



CORROSION OF CERAMIC SILICON CARBIDE IN HYDROFLUORIC ACID

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Silicon carbide usable in mechanical or electrical engineering is produced in various purity grades and exhibits a large number of crystal structure variants. As for use in the chemical field, it is commonly stated that it is highly resistant in acid media but not suitable for use in alkaline media. This paper discusses the resistance of compact silicon carbide to hydrofluoric acid. The compact silicon carbide has been prepared by sintering using the SSiC method with or without binders based on scandium oxide Sc_2O_3 and calcium fluoride CaF_2 . The purest silicon carbide sample of cubic 3C structure sintered without a binder was almost insoluble in hydrofluoric acid. It has been shown, however, that pure silicon carbide is perfectly insoluble in hydrofluoric acid irrespective of the structure variants detected in the samples (3C, 4H, 6H, 15R). The corrosion stability of the compact ceramics is affected by the residual SiO₂ content (together with other impurities) in imperfect SiC preparations, and it is influenced by the choice and chemical properties of the chosen ceramic binder as well.

INTRODUCTION

The field of industrial use of silicon carbide, produced according to Acheson's U.S.Patent 492.767 of 1893, is wider and wider [1]. Besides its primordial use for cutting and grinding tools or abrasion-proof parts making, for which it is ideally suited due to its third highest hardness [2, 3], it is used nowadays in electrical engineering, e.g. for heating elements [4, 5], for microwave heating [6], for antiballistic materials [7, 8] and in many other applications [9]. Silicon carbide figures prominently in power electronics and microelectronics [10, 11], because it ranks among the semiconductors having a wide bandgap (2.2 to 3.2 eV), high dielectric strength and electron mobility, and excellent thermal conductivity, which makes it a promising candidate for the production of electronic devices capable of processing high powers and frequencies as well as operating at extreme temperatures. Actually, power electronics based on 4H-SiC single crystals has become a serious competitor for silicon-based components [12]. The outstanding feature of components made of silicon carbide is their high radiation resistance, which makes them suitable for the use in extreme conditions both on the Earth and in the outer space [13, 14].

One of the positive properties of silicon carbide, albeit less frequently emphasized, is also its unusally high corrosion resistance to almost all acids [15, 16], even at high temperatures, which is in contrast with its lower resistance to alkaline media [17]. However, the only proved fact so far concerning the insolubility of SiC in hydrofluoric acid refers to the mineral moissanite, which is not relevant from the viewpoint of technical practice [18]. With respect to high-temperature processing of aggressive chemicals, halogenated hydrocarbons in particular (especially fluorinated hydrocarbons), SiC-based materials are very perspective. One of the many examples is a plasmachemical reactor allowing the elimination of halogenated hydrocarbons, which would otherwise escape into the atmosphere and contribute to the greenhouse effect [19, 20]. The plasmachemical reactor design with protective structural elements made of SiC carbide extends its service life and increases its usability at extremely high running temperatures.

In industrial practice, compact ceramic products made of silicon carbide SiC are prepared by sintering silicon carbide powders with different inorganic binders by two different technologies. In the first case, these are high-temperature inorganic binders, e.g. from the $Al_2O_3-Y_2O_3$ or $Al_2O_3-ZrO_2$ systems. This technology is called S-SiC. The second case is the so-called reactive sintering, in which powdered SiC is sintered with a mixture of elemental silicon and carbon at temperatures up to 1600 °C. This technology is called Si-SiC or LP–SiC (liquid phase sintered SiC). An example can be Rocar[®] products sintered by the S-SiC method at temperatures of 1800 °C to 2200 °C, i.e. higher than the Si–SiC technology, but due to chemical differences and the amount of binders used, they have a wider spectrum of chemical properties and corrosion resistance. The situation is complicated here, because the choice of binders in terms of their chemical composition and structure is very wide. In addition to high-temperature sintering technology, polymeric organic binders are also widely used in another category of silicon carbide products. This fact is one of the main causes of contradictory published or advertised data on the corrosion resistance of silicon carbide in strong acids, bases, or melts.

