

# Dense SiC-Ceramics with Specifically Adjusted Electrical Resistance (or Electrical Conductivity)

Dense, solid-state sintered SiC-ceramics and structural components produced therefrom are established over a wide range of industrial applications due to their outstanding combination of technically interesting properties (high strength and oxidation resistance up to very high temperatures, high hardness and wear resistance, comprehensive corrosion resistance, low thermal expansion, very good thermal conductivity, and favorable tribological properties). Concerning electrical properties, they usually show semiconductor behavior, which is not suitable for certain applications. By means of the described developments, such limitations were eliminated, providing special SiC-grades with adjustable high or low electrical resistance.

## Background of the development

Dense, SiC-based ceramic materials and structural components produced therefrom are established over a wide range of industrial applications due to their outstanding combination of technically interesting properties. Especially the property profile of solid-state sintered SiC is characterized by high strength and oxidation resistance up to high temperatures of 1500 °C in air and even higher under inert gas, high hardness and wear resistance, a comprehensive corrosion resistance from strongly acidic to the highly basic region, a low thermal expansion, a very good thermal conductivity, good tribological properties and usually electrical semiconductor properties (about:  $10^2$ – $10^5 \Omega \cdot \text{cm}$ ). Therefore, such components find various applications as e.g. seal-rings in mechanical seals, sliding bearings and shaft-protection sleeves, as wear-resistant compon-

## Keywords

silicon carbide (SiC), wear-resistant components, electrical conductivity, semiconductor properties, tribology

ents in materials preparation technology, as structural components of high-temperature and chemical plants such as heat exchanger, in semiconductor manufacturing, the sputtering technique as well as the electronics and sensor technology [1–4]. On the other hand, however, there were some restrictions on certain applications, resulting from the fact that although the SiC material would be well suited in terms of its mechanical, chemical and/or thermal properties, the electrical conductivity resp. the electrical resistance was inappropriate. To overcome these limitations in application, own development work has been carried out to selectively adjust the electrical resistance of dense, sintered SiC, without affecting other important properties to an unacceptable extent. Another objective was a cost-effective and competitive manufacturing of these materials and components by using raw materials of technical purity and applying conventional ceramic technology like an economically advantageous sintering process, to achieve cost acceptance by users and markets [5].

## Mechanism of the electrical conductivity of silicon carbide

Quite a number of solid-state physical examinations indicate that the semiconductor properties of crystalline SiC results from a relatively large gap of the electron conductivity bands, which is about three times larger than that of silicon. This “band-gap” specifically can be increased or decreased by doping with donors such as N or P or acceptors like Al or B, which dissolve in the SiC crystal lattice. Thus, SiC becomes p-semiconductive when 3-valent Al or B replace parts of the 4-valent Si or of the n-type when 5-valent N or P partially occupy 4-valent C-spaces. However, the resulting conductivity does not follow the rule of mixture, but influences the “band-gap” depending on the combin-

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ation and concentration of dopants up to the solubility saturation [6].

These concepts work reliably in semiconductor technology with high-purity starting materials and strictly controlled process conditions, but are no more applicable in processes using raw materials of technical purity, which already have a certain range of impurity elements. In addition, it must be considered that due to the high proportion of covalent bonding, the solid-state sintering of SiC is only possible by the addition of sintering additives, such as B and/or Al (in combination with C), which on its own terms are conductivity-relevant additives. Thus, the physical aspects are not well suited to realize specifically adjustable electrical conductivities of technical grades of sintered SiC-ceramics. That's why a more pragmatic approach has been chosen for the own developmental work.

The further request that basic properties of the SiC-materials should only be influenced by a minimal extent, excluded concepts like liquid phase sintering with a resulting continuous grain boundary phase in the microstructure of the material or the composite concept of mixed ceramics with well or poorly conductive phases with concentrations up to the so-called percolation structure of  $\geq 33$  vol.-%.

