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Silicon Carbide and Silicon Nitride Ceramics for High Performance Structural Applications
- Development Status and Potential -

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Substantial progress has been made worldwide in recent years to enhance mechanical properties and reliability of SiC and Si_3N_4 ceramics. An overview will be presented on developments in processing, sintering as well as materials characterization and testing. Microstructural engineering has become of major interest in improving strength and fracture toughness. Sintering aids promoting liquid phase sintering have been studied extensively with both ceramics.
Pressureless sintered silicon carbide has reached strength levels of about 900 MPa with over 50 % increase in fracture toughness compared to materials sintered by solid state diffusion, making it attractive for gas turbine applications. Strength levels of gas pressure sintered silicon nitride have exceeded 1400 MPa with good high temperature strength retention.
In automotive applications SiC has been commercially introduced as a water pump seal while Si_3N_4 is being evaluated as inlet and exhaust valves besides other promising engine components. Results of extended road tests in cars have shown expected benefits. Further cost reduction is still a key issue for successful commercialization of these non-oxide ceramics.

1. INTRODUCTION

Silicon nitride and silicon carbide ceramics are the most promising materials for high performance structural applications. A deeper understanding of powder properties, processing conditions, effects of sintering aids and sintering parameters, and microstructure properties correlation has led to materials with strength levels and reliability nearly doubled over the past few years. Some key aspects of materials development will be adressed with specific examples and commercial applications.

2. PROCESSING

At the beginning of the development of high performance ceramic materials, properties were mainly influenced by powders quality. Meanwhile, a variety of powders are offered with low impurities, designed surface areas and specially low oxygen contents (Tab.1). So the quality and

Table 1
Ceramic Powder Properties

Powder	Specific Surface Area (BET) [m^2/g]	Mean Particle Size [µm]	Metallic Impurities [ppm]	Oxygen Content [weight %]
α - Si_3N_4	15...20	0,6...0,4	< 150	0,8...1,6
α - SiC	10...15	0,7...0,4	< 800	0,4...0,8

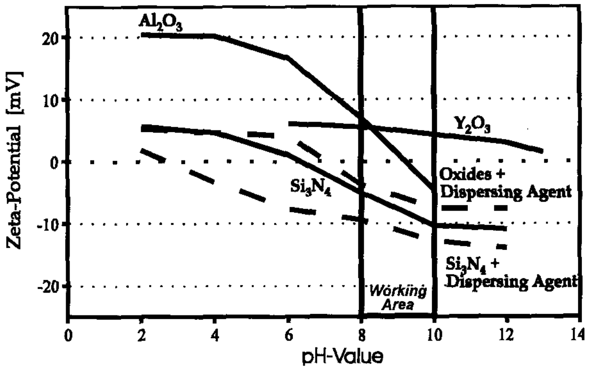

Figure 1. Zeta-potential of powders in water

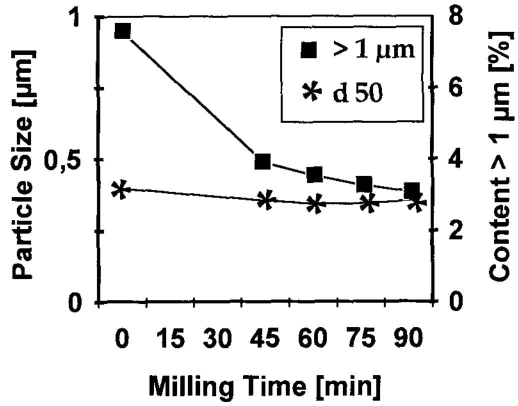

Figure 2. Particle sizes of milled Si_3N_4 slurries

reliability problem is now transferred to the processing and sintering steps, where the main goal is the avoidance of structural defects. For milling and mixing it is very important to achieve a homogeneous dis-persion, where water as the milling media is preferred because of environmental and cost aspects. Fig. 1 shows the zeta-potential of a typical raw Si_3N_4 powder and the most common additives yttria (Y_2O_3) and alumina (Al_2O_3) versus pH-value (full lines). Without any surface modification there can't be a intimate mixture because of different surface charges. By using specific surface (dispersing) agents all components show a negative charge (dashed lines), which results in a very homogeneous slurry in the working area between pH-value of 8 and 9 [1].