Apart from other things, the diversity of physical and chemical properties of sintered silicon carbide is caused by the sophisticated crystal structure of the starting material - SiC powder. It is known that there are dozens of structural polytypes of SiC differing in the Ramsdell symbols nX, where n indicates the number of layers creating one repetitive sequence in the polytype structure, and X designates the crystal system [21]. As for the SiC used in this work, C=cubic, H=hexagonal, and R=trigonal (with rhombohedral lattice) polytypes, i.e. 4H, 6H, and 15R, are taken into account. Exceptionally, cubic β -SiC (3C–SiC) can also be prepared in industrial production. The phase composition of SiC polycrystals made from siliceous raw materials retains in most cases the quantitative sequence 4H > 6H > 15R. On the other hand, the specific surface of commercial SiC powders of different producers varies greatly. The size distribution is usually in the range $0.1 - 100 \,\mu\text{m}$, while the corresponding BET specific surfaces vary in the range 0.2 to 40 $m^2 \cdot g^{-1}$. Metallic impurities or accessory elements can be either primary ones from the starting raw materials or secondary ones introduced during mechanical processing, milling, and screening.

The presence of SiO_2 in the interplanar layers of individual SiC crystals is the main factor influencing different numerical data relevant to SiC corrosion in hydrofluoric acid and other strong acids. Simplified information about metallic as well as non-metallic impurities in SiC products is presented in Figure 1 and Table 1. The existence and distribution of SiO₂ interlayers in SiC crystals is also very well documented in [22], see also Figure 2, which shows oxide layers in SiC crystals.



Figure 1. SiC crystals with surface impurities.

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Early work on the stability of SiC treated with hydrofluoric acid [23] alone and in a mixture with sulfuric and nitric acids [24] concluded that hexagonal α -SiC (6H-SiC) is stable to acids, while cubic β -SiC (3C-SiC) decomposes in acids (with increasing rate as the synthesis temperature decreases). The higher corrosion resistance observed with materials prepared at higher temperatures is mainly due to better crystallization. These corrosion results correspond to the work of Cambaz et al. [25], in which SiC whiskers were etched with a mixture of HF and HNO₃ to form so-called nano-pallets. Lutsenko [26] has studied the composition, surface state and morphology



a) Electron image 1



b) O Kal

Figure 2. Distribution of SiO_2 interlayers and impurities in SiC crystals.

of green technical SiC powder using also a mixture of HF and HNO₃ to dissolve impurities and β -SiC phase. As reported in [15], Si-based polycrystalline carbides (i.e. SiC) showed excellent corrosion resistance when exposed to a hydrofluorid acid azeotrope (38.26 %) at 90 °C, in contrast to Si-based nitride ceramics. It has been found that corrosion usually occurs at grain boundaries by dissolving the siliceous phases of the grain boundaries. This work aims at assessing the corrosion resistance of SiC-based ceramic materials in hydrofluoric acid.

EXPERIMENTAL

Characteristics of SiC starting powders

Commercially produced SiC powders, produced with different quality and granulometry (according to the FEPA standard F 42-D-1984, now FEPA Standard 42-1:2006, denoted as SiC F240 and SiC F1200), were chosen for the experiments in this work. Volume-weighted particle size distributions were measured via laser diffraction (Fritsch Particle Sizer Analysette 22 NanoTec). Granulometric and chemical characteristics are given in Table 1. Diffraction patterns of all samples showed a mixture of modifications 4H, 6H, 15R in the approximate ratio 50:40:10 %, as well as the presence of silica SiO_2 in maximum amounts of 2 - 3 %. Specific surface area and pore size distribution were analyzed using gas adsorption (Beckman Coulter SA 3100) after degassing at 150°C in vacuum for 240 min. The analysis of oxygen content was performed using the LECO method in a combustion analyser (LECO ON836), and the content of accessory elements was determined via X-ray fluorescence analysis (XRF PANalytical Axios) separately for each sample series. Silica is the dominant impurity in the SiC used. The content of other metallic as well as non-metallic accessory elements did not exceed 0.5 % in total.

Table 1. Characteristics of SiC feedstock powders.

Spark plasma sintering (SPS) of silicon carbide

Four series of original samples were prepared for corrosion resistance tests of the sintered SiC in hydrofluoric acid, as well as in other acids for comparison. The pulverized and homogenized mixtures of powder precursors were compacted by spark plasma sintering (SPS) in a graphite die with 20 mm internal diameter (SPS 10-4 Thermal Technology LLC, USA). Additional information on the SPS process and the equipment used can be found in a recent paper [27]. The maximum SPS temperature was 1600 °C (with 10 min dwell time), the maximum pressure 60 MPa. The SPS schedule was the same for all sample series and is given in Figure 3.



Figure 3. SPS schedule used for the preparation of silicon carbide samples.

The sample series prepared are as follows:

 I^{st} series: Original SiC powder F240 and SiC powder F1200 were prepared by SPS, without any binder addition. Silica (SiO₂), built-in in the interlayers of SiC crystals in amounts of 2 - 3 wt. %, acted as a binder (see Figure 2).

