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ON THE SINTERING OF SILICON CARBIDE

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16. Abstract

This document deals with the sintering of silicon carbide using pressureless sintering. This technique makes it possible to sinter a primarily covalent material to usable densities up to over 98% thD without having to use a high amount of sinter additives as is the case with other non-oxide ceramic materials. The process takes place rapidly, and it is also possible to produce relatively thick-walled structural parts without major problems. This sheds more light on the true characteristics of silicon carbide in one structural part, since there is no second or nearly no second phase. Heat pressing has improved stability.

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ON THE SINTERING OF SILICON CARBIDE

E. Gugel
Dedicated to Professor J Oel
on his 60th Birthday

In numerous scientific treatises, Prof. Oel has /89* demonstrated his intensive interest in sintering. Consequently, the author takes the liberty of expressing a few thoughts on still unresolved questions as to the nature of the silicon carbide sintering mechanism. In due consideration of observations quoted in relevant literature and gleaned from the author's own investigations[1], these considerations would indicate that an initial liquid-phase sintering is ultimately followed by solid-state sintering in the final stage, whereby both are only possible following "purification" with the aid of a reducing agent. The relatively modest strength of pressureless-sintered SiC (SSiC) is chiefly attributable to the hardly avoidable presence of excess reductive carbon.

1. Introduction

The most notable discovery among the many noteworthy developments in the field of non-oxide ceramics in the last two decades is that of pressureless-sintered silicon carbide. In this discovery it has been possible to sinter a primarily covalent material to usable densities up to over 98% thD without having to use a high amount of sinter additives as is the case with other non-oxide ceramic materials. Moreover, the sintering process takes place amazingly rapidly, and it is also possible to

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*Numbers in the margin indicate pagination in the foreign text.

[1] The extensive results of investigations conducted within the scope of a commission from the German Federal Ministry for Research and Technology (BMFT) have been summarized and published in the form of semi-annual and final reports [1,2] in cooperation with the author's former associate, Dr. Gerhard Leimer.

produce relatively thick-walled structural parts without major problems. This means that we are nearing the goal of realizing the true characteristics of silicon carbide--whereby mechanical characteristics are of the greatest interest--in one structural part, since there is no second or nearly no second phase. However, it has been shown that the stability attained to date at a level of 400 N/mm^2 (bending strength, 4-point) cannot be considered satisfactory, so that the question arises, what can be done to improve stability. Nonetheless, heat compressing has made it possible to attain bending stabilities up to 600 N/mm^2.

2. Historical Background of Sintering

Attempts to process silicon carbide in its purest possible form into a dense substance go back as far as the early stages of its technical production beginning in 1893. As early as 1899, it was suggested [3] that silicon carbide granules be processed into a molded body by means of heat treatment, a process which is possible using a combination of vaporization and separation. This process led to the fireproof substance designated as recrystallized silicon carbide, available on the market today. This coarse-pored product is produced at temperatures exceeding 2300°C without exhibiting any shrinkage, a fact which clearly proves the stability of SiC.

No necessary volume diffusion takes place in sintering effected by shrinkage, with conditions for this becoming even less suitable as recrystallization, making the crystal coarser, progresses.

In 1956 silicon carbide was sintered to density for the first time. This was accomplished using heat pressure [4], whereby relatively small amounts of boron, aluminum, and iron acted in elementary state or in compounds as the sintering agent. This provided evidence that the graphite matrices provide a reducing atmosphere. We note this here, because, as is known, use of pressure during sintering provides only limited relief for the densification process, but does not introduce any basically different sintering process, especially since the pressure is relatively low due to graphite stamps which must be used. Increased densification through grain destruction and slipping procedures takes place only under extremely high pressure [5].

In addition to this, reference is also made [5] to the later discovery of boron's effect on sintering: During experiments on SiC preparations made from carbon and SiO_2 and intended for semiconductor purposes, a fritted crystal cake was observed instead of the usual loose powder when boron was used as the doping agent.

