Ralf Westerheide
Fraunhofer-Institut für
Werkstoffmechanik
Wöhlerstr. 11
79108 Freiburg, Germany
Phone ++ 49 761 5142-206
Fax   ++ 49 761 5142-403
Email wh@iwm.fhg.de

Christina von der Wehd
Fraunhofer-Institut für
Werkstoffmechanik
Wöhlerstr. 11
79108 Freiburg, Germany
Phone ++ 49 761 5142-258
Fax   ++ 49 761 5142-403
Email vdw@iwm.fhg.de

Jörg Adler
Fraunhofer-Institut für Keramische
Technologien und Sinterwerkstoffe
Winterbergstr. 28
01277 Dresden, Germany
Phone ++ 49 351 2553-515
Fax   ++ 49 351 2554-333
Email adler@ikts.fhg.de

Petra Rehak
Fraunhofer-Institut für Keramische
Technologien und Sinterwerkstoffe
Winterbergstr. 28
01277 Dresden, Germany
Phone ++ 49 351 2553-704
Fax   ++ 49 351 2554-333
Email rehak@ikts.fhg.de

Evaluation of Mechanical Properties and Structural Changes of Ceramic Filter Materials for Hot Gas Cleaning under Simulated Process Conditions

Keywords: ceramic filter materials, (thermo)-mechanical properties, silicon carbide, oxide based ceramics

Introduction
The combined cycle technology for advanced coal fired power plants enables higher generation efficiencies than the only steam cycle based technology. However, temperatures up to 950 °C by using the circulating pressurized fluidized bed combustion (PFBC) are leading to increased demands to the materials in the whole plant. One of the main components in the hot sections of the combined cycle technology is the filtration unit in which the removal of particles from the stream to the gas turbine takes place.

For a stable long term operation of the filter elements, a good resistance towards thermal, mechanical and chemical loading is crucial. Additionally, the filter media must ensure a minimum pressure drop in order to reach maximum operation efficiency and to minimize cost of operation. These requirements are met by ceramic materials. Rigid ceramic filter elements are state of the art for the removal of particles from gases. However, their application depends on the properties of the dust being separated from the raw gas (Grannel et al. 1996).

The structure of ceramic filter elements consists usually of a highly porous support which ensures the mechanical strength and a layer which operates as the functional part for the particle removal. The durability of the ceramic filter elements is limited in principal by chemical reactions between gas and ceramic material, mechanical loading or thermal shock during pulse cleaning. Thereby the lifetime of the whole element is mainly determined by the lifetime of the support material and not by the functional layer.

Objectives
The objective of this study is to evaluate changes in structure and mechanical properties of ceramic filter materials under simulated corrosive process conditions. Due to an analysis of the mechanisms of degradation firstly an optimization of materials shall be enabled and sec-

ondly a material selection for specific applications shall be relieved. This publication describes the investigations made on many ceramic support materials based on oxides and carbides. Both commercially available and newly developed support materials have been evaluated for specific applications in hot gas cleaning.

Approach

Ceramic filter materials made from different oxides and silicon carbides respectively have been exposed to reducing and oxidizing atmospheres in a continuous flow reactor with temperatures up to 850 °C and a gas pressure of 10 bar. In some experiments alkali salts have been added to the gas stream. In other experiments the alkali load was given by a soaking of the specimens in alkali solutions. The specimen were dried after soaking and than exposed to a gas stream without additional alkali load. Therefore it can be assured that a maximum of inner and outer surface was in contact to alkali. All exposures were performed by the TU-Bergakademie in Freiberg, Germany. Details of the exposure are described elsewhere (Angermann et al. 2002). After these exposures (t = 100 h) changes in porosity, density and structure have been determined. Furthermore fundamental mechanical properties as strength, modulus of elasticity and the softening behavior have been measured. The mechanisms of degradation were discussed and finally new approaches for a materials optimization were found.

Considering the demands to lifetime up to 16.000 h the question arise, whether an exposure of only 100 h leads to reliable results with respect to mechanical properties. Earlier results obtained by Alvin et al. (Alvin et al. 1998 and 1999) have shown by experiments up to 3000 h that a strength degradation of filter elements in operation occurs in the beginning of service. Afterwards the strength remains on a constant level for most of the investigated materials. Therefore a prediction of changes in mechanical properties based on results obtained after 100 h seems to be acceptable for long term exposure.