SiC powder, standard FEPA F 42-D-1984	F240	F1200
Mode diameter [µm]	46.5	4.8
Median diameter [µm]	45.1	4.8
Specific surface area (BET) [m ² ·g ⁻¹]	0.15 - 0.18	43 – 49
Oxygen content by LECO [wt. % O ₂]	0.41 - 0.53	0.68 - 0.87
Oxygen content by EDS analysis [wt. % O ₂]	1.5	2.0
Conversion to SiO ₂ content [wt. %]	2.81	3.75
Impurity content [wt. %]		
Al	0.076 - 0.082	0.036 - 0.082
Ca	0.009 - 0.014	0.004 - 0.006
Ti	0.017 - 0.018	0.028 - 0.037
V	0.018 - 0.026	0.044 - 0.060
Fe	0.166 - 0.180	0.089 - 0.105
Ni	0.014 - 0.029	0.012 - 0.028
Sum of metallic impurities [wt. %]	0.300 - 0.349	0.213 - 0.318

Corrosion	of	ceramic	silicon	carbide	in	hydrofluoi	ric	acia
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Table 2. Characteristics of the Sc₂O₃ and CaF₂ powder binders.

	Sc_2O_3		CaF_2	
Mode diameter [µm]	24.3 - 26.8 10			.4
Median diameter [µm]	13.0	- 18.8	8	.4
Specific surface area (BET) [m ² ·g ⁻¹]	2	6.0	1.20	
	Al	0.04	Na	0.14
	Si	0.04	Mg	0.15
	Ca	0.40	Al	0.10
Impurity content (XRF) [wt. %]	Fe	0.04	Si	0.20
	Cu	0.01	Cl	0.02
	Sn	0.02	_	_
	Th	0.03	-	_
Sum of impurities [wt. %]	0.56 0.61		.61	

 2^{nd} series: SiC original powder F1200, sintered with 5 wt. % Sc₂O₃ ceramic binder. Characteristics of the Sc₂O₃ powder are given in Table 2.

 3^{rd} series: SiC original powders, SiC F240 and SiC F1200, sintered with 5 wt. % CaF₂ ceramic binder. Characteristics of the CaF₂ powder are given in Table 2.

4th series: Ultrapure SiC, without accessory elements, sintered by reaction of elemental silicon (Crytur, s.r.o. Turnov, Si purity 6N) with carbon powder (Carbon black Arosperse Palmer Holland, Inc., purity 5N).

Leaching of SiC in hydrofluoric acid

The acid resistance of SiC starting powders and SiC ceramics prepared by SPS in 22.5 M (40 wt. %) hydrofluoric acid was tested during long-term exposure at a standard temperature of 20 °C for 100 - 1000 h, and also in short-term experiments for 5 - 10 h during heating to a temperature of 100 °C. In view of the hazards when working with hydrofluoric acid, the technique used was as follows: weighed amounts of SiC powder F240 and/or SiC F1200 in a Teflon bottle were poured over with a specified amount of 22.5 M solution of hydrofluoric acid HF and left for 100 - 1000 h at a temperature of 20 °C, stirring up at times. After ending the exposure time and allowing the SiC powder to settle down, a sample of the solution was taken and neutralized by titration with 1 M NaOH solution. The content of the main impurity elements (Al, Ca, Ti, V, Fe etc.) was determined via atomic absorption spectrometry (AAS Agilent 280 FSAA) with combustion flame atomization. A similar experiment was made with powder precursors at a temperature of 20 °C for 1000 h. Then changes in the content of leached elements were analyzed by XRF.

The compact samples of all series, leached in 22.5 M hydrofluoric acid HF at a standard temperature, were analyzed gravimetrically as well. Then a series of experiments was carried out as follows: the compact samples were leached in 22.5 M hydrofluoric acid solution for 5 h at a temperature of 100 °C or 250 h at 20 °C, and the roughness parameters R_a , R_q , and R_z (DIN EN ISO 4287:1988) of corroded surfaces were measured using profilometry (Mitutoyo Surftest SJ-210). The structural characteristics of the sample were obtained using mercury porosimetry (Micromeritics AutoPore IV 9500). The analysis was performed in the range of macropores and mesopores in the pressure range from 0.01 - 400 MPa, i.e. for pore radii from about 100 µm down to 1.5 nm.

Table 3. Changes in the content of impurity elements in SiC powder after leaching in 22.5 M hydrofluoric acid for 1000 h (AAS analysis).

