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**CHARACTERIZATION OF SiC POWDERS  
AND THE INFLUENCE OF POWDER  
PROPERTIES ON SINTERING**

(Technical Report)

*Prepared for publication by*

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# Characterization of SiC powders and the influence of powder properties on sintering (Technical Report)

*Synopsis.* The report summarises the characteristics of SiC powders which influence the ability to obtain fully dense (non porous) ceramics, with good mechanical properties, via the sintering process. Methods for characterising powder properties, such as particle size, morphology, bulk and surface chemistry, are outlined and specific examples are referenced. The characteristics of typical commercial SiC powders are tabulated.

## Introduction

Silicon carbide components with the highest density and strength may be produced by direct sintering, hot-pressing or hot-isostatic-pressing from fine SiC-powders with sintering additives. High performance structural components require a sophisticated and controlled processing technology which necessitates the use of fine SiC-powders, which are generally characterized by high homogeneity and purity.

Such high quality silicon carbide powders can be produced by different methods, in the  $\alpha$  or  $\beta$  polymorphic forms in different particle sizes and purities. Depending on the manufacturing method the powders have specific properties, which have to be considered in their processing to obtain optimum final product properties. The powder properties which have to be characterized occupy the three categories; morphology, constitution and chemical composition.

In this report a survey is given of characterisation methods and typical SiC powder properties. This is preceded by an introduction to SiC sintering science which emphasises the importance of powder properties.

## Influence of powder properties and processing on microstructure and properties of SiC-Ceramics

The most convenient method for producing dense SiC is pressureless sintering [1,2]. Due to the strongly covalent character of the Si-C chemical bond and hence slow diffusion kinetics the addition of sintering aids is necessary, if a high degree of densification is required. The most frequently used combinations B+C or Al+C allow sintered densities of  $\geq 97\%$  of the theoretical value. A number of studies of the sintering behaviour of SiC have been made, but some of the underlying mechanisms have only recently been identified. In Al-doped sintering compositions there are indications of the formation of a liquid phase, at least in a transient state, whereas the sintering kinetics and the lack of a continuous grain boundary phase in B-containing compositions suggest a solid state diffusion reaction [3, 4].

The stable high temperature modifications, known generically as ' $\alpha$ -SiC', show a great number of hexagonal (H) and rhombohedral (R) polytypes which only differ in stacking sequence in the  $\langle 0001 \rangle_H$ -direction. The crystal type which is formed during the sintering process depends on the additives used [5,6]. Research shows that B promotes the formation of the 6H polytype which tends to promote discontinuous grain growth, with plate-like crystals of high aspect ratio, whereas the addition of Al leads to isotropic grain growth in the later stage of sintering. The

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risk of grain coarsening due to oversintering requires a strict optimization of the sintering parameters in relation to starting powder and sintering aid formulation.

Because of the sensitivity of sintering phenomena to small additions of sintering aids (e.g. 0.5 % B, 2 % C) homogeneous compositions and green bodies are preconditions for a homogeneous, fine microstructure.

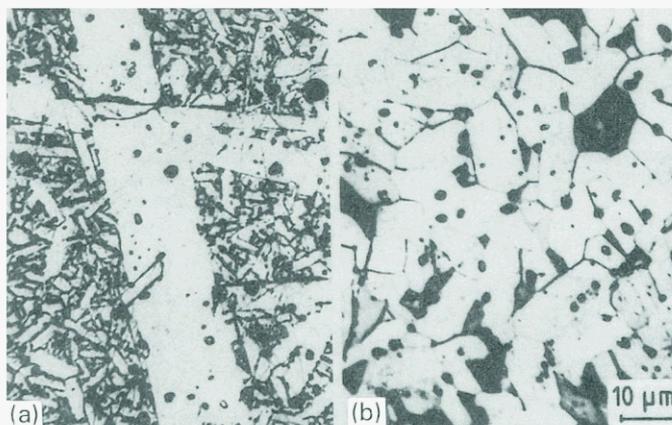


Fig.1 Influence of sintering additives on the microstructure of  $\alpha$ -SiC

- a) Additives: 0.5 wt% B, 2.0 wt% C; density: 3.11 g/cm<sup>3</sup>  
 b) Additives: 1.4 wt% Al, 0.1 wt% B, 2.0 wt% C; density: 3.03 g/cm<sup>3</sup>  
 Sintering condition a) and b): T=2090 °C; t = 20 min

