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Synthesis of Nanocrystalline Silicon Carbide Powder by Carbothermal Reduction

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Abstract

A solution of sugar in silica sol was used as parent material for the manufacture of nanocrystalline SiC powders. After mixing and freeze drying of the components the conversion was performed in two steps. First the sugar was converted to carbon particles and secondly the silica carbon mixture was heated up to the approved reaction temperatures between 1550 and 1800°C under an argon pressure of 180 kPa. When the synthesis temperature was reached the pressure was reduced to 0·02 kPa what leads to a vigorous reaction resulting in extremely fine particles. The obtained powders were characterized with regard to the particle and crystallite size, the BET surface and their chemical composition. The oxygen content was $< 0{\cdot}5\,wt\%$ *and the particles were* $< 0{\cdot}5\,\mu m$ *with crystallites* $< 100\,nm$ *and specific surface areas in the range of* $20\text{–}30\,m^2\,g^{-1}$*. Conclusions concerning the synthesis parameters to the resulting powder properties are given in this paper. © 1998 Elsevier Science Limited. All rights reserved*

1 Introduction

Silicon carbide is a commonly used ceramic material with attractive properties such as high strength, stiffness, good wear and corrosion resistance and semiconductivity, which are mainly characteristic of covalent bonded ceramic materials. Therefore SiC is a promising material for thermomechanical and electronic applications. The industrial manufacture of SiC is widely performed by the Acheson Process, which includes a carbothermal reduction of sand by petrol coke at about 2400°C. The produced SiC possess large grains and batches which demand grinding and purification processes for further usage. The manufacture of nanosize powders by milling of Acheson SiC products are not successful. Nanosize particles can be obtained by several advanced technologies as for rice hull conversion, CVD processes, sol–gel processes and laser gas phase pyrolysis or laser evaporation processes as reported.[1–6] A still existing problem of nanoparticle production is the economy and the quantities which are synthesized by the available processes. An efficient and economic process of SiC synthesis could be the reaction of silica sol and sugar as it was already reported by other authors.[7–11] But the lack of these processes is the agglomeration of the nanocrystalline particles and the subsequent crystallite growth during the synthesis process. A drop of the synthesis temperature or of the synthesis time is limited by the demand of complete conversion which is necessary to avoid subsequent purification of the powder from unreacted carbon and silica.

This paper describes a technology which combines pressure and temperature parameters to obtain nanoparticles which are completely converted from the parent silica sol and sugar and additionally not agglomerated in stable ensembles.

2 Thermodynamic aspects

The carbothermal reduction of SiO_2 is controlled by atmosphere, pressure, temperature and time. It can be described as depicted in eqn (1).

$$SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(g) \qquad (1)$$

The reaction is strongly endothermic with $\Delta H^{298} = 618{\cdot}5\,kJ\,mol^{-1}$ and performs in two steps. The initiation reaction is also endothermic (2) whereas the second reaction is exothermic (3).

$$SiO_2(s) + C(s) \rightarrow SiO(g) + CO(g) \qquad (2)$$

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$$\mathrm{SiO(g) + 2C(s) \rightarrow SiC(s) + CO(g)} \qquad (3)$$

The temperature, at which the reaction is initiated, is strongly dependent on pressure and atmosphere composition. A high pressure will shift the start of reaction (2) to higher temperatures as it is shown for the pressure dependence in Fig. 1 which is derived from $\Delta G = \Delta G^\circ + \Delta nRT\ \ln(p/p^\circ)$ with $\Delta G^\circ = G_{\mathrm{SiO}} + G_{\mathrm{CO}} - G_{\mathrm{SiO_2}}$. The data of G are obtained from Ref. 12 ($\Delta n = 2$ for (2), R = gas constant, T = temperature). One can also reach this shift to higher temperatures by a high carbon monoxide partial pressure. When reaction (2) is inhibited the SiO content is rather low and reaction (3) will be also inhibited. In this situation no SiC is formed over the whole temperature range where $\Delta H > 0$ kJ mol^{-1}. Consequently no silicon carbide exists up to 1700°C at a pressure $>$ 180 kPa and no silicon carbide crystals will growth and coarsen in this period. If the pressure is rapidly decreased at a temperature of more than 1550°C the reactions (2) and (3) start extremely vigorously. It can be expected that the complete mixture of silica and carbon is converted in a short period under these conditions especially when they are intrinsic mixed in a colloidal level which will shorten the diffusion paths of the parent components so that the reaction kinetics are not limiting the conversion progress. This principle was applied in our investigations and the results are discussed in this paper in continuation to the results of Ref. 13.