		Al	Ca	Ti	V	Fe	Sum
SiC F240	Impurity content in 10 g SiC powder F240 before leaching [wt. %]	0.082	0.014	0.018	0.026	0.185	0.325
SiC F240	Impurity content in 10 g SiC powder F240 before leaching [mg]	8.2	1.4	1.8	2.6	18.5	32.5
SiC F240	Content of leached impurities in the extract 50 ml 22.5 M HF after 1000 h leaching [mg]	0.85	0.35	1.05	0.85	1.51	4.61
Total amoun leached from	t of metallic impurities 1 the 10 g SiC batch		4.61 n	ng, i.e. 0.046	5 wt. %		
		Al	Ca	Ti	V	Fe	Sum
SiC F1200	Impurity content in 10 g SiC powder F1200 before leaching [wt. %]	0.060	0.004	0.048	0.074	0.085	0.271
SiC F1200	Impurity content in 10 g SiC powder F1200 before leaching [mg]	6.0	0.4	4.8	7.4	8.5	27.1
SiC F12040	Content of leached impurities in the extract 50 ml 22.5 M HF after 1000 h leaching [mg]	0.64	0.08	1.12	1.8	1.2	4.84
Total amount leached from	t of metallic impurities 1 the 10 g SiC batch	4.84 mg, i.e. 0.048 wt. %					

RESULTS AND DISCUSSION

Regarding the stability of the SiC powder precursors SiC F240 and SiC F1200 in 22.5 M hydrofluoric acid, basic information was obtained during leaching at a temperature of 20 °C (leaching time 1000 h). Due to the slight weight loss by leaching, the amount of leached metallic elements could be determined by AAS analysis. After neutralization with sodium hydroxide, the extract of the metallic impurity elements was analyzed by AAS. The results are summarized in Table 3.

During the second experiment concerning SiC powder leaching for 1000 h, the leached SiC powder was decanted several times with distilled water. The remaining sediment of SiC powder (3 mm high) was dried and subsequently analyzed by XRF. For comparison, a similar experiment was carried out with SiC F1200 in a 15.5 M solution of nitric acid HNO₃. Concentrations of accessory elements and impurities in weight percentage, given in Table 4, show that quantitative data relevant to etching or dissolving of impurities depend on the contact surface of reacting components, i.e. on their grain size distribution. However, the weight loss of the fine-grained SiC F1200 with the specific surface 43 - 49 $m^2 \cdot g^{-1}$ is only insignificantly higher than that of the coarse-grained SiC F240 with the specific surface $0.16 - 0.18 \text{ m}^2 \cdot \text{g}^{-1}$. The weight loss is lowest after etching with nitric acid.

About 80% of impurities were leached from the total amount, depending on the grain size distribution of SiC powders. The results of this experiment, which can be regarded as powder washing or cleaning, indicated that the purity of commercial SiC materials can be increased by some tenths of percent during further washing or leaching in hydrofluoric acid. This result is obviously related to the surface impurities illustrated in Figures 1 and 2. Corrosion losses of the compact samples of sintered SiC in hydrofluoric acid HF were evaluated separately based on the particular chemical composition and conditions of their preparation. It is important to note that in this work the corrosion rate is not evaluated in usual units such as $mg \cdot cm^{-2}$.year or $\mu m/year$, because as the impurities and SiO₂ present in the sintered SiC crystals leach only from the surface and open pores, weight losses converted to the usual units are somewhat misleading.

First, the samples of the 1st series, obtained by sintering of the original commercial untreated SiC powders F240 and F1200 without any sintering additive (binder), were evaluated by XRF analysis. Silica/SiO₂, found in amounts of approximately 2 wt. % in the SiC powder F240, and maximally 3 wt. % in the SiC powder F1200, was identified as the only sintering additive (binder) in this case. It should be emphasized, however, that the quantitative analysis of the amount of SiO₂ in silicon carbide products is problematic and a little vague for experimental reasons. SiO₂ crystallizes in more than 10 modifications [28] and melts at temperatures above 1600 °C, depending on the silica phase and the conditions (cristobalite at 1710 - 1720 °C), with the melt undergoing a transition to an amorphous (glassy) state upon cooling. Since the history of the heat treatment and subsequent sintering during the industrial production of SiC is usually not known, the exact content of undesirable SiO₂ (responsible for increased solubility in hydrofluoric acid HF) can be measured only with difficulty. X-ray diffractometry as well as the evaluated EDS spectra showed a maximum of 2 wt. % SiO₂ in coarse-grained commercial SiC powders. Moreover, in many cases the content of SiO₂ is not more than a "trace", i.e. close to the detection limit of X-ray diffraction (PANalytical X-Pert Powder). Therefore, the oxygen content was