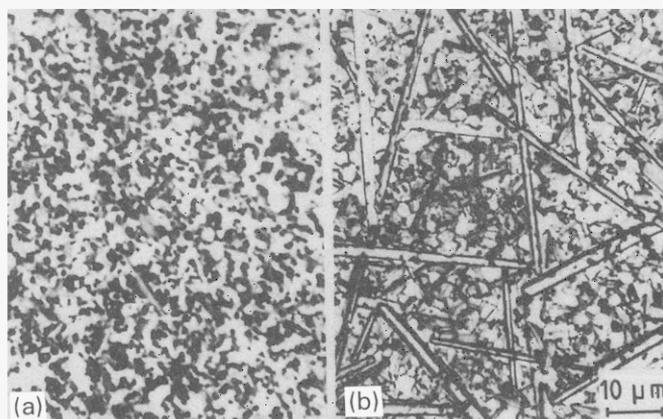


Fig.2 Influence of sintering conditions on the microstructure of  $\beta$ -SiC

- a) T = 2030 °C; t = 5 min; density: 3.05 g/cm<sup>3</sup>  
 b) T = 2050 °C; t = 20 min; density: 3.12 g/cm<sup>3</sup>  
 Sintering additives a) and b): 0.5 wt% B/1.0 wt% C

Excess carbon (above the stoichiometric SiC level) is an effective agent for microstructural control due to inhibition of secondary grain growth when finely dispersed in the SiC-matrix [7]. However, the major function of free carbon [8], which is necessary to obtain high sintered densities, is explained by its reaction with the SiO<sub>2</sub>-layer on the powder surface resulting in deoxidation with formation of fine SiC. At the same time evaporation and condensation reactions at high temperatures, which lead to sintering reactions without volume shrinkage, are suppressed in favour of bulk diffusion and the elimination of pore volume so that densification is promoted. Some examples of the influence of additives and sintering conditions on microstructure, described above, are given in figures 1 and 2.

Generally, pressureless sintering requires the finest SiC-powders which are in the submicron range. Examination of powders with different particle size distribution, and hence specific surface area, shows that high densification is only obtainable within a particular size range (Figure 3) dictated by reduced diffusion paths, and high sintering activity. The width of the particle size distribution determines the homogeneity of sintering reactions; a broad spectrum increases the tendency to oversintering and secondary grain growth.