For the milling step itself the control of mixing energy is necessary. It should be high enough to destroy remaining powder agglomerates but not too high to avoid the generation of new surfaces with an increase of the oxygen content. Fig. 2 shows an optimized milling step, in which the particles (agglomerates) with a size of more than 1 µm are clearly reduced while the mean particle size is hardly influenced [1].

The drying step is determined by the following shaping method. In the slip casting process the molding could be carried out directly after milling. A predrying step is required for the injection molding process requiring organic additives independent of the selected binder system. For cold isostatic pressing (CIP) the control of drying ist most important because of structural defects in the granulates which could become the main failure origin in the sintered body. The dried granulates must have a certain size, shape, and strength high enough to allow a homogeneous filling of the mold, but must be completely destroyed by increasing pressure during compaction resulting in a green body with high density. Only a careful control of binders and plasticizers can lead to such an optimized granulated powder.

3. MATERIALS DEVELOPMENT

The main parameters for materials development are Si_3N_4-powder choice, amount of sintering additives, and control of the sintering step, by which the resulting mechanical, thermal, or chemical properties can be widely influenced. Because of the high number of potential factors statistical methods can be used to reduce the efforts in R&D work and specifically development time. Table 2 shows the result of a Taguchi L_9-array trial for gas pressure sintering parameters for Si_3N_4. A traditional full factorial experimental design of 4 factors with 3 levels would consist of 81 trials instead of 9 in the L_9-array. Besides the optimum levels of fac-

Table 2
Influence of gas pressure sintering parameters

Process Factors	Contribution to Flexural Strength [%]	
	Room Temp.	1000 C
Maximum Temp.	54,5	15,6
Holding Time	27,35	32,5
Gas Pressure	0,05	14,9
Pt. of Pressure Increase	18,1	37,0

tors the calculation of ANOVA-tabel gives as a result the influence of the examined factors on a certain property (in this case flexural strength).

For superior mechanical properties an optimized microstructure is essential. Fig. 3 shows the microstructure of two silicon nitride materials, Fig. 4 the affiliated grain size distributions. The very fine grained material is based on a diimide Si_3N_4 powder and characterized by excellent flexural strength properties (see below). The broad grain size distribution is based on Si_3N_4 powder synthesized by direct nitridation, resulting in medium strength.

The development and application of SiC high performance ceramics was enhanced by the possibility of pressureless, solid state sintering with addition of boron and carbon discovered by Prochazka in 1975 [2]. A further breakthrough was achieved by the liquid phase sintering of SiC using Al-compounds and yttria (LP-SiC) [3].

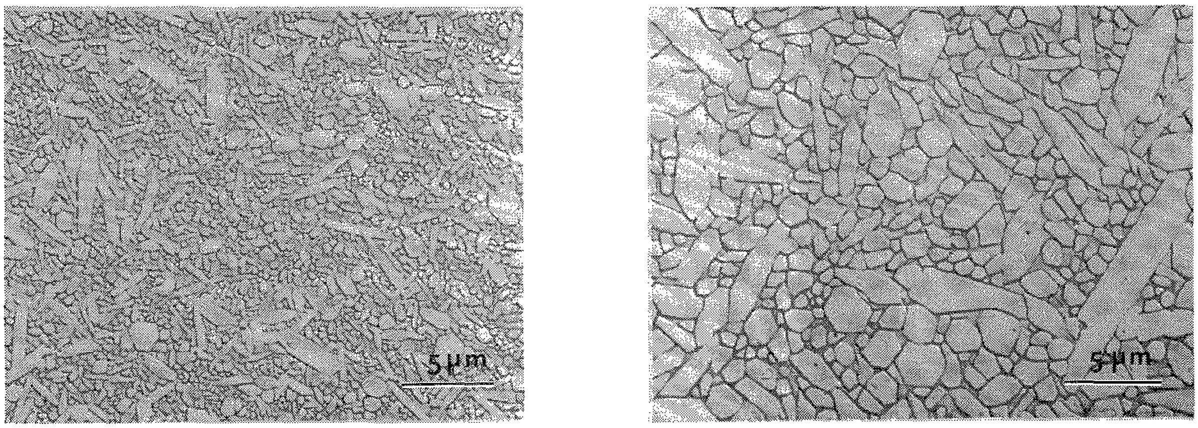

Figure 3. Optimized microstructure (left) and standard Si_3N_4microstructure (right)