Elements	SiC F240 before leaching in HF [wt. %]	SiC F240 after leaching in HF [wt. %]	SiC F1200 before leaching in HF [wt. %]	SiC F1200 after leaching in HF [wt. %]	SiC F1200 after leaching in HNO ₃ [wt. %]
Al	0.043	0.006	0.031	0.006	0.030
Ca	0.014	0.004	0.011	0.004	0.008
Ti	0.011	0.003	0.035	0.006	0.016
V	0.008	0.003	0.030	0.005	0.008
Cr	0.044	0.006	0.003	0.002	0.003
Mn	0.005	0.002	0.003	0.001	0.002
Fe	0.063	0.020	0.045	0.006	0.038
Ni	0.021	0.004	0.009	0.003	0.006
Sum of the impurit elements	^y 0.209	0.048	0.167	0.033	0.081
Relative amount (p of leached impuriti	ercentage) ies	77 %		81 %	51 %

Table 4. Changes in the content of impurities in the sediment of SiC powder after leaching in 22.5 M HF and 15.5 M HNO_3 for 1000 h (XRF analysis).

analyzed with the LECO method (LECO ON836) with the aim of calculating the amount of SiO₂ from the oxygen content measured. For this purpose, the samples in graphite crucibles were burnt in an impulse resistance furnace, forming CO and CO₂, which was subsequently detected in infrared cells (NDIR). A discrepancy between the analytical values of the oxygen content and its conversion into the amount of SiO₂ became evident depending on the SiC granulometry. The coarse-grained SiC F240 exhibited lowest values of oxygen content, while the fine-grained SiC F1200 showed values higher by an order of magnitude. Therefore, it has been surmised that the LECO apparatus - if the preset programme of temperature and pressure of the measured gases is used - is not capable to register and analyze all SiO₂ embedded in inside layers of SiC crystals. This view was confirmed experimentally as follows: SiC F240 powder with specific surface 0.15 m²·g⁻¹ and median diameter 45 µm containing oxygen bonded as SiO₂ was milled and then analyzed. The original value of oxygen content was 0.43 wt. %, but after milling of the same sample in a crusher made of sintered tungsten carbide the oxygen content increased almost three times to a value of 1.13 wt. %. A total content of 2.2 wt. % SiO₂ then results from this value.

This experiment can serve as a support for the view of the important role played by SiO_2 in the corrosion of SiC in hydrofluoric acid. Unfortunately there are no reliable analytical methods for the exact quantitative analysis of the SiO_2 content in SiC materials. It is possible that in the past many authors had not been aware of this fact and thus arrived at incorrect conclusions when interpreting measured data relevant to SiC corrosion in acid media. If the corrosion medium does not get into contact with all SiO₂ layers in the SiC crystals, then the result of the measurements is only a "quasi-resistance", i.e. a relative value for comparing geometrically identical samples. We note in passing that in the case of oxygen analysis via the LECO method, the carbonaceous reaction medium can also be considered as a "corrosion agent" in a certain sense.

Pressed compacts of silicon carbide sintered without binder at 1600 °C had a suitable mechanical strength to cut them into prisms with rectangular cross-section for the subsequent analyses. During fracture tests, an approximate flexural strength of 150 ± 50 MPa was measured. Similar values have been found by other authors [29]. Cylindrical compacts (diameter 20 mm and length/ height 5 ± 0.2 mm, volume 1.4 - 1.7 cm³, surface area approximately 9.4 cm²) were ground to parallel surfaces and metallographically polished. Then the samples (4.4 - 5.3 g) were put into a Teflon container, poured over with 22.5 M HF solution, heated up to 100 °C and held at that temperature for 5 h. The leaching extracts were analyzed via the AAS method. The results are summarized in Table 5.

From the weight losses presented in Table 5, the corrosion rate cannot be calculated in the usual units linear dimension/time, e.g. μ m/year, as the geometric dimension of the samples does not change. From the

Table 5. Analysis of leaching extracts from sintered SiC F240 and SiC F1200 prepared without binder after 5 h in 22.5 M hydro-fluoric acid at 100 °C.