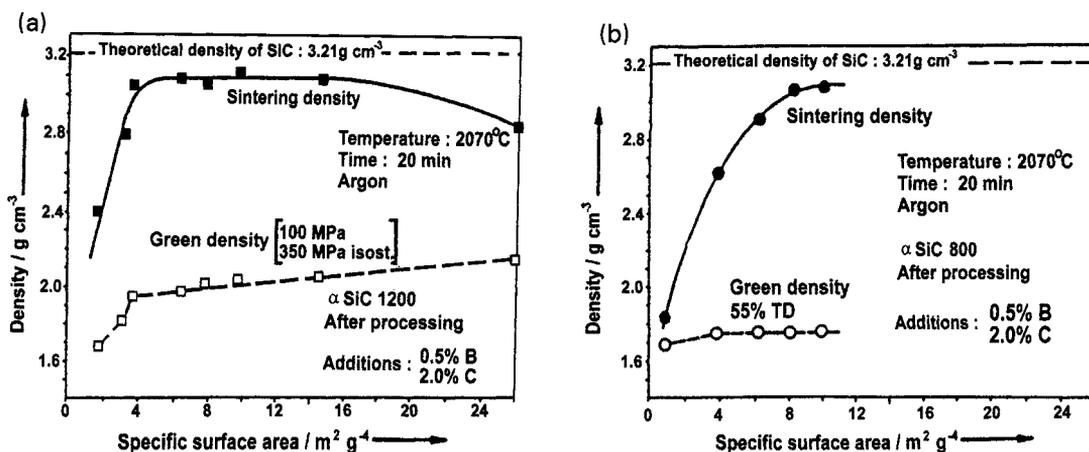


Fig. 3 Influence of physical properties on the sintered density. Experiments were performed with two different starting powders, SiC 1200 and SiC 800, which had been milled to increase the surface area. At comparable surface areas the powders differed in their grain size distribution; the powder in 3b had a higher mean grain size. (Courtesy of Prof. Hans Hausner)

$\beta$ -SiC transforms during sintering to  $\alpha$ -SiC by nucleation and growth and, therefore, has a greater susceptibility to discontinuous grain growth than alpha SiC starting material. However, suitable particle and sintering parameters allow high sintered densities and controlled microstructures with  $\beta$ -SiC as well [4].

SiC powder purity also has an influence on the sintered microstructure. Similar to the effect of sintering additives, impurities can induce the formation of specific preferred crystal structures, influence surface reactions or produce local liquid formation and other microstructural defects if they are heterogeneous. The oxygen content is of special interest as it influences the sintering reaction and can inhibit densification [8]. The oxygen content should be as low as possible, although, within limits, it can be balanced by the addition of free carbon.

Microstructural development during sintering is mainly responsible for the property profile of ceramics. The mechanical data, for example fracture stress, is a function of defect size, grain morphology and grain boundary characteristics. High temperature creep and stress rupture are especially sensitive to grain boundary phases, and hence to sintering additives and purity. A specific service stress or environment may dictate variations in powder property and additive. The requirements which have to be fulfilled are summarized in the following sections, together with a more detailed description of powder characterization.

## **Property Requirements for SiC-Powders**

### **Requirements for Sintering**

Because of the low sintering activity of pure SiC, fine powders are required. Agglomerates in fine powders should be weak and dispersible in processing [9, 10]. The purity should be as high as possible. The following categories of powder characterization and the general requirements of ceramic powders for sintering also apply to SiC:

- Fineness; 0.5  $\mu\text{m}$  average particle size, within a size distribution under 5  $\mu\text{m}$  and preferably under 3  $\mu\text{m}$
- Composition; greater than 99% purity, preferably 99.9% with respect to metallic impurities, high homogeneity, no heterogeneous contaminants
- Constitution/  
Phases  $\alpha$ -SiC or  $\beta$ -SiC are both suitable

The commonly used densification method is pressureless sintering under an Argon-atmosphere, using the finest SiC-powders. By pressure-sintering, e.g. hot-pressing or hot-isostatic-pressing [12, 13] coarser powders than mentioned under 3.1 can also be densified.

#### Requirements Dictated by Ceramic Preform Shaping Methods

According to the shaping technology different powder properties are significant:

- Dry-processing; fine particle size together with an equiaxed to spherical particle shape within a variable size distribution is important for a high green density
- Slip casting; surface chemistry and manufacturing methods of the powders as well as size characteristics have to be considered [11]
- Injection moulding; specific surface area, particle shape, and size distribution are important parameters.

#### Powder Characterization

Due to different requirements for SiC-sintering powders, there is a necessity to determine a range of powder characteristics. A comprehensive powder characterization is important as a control instrument for reproducible production of those powders as well as a quality control reference for the user.

#### Essential Aspects of Powder Characterization

Powders are characterized comprehensively in three property categories:

##### I. Morphology:

Characterization of single particles and particle agglomerates concerning size and shape as well as microstructure.

##### II. Constitution:

Material characterization of the powder concerning the nature and quantity of known mineralogical phases.

##### III. Chemical Composition

Characterization of the powder concerning the average chemical element content and surface chemistry.

Table 1 summarises possible characterization methods applicable to fine SiC-powders.