3 Experimental Procedure

The raw materials used for the synthesis of SiC are silica sol, with 15 wt% SiO_2 of a mean particle size of 10 nm and sugar. The ratio of the SiO_2 and carbon content in the solution was SiO_2/C 0·96–1·02 by weight which is associated with a carbon amount of 1·6–1·7 times of that needed by reaction (1). After complete dissolution of sugar in silica sol the solution was frozen and freeze-dried. The dried gel powder was pre-treated at 800°C in flowing argon atmosphere to prevent the high temperature furnace against hydrocarbon condensed liquids resulting from the sugar conversion into carbon. The resulting SiO_2/C mixture, which showed homogeneity and fine grains was used for the SiC synthesis. The SiC formation was carried out in a high temperature furnace with changing the atmosphere and pressure conditions. An argon pressure of 180 kPa suppressed the conversion of SiO_2/C into SiO gas and CO while heated up, as discussed in thermodynamic aspects. When reaching the reaction temperature (1500–1800°C) the pressure was reduced to vacuum (0·02 kPa). Reaction times were varied between 15 and 30 min for the mentioned conditions.

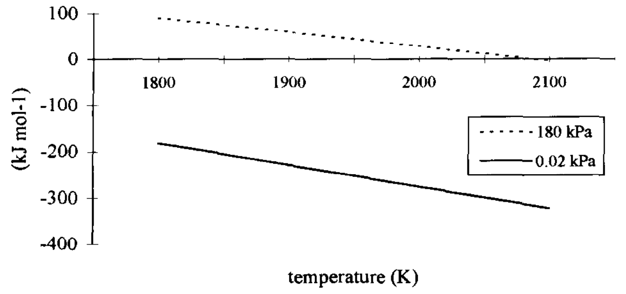

Fig. 1. Change of free energy ΔG for reaction (2) depending on temperature and pressure.

The synthesized SiC powder was characterized by several methods. The oxygen content in the powder was determined by combustion analysis under helium and IR detection of the CO_2-vibration. Combustion method was also used to determine the carbon content. The SiC powder was heated in an oxygen flow. Added Fe powder was used to assist the combustion. The formed CO_2 was used again to detect the carbon content. Microtrac-Ultrafine-Particle-Analyzer of Leeds and Northrup Corp. was employed to determine the grain size. Sodium tetrapyrophosphate (TNPP) as solution (1 mg ml^{-1}) was used for dispersion of SiC powder.

Specific surface area was determined by the BET method. A helium pycnometer was applied for powder density characterization.

4 Results and Discussion

4.1 Oxygen content

The conversion ratio of pyrolysis is indicated by the remaining oxygen content in the obtained SiC powders. Oxygen values $<$ 1 wt% without chemical follow-up treatment should be reached because higher oxygen contents have a negative effect on sintering. The oxygen values range between 0·2 and 5·6 wt%. At least 1550°C should be applied to reach a complete conversion and low oxygen contents. Then a significant dependence on temperature and reaction time is not observed regarding for the range 1550–1800°C. The detected variation of the oxygen content is obviously caused by processing instabilities of the applied vacuum. Samples of a reaction time of 30 min show very small values with low dependence on temperature. Whereas samples with only 15 min reaction time fluctuate strongly in their oxygen contents. Obviously, this is mainly the result of irregular running of the vacuum pump. Although, the results imply a complete conversion of the parent materials even after

Table 1. Density, specific surface area, particle size from laser light scattering of the obtained powders depending on the synthesis parameters

