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Determination of impurities in silicon carbide powders*

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Summary. The analysis of SiC powders used for the production of high-performance ceramics was investigated by combined procedures as well as by a direct technique including atomic spectrometric detection. For the combined chemical procedure, SiC powders (0.25 g) were completely dissolved in a mixture of HNO_3, HF and fuming H_2SO_4 in an autoclave at 240°C within 8 to 20 h. In the final 0.5% w/v solution 13 elements were determined by electrothermal atomic absorption spectrometry (ETAAS) and by inductively coupled plasma atomic emission spectrometry (ICP-AES). With acid decomposition the detection limits for Ca, Cd, Cr, Cu, Mg, Mn and Zn were found to be in the range of 0.1–1 µg/g; those for Al, B, Fe, Ni, Ti and V are at the 1–5 µg/g level. With a Babington-type nebulizer 1% slurries of SiC can be directly analyzed by ICP-AES. Calibration was performed by standard addition of aqueous solutions of the elements to be determined and the detection limits are close to those of ETAAS subsequent to pressure decomposition. The required analysis time was reduced from approx. 24 h to 30 min. First results for Ca, Cr, Cu, Mg, Mn, Ti and V as well as the needs to overcome systematic errors of this method, e.g. for Fe, are communicated.

Introduction

High-performance ceramic materials, such as SiC, are of important use in high-temperature technology, for instance, in engines, as coatings in nuclear fusion equipment, for working tools; they are also used in micro electronics etc. [1]. In these applications trace impurities of different elements are already known to considerably influence the properties of the final product. Today, however, there is still a substantial lack of reliable methodology for trace analysis of ceramic materials [2], as they are difficult to be dissolved.

Fusion is the most applied procedure for the decomposition of SiC [3]. For this purpose, alkaline oxidative mixtures of NaOH or Na_2CO_3 with KNO_3 and Na_2O_2, respectively, have been used [4–9], as well as mixtures of various agents: Pb_3O_4 with Na_3AlF_6 [10] or with NaF [11], B_2O_3 with Li_2CO_3 [12], $PbCrO_4$, PbO_2, Pb_3O_4 [13], $Na_2B_4O_7$ [14] and probably $K_2S_2O_7$ with $K_2S_2O_8$ and KNO_3 [15]. Decomposition by chlorine at temperatures of 1200° C in a quartz apparatus has also been performed [16]. The treatment with various acids and their mixtures [3] such as HCl [17], HNO_3 with HCl [5], $HClO_4$ with HNO_3 and HF [18], both in open and in high-pressure systems, has led to an incomplete dissolution of SiC. Consequently, one had to use fusion of the residue to ensure quantitative solubilization. Due to a possible contamination or analyte loss arising from fusion as well as due to an incomplete acidic decomposition, these procedures, including the recommended ones [19], are of no practical analytical importance for the determination of trace impurities in SiC.

To overcome contamination and dissolution problems in the analysis of finely powdered refractory materials, the nebulization of slurries with the aid of a suitable pneumatic nebulizer as it has been used for ETAAS or ICP-AES [20–24] may be a viable alternative. This paper deals with a new wet-chemical high-pressure procedure, which enables it to completely dissolve fine SiC powders with the aid of high-purity acids and to determine trace elements in the solutions by ETAAS and ICP-AES. Also the possibilities of slurry nebulization ICP-AES for a direct analysis of SiC powders are investigated.

Experimental

Reagents and samples

"Suprapur" grade (Merck, Darmstadt, FRG) NaOH, KNO_3, Na_2CO_3, K_2SO_4 and KF were chosen for preliminary fusion experiments. For the high-pressure dissolution, concentrated acids (HNO_3, HCl, HF, H_2SO_4) only were used. $HClO_4$, H_3PO_4 and H_2O_2 were of "Suprapur" grade (Merck, Darmstadt, FRG). Pure fuming sulfuric acid, which contained about 30% of SO_3, was prepared by isopiestic

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Table 1. Instrumental parameters for atomic absorption measurement