*Particle size.* Powder dimensions are described by crystallite size, primary particle size, aggregate size and specific surface area. These characteristics are partially dependent on one another.

The crystallite size can be estimated indirectly from X-ray line broadening, based on Scherrer's equation which compares the characteristic peak widths at half height [18]. Besides the crystallite size lattice defects and internal stress contribute to line broadening as well as instrumental precision. This method gives average data and does not always distinguish between crystallite and particle size and hence is not comparable with direct TEM-imaging.

TEM or SEM-micrographs define the size of individual primary particles which can be monocrystalline (crystallites) as well as polycrystalline, but which are not agglomerates. Ideal, well dispersed, powders, should consist of primary particles, at least after processing. Real powders are partially agglomerated. The finer the powders the greater the danger that such agglomerates survive in the processing during the production of sintering mixtures. This will lead to inhomogeneity and defects in the sintered microstructure.

The size of primary particles can be determined directly from electron micrographs and indirectly by the specific surface area or by other particle size measuring methods which are applied to dispersed powders [19]. All methods will show different results. Primary particle size in particular, calculated from the specific surface area, will be influenced by particle shape, surface-roughness, surface phases like amorphous SiO<sub>2</sub>-layers or adsorbed chemical residues from the powder production.

Direct imaging methods using TEM or SEM suffer from errors due to small sample population and are tedious for routine use. The Fisher Sub Sieve Sizer (FSSS) is both rapid and requires minimum operator skills in its use and is commonly used in industry for routine quality control of average particle size [20] and specific surface area (SSA). However, the most common method to measure the SSA of a powder is by nitrogen desorption/adsorption according to BET theory. Whilst multi point determinations are somewhat tedious and more suited to the research environment, single point measurements are rapid and can be used for routine quality control.

For a variety of reasons, principally the long times which are involved, classical sedimentation methods under gravity have lost their importance for the measurement of particle size distribution (PSD) of submicron powders. Nowadays the techniques usually employed are centrifugal sedimentation and laser light scattering both of which involve short measurement times and generally yield results of high reproducibility. Laser diffraction analysis in particular has made rapid strides in the last few years and a variety of commercial instruments are available. It should be emphasised however that the results of PSD analysis are strongly dependent on the technique of sample preparation e.g. use of specific agents and/or ultrasonic techniques for deagglomerating the powder and therefore the method and other conditions have to be specified when comparing data.

It is useful to analyze the particle size distributions of the original powder as well as that of the dispersed (deagglomerated) powder. The comparison of both distributions gives information on the agglomeration of primary particles. A deagglomerated powder, which should effectively consist of primary particles, can be obtained by intensive ultrasonic treatment of the powder suspension before the particle size distribution measurement, possibly with addition of dispersing agents. 'Weak' agglomerates are dispersed by this method but hard agglomerates may survive and will be analyzed as coarse particles. A good sintering powder should therefore show a particle size distribution of less than 3 μm in the deagglomerated state, to avoid, in the sintered parts, strength-determining inhomogeneities as a result of coarse grains or agglomerates.

*Particle Shape.* The particle shape, i.e. both the agglomerate and primary particle shape in a powder affects compacting/shaping and sintering properties. A rounded or equiaxed particle is desirable. SEM- and TEM- micrographs allow a characterization of average particle shape or particle shape distribution. The latter is more a function of the particle size, as larger particles or agglomerates mostly deviate from the equiaxed particle shape. The particle shape is defined by shape factor  $F_1$  [21]

$$F_1 = 4\pi A/U^2$$

TABLE 1. Characterization of SiC-powders

## Category

Main Characteristics	Property/Parameter	Technique
1.1. Particle and crystallite size	1.1.1. Crystallite size - average - individual	X-ray line broadening TEM
	1.1.2. Primary particle size - average - individual	partly by FSSS, BET TEM, SEM Microscopy
	1.1.3. Aggregate particle Size - average	FSSS = Permeability (ASTM B-330) calc. from BET and size distributions
	- distributions	Sieving, wet microsieving Sedimentation, centrifuge, light scattering
1.2. Particle shape	1.1.4. Specific Surface Area Crystallite/Particle shape	BET (gas adsorption) TEM, SEM Powder Micrograph
1.3 Microstructure of particles		TEM, SEM Microscopy