#### Pursued developmental concept

Own developments followed the pragmatic approach, to dope an established and well-characterized SiC sintering composition with the sintering additives B and C needed for solid state sintering, with N donors in the form of a high-temperature resistant Si-N compound and/or with Al in the form of a fine metal powder. These developmental grades were characterized concerning their sintering behavior and resulting mechanical properties as well as the electrical resistivity at room temperature according to the *ASTM* test instruction. In order to achieve very low values of electrical resistance, it pointed out that an increase of the content of free carbon resp. graphite is the most suitable solution.

#### Variation-range of the electrical resistance

In order to increase the electrical resistivity compared to the sintered standard SiC-grade S-SiC #135 of *FCT Hartbearbeitungs*

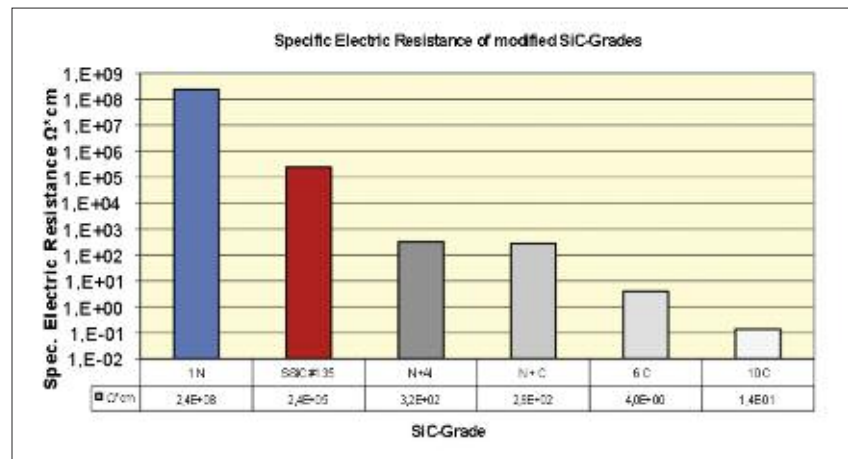


Fig. 1  
Specific electrical resistance of the modified SiC variants at room temperature

GmbH, increasing amounts of the powdered Si-N-compound were added to this basic composition. This measure indeed increased the specific electrical resistance at room temperature while surprisingly, up to a content of about 2 mass-% N, no negative impact on the achieved sintering densities is observed. An increase of the electrical resistivity, however, only occurs up to a content of about 1 mass-% N and falls again with higher contents. A physical explanation cannot be given for this, possibly the effect is connected with the achievement of a solubility limit of N in SiC. With an increase of the resistance value by over three orders of magnitude to about  $10^8 \Omega \cdot \text{cm}$ , compared to the standard SiC #135, this measure can be rated as quite successful (Fig. 1).

To realize also variants with lower electrical conductivity than the one of the standard material SiC #135, additions of Al to the B + C-doped basic SiC sintering composition were tested. Surprisingly, these attempts showed that additions of  $\geq 2$  mass-% Al disturb the sintering behavior of the standard material and are not a suitable measure to reduce the electrical resistance. On the other hand, a simultaneous addition of  $\leq 1.5$  mass-% Al in combination with the Si-N compound hardly hindered the sintering behavior and reduced the electric resistance compared to the reference SiC #135 by about 3 orders of magnitude to a value  $3 \cdot 10^2 \Omega \cdot \text{cm}$  (Fig. 1: N + Al). Again, no physical explana-

tion can be given for this, may be the presence of N by the Si-N-compound prevents a premature evaporation of Al by reaction to a stable compound, so that the Al is effective as a dopant only in combination with N. Thus, this measure points out to be suitable to realize a SiC-sintered material with relatively low electrical resistance. Further increased Al additions, however, do not result in any further reduced resistance values. Besides this, also a combination of N + C was found to lead to a similar reduction in electrical resistance.