Element	Wavelength [nm]	Spectral bandwidth [nm]	HCL [mA]	Temperature programme[a]				
				Charring			Atomization	
				Temp. [°C]	Ramp [s]	Hold [s]	Temp. [°C]	Hold [s]
Al	309.3	2.2	7.5	550	60	–	2700	7
Ca	422.7	2.2	8	650	55	–	2700	7
Cd	228.8	1.1	15	200	–	20	1700	5
Cr	359.3	2.2	10	550	50	–	2700	5
Cu	324.7	2.2	5	500	45	–	2400	5
Fe	248.3	0.4	15	500	40	–	2500	5
Mg	285.2	2.2	10	450	35	–	2000	7
Mn	279.8	1.1	15	400	55	–	2200	5
Ni	232.0	0.4	20	550	50	–	2700	5
Zn	213.9	1.1	7.5	350	35	–	1700	5

[a] Drying at 160°C for 40 s

distillation. Therefore SO_3, which escapes from analytical-reagent grade fumic acid (65% SO_3) was adsorbed in "sub-boiling" grade acid during a storage of both liquids in quartz vessels placed in a closed system (desiccator). Water which has been bidistilled in quartz vessels was used for the preparation of all solutions.

Commercially available SiC powders supplied by H. C. Starck (Goslar, FRG; 2 samples of type A 10 and B 10) and Lonza (Waldshut, FRG; type UF15) were analyzed, marked with the symbols I–IV.

After ultrasonic pretreatment, the largest particles found did not exceed 5 μm and the mean particle size of these powders was at 0.4–0.5 μm, as it was found by electron probe microscopic investigations. Excepted for the ultrasonic treatment, no further pretreatment of the powders such as grinding or fractionation, which could introduce contamination, was applied.

A solution of silicic acid (Lachema, Brno, CSFR), which is commonly prepared for the production of silicagel, was used as soluble form of the matrix element for comparative measurements.

Apparatus

The acid decomposition of the powder samples was performed with a high-pressure system DA III (Berghof, Tübingen, FRG) using PTFE inserts of 150 ml volume.

ETAAS determinations were made with an Hitachi 170-70 Zeeman (inverse transversal DC system) spectrometer equipped with a Perkin-Elmer 56 recorder. For the determination a normal graphite furnace was used excepted for Cr, Cu, Fe, Mn, Ni, where pyrolytically-coated tubes were employed. Argon was used as sheathing gas with internal and external flows of 100 and 3400 ml min^{-1}, respectively. The instrumental parameters are summarized in Table 1.

The ICP-AES measurement system includes an FS-10 free-running rf generator (Linn GmbH, Hirschbach, FRG), which operates at a frequency of 27.12 MHz and at a forward power between 2 and 4 kW, and a 0.9 m micro-computer controlled Czerny-Turner monochromator [25]. A Greenfield-type torch was used with outer and intermediate argon flow rates of 22 and 8 ml min^{-1}, respectively. For the pneumatic nebulization of solutions, a Perkin-Elmer (Überlingen, FRG) HF-resistant cross-flow nebulizer was operated at an argon pressure of 120 kPa and fed with a Minipuls 2 peristaltic pump (Gilson, Viliers le Bel, France) at a sampling rate of 1.8 ml min^{-1} (i.d. of the sampling capillary: 1 mm). For the nebulization of the SiC slurries, a modified Babington-type nebulizer made of glass (G.M.K., Labtest, Ratingen, FRG) equipped with a capillary No. 4.7 was used. The pumping rate was between 0.4 and 2.2 ml min^{-1} and the nebulizer gas flow between 0.5 and 1 l min^{-1} Ar at a pressure of 200–400 kPa. The instrumental parameters for the analysis of solutions are summarized in Table 2.

The working conditions (forward power, sampling rate, nebulizer gas flow and impact bead distance) were selected in order to get optimum line-to-background ratios and power of detection. A trial-and-error procedure was followed for this aim. The observation height experienced as optimum depends on the elements and their lines selected. As the spectra hardly suffered from interferences, this point could be practically neglected and the most sensitive lines selected.