If SEM- or TEM-powder micrographs are used, the particle diameter  $A$  and the particle circumference  $U$  can be determined by a semi-automatic image analysis. A sphere has the value  $F = 1$  and irregular particles have values which are much smaller. Effects of shape factors on particle surface and particle volume are shown in [22].

*Additional Powder Properties Dependent on Morphology.* The particle size and shape affect the densities, green strength and flowability of the powder. Measurements should be made on dry powders, because the adsorbed humidity may have disturbing effects. Different densities can be measured: Bulk density or apparent density (Scott density, [23]), tap density [24] or a green density after cold pressing.

For coarser or agglomerated powders, which have a particular flowability, the 'Hall-Flow' value can be characterised [25]. This value specifies the time taken for a certain powder quantity to flow out of a funnel.

For the fine sinter-active powders only the green density may be usefully measured and this value provides information about compaction behaviour and amount of shrinkage to be expected during sintering. Green densities, which have been obtained on coupons pressed under controlled conditions can serve to reflect production-specific powder properties, such as particle size distribution, particle shape and agglomeration.

The chemical composition may also influence the green density if, for example, significant quantities of other phases of different specific gravity are present, for example, SiC with amorphous SiO<sub>2</sub>-films on the particle surface [26].

### Constitution/Phase Analysis

Phase analysis may be used to determine -

- (1) impurity phases which in SiC normally consist of SiO<sub>2</sub>, Si and C. Apart from crystalline Si the other phases cannot be analysed quantitatively using X-ray diffraction because either they are near the limit of detection or are non crystalline (e.g. SiO<sub>2</sub>).
- (2) the polytypes present within the nominal hexagonal  $\alpha$  or cubic  $\beta$  phases.

Typical  $\alpha$ -SiC powders, which originate from the high-temperature Acheson process, show a range of polytypes (mainly 6 H, 4 H and 15 R). It is not possible to quantify these individual polytypes exactly, but the method of J. Ruska and L.I. Gauckler using X-ray diffraction is mainly used [16]. SiC-powders originating from process reactions below 2000°C are mostly  $\beta$ -SiC-powders. The  $\alpha$ -SiC content in these  $\beta$ -SiC-powders can be determined from the intensity of the  $\alpha$ -SiC-diffraction line at  $d=0.2352\text{nm}$ . The percentage of  $\alpha$ -SiC (6 H here) will be taken directly from a calibration curve from known  $\alpha$ -SiC/ $\beta$ -SiC mixtures. Recent methods for determination of relative polytype content are based on chemical-shifts of NMR spectral peaks but to achieve the required spectral resolution access to a high-field 'magic-angle-spinning' system (MAS NMR) is required.

Phase content is important for sintering behaviour of SiC-powders.  $\beta$ -SiC powders may transform largely to the  $\alpha$ -phase during sintering and show a greater tendency to excessive grain growth up to ~100 microns. Therefore  $\beta$ -SiC powders have to be sintered more carefully to control grain size. Otherwise, complete removal of porosity will be inhibited, resulting in larger critical flaw sizes and reduced fracture stress. However, anomalous grain growth has been shown to enhance fracture toughness ( $K_{IC}$ ) via crack 'bridging' mechanisms.

### Chemical Composition

Chemical analyses of fine SiC-powders are necessary to determine carbon and oxygen contents, which have to be considered for the addition of sintering additives, and characterization of other impurities, which can influence the high temperature properties in the final product.

It is difficult to identify heterogeneously distributed impurities within the typically small samples used for analysis - even if representative sampling methods are applied. Specific "searching methods" are therefore necessary.