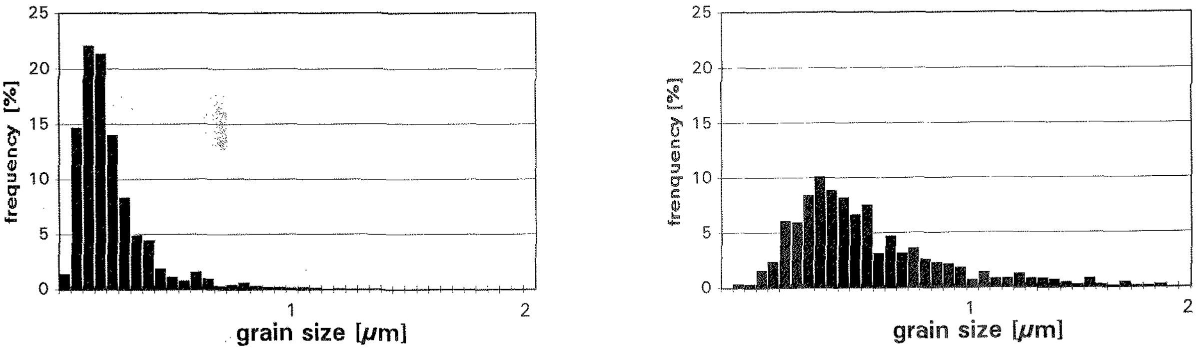

Figure 4. Grain size distributions for above microstructures (small base dimension)

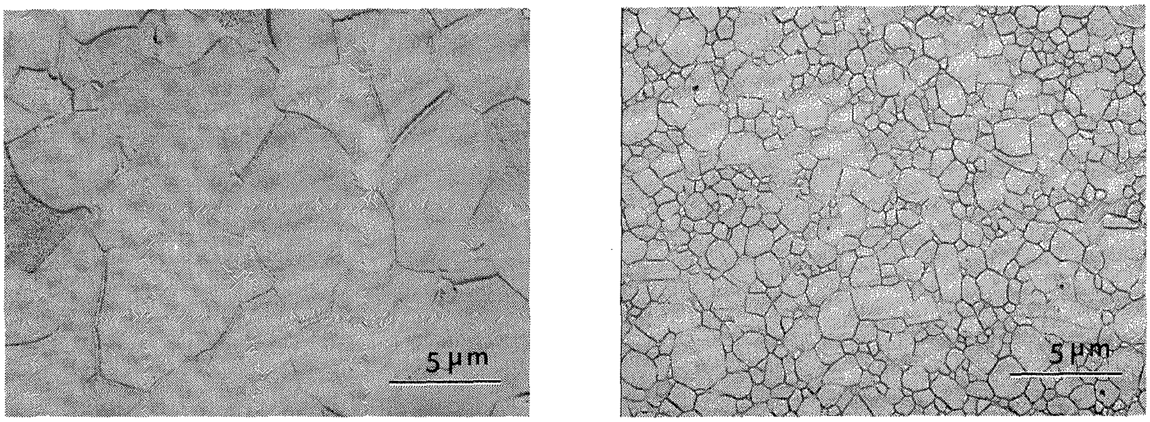

Figure 5. Comparison of microstructures of SiC, solid state sintered (left) and liquid phase sintered SiC (right)