Results and discussion

Wet chemical procedure

Fusion decomposition

In order to minimize analyte losses and contamination, only crucibles made of glassy carbon, platinum or quartz were used throughout. About 0.1 g of sample were mixed with an excess of flux (1:10), heated carefully to the final temperature and held at this temperature for a few minutes. The molten mass was allowed to cool and was then treated with water and acids, respectively.

Mixtures of $NaOH + KNO_3$ (10:1), $Na_2CO_3 + KNO_3 + NaOH$ (1:1:1) were molten for 10 min in glassy carbon crucibles at temperatures of up to 650°C and under argon atmosphere. A mixture of $K_2S_2O_7 + KF$ (1:1) was used for 30 min in Pt crucibles at about 900°C. K_2SO_4 or KNO_3 were used in quartz crucibles at 700°C and 400°C for 30 and 20 min, respectively.

Table 2. Instrumental parameters for ICP-AES using an argon plasma

		Solutions	Slurries
Forward power [kW]		2.2	3
Sampling rate [ml min^{-1}]		1.8	2.2
Nebulizer gas flow at [kPa]		120	300
Impact bead distance [mm]		8	8
Observation height [a] above coil:			
Element/line [nm]		[mm]	[mm]
Al I	396.15	13	24
B I	249.77	9	22
Ca II	393.36	10	19
Cd II	214.43	10	–
Cr II	267.71	11	21
Cu I	327.39	11	5
Fe II	238.20	10	10
Mg II	279.55	9	8–18
Mn II	257.61	9	24
Ni I	232.00	13	–
Ni II	216.55 [b]	–	8–16
Ti II	336.12	9	18–24
V II	290.80	9	24
Zn I	213.85	10	–

[a] Over the upper edge of rf coil
[b] For slurry ICP-AES only
Ni II 221.64 nm is interfered by Si I 221.66 nm
Ni I 232.00 nm is interfered by SiO bands (222–242 nm, degrading to longer wavelengths) [26, 27]

Only with a Na_2CO_3 + KNO_3 + NaOH (1:1:1) mixture it was possible to decompose the SiC and to completely dissolve the flux in water. In all other cases, even if the dissolution of the flux was performed in the presence of a large excess of HF, insoluble residues were observed. Nevertheless, the application of the fusion procedure was not pursued because of the necessity to use a large quantity of fluxes, especially of NaOH or KF, which are difficult to purify. In addition large amounts of insoluble silicic acid are obtained after the acidification of the solution, which can sorb the trace impurities to be determined.

High-pressure decomposition

Preliminary experiments on acid dissolution were performed in a PTFE autoclave with 0.1 g amounts of SiC powder and various concentrated acids or mixtures of acids (HCl, HNO_3, $HClO_4$, H_2SO_4, HF, H_3PO_4, and H_2O_2). These experiments showed that a total decomposition of SiC only is achieved when oxidizing agents and HF act together, e.g. in the mixtures of HCl + H_2O_2 + HF, HCl + HNO_3 + HF or HNO_3 + H_2SO_4 + HF. The presence of fuming sulphuric acid enhances the oxidative strength of the mixture due to desolvatation effects (nitronium ions). Fuming sulphuric acid alone, however, did not noticeably dissolve SiC. For a quantitative dissolution, it was necessary to heat the mixtures (4 ml of each of the acids) to temperatures of 240° C during 24 to 100 h. Fuming H_2SO_4 in combination with conc. HNO_3 and HF was most efficient, as up to 0.25 g of SiC powder could be decomposed within 8 h. For bigger amounts of SiC, a proportional increase of all reagents is necessary and leds to additional contamination and considerable prolongation of the decomposition time.

It was also observed that the decomposition time relates to the concentrations of some admixtures and impurities and directly depends on the grain sizes of the sample. For example, from a compact sample (single crystal of 0.176 g) only 6% could be decomposed during 1 week at 240° C.

Results for the determination of 13 elements in 4 SiC samples by ETAAS and ICP-AES, subsequent to the wet chemical dissolution procedure described together with the corresponding detection limits, are given in Table 3. No considerable interferences are caused by the acids present in the solutions, excepted in the determination of aluminium by ETAAS. The results of both determination methods agree well for most elements. For many elements the detection limits showed to be influenced by the spectral background and its fluctuations. Only for Ca, Fe and Mg fluctuations of blank values were found to be limitative. Thus, here a progress in power of detection can still be expected from an efficient purification of the acids by subboiling distillation. No memory effects were found to arise from the PTFE inserts during all experiments.