Heat treatment	*Density ($g\,cm^{-3}$)*	*Specific surface area ($m^2\,g^{-1}$)*	*Mean particle size (derived from specific surface area) (nm)*	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
1500°C/15 min	2·83	26·6	80	0·34	0·5	10·1
1550°C/15 min	3·04	26·7	74	0·28	0·45	0·99
1550°C/20 min	2·72	31·1	71	0·58	1·17	1·80
1600°C/15 min	2·99	23·7	85	0·33	0·43	0·68
1600°C/30 min	2·78	19·0	114	0·76	2·86	4·78
1700°C/15 min	2·84	29·6	71	0·24	0·33	0·88
1700°C/30 min	2·81	27·0	79	0·73	1·42	2·09
1800°C/15 min	2·94	28·0	73	0·23	0·39	0·89
1800°C/20 min	2·96	27·2	74	0·73	3·32	5·04
1800°C/30 min	2·89	6·8	305	0·96	3·23	5·5

short reaction times for the sample after 1550°C/15 min.

4.2 Carbon content

The carbon content was analyzed by a combustion method. Its mean value of 36 wt% shows only small variations (±2 wt%) which do not depent significantly on the synthesis temperature. The value of free carbon was determined by chemical calculations using the oxygen (SiO_2) and silicon (SiO_2, SiC) content. Consequently samples with higher oxygen content show also higher contents of free carbon which did not react with the silica according to reaction (2). The free carbon content varies between 6 and 15 wt%, but a significant trend is only observable for samples after 30 min reaction time where the content obviously decreases with higher reaction temperature. This is a result of a silicon loss, as already found by Poch and Dietzel,[14] caused by the formation of escaping gaseous SiO for lower temperatures. Below 1650°C reaction (2) is the slowest and therefore speed limiting. SiO formation and loss are in balance up to approximately 1700°C.

4.3 Density, specific surface area, particle size (Table 1)

Generally the measured densities have a lower value as the theoretical density of SiC. The still contained SiO_2 and the free carbon decrease the density of the powder. The samples with the highest SiO_2 and carbon contents have consequently the lowest measured density. But also the density calculated from the components of the powders is higher than the measured so that a lower density is also caused by a large portion of disordered material in the nanocrystalline material. The volume fraction of grain boundaries in nanocrystalline materials are much higher than in conventional materials. The use of raw materials with high specific surface area, amorphous silica sol and amorphous carbon after decomposition of sugar, promises a high conversion rate and consequently also a high specific surface area of the resulting SiC powder. Extremely fine amorphous carbon shows higher reactivity and leads to finer β-SiC powders.[10,11] The vigorous gas formation (SiO, CO) results in an increase of the surface on account of eruption of SiO_2 particles. The reaction temperature has a significant influence on completeness of reaction (1) caused by the an endothermic course. But after SiC formation, the surface reduces quickly at high temperatures for energetic reasons. The higher the reaction temperature is, the higher the surface reduction is. If SiC formation is complete, heat treatment should be stopped to avoid a decrease of the specific surface area.

SiC-powders with higher SiO_2 and carbon contents show the larger surface areas, because the conversion was incomplete so that the porous parent material still exists and due to the finely divided particles of free carbon. But also a complete conversion cycles can result in a high specific surface area if the reaction time is short. The powders after 1800°C synthesis elucidate the influence of reaction time to surface area (Table 2). A drastic drop of the specific surface area is observed after 30 min reaction time. This proves the great sintering force of the powder particles especially at higher temperatures. But the particle size is very similar with regard to the d_{50} and d_{90} data which are obtained by the particle size analyzer. An explanation of this observation is that the porous particles form more

Table 2. Average crystallite size calculated from the (220) peak

Heat treatment	*Mean crystallite size (nm)*
1500°C/15 min	18
1550°C/15 min	20
1550°C/20 min	20
1600°C/15 min	20
1700°C/15 min	21
1800°C/15 min	22
1800°C/20 min	22