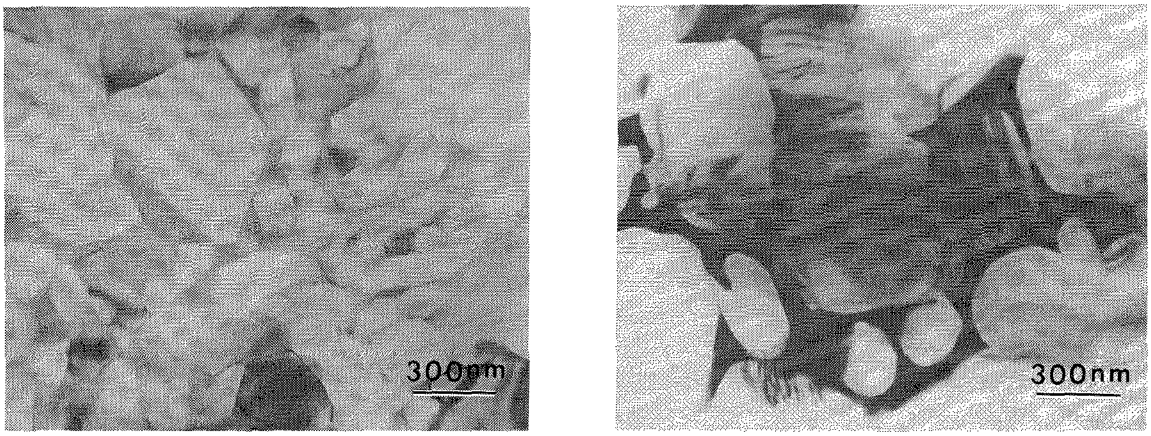

Figure 6. STEM-Micrographs of the microstructures of Si_3N_4 (left) and LP-SiC (right)

Fig. 5 illustrates the quite different microstructure in comparison with a solid state sintered SiC. Two STEM-micrographs (Fig. 6) show the difference in second phase distribution of LP-SiC and GPSN (gas pressure sintered silicon nitride).
While the intergranular phase of Si_3N_4 is completely amorphous, in the case of LP-SiC the intergranular phase is highly crystallized (YAG-phase).

4. CHARACTERIZATION AND PROPERTIES

A complete process development with specific optimization of each step leads to ceramic materials with superior mechanical

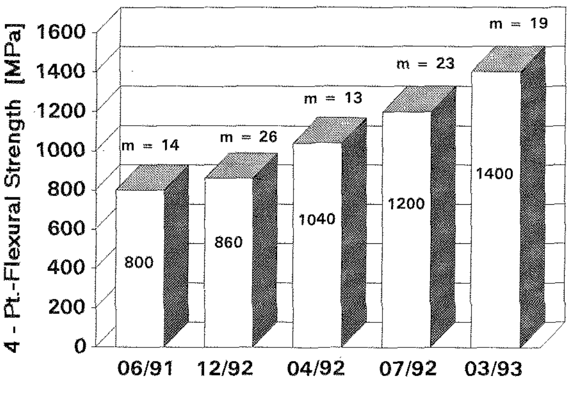

Figure 7. Strength development of Si_3N_4

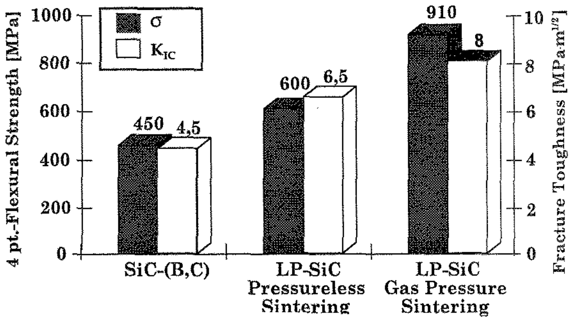

Figure 8. Mechanical properties of SiC-materials

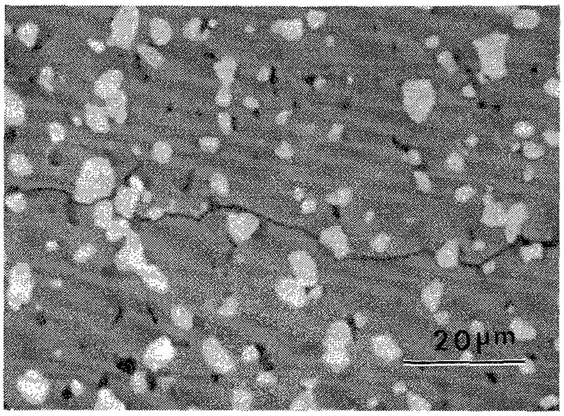

Figure 9. Microcrack propagation in $SiC\text{-}TiB_2$

properties. Fig. 7 shows the increase of 4.-pt. flexural strength for the last two years. Starting from 800 MPa presently a strength of 1400 MPa is achieved by consequent reduction of possible failure sources in all processing steps.