Procedure. 0.25 g of SiC powder are transferred into an autoclave insert and 4 ml of conc. HNO_3, 4 ml of HF (40%) and finally 4 ml of fuming H_2SO_4 are carefully added. The autoclave is heated at 240° C for 8–20 h, depending on the particle size and the impurity level in the powder. After cooling the resulting solution is transferred into a polypropylene flask and then diluted with water to the final volume of 50 ml resulting in 0.5% w/v Si-solutions. 6 replicates are analyzed by ETAAS and ICP-AES (see Tables 1 and 2). Calibration is done by standard addition. A similar number of experiments has to be made without sample to evaluate the blank values and to determine the detection limits.

Slurry nebulization ICP-AES

Finely powdered materials with grain size up to 5 μm can also be introduced into the inductively coupled argon plasma by generating aerosols from their aqueous (1% w/w) slurries [21]. Lengthy and laborious wet-chemical attack and problems arising from analyte loss and contamination therewith can be circumvented. However, the calibration of such direct procedures remains generally problematic since well-characterized SiC powders are not readily available. Standard addition with aqueous solutions of the elements to be determined to the slurry is a viable way to go. However, it must then be controlled if the analyte in solution which is added to the slurry behaves in any respect similar as the analyte in the particles of the suspended powder.

It is guaranteed that no differences occur, e.g. due to aerosol transport, particle evaporation etc., when the element line intensities of slurries and solutions containing the same amounts of analyte deliver the same signals.

This can only be achieved after a careful optimization of the working conditions of slurry ICP-AES, namely the uptake rate, the nebulizer gas flow, the forward power of the ICP, the observation height, etc. Two main optimization criteria were selected, first one optimizes towards highest signal-to-background ratio and second one has to look after conditions where solutions and slurries with the same analyte concentrations give the same signals. It is apparent, that

Table 3. Results of comparative analysis of silicon carbide samples (concentration [b] of impurity in ppm

Sample No.	I			II			III			IV			DL		
Method[a]	a	e	s	a	e	s	a	e	s	a	e	s	a	e	s
Element															
Al	–	267	214	–	347	265	–	461	383	–	193	162	–	20	
±		3	3		2	2		2	6		2	1			
B		<4	≈1	–	4.5	3.0	–	13.4	8.9	–	920	1070	–	4	
±						0.4		0.6	0.5		4	15			
Ca	134	140	114	–	21.0	16.7	–	362	345	–	15.4	13.8	0.4	0.6	0.2
±	2	3	1		0.3	0.2		5	1		0.3	0.2			
Cd	0.23	<3	–	<0.07	<3	–	<0.07	<3	–	–	–	–	0.07	3	–
±	0.04														
Cr	3.0	≈3	≈2.8	18.2	15.8	15.1	2.4	<3	≈2	5.6	–	5.0	0.2	3	2
±	0.1			0.2	0.1	0.1	0.1			0.2		0.1			
Cu	5.3	–	≈2.5	7.4	8.6	6.4	1.85	<5	<2	≈1	–	<2	0.6	5	2
±	0.4			0.1	0.2	0.4	0.05								
Fe	246	256	205	–	656	556	–	17.0	13.8	–	134	117	1.5	6	–
±	3	4	1		16	8		0.7	0.3		1	4			
Mg	33.7	33.6	29.8	–	12.6	11.0	–	5.0	5.0	–	1.8	1.8	0.3	0.3	0.04
±	0.5	0.6	0.8		0.3	0.3		0.1	0.1		0.1	0.1			
Mn	6.96	7.0	6.9	3.49	3.8	3.3	≈0.2	<0.8	≈0.3	0.69	–	0.8	0.2	0.8	0.1
±	0.06	0.2	0.2	0.02	0.03	0.2				0.02		0.1			
Ni	24.0	<100	18	12.9	<40	12	≈2	<40	<11	≈2	–	<11	2	40	11
±	0.1		3	0.1		3									
Ti	–	102	109	–	82.4	79	–	64.8	60	–	40	40	–	2	2
±		1.6	1		1.4	2		0.7	2		1.6	3			
V	–	35.6	35.3	–	26.1	24.9	–	27.8	24.4	–	12.0	9.5	–	5	4
±		1.1	4		0.3	3		1.3	3		0.5	2			
Zn	0.8	<2	–	<0.15	<2	–	0.11	<2	–	–	–	–	0.03	2	–
±	0.15						0.01								

