sub>3</sub>

#### 4. MICROSTRUCTURE OF SiC CERAMICS

Microstructure development during sintering of silicon carbide ceramics has been extensively studied ever since Prochazka reported that sub-micron powders of β-SiC with small additions of boron and carbon (approximately 0.5 w/o of each) can be densified to greater than 98% of theoretical density by solid state sintering in the vicinity of 2100°C [31]. Subsequent work by Coppola and McMurry [32] has shown that the same approach was successful in the case of α-SiC powders.

The SiC microstructure is prone to exaggerated grain growth, which should be avoided to achieve high density and good mechanical properties. It is well known that β-SiC powders are more vulnerable to this phenomenon than α-SiC powders.

If the proper care is not taken, the microstructure of SiC ceramics prepared from β-SiC powder may contain extremely large plate-shaped grains of α-SiC in a matrix of much smaller slightly anisotropic β-SiC grains. At higher

temperatures, the microstructure may be fully recrystallized (Fig. 4).

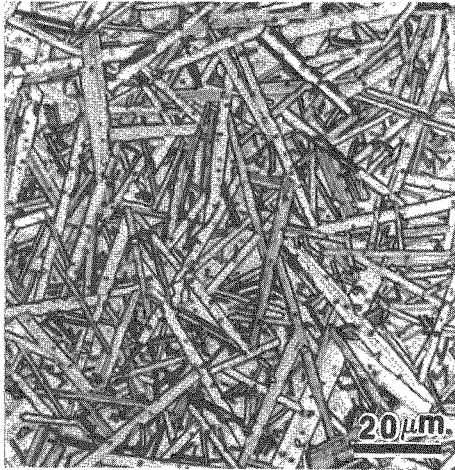


Figure 4. Microstructure of SiC ceramic sintered from  $\beta$ -SiC powder (0,5 wt%  $B_4C$ , 4 wt% C) to 97,8 % TD (2065°C, 1 hour, static Ar atmosphere. Courtesy V. M. Kevorkijan.

The origin of this phenomenon in the case of  $\beta$ -SiC powders is accepted to be phase transformation of  $\beta$ -SiC which is cubic and transforms in the sintering temperature range (2000-2200°C) into one or more  $\alpha$  polytypes with hexagonal or rhombohedral symmetry.

In general, the anisotropy of grain shape may be due to anisotropic growth kinetics (determined by the mobility term in Eq. (1), or due to anisotropic grain boundary energies. It was concluded that "normal", slightly elongated, plate shaped grains of sintered cubic ( $\beta$ ) SiC develop due to stacking faults on {111} planes and are therefore of kinetic origin [33]. During the early stage of sintering, the grains grow predominantly in the fault plane, but later in the densification process, they return to more equiaxial shape by the lateral growth of unfaulted  $\beta$ -SiC.

This is according to expectations, since the equilibrium grain shape of cubic materials must be closer to equiaxial in order to minimize the total grain boundary energy.

The morphology of extremely large  $\alpha$ -SiC grains embedded in a  $\beta$ -SiC matrix was studied by Shinozaki and Kinsman [34]. The authors observed that each  $\alpha$ -platelet was completely surrounded by a  $\beta$ -SiC envelope. Basal planes of  $\alpha$  grains coincided with {111} planes of the  $\beta$  envelope. It was proposed that after a critical sized nucleus of an  $\alpha$  polytype has developed in the  $\beta$ -SiC matrix, it grows rapidly in the basal plane by a variant of the reentrant-angle edge mechanism [33]. As in the previous case, the reason for exaggerated growth should be kinetic rather than due to a difference in surface energy of the various planes, although the hexagonal structure allows larger energy differences.

In contrast to  $\beta$ -SiC powders, similarly doped  $\alpha$ -SiC powders under comparable sintering conditions develop a microstructure with fairly equiaxial grains [35,36]. However, at higher sintering temperatures, exaggerated grain growth takes place even in SiC ceramics made of  $\alpha$  powders in which no  $\beta$  phase was detected (Fig. 5) [37-39]. This phenomenon is less well understood than in the case of  $\beta$ -SiC.