By the development of LP-SiC the flexural strength could be increased to 600 MPa, by using gas pressure sintering even up to 900 MPa. Additionally the fracture toughness is increased to $8\,MPa\sqrt{m}$ (fig. 8). LP-SiC shows now similar room temperature properties like a standard Si_3N_4 material but with better high temperature and tribological properties. A special type of SiC material developed by Carborundum Company is shown in fig. 9, where the SiC matrix is strengthened by TiB_2 particles which results in improved resistance

Table 3
Non-oxide ceramic components of engines in production

Component	Engine Manufacturers (1980 1982 1984 1986 1988 1990 1992)	Accumulated Number of Parts	Current Production Parts/Month
Glow Plug (Si_3N_4)	ISUZU	6 Mill.	20 000
	MITSUBISHI		12 000
	ISUZU		unknown
	MAZDA		6 000
	NISSAN		7 200
Precombustion Chamber (Si_3N_4)	ISUZU		8 000
	TOYOTA		5 000
	FORD		unknown
Cam Roller Follower (Si_3N_4)	DETROIT DIESEL	unknown	4 000
Rocker Arm Pad (Si_3N_4)	MITSUBISHI	unknown	16 000
	NISSAN	unknown	8 000
Turbocharger Rotor (Si_3N_4)	NISSAN	500 000	22 000
	ISUZU	unknown	unknown
	TOYOTA	unknown	13 000
Water Pump Seal Ring (SiC)	VW, AUDI, DB	> 20 Mill.	400 000
	FORD, PORSCHE		
Injection Pump nozzle (SiC)	CUMMINS	unknown	20 000

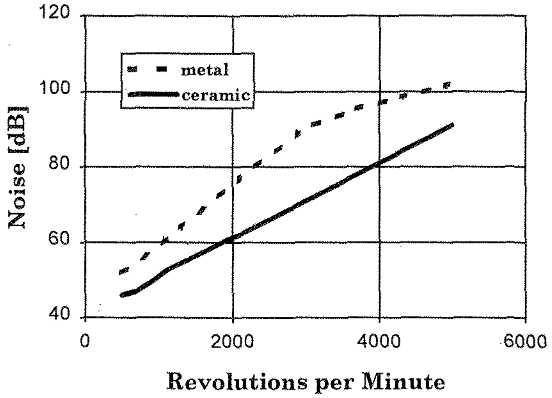

Figure 10. Noise emission of cylinder head with metal and ceramic valves [5]

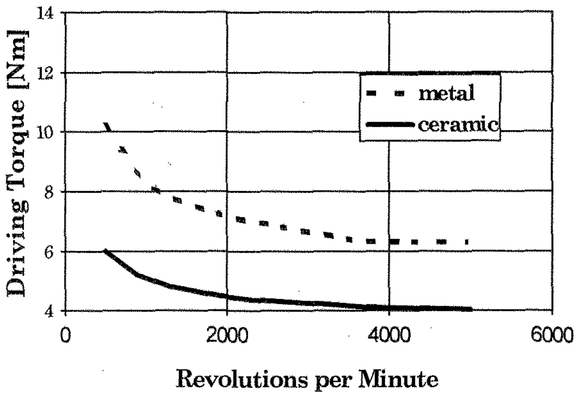

Figure 11. Driving torque for cylinder head with metal and ceramic valves [5]

against crack propagation. This material contains about 20 vol.-% of micron-sized TiB_2 particles which cause crack-tip deflection due to their higher Young's modulus than the SiC matrix.