Sintered sample SiC F240 we	ighing 5.0 g v	vith a surface	area of 9.4 cm ²	2	
	Al	Ti	V	Fe	Sum of analyzed impurities 0.300 wt. %
Content of impurities* in sintered SiC F240 without binder before leaching [wt. %]	0.080	0.020	0.020	0.180	_
Content of impurities in sintered SiC F240 without binder after leaching in 22.5 M HF, 5 h, 100° C [wt. %]	0.043	0.014	0.005	0.065	0.127 wt.%
Amount of leached elements from the samples weight 5 g, determined by AAS [mg]	1.70	0.22	0.24	3.00	5.16 mg, i.e. 0.103 wt. %
Sintered sample SiC F1200 we	eighing 5.0 g	with a surface	area of 8.3 cm	2	
	Al	Ti	V	Fe	Sum of analyzed impurities 0.220 wt. %
Content of impurities* in sintered SiC F1200 without binder before leaching [wt. %]	0.070	0.030	0.040	0.080	_
Content of impurities in sintered SiC F1200 without binder after leaching in 22.5 M HF, 5 h, 100° C [wt. %]	0.012	0.004	0.007	0.048	0.071 wt. %
Amount of leached elements from the samples weight 5 g, determined by AAS [mg]	0.60	0.20	0.36	2.44	3.60 mg, i.e. 0.072 wt. %

* Note: Only the content of selected elements with the highest concentration was analyzed.

weight loss, only the rate of etching or dissolution of impurities (or sintering additives) can be determined. In this case, we arrive at approximate values of 0.93 g·m⁻² year for coarse-grained SiC F240 and 0.67 g·m⁻² year for fine-grained SiC F1200. The latter value is lower be-cause sintered SiC F1200 samples are less porous (see Table 6) and thus have a lower value of attackable surface (although the initial particle size of the powders was smaller).

Furthermore, the samples were processed with metallographic methods (cutting, grinding, polishing) with the aim of obtaining micrographs of the structure.



Figure 4. Structure of sintered SiC F240 without binder (1st series) non-etched surface.

Another part of the cut samples was used for mercury porosimetry. Micrographs of the original structure and the leached sample surfaces are presented in Figures 4-7. Results of mercury porosimetry are given in the first part of Table 6.

During the 2^{nd} series of experiments the original powder SiC F1200 was sintered after adding 5 wt. % of scandium oxide Sc₂O₃ as a ceramic binder. Characteristics of the used Sc₂O₃ powder are listed in Table 2.

For the conditions of SPS see the sintering schedule in Figure 3. The Sc_2O_3 binder microstructure and its uniform distribution are presented in Figures 8 and 9.



Figure 6. Structure of sintered SiC F1200 without binder (1st series) non-etched surface.



Figure 5. Structure of sintered SiC F240 without binder (1st series) etched in 22.5 M HF.



Figure 7. Structure of sintered SiC F1200 without binder (^{1st} series) etched in 22.5 M HF.

The diffraction pattern in Figure 10 proves that scandium oxide reacted with the SiO_2 present in the original SiC powder to scandium silicate Sc_2SiO_5 or $Sc_2[SiO_4]O$ [30].

The 2^{nd} series of SiC samples prepared with Sc_2O_3 binder followed another objective, namely the reaction of the primarily present SiO₂ incorporated in the silicon carbide crystals with this binder. Diffraction patterns of the sintered compact of fine-grained SiC F1200 with scandium oxide (Figure 10) corroborate the generation of Sc_2SiO_5 , the structure [30] and other properties of which are described well in works dealing with pumped laser diode traps, e.g. [31, 32]. Besides Sc_2SiO_5 phase also a residual unreacted fraction of SiO₂ was found in the diffraction pattern of coarse-grained SiC F240 with Sc_2O_3 binder, which can be explained by the inhomogeneous course of the reaction, and by the insufficient contact of the binder with SiO_2 interlayers in the coarse-grained reaction mixture. During this experiment a qualitative proof of the presence of scandium ions in the fluoride extract was carried out by determining the solubility of sintered samples containing scandium in 22.5 M HF solution by means of AAS. It was found that the Sc³⁺ content in the fluoride extract is 0.27 - 0.30 wt. %.

Another, semiquantitative proof of the leaching of scandium binder in the form of scandium fluoride was provided by XRF after drying of an extract absorbed on an ultrapure carbon fibre filter (Insul Trade). After 5 h leaching of SiC sintered with 5 wt. % Sc₂O₃ in HF at 100 °C, a solution volume of approximately 10 ml was retained on the surface of the carbon-fibre filter, dried and analyzed by XRF. The result given in Table 7 corroborated that besides Sc also other impurity elements were leached.

Table 6. Mercury porosimetry of SiC compacts.