*Average Contents.* The overall Si and C content can be determined by different methods, but does not define their distribution. For example, these elements may exist as a SiC-phase or in the form of impurities like SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, free Si, free C or silicides such as FeSi<sub>2</sub>.

- Si: The determination of total Si-content can be made by wet chemical/gravimetric methods after an alkaline decomposition. This analysis is not very exact.
- C: The determination of total C-content may be achieved by coulometric titration of CO<sub>2</sub> formed by oxidation of SiC with oxygen at 1250°C using lead borate as a fluxing agent. Determination of free C can be made by the same method after its oxidative removal from coarser SiC-powders (>2 $\mu\text{m}$  average particle size), but this method is not suitable for finer SiC powders, because they will be simultaneously oxidized. For these powders a method of wet chemical oxidation may be useful [14].

For the analysis of metallic impurities the SiC-powders are dissolved, preferably in acid mixtures such as HF/HNO<sub>3</sub>, at 200°C in a teflon pressure vessel or in an alkali carbonate melt. The small content of metallic elements may be precisely determined from these solutions by spectrometric methods such as DCP, ICP or ICP-AES with the help of calibration solutions [27].

Oxygen and nitrogen contents are usually determined by a carrier gas hot extraction method (decomposition of SiC at a temperature of 2600°C). Oxygen content is partially dependent on surface area and hence particle size, but also on the manufacturing method. Generally low oxygen SiC-powders are preferred for sintering in order to decrease CO-formation. However, the oxygen content in fine SiC-powders may be up to 1.5wt% and is normally the dominant impurity. It originates in the SiO<sub>2</sub> oxidation films on SiC particle surfaces.

The sum of metallic impurities is mostly less than 1% and is considered harmless if homogeneously distributed but may give rise to microstructural defects if heterogeneously distributed. Some SiC-powders show anionic contaminations, such as Cl<sup>-</sup> and F<sup>-</sup> which can result from the final acid cleaning or from halides used for SiC-powder synthesis by the gas phase method. The content can be measured spectroscopically with EDX but the low energy fluorine X-rays are not normally detectable.

*Homogeneity and Surface Chemistry.* The homogeneity of the "pure" SiC-powder is as difficult to define as the homogeneity of the green bodies mixed with sintering additives, especially as the light element X-ray emission (C,O) is difficult to detect and quantify with X-ray fluorescence or EPMA.

Particle surface elements may be examined qualitatively by Auger-electron-spectroscopy (AES) or X-ray photoelectron spectroscopy (XPS). Moulded pieces or sintered bodies are more suitable than powders for the determination of heterogeneous impurities. Element mapping may be made with back-scattered electrons in SEM concerning size and distribution supplemented by X-ray imaging or spectroscopy (EDX) for compositional analysis.

Wetting behaviour, dispersion stability, viscosity and pH-value of suspensions are strongly dependent on the surface chemistry of SiC-powders. The latter is normally dependent on powder manufacturing method and it is important, especially for aqueous processing, to characterize such powder properties; for example, wet milling may increase surface oxygen above the initially manufactured level. Thus Zeta potential measurements or settling tests and viscosity measurements as a function of the pH-value are used to supplement direct measurements of surface chemistry and to predict powder behaviour during wet mixing and preforming (e.g. slip casting).

### **Production of Fine SiC-Powders**

There is a special requirement for high grade SiC powders for sintering, in relation to shaping behaviour, sintering ability, and formation of refined microstructures with good engineering properties. The choice of manufacturing method may also be influenced by economy, raw material availability, required volume of powder production and disposal of by-products. The three powder manufacturing methods most frequently used are;

- carbothermal reduction of SiO<sub>2</sub>
- direct carburization of Si
- gas phase reactions of gaseous Si- and C-compounds or thermal decomposition of organic precursors in the gas phase.