5. APPLICATIONS

Contrary to the expected market growth of structural ceramics only a few components found their application in industry. Table 3 gives an overview about SiC and Si_3N_4 parts in automotive industries [4]. The most commonly used SiC component (solid state sintered) is the seal ring for water pumps in engines. The production of the rather complex shaped Si_3N_4 turbocharger rotor is remaining on a relatively low level. So the most promising Si_3N_4 components at the moment are the inlet and exhaust valves in the cylinder heads of automotive engines. Fig. 10 and 11 show the advantages of ceramic valves. Because of the low density the valve spring force can be reduced by which noise but more important the driving torque in the cylinder head can be reduced significantly [5]. By that a reduction of fuel consumption up to 5% can be observed.

In Hoechst AG four cars are presently running with ceramic valves (fig. 12) with no

Table 4
Properties of Si_3N_4 materials for engine valves

	Material HCT 90	Material HOE 120	Preliminary Valve Specification
σ_{RT} (4-pt.) [MPa]	922	1202	>900
$\sigma_{1000°C}$ (4-pt.) [MPa]	700	870	900
Weibull Modulus	19	23	>20
Density [g/cm^3]	3,27	3,26	-
K_{IC} [$MPa\sqrt{m}$]	7	9	-
Young's Modulus [GPa]	320	310	-
Hardness (HV 10) [GPa]	15	15	-

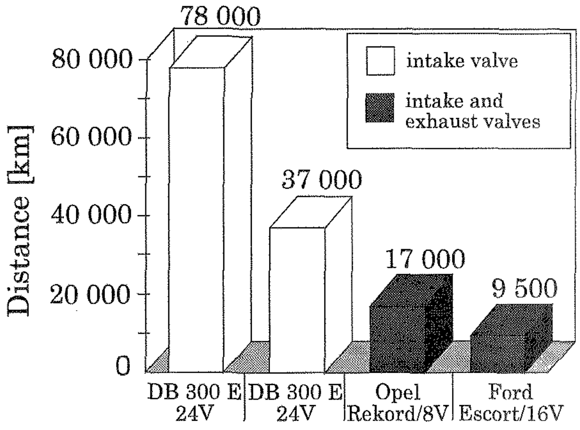

Figure 12. Road test with Hoechst AG cars

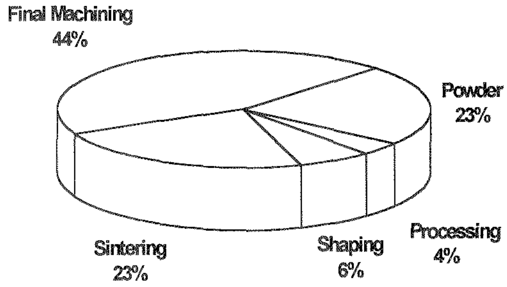

Figure 13. Relative costs of valve production

problems observed. Two Si_3N_4 materials have been specially developed for this application, the data are shown in table 4.

A major constraint for introducing ceramic valves in automotive engines are their manufacturing costs. Based on medium scale serial production, costs can easily be 2-5 times higher than those of metal valves depending on design and size. In case of sodium-cooled metal outlet valves, the costs may even be approximately equal because with ceramic the cooling is not needed. A relative cost calculation for ceramic valve production is shown in fig. 13. The largest cost contribution is in final machining which is determined by the required grinding time based on stock removal. Preliminary grinding studies using special tools have shown that grinding times of less than 2 minutes are realistic and close to 1 minute may be achievable.

Precondition for this is that accurately shaped parts with close tolerances have to be obtained by sintering in order to reduce the amount of material to be removed by the grinding process. Therefore it is most important to minimize the skin effect on as-fired surfaces of Si_3N_4 components as shown in cross sections of valve stems in fig. 14. These porous defects leading to strength degradation up to 40% are based on additive migrations and thermal decomposition of Si_3N_4 during sintering. Through proper control of sintering parameters these defects can be minimized as shown on the left picture in fig. 14.