	1 st series		2 nd se	eries	3 rd series		
	SPS SiC F240 sintered without binder	SPS SiC F240 etched 5 h at 100 °C	SPS SiC F1200 + 5 % Sc ₂ O ₃	SPS SiC F1200 +5 % Sc ₂ O ₃ etched 5 h at 100 °C	SPS SiC F1200 +5 % CaF2	$\begin{array}{c} \text{SPS SiC F1200} \\ + 5 \% \text{ CaF}_2 \\ \text{etched 5 h at 100 °C} \end{array}$	
Total intrusion volume [ml·g ⁻¹]	0.16	0.16	0.13	0.14	< 0.001	< 0.001	
Total pore area [m ² ·g ⁻¹]	6.71	6.73	7.43	7.40	0.002*	0.00*	
Median pore radius [µm]	0.05	0.04	0.03	0.08	0.01*	0.01*	
Apparent (skelet density [g·ml ⁻¹]	tal) 3.16	3.15	3.09	3.08	3.16	3.06	
Open porosity [%]	33.9	34.1	30.0	30.7	0.07	0.11	

* Note: Within statistical measurement errors (1 %).





Figure 8. Microstructure of sintered SiC with 5 % Sc_2O_3 binder.

Sc Ka1



Figure 9. EDS map of the distribution of Sc_2O_3 in the sintered samples.



Figure 10. XRD pattern of sintered SiC with Sc_2O_3 binder and $Sc_2[SiO_4]O$ phase.

Table 7. Amount of leached impurity elements from sintered sample SiC + 5 wt. $\%~Sc_2O_3.$

C (filter)	Mg	Al	Si	Ca	Sc	Ti	Fe
[wt. %]							
99.34	0.025	0.112	0.303	0.037	0.045	0.005	0.072

This experiment indicated that the SiO_2 present in the SiC crystals is able to react with every suitable chemical compound added not only as a binder, but also as a solvent or corrosion medium.

 3^{rd} series: SiC original powder F240 and F1200 with 5 wt. % CaF₂ ceramic binder. Sintering conditions are the same as for the 1st series. Microstructures of products are shown in Figure 11, and the uniform distribution of the added CaF₂ binder is documented in Figure 12.

The 3rd series of silicon carbide samples sintered with CaF_2 binder showed better results, i.e. the lowest corrosion loss in weight, again within analytical limits at a level of 10^{-3} %. Owing to the relatively low melting temperature of 1418 °C, the CaF_2 binder covered the SiC grains very efficiently at the sintering temperature of 1600 °C. As a consequence the samples had the lowest porosity of 0.11 vol. % (see Table 6), and thus the corrosion medium could not penetrate deeply into the sample. Weight losses were undetectable with an analytical balance of response 10^{-3} g.

In the 4th series experiments were carried out involving the preparation of ultrapure SiC without accessory elements. SiC samples without oxygen (or more precisely without SiO₂) were prepared by sintering silicon semiconductor powder (Crytur, s.r.o Turnov, Si purity 6N) in stoichiometric ratio with carbon powder (Carbon black Arosperse Palmer Holland, Inc., purity 5N). Sintering conditions: temperature 1600 °C, pressure 60 MPa, see Figure 3. The fracture surface structure of the compact sample is shown in Figure 13, the porous microstructure in Figure 14. Based on the diffraction pattern in Figure 15, the single-phase structure was identified as cubic SiC (3C-SiC, space group T_dF-43m).

An almost ideal result was obtained for 4th series samples of ultrapure SiC prepared from semiconductor pure silicon. In contrast to the 1st, 2nd and 3rd series samples, which showed a three-phase SiC crystal structure, in this case only a single-phase product was formed, silicon carbide with a cubic structure (β -SiC, polytype 3C, space group F-43m). In addition, the diffractogram of Figure 15 shows lines 2θ at 26.8° and 55.1° , which belong to graphite, the amount of which corresponds to a possible stoichiometric excess when homogenizing the Si + C mixture, or an additional contribution from the graphite pistons and walls of the graphite die of the SPS apparatus. The exposure time of leaching of these samples in 40 % HF was 250 h, and no weight loss or visible attack of the sample surface occurred. This can be documented, among other things, by measuring the surface roughness.



Figure 11. Microstructure of sintered SiC F1200 + 5 % CaF₂.



Figure 12. EDS map showing the uniform distribution of the CaF_2 binder.

Surface roughness measurements were performed according to EN ISO 4288 and CSN EN ISO 4287: 1988 (with the roughness tester Mitutoyo VR-5000 Surftest SJ-210). The measured values are given in Table 8. The values of R_a and R_q in Table 8 represent the arithmetic and quadratic mean deviations of the roughness from the center line of the profile. The R_Z parameter indicates the height of the unevenness of the etched surface.