Finally, the breakthrough came in 1973 by adding small amounts of boron (or B_4C) and carbon while using submicron-fine powder [6]. The original assumption that crystal modification is decisive led to the belief, at first, that sinterability was a characteristic of only β-SiC. This was later disproved when the same effect with fine-grained α-SiC was attained [7]. This led above all to ongoing arguments with regard to patent rights.

The favorable effect of boron during heat pressing was, without a doubt, the inspiration for using this additive in pressureless sintering. The similar effect of aluminum, discovered at a later date [8], also originates with heat pressing [4].

It is also important to mention that metals with a reducing effect used in place of carbon likewise lead to a sintering effect when used in combination with boron.

Naturally, this development had a positive effect on patent literature, a fact, however, which is of little substantial importance. Thus, for example, Fe, Ti, W, Mg, but also Ca, Ga, Ni, Cr, Mn, Zr, In, and Sc were recognized as having the same effect as boron or aluminum (for example, [9]).

3. Arrangement of Structure

The structure of silicon carbide sintered under optimum conditions is characterized by a relatively uniform grain structure with maximum measurements seldom exceeding 5 μm. Through volume diffusion, it resembles highly sinterably material, for example, aluminum oxide. Sintering conditions which are too severe make the grain structure coarser, /90 particularly lengthwise-oriented crystals to the point of extremely needle-shaped giant grain growths. Such conditions also make the residual spores coarser and, at the same time, they lower stability. The structural picture differs markedly from that of the dense silicon nitride which always contains a higher portion of secondary phases. Silicon nitride results from recrystallization caused by a dissolution-separation mechanism employing a glass phase.

Occlusions made of carbon and diverse impurities can always be found in the SSiC structure [2, 10]. The existence of a very thin, uninterrupted grain boundary phase was suspected in only one case [11], but was not discovered in other investigations, even those using high-dissolution instruments [10, 12]. Boron is distributed uniformly over the entire cross section of the structure. A discontinuous second phase with high boron content is discovered only with larger additive amounts [13].

4. Sintering Mechanisms

The development of silicon carbide produced through pressureless sintering naturally gave rise to intensive considerations on how this sintering of a primarily covalent material occurs at all. Originally, it was assumed that activating the driving forces by means of sinter additives was sufficient to support material transport [6]. This statement is supported by thermodynamic observations of processes in which sintering is fundamentally possible on the way over the collar formation having a seal [14]. Further, the self-diffusion data measured to date [15] show that silicon carbide develops sinterability more readily than silicon nitride does. It is well known that silicon nitride cannot be condensed without larger portions of sintering additive. (However, this can be traced back to the fact that silicon nitride never reaches the high temperatures necessary for sintering because of its early decomposition at 1900°C.)

On the other hand, there are investigation results which indicate the possibility of sintering affected or supported by liquid phases [11, 13].

Already in 1976, the author drew attention to the fact that both liquid phase and solid body sintering mechanisms might be decisive [16]. This will be dealt with in greater detail here, whereby Table I lists the measures which lead to SiC sintering, with attention being paid to their special effects according to present knowledge.

Increased surface energy and decreased grain boundary energy enhance sintering because the superimposed drifting power is increased. To attain densification of the material, material transport must take place primarily by volume diffusion, but also by grain boundary diffusion or by dissolution and reseparating through a liquid phase. Evaporation-condensation processes and surface diffusion should be prevented.

The use of submicron-fine powder means increased surface energy and influences the individual sintering mechanisms positively, as can be seen in Table I.

The effect of carbon as a reduction agent is indisputable; oxygen contents in SiC-powder up to > 2% were reduced to < 0.1%. Other reduction agents also exhibit a similar effect. The

SiO_2 which is present at least as a mono-molecular surface layer is eliminated. On the one hand, this influences surface energy, and, on the other, surface diffusion. The amount of carbon required is dictated by the oxygen content. Too little additive markedly worsens the sintering effect. Excessive amounts lead, of course, to a well condensed product, but their excess represents a structural characteristic which affects stability unfavorably.

Inserting carbon into the SiC lattice would certainly alter the sintering activity; however, this cannot be expected on the basis of knowledge to date.