In order to achieve even higher electrical conductivities, the addition of excess carbon appears as a suitable measure. One recommended measure described in literature is the addition of carbon nanotubes (CNTs), but their processing concerning dispersion is still difficult and frequently leads to defects by non-dispersed CNT-clusters and catalyst residues, influencing the mechanical properties and reliability of the resulting SiC-material in a very negative way. Alternatively, attempts performed with finely dispersed graphite suspensions showed that they enable a further reduction of the electrical resistance even with relatively low concentrations. Thus, the addition of 6 mass-% graphite by such a suspension resulted in a resistance of only  $4 \Omega \cdot \text{cm}$ , a value reduced by 5 orders of magnitude compared to the reference SiC #135 (Fig. 1: 6 C), without affecting the sintering behavior markedly negative. Increasing the graphite addition to 10 mass-% provides a further

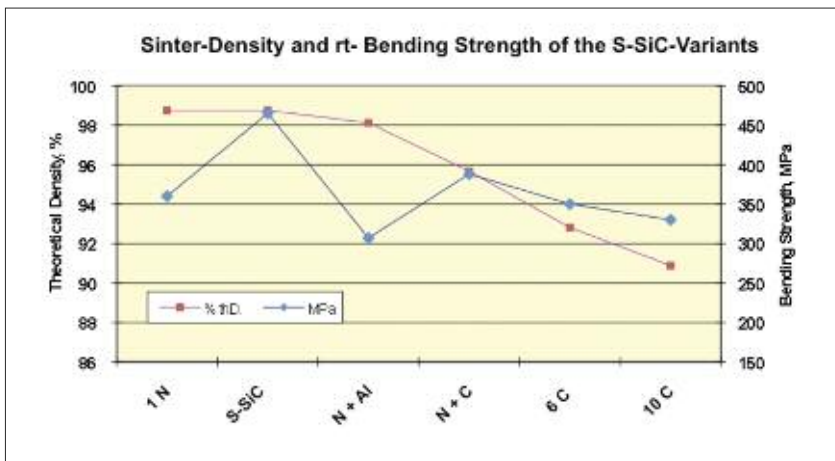


Fig. 2 Sintering densities [%] of the theoretical density and bending strength of the SiC-variants

reduced electrical resistance by one order of magnitude, however, this composition achieves only a sintering density of 2,8 g/cm<sup>3</sup>, which corresponds to about 91 % of the theoretical density, affecting the oxidation behavior in a negative way. To improve these highly graphite-loaded SiC-variants, a post-HIP treatment pointed out as successful, however on the expense of additional cost.

**Technological aspects: sintering behavior and mechanical properties**

In addition to the desired adjustment of the electrical resistivity, the material compositions shall be able to be densified by sintering and provide an acceptable level

of mechanical properties. The sintering behavior has been mentioned several times in the foregoing description and is also shown graphically in Fig. 2, represented as percentage of the theoretical density (th.d.) of their overall composition. From this graph it can be seen that the N- and Al-additions in the applied concentrations hardly influence the obtained sintered density. Increased additions of C, however, lead to decreased sintering densities, but even with 10 mass-% C still a density level of >90 % th.d. is reached. Therefore, the question is of interest, how such reduced densities affect the resulting strength, which was determined as 4-point bending strength (span length 40/20 mm)

at room temperature; mean values of the bending strength are shown as the second curve in Fig. 2.

Fig. 2 shows that all modified SiC-variants have a lower strength compared with the standard SiC #135, the largest decrease occurs with the Al-doped variant. As an explanation for this, again difficulties to achieve a homogeneous distribution of the added Al-particles can be given, comparable to the difficulties with CNTs. Relatively moderate, however, are the decreases in strength for the variants with excess C, despite of the significantly higher concentrations added. This is obviously related with the very uniform and defect-free distribution of the graphite phase, obtained by means of fine graphite suspensions, as can be seen from the following SEM micrographs (analyzed by *Fhg-IKTS*):

Overall, it can be considered positive that the strength level of all variants remains above 300 MPa, which is a common value for sintered SiC-based materials and makes their technical use possible. Besides this, there is also the possibility of increasing the density and the strength level by post-HIPing. With the variants tested in this regard in each case a strength increase to about 450 MPa could be achieved, corresponding to the strength-level of the standard SiC #135.