When the exaggerated growth starts, the large grains grow with a constant growth rate (grain growth exponent 1) until they impinge with other grains and growth stops (Fig. 6). Large pores appear within the grains. Grain growth is anisotropic and the grain size distribution curve broadens with time [39]. The grains are strongly faceted. This picture is typical of grain growth in the presence of a small amount of liquid phase, although the liquid phase was not detected.

It was repeatedly observed that the additives (B+C) are uniformly distributed among the SiC grains at the beginning of sintering. At high temperatures, carbon reduces the oxidized surface of SiC grains, whereas excess C hinders grain growth. Diffusion of B into SiC grains is a slow process at 2000°C [40] and it is likely that B together with SiC and Si form a finely distributed eutectic liquid, which accelerates sintering and grain growth by the solution-precipitation process. The liquid phase sintering mechanism was hypothesized by several

authors [35, 41, 42] but it was not accepted, mainly because examination of grain boundaries in SiC ceramics by high resolution transmission electron microscopy failed to detect a continuous second phase, expected in the case of a liquid phase mechanism [43, 44]. However, it was also pointed out that the second phase may be transient in nature [42]. During the sintering process, B dissolves in the SiC grains, whereas Si evaporates and/or reacts with carbon to form secondary SiC. A "clean" grain boundary may result.

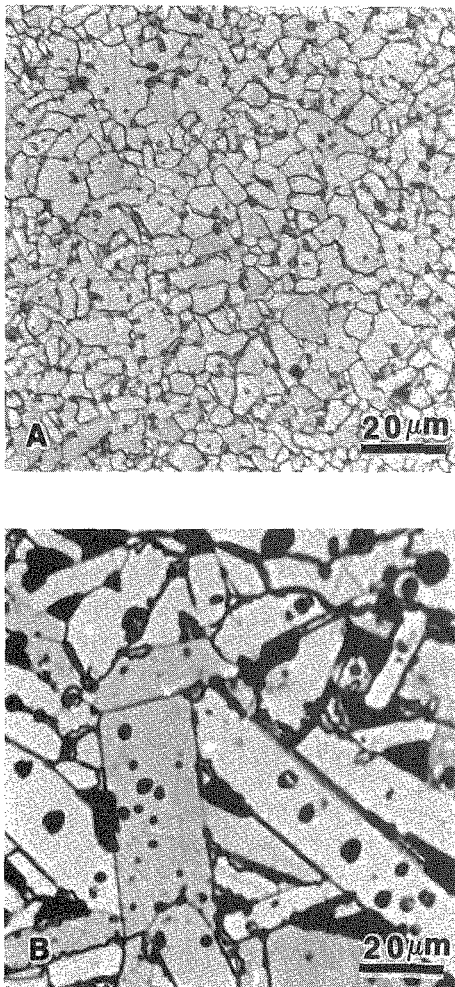


Figure 5. Microstructure of SiC ceramic sintered from  $\alpha$ -SiC powder (0,5 wt% B<sub>4</sub>C, 4 wt% C)

A: 2080°C, 0,5 hour, 97,8 % TD

B: 2020°C, 0,5 hour, 95,6 % TD [39]

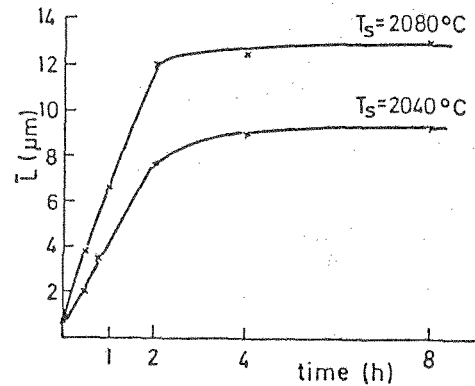


Figure 6. Linear intercept length of SiC grains vs. sintering time ( $\alpha$ -SiC, 0,5 wt% B<sub>4</sub>C, 4 wt% C) [39]

Rollett et al [45] have shown by Monte Carlo computer simulation that the abnormal grain growth may be related to anisotropy in the properties of grain boundaries. In an attempt to understand the mechanism of anisotropic grain growth in  $\alpha$ -SiC, we modified the model presented by Srolowitz et al [9] to allow anisotropic grain growth. Simulated anisotropic grain growth of a single grain embedded in a matrix of normally growing grains exhibited a nearly constant growth rate and an aspect ratio dependent on the cube root of time [46]. It was also shown that the growth rate is linearly proportional to the ratio between the energies in the promoted direction and the direction perpendicular to it. Simulations with less than 50 % of anisotropic grains developed bimodal microstructures, similar to the ones obtained experimentally (Fig. 7). Simulated distributions of aspect ratio vs. time were in excellent agreement with experimental data published in [47] for SiC (Fig. 8).