Inserting boron into the SiC lattice, however, is probably possible, because SiC possesses a considerable solubility for boron [17]. The optimum mixture of the auxiliary sintering agent depends on this solubility [18]. This increases self-diffusion, which subsequently makes an improved material transport possible through volume diffusion.

Before boron is inserted in the SiC lattice, it is situated on the grain boundary, where it favorably influences grain boundary diffusion.

An important possibility is the formation of a eutectic mixture which melts beginning at 1400°C in the Si-B-C system [17]; this is a prerequisite for liquid phase sintering.

Further, in [14] boron is said to prevent SiC surface diffusion and decomposition, or else cause it to happen only at higher temperatures, thereby preventing grains from becoming coarser and/or surface reduction before the other sintering mechanisms start. However, boron itself disperses uniformly over the SiC surface beginning at 1350°C [11], which is a prerequisite for this effect. If one draws upon all these observations and considerations for a conclusion, we see that both solid body and liquid phase sintering mechanisms play a role in pressureless sintering of silicon carbide. The additives, carbon and boron, come from original mixture between the SiC grains, that is, on their surfaces. Before sintering can begin, oxygen must be cleaned from the surface using carbon. Then the boron combines with the silicon carbide to form a eutectic liquid phase, which also requires silicon for its formation. This silicon can be supplied by the SiO_2 reduction or else by SiC decomposition of the extremely fine powder. The finely distributed liquid phase serves as an agent for material transport (dissolution and reseparation) of silicon carbide so long as the phase is slowly dissolved in the SiC-lattice by the boron drift. In the process--in accordance with the continuously detectable weight loss--evaporation of the silicon which is released must be assumed. The silicon may also combine with the constant excess reduction carbon, thus forming SiC. This explains the resulting C loss according to calculations --using C and O content before and after combustion [1].

Doping SiC with boron increases volume diffusion to the point that solid body mass transport can now occur simultaneously. This leads to the final SSiC structure arrangement which is common for this sintering mechanism.

5. Stability

The sintering process just discussed naturally influences stability development in sintered silicon carbide. Disregarding coarse occlusions which impair stability substantially and which were observed as structural errors [2, 10], the carbon additive necessary for reduction plays a decisive role.

Microanalytical investigations [10, 19] have proven the presence of carbon in sintered silicon carbide, more precisely, in singular grains not larger than 1-2 μm on the grain boundary. Preferably, it occurs in connection with residual pores.

To totally remove the oxygen content in SiC powder, which can amount to up to > 2%, carbon equal stoichiometrically to only 75% of the oxygen content is required. Practically, however, much more is required to guarantee a sufficiently high densification at all. In the process, the type of carbon used takes on increased importance, since it determines the attainable distribution level. Both relatively too low and too high carbon content--in both cases, poor densification will result--can be balanced to a certain extent by higher combustion temperature. This, however, involves the danger of making the structure coarser, with a negative effect on stability.

Thus, to execute reduction with regard to optimum sintering, a carbon amount calculated exactly for the oxygen content at hand is not sufficient because an ideal mixture cannot be expected. Accordingly, so that sintering is not prevented by remaining oxide, a certain carbon excess must be figured for a well-condensed material composed of small grains.

Table 1: Effect of Measures for Sintering of Silicon Carbide

		Effect on \ Measure	Submicron Powder			B-Additive	C-Additive
Driving Power		Surface Energy ↑	Large Surface, much disturbed			Sinter Agent	Sinter Agent Removal of SiO_2 Layer
		Granule Boundary Energy ↓				Insert at Granule Boundary	
Sinter Mechanism	Material Transport by	Evaporation Condensation ↓	Lattice Disturbances			Prevents Evaporation (Coarsens Structure) →	
		Surface Diffusion ↓		Short Transport			
		Liquid Phase Sintering ↑			Many Contact Points	Low Melting Eutectic	
		Granule Boundary Diffusion ↑				B-Insert in Lattice	Removal of SiO_2 Layer (C-Insert in Lattice?)
		Volume Diffusion ↑					

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