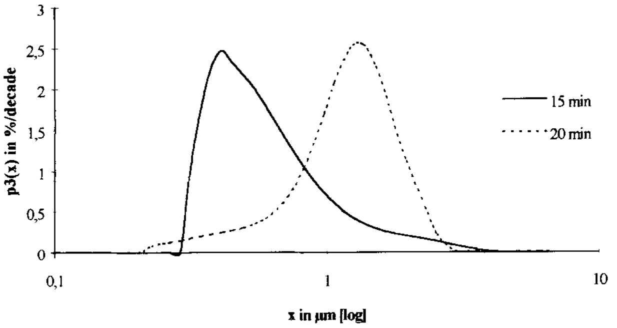

Fig. 2. Volume density distribution in dependence on reaction time at 1550°C. Since a logarithmical scale is used for the distribution p^3 (x) the unit for the ordinate is related to the ratio (%) per fixed distance of the logarithmically increasing length (decade).

dense particles with longer time what only would influence the specific surface especially if the smallest particles are incorporated into the larger particles as it is probable with regard to the increasing d_{10} value. A reaction time of 15 min keeps the temperature influence to surface reduction to a minimum, because the high temperature only effects the reaction period and is interrupted before sintering effects become efficient. For all these reasons a optimum of temperature and time for the nanoparticle manufacture has to be recognized. A high temperature leads to a rapid conversion and to a higher driving force for sintering. Thus short times with high temperatures produce the smallest powder particles.

Furthermore higher temperatures support the endothermic reaction so that the gas formation is more vigorous. A rapid gas formation promotes the increase of the specific surface area and the development of small crystals. But as higher the temperature is, as larger the efficiency of the final specific surface area reduction. Especially fine particles form rapidly agglomerates by sintering of the primary nanocrystalline particles. The resulting particle ensembles have still a high specific surface area. But these permanent agglomerates can not be destroyed by ultrasonic treatment or milling and are made out as particle agglomerates by the Microtrac-Particle-Analyzer where the powder is suspended in a fluid and is analysed by dynamic laser light scattering

The comparison of the particle size distribution curves after different reaction times illustrates the grain coarsening process with longer reaction times (Fig. 2). A longer reaction time of 15 to 20 min causes a doubling of d_{50} and d_{90} at 1550°C. The effect at 1800°C is much greater. But there are only small differences between the distributions after reaction times of 20 and 30 min.

4.4 X-ray diffraction

The XRD patterns show pure β-SiC phase with peak shoulders which may be derived from α-SiC or stacking faults. The samples with higher oxygen content did not show SiO_2-peaks, because the contents are under the detecting limit or due to an amorphous silica phase. The shoulder on the (111) peak at $2\Theta = 36°$ results from stacking faults in the grain as they were already described by Seo and Koumoto[15] and has been observed by our TEM investigations (Figs 3 and 4).

The crystallite size distribution of β-SiC was derived from the physical profile of the (220) diffraction peak by means of a deconvolution of the experimental profil and by fitting it by model profiles. Thus, a subsequent calculation of the Fourier coefficients was possible which were used for calculating the size distribution function.[16] An analysis of the x-ray peak profiles was only feasible by combination of several distribution functions to fit the peak profile. This is an indication of the complex structure of formed SiC which consists of nanocrystallites and amorphous fractions.

The mean crystallite sizes do not vary significantly with the applied reaction temperatures. At higher temperatures a small growth of crystallites is observed. Variation of the reaction time from 15 to

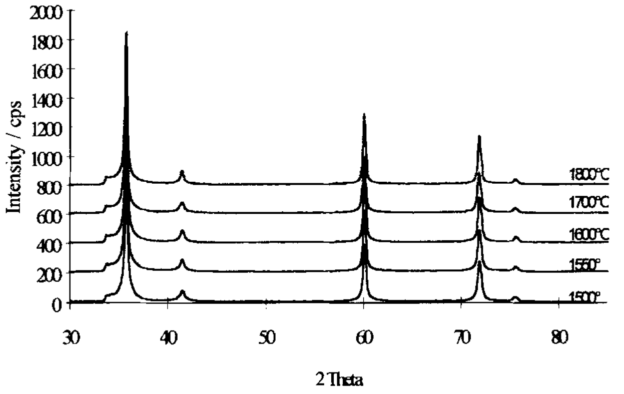

Fig. 3. X-ray diffraction patterns depending on synthesis temperature.