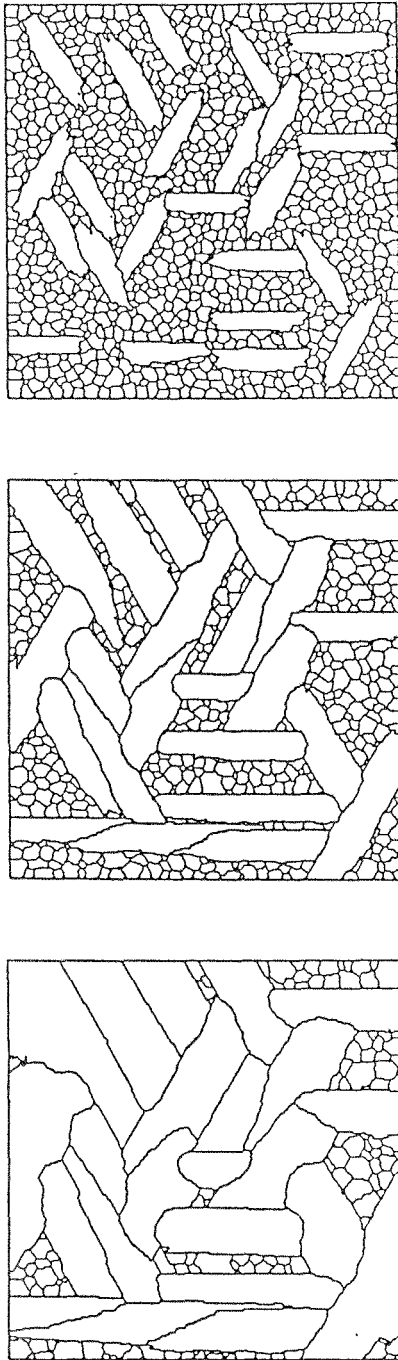


Figure 7. Time lapse sequence of microstructure development with 2 % of anisotropically growing grains and an energy ratio 1:4. From top to bottom: 40 MCS, 10 MCS, 200 MCS; MCS = time unit [46].

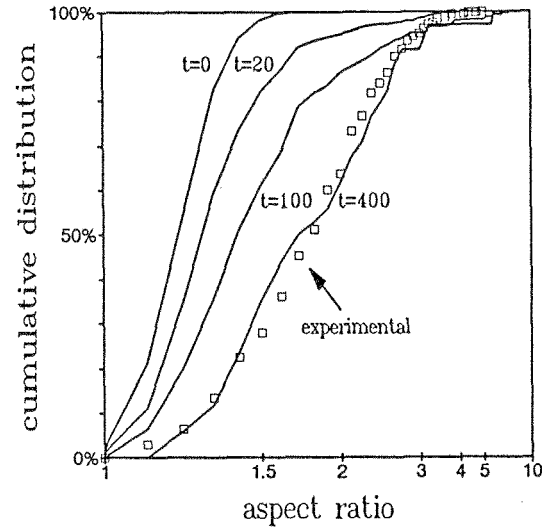


Figure 8. Time dependence of weighted aspect ratio cumulative distributions for a microstructure with 2 % of anisotropic grains and energy ratio 1:4. Squares represent experimental data for SiC from ref. [47].

## 5. CONCLUSIONS

1. The important features of ceramic microstructures which strongly influence the properties of ceramic products are (1) grain size and grain morphology, and (2), the chemical and structural characteristics of grain boundaries
2. Whereas the basic principles of microstructure evolution during sintering are well known, each particular system needs thorough investigation regarding the chemical reactions which may take place during sintering. In particular, the influence of additives and impurities must be analyzed to achieve reproducibility and optimal characteristics.
3. The principles of microstructure evolution in particular multicomponent systems may be generalized, provided that the systems are thoroughly investigated. With an increasing number of well described systems, the range of applications of high performance ceramics will steadily grow.



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