If we start from the assumption of ideal evenness or smoothness of the initial investigated surface, then the hydrofluoric acid will etch the material to the maximum depth R_z (µm). The R_z value in this case is the most concise to characterize the change in the etched surface, as it expresses in some way the amount of etched material.

Table 8 shows the roughness values of the original diamond paste-polished surface of the compact sample in two directions, parallel to the pressing axis in the SPS apparatus and perpendicular to the pressing axis. The same measurement was then performed on the surfaces etched in hydrofluoric acid for 250 h.

The extraordinary corrosion resistance of the ultrapure β -SiC described above is in contrast to an earlier study [23], where the authors found their samples of β -SiC to some extent soluble in hydrofluoric acid. The solubility of β -SiC samples in hydrofluoric acid as reported in [24] was increasing as the sintering temperature (temperature of SiC synthesis) decreased. The authors attributed this observed trend to an increasing amount of imperfections in the crystal lattice with decreasing processing temperature. They also found that the presence of impurities retards the solubility of the β -SiC itself. However, the results obtained here for ultrapure SiC do not confirm these findings. A study of the influence of lattice imperfections, depending on different conditions of the sintering process, is beyond the scope of the present work but could be the subject of further investigations.

Silicon oxide occurs in the form of interlayers or on the surface of individual SiC crystals and enables the sintering of the SiC powder grains without any external binder. A similar sintering mechanism via oxide



Figure 13. Fracture surface structure of the sintered ultrapure SiC (4^{th} series).



Figure 14. Porous microstructure of the sintered ultrapure SiC (4th series)

Surface roughness of the initial polished surface (perpendicular to the pressing direction)			Surface roughness of the same sample after 250 h (perpendicular to the pressing direction)			
R _a	R_q	R_z	$\overline{R_a}$ R_q			
0.552 μm	0.717 μm	3.327 µm	0.486 µm	0.600 µm	3.450 μm	
	Surface roughness of the initial polished surface (parallel to the pressing direct	Surface roughness of the same sample after 250 h of etching in 40 % HF (parallel to the pressing direction)				
R _a	R_q	R_z	R_a	R_q	R_z	
0.566 µm	0.720 μm	3.707 µm	0.581 μm	0.753 μm	3.778 μm	
EN ISO 4287	and EN ISO 4288					

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layers has also been described for plasma spraying of SiC layers. In this technology, the SiO₂ surface layer is generated by SiC oxidation during plasma spraying [33]. However, the mechanical strength of these sintered products is much lower than the mechanical strength of sintered SiC products which have a higher content of a suitable ceramic binder.

Note that lower contents of SiO_2 are generally detected in SiC products sintered via the Si-SiC method, i.e. in samples sintered with elemental silicon as a binder, because commercially supplied silicon powder is chemically purer by a few orders of magnitude compared to SiC powder at approximately the same price level.



Figure 15. Diffractogram of ultrapure sintered SiC (4^{th} series), cubic F-43m structure.

CONCLUSION

The experiments described in this paper have shown that chemically pure SiC is not soluble in hydrofluoric acid. Importantly, the results of this work showed that the solubility of SiC samples in hydrofluoric acid does not depend on the crystalline structure of SiC. This finding does not confirm the previous results of some authors, e.g. [24], which led to the conclusion that the β -SiC (3C) phase decomposes in HF. The corrosion resistance of SiC ceramics depends on the content of other substances contained in the SiC-ceramic binder system. In this work, the corrosion resistance was measured using commercially available industrial silicon carbide raw materials in which the residual SiO₂ content remains at the level of a few weight percent. Silicon oxide occurs in the form of interlayers or on the surface of individual SiC crystals.

The content of silicon oxide in SiC crystals is the main cause for a different corrosion resistance of ceramic products made of SiC. The point is that silicon oxide is soluble only in hydrofluorid acid, while the other additions functioning as a binder or primary metallic impurities are soluble in a broad range of other strong mineral acids as well. An obvious difference in the corrosion resistance of sintered SiC was exhibited by Sc_2O_3 binder, which is soluble in hydrofluoric acid. In the

case of CaF_2 binder, which is insoluble in hydrofluoric acid, the corrosion resistance was higher by an order of magnitude. In all cases, however, the corrosion rate is very low, of order $1g \div 2 \text{ g} \cdot \text{m}^{-2}$ year, and depends only on the chemical composition and the amount of ceramic binder used and, of course, on the content of primary impurities, especially the residual silica content. Absolutely pure SiC does not react with hydrofluoric acid.

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