[a] Method: a – wet procedure with GF AAS, e – wet procedure with ICP-AES, s – slurry technique for ICP-AES

[b] Average value obtained for 6 parallel determinations ± standard deviation of average value

– Not estimated

< Lower than detection limit (3-fold of stand. deviation of blank value)

these criteria can lead to contradictionary requirements and compromise conditions have to be accepted.

The optimized parameters were determined for an analyte line namely Ca II 393.36 nm and the matrix line Si I 251.61 nm. Only for a 1% w/w slurry of SiC in water the same set of values could be used for the sampling rate, the nebulizer gas flow, the distance between the impact bead and the capillary orifice, the observation height and the forward power. These were varied in the ranges: 0.4 – 2.2 ml min^{-1}, 0.5 – 1 l min^{-1}, 4 – 20 mm, 0 – 25 mm and 2 – 3 kW, respectively. The position of the impact bead was found to have almost no influence on the signals. A sampling rate of 2.2 ml min^{-1} gave maximum signal-to-background ratios. At an increasing nebulizer gas flow rate the calcium signal increased until the flow rate of 1 l min^{-1}. The maximum intensity of the silicon signal, however, was achieved at 0.73 l min^{-1} for all power settings. Accordingly, a forward power of 3 kW and a nebulizer gas flow of 0.73 l argon min^{-1} were used for all further experiments.

Under these conditions delivering the highest power of detection, the slurry should behave as a real solution of the same composition also for elements such as Al, B, and Fe.

In order to reach this point, we performed for each powder such an optimization of the working conditions until the intensity ratios of a Si matrix line for slurries and solutions are as close to 1 as possible.

A trial-and-error procedure leads to the conditions listed in Table 2. It can be understood that the forward power and the observation height should be generally higher, so as to come to a complete particle decomposition required for the above mentioned aim. It was found that only for a few elements (Cd, Co, Mg, Mn and Ti) the results of slurry atomization are in agreement with the values obtained after wet chemical decomposition (Table 3). However, it should be mentioned that as reported earlier, the particle size distribution of the powders must be determined so as to be able to estimate implications for the nebulization, transport and evaporation processes taking place. These points together with a systematic optimization of the working conditions are required so as to achieve the same performance for SiC as with other ceramic powders.

Procedure. An amount of SiC powder resulting in a 1% w/w suspension was weighed directly into a polypropylene vessel and suspended in water. To break agglomerates of SiC particles, the slurry was treated in an ultrasonic bath [Bransonic 12 (55 kHz), Heusenstamm, FRG] for 15 min. During the measurement, the slurry was continuously homogenized by stirring with a PTFE-coated magnetic bar and sampled by the peristaltic pump. The instrumental parameters for the ICP measurements are listed in Table 2. For calibration the slurries were spiked with appropriate amounts of aqueous standard solutions.

Conclusion

SiC powders used for the production of high-performance ceramics can be completely dissolved by high-pressure treatment in a PTFE-lined autoclave system with a mixture of conc. hydrochloric, nitric and fumic sulphuric acids. When using high-purity agents, the detection limits in SiC are as low as 0.1 – 1 µg/g for a series of elements and a good agreement is obtained between results of ET-AAS and those of ICP-AES.

With a modified Babington-type G.M.K. nebulizer direct analysis of SiC powders by slurry nebulization ICP-AES is possible. The detection limits of this technique are close to those obtained by ETAAS combined with a wet procedure. A careful optimization of instrumental parameters, and an estimation of the particle size distribution are still required to make the technique for the analysis of SiC more reliable.

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