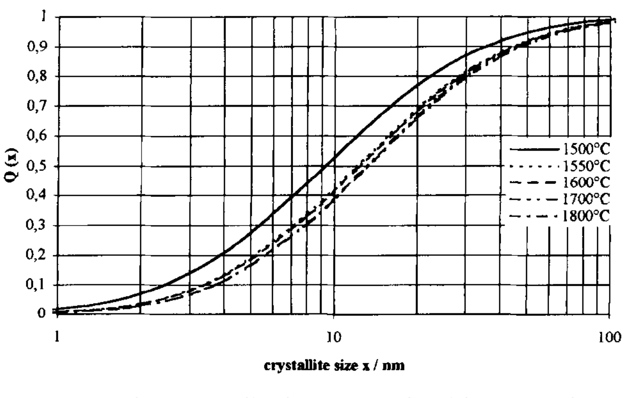

Fig. 4. Cumulative distribution of the chord length in dependence on synthesis temperature with 15 min reaction time. (The distribution functions for 1550 and 1600°C as well as for 1700 and 1800°C almost coincide.)

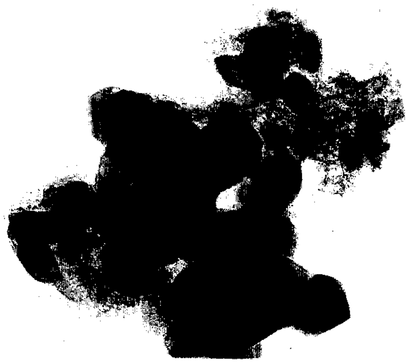

Fig. 5. TEM image of the SiC powder after synthesis at 1550°C/20 min. 100 nm.

Fig. 6. TEM image of the SiC powder after synthesis at 1800°C/20 min. 200 nm.

20 min does not show a clear influence to the crystallite size. The comparison with the grain size (Fig. 2) demonstrates the formation of agglomerates. The single nanocrystallites do not growth but sinter to larger agglomerates with longer reaction time.

4.5 TEM-investigations

Figures 5 and 6 show typical powder particles after 1550 and 1800°C. There are single crystalline particles with polygonal shape. The diffraction effects result from electron scattering on stacking faults inside the crystallites. The particles are composed of β-SiC, what was confirmed by EDX analysis and electron diffraction. But also the particles without diffraction contrasts consist of Si and C. Figure 5 shows additionally to the crystalline SiC particles also particles of an amorphous structure. These amorphous particles consist of Si, C and O. After 1800°C there are also amorphous components, but their incidence is rarer than those after 1550°C. The higher content of oxygen and free carbon results in higher content of amorphous components.

Regarding the different physical effects, the results of the applied grain size analysis methods are consistent.

5 Conclusion

The synthesis of nanocrystalline SiC powders from silica sol and sugar is confirmed to be feasible, with three conditions:

1. fine starting materials and their molecular or colloidal mixing;
2. suppress the initiation reaction up to desired reaction time, then pressure reduction to vacuum for promotion of the reactions (2), (3); and
3. short reaction times.

Oxygen contents <0·5 wt% are attainable without chemical follow-up treatment. The free carbon content is dependent on the used weight ratio of SiO_2/C. A surplus of carbon is advisable, because it improves the SiC yield and compensates the carbon loss during the sugar decomposition.

Reaction time and temperature have a large effect on the powder properties of SiC. Specific surface area, crystallite and grain size are controllable by the processing parameters, these properties influence the sintering behavior of the obtained SiC-powder. The reaction time is the most significant parameter. The shorter the reaction time, the smaller the temperature influence on the particle properties is. Longer reaction time reduces the specific surface area, grain and crystallite coarsening appear. The conversion progress is supported by a higher reaction temperature. The reaction time should cover only the complete reaction run to obtain small particles. A high temperature has a positive effect on the properties in this stage. With higher temperatures the gas reactions run more quickly and more violently and result in larger specific surface areas and smaller grains caused by eruption effect on the parent particles during the rapid conversion into SiC.

To avoid agglomeration of the synthesized fine SiC particles additionally to a short reaction time the quenching period should be short as possible. Furthermore the particles should also separated during the hole synthesis course what demands a suited construction of the synthesis equipment.

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