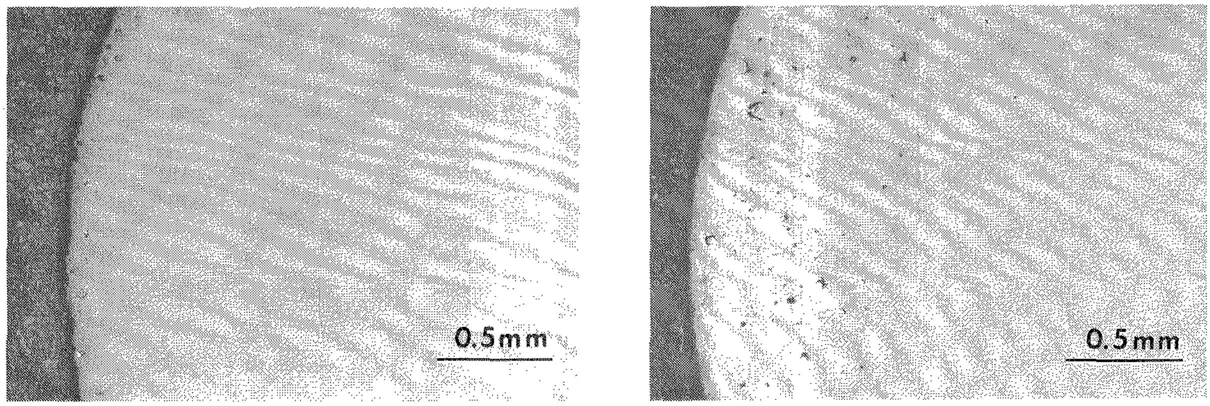

Figure 14. Skin effect of Si_3N_4-materials. Standard sintering cycle (right) and optimized sintering cycle (left)

The second main problem for the application of ceramics in engines is to achieve the required reliability. For large scale serial production parts the desired probability of failure is in the region of 10^{-8}. The potential of the material to meet these requirements is characterized by the mean strength and the Weibull modulus, where the latter becomes dominant in case of such high reliability level. If both material parameters are known (e.g. by statistical evaluation of 4-point-bending-tests) for a given stress level and stressed volume based on Weibull theory the corresponding reliability can be calculated. For automotive valves a realistic stress level is difficult to obtain because of the complex combination of dynamic thermal and mechanical loads. Nevertheless conservative estimations using finite element methods as well as experimental results, both in test rigs and in vehicles, have previously shown that even moderate strength Si_3N_4-materials had the potential for valve application [7,8]. For the new Si_3N_4-qualities there is no doubt that also the reliability demands of the automotive industry for large scale serial production can be satisfied.

6. SUMMARY AND OUTLOOK

SiC and Si_3N_4 monolithic materials are developed to high standards meeting property requirements for most commercial applications. Both ceramics have found a broad range of industrial usage in the field of wear, and corrosion, and thermal management in many engineering components. Manufacturing costs are still a major hurdle for successful introduction of new applications. Near net-shape forming techniques play a significant role in economic targets. High temperature properties of these ceramics like strength, creep, and oxidation resistance as well as reliability still need focused attention for high performance components, e.g. in gas turbines. Microstructural engineering plays a key role in all aspects of these property enhancements.

Significant progress has been made worldwide in the area of particulate composites and fiber reinforced composites. Ceramic reinforcements based on SiC have been developed which meet the high temperature stability requirements [9]. Great expectations are presently placed on nanocomposite materials which have shown superior strength and fracture toughness compared to monolithic materials [10]. Some of these nanocomposites exhibit superplastic behavior which offers interesting possibilities for shaping of components. These recent developments, although the commercial success is still lacking, will significantly impact the long range growth of high performance ceramics.

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Short Biography

Wolfgang D.G. Boecker ist manager of the Materials Research Department within Corporate Research at Hoechst Aktiengesellschaft in Frankfurt, Germany.
A graduate of the Technical University of Berlin, he received his diploma in chemical engineering in 1970 and his doctorate of engineering in 1979 while working at the Institute of Nonmetallic Inorganic Materials. In 1979 he joined the Carborundum Company in Niagara Falls, New York where he held managerial positions in R & D and manufacturing of high performance ceramics.
His research activities were in the areas of powder synthesis, processing and properties of oxide and non-oxide ceramics for structural and electronic applications as well as composites resulting in numerous patents.
In 1990 he returned to Germany joining Hoechst AG where he heads the R & D efforts in engineering and functional ceramics as well as high temperature superconductors.
He is member and fellow of the American Ceramic Society, member of the German Ceramic Society (DKG) and board member of the German Society for Materials Research (DGM).

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