**Summary**

With the development described, it is possible to realize dense, sintered SiC-materials with up to 3 orders of magnitude (up

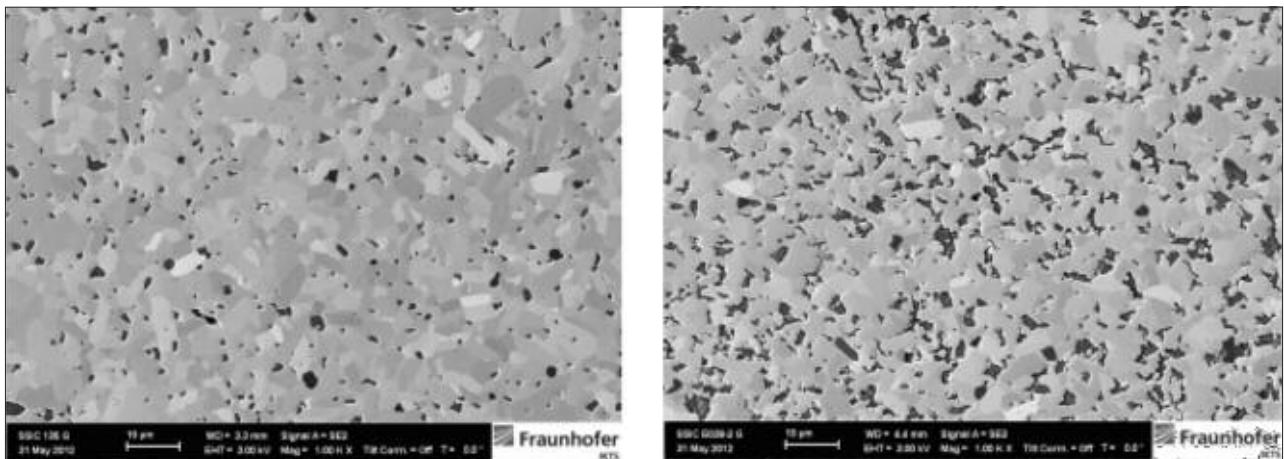


Fig. 3 FE-SEM micrographs of the standard SiC #135 and the SiC-variant with 10 mass-% C

to  $\geq 10^8 \Omega \cdot \text{cm}$ ) higher or down to 5 orders of magnitude (to  $10^{-1} \Omega \cdot \text{cm}$ ) lower specific electrical resistivity at room temperature compared to the standard or reference SiC #135. These developments were performed under particular attention to affect the characteristic, favorable properties of the solid-state sintered SiC only as low as possible. Compared to the standard SiC #135 with its very good strength of about 450 MPa, the bending strength of the modified SiC-variants is 100–150 MPa lower. However, they still provide properties, which make them suitable for many common as well as new technical applications. As examples for the high-resistance SiC-variant, there are pos-

sible applications as heat-sinks, insulating furnace components and structural parts for the solar and semiconductor industry, possibly as a replacement for low-strength BN-parts. Because of a still good thermal stability despite the presence of higher levels of free C, the low-resistance SiC-materials appear suitable for applications like new concepts of heating elements as well as sputtering materials and targets. Furthermore, these low-resistance SiC-variants allow an electrical discharge machining (EDM), which enables the introduction of fine holes or the production of complex structures, which cannot be realized or only with great effort by other methods. First EDM-attempts have been successful

and open up a potential for completely new design possibilities for SiC-components in the future [7]. Another interesting aspect is, that according to new research results by FhG, the tribological behavior of SiC-sliding pairs in an electrolyte medium can specifically be influenced by the application of electrical potentials, for which also SiC-materials with a specifically adjusted electrical conductivity or electrical resistivity are needed [8].

Overall, besides the examples outlined, much more innovative applications for these SiC-materials will develop, encouraged by the aspect that all these SiC-variants can be produced by an established ceramic technology at adequate cost.

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