**TABLE 2** Characteristics of Fine  $\alpha$ -SiC-powders obtained from the Acheson-Process

1. Morphology Data		1	2	3	4	5
BET	m <sup>2</sup> /g	15.8	15.1	17.0	14.8	15.0
FSSS	$\mu$ m	0.60	0.65	0.67	0.60	0.60
Microtrac d50	$\mu$ m	0.7	0.8	0.8	0.8	0.7
Scott density	g/cm <sup>3</sup>	0.49	0.45	0.52	0.38	0.4
Green density	g/cm <sup>3</sup>	16	2.0	2.0	1.6	1.7
2. Constitution						
$\alpha$ -SiC-Polytype mixture, mainly 6H		x	x	x	x	x
3. Chemical Composition, mass fraction						
C total	%	29.4	30.2	29.9	29.4	29.6
O total	%	1.3	0.7	0.8	1.8	1.3
N	%	0.01	0.03	0.04	0.01	0.02
$\Sigma$ Fe, Al, Ca	%	0.08	0.03	0.04	0.08	0.03

1. H.C. Starck/Germany; 2. H.C. Starck/Germany; 3. Showa Denko/Japan; 4. Fukim/Japan; 5. Onoda Cement/Japan.

$\alpha$ -SiC only will be obtained by carbothermal reduction of SiO<sub>2</sub> at high temperatures, known as the "Acheson" method.  $\beta$ -SiC or amorphous SiC will be obtained by the other methods. Fine, high purity, SiC-powders can be produced by varied methods described in a large number of patents and scientific papers. However, production on a larger and economical scale is only possible by a few methods at present [28].

The following methods are the most promising:

- Milling methods for coarser  $\alpha$ - or  $\beta$ -SiC powders. The intensively milled powders have to undergo a cleaning to remove contamination especially if the milling has not been carried out with pure SiC media.
- A nearly direct production of fine powders by continuous carbothermal reduction of SiO<sub>2</sub>. In this method gaseous SiO is an intermediate reactant and ensures a fine Beta-SiC primary crystallite formation in an agglomerated powder which requires dispersion.
- Fine  $\beta$ -SiC-powders may be obtained directly by gas phase reactions. An excellent example is provided by the Mitsui Toatsu process in which SiCl<sub>4</sub> and heavy oil, as a source of carbon, are reacted in the vapour phase, excess carbon being subsequently removed by oxidation in air at 700°C.

Properties of fine  $\alpha$ -SiC-powders, which are produced in large volume by milling methods from readily available Acheson-SiC, are listed in Table 2. Fine  $\beta$ -SiC-powders are also produced on a significant scale by carbothermal reduction of SiO<sub>2</sub> and by carburization of Si. Table 3 compares the characteristics of  $\beta$ -SiC powders made by these methods, from different sources.

Beta-SiC-powders, produced by gas phase methods, are under development or at the pilot plant stage.

**TABLE 3** Characteristics of Fine -SiC-powders obtained from different processes

1. Morphology Data		1	2	3	4	5
BET	m <sup>2</sup> /g	15.8	18.1	16.8	18.3	10-20
FSSS	μm	(1.6) agglomerated	0.5	0,6	0.8	
Microtrac d50	μm	0.6	0.6	0,8	0.5	
Scott	g/cm <sup>3</sup>	0.7	0.5	0,5	0.6	
Green density	g/cm <sup>3</sup>	2.0	1.8	2,0	2.0	
2. Constitution						
β-SiC	%	99	97	99	99	mainly β
α-SiC	%	1	3	3	1	
3. Chemical Composition, mass fraction						
C total	%	30.4	29.9	30.6	30.1	0.1-0.6
O total	%	0.8	0.9	1.0	1.3	
N	%	0.2	0.3	0.2	0.3	
ΣFe, Al, Ca	%	0.08	0.18	0.08	0.09	
Process		Carbothermal Reduction of SiO <sub>2</sub>		Carburization of Si	Experimental from gasphase	

1. Superior Graphit/USA; 2. Ibidem/Japan; 3. H.C. Starck/Germany; 4. Showa Denko/Japan; 5. Experimental powder: Alcoa/USA, Nippon Steel/Japan, Standard Oil/USA.

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