Project Description

To ensure that for all specific applications at minimum one material is favorable, three different types of materials have been investigated. Oxides, self-bonded silicon carbide and clay bonded silicon carbide were taken into consideration. The oxides are spinel (S) and alumina (A). Both materials are newly developed materials without any experience in filtration operation at high temperatures. The self bonded silicon carbides were delivered by different companies. Two of these materials (R1 and R2) are in the state of new developed materials and one material (R3), bought as tubes for filter elements, is still under investigation in other plants and is well described in the literature (Eggerstedt and Zievers 1999). The third group of materials are the well known clay bonded silicon carbides and a liquid phase sintered silicon carbide. The clay bonded silicon carbides are standard materials for these applications. Therefore several results from filtration operation are existing. However the results were often obtained at process conditions not comparable to those applied in this project (compare with Montanaro et al. 2000 and Pastila et al. 2001). Three of the materials were produced by the Fraunhofer-IKTS as small sized specimens (B1, B2 and L1) whereas the other materials were delivered as filter elements and then cut to specimen. The clay bonded materials have a porosity of about 30 to 40 %. The RSiC-Materials have a lower porosity of 20 to 25 %, whereas the alumina has 46 % porosity. Table I summarizes the basic properties of the materials.

The main differences of the microstructures for the investigated groups of materials can be seen in figure 1. The fine grained spinel material (S) has a small mean pore size. Whereas the

coarse grained RSiC-material (R3) has a relatively big mean pore size. A correlation between pore size, grain size and strength does not exist due to the different types of bonding.

All materials were cut to specimen of the size 5x6x45mm or 6x8x60mm respectively. The grinding of the surface was performed by a conventional diamond wheel with respect to the dimension and not to the surface roughness. For each material and for each exposure at least 10 specimen were prepared. The specimen were characterized before exposure with regard to their phase composition by X-ray, to their density by the Archimedes method and to their porosity by mercury porosimetry. The microstructure before and after exposure was investigated using a FE-SEM. The bending strength was measured using a 4-point-bending device with an inner span of 20 mm and an outer span of 40 mm. The deformation behavior was measured using the same 4-pont-bending device coupled with a displacement measurement system contacted directly to the specimen. The temperature during the deformation measurement was increased stepwise from 850°C to 1000°C (each 5h the temperature was increased about 50°C). The applied load was 5 MPa for the whole time of the experiment.

The exposure conditions for the experiment are given in table 2. The alkali load was added by subliming solid salts to the gas phase. Some experiments were additionally performed by soaking the porous specimen with an alkali solution before thermal treatment. After the different exposures the specimen were characterized again in a similar way to those characterized before.

Results
Microstructure
The thermochemical loading during the different exposure conditions can lead to alterations of the surface of the grains. This can be caused mainly by reactions between alkali and the material or by reduction respectively oxidation at high temperatures. An alteration of the microstructure can lead to changes in pore size and therefore to an increased pressure drop during filtration or they can lead to a decrease in the values for mechanical properties.

- Reducing atmospheres
The density and the porosity of all materials after exposures 1, 2 and 3 are similar to those measured before exposure. Also the X-ray analysis has shown no differences in crystalline phase content between the as sintered state and the exposed materials. Furthermore no changes in the microstructure by SEM-investigation could be observed after exposures 1 and 2. However, after exposure 3 with alkali load at 650 °C the material L1 has shown traces of whisker formation and the oxide based materials have shown slight changes in the surface structure of the grains. These changes seem to be of minor importance for mechanical properties.

Due to a soaking of the specimen in alkali solutions the outer and the inner surface of the materials are in contact to the alkali load. This was not ensured by the exposition in the alkali loaded gas stream, because the specimen does not act as a filter in those exposures. The temperature for the exposure of soaked specimen in reducing atmosphere was increased to 750 °C. This was done with respect to the small effects to the microstructure during exposure up to 650 °C.

After exposure 3* the density of the skeleton (which is the density of the material without the open porosity) is significant lower compared to the density of the skeleton in the as sintered

state for most of the materials. However, the skeleton density of R3, B3 and the Spinel is not decreased (table 3).

The skeleton density can be influenced by phase transformation, by bubble formation in the binder material, by oxidation of the grain surfaces or by the formation of closed porosity. Phase transformations could not be observed. However, the formation of bubbles in the siliceous bonding of the SiC-grains was observed for materials B3 and B4 (see figure 2). The bubble formation has no significant influence to the porosity for these materials. For materials R3 and L1 a strong decrease of porosity was determined (table 3). In the case of L1 this can be caused by the small pore size which correlated with the high amount of inner surface, able to react with the alkali load.

- Oxidizing atmospheres
The temperature at exposures with oxidizing atmospheres was 100 °C to 200 °C higher compared to the reduzing atmospheres. Only minor changes of the skeleton density could be measured for all materials after exposure of not soaked specimens. Also the amount of porosity was not affected by the oxidizing atmosphere with and without alkali load (table 3). However, in X-ray investigation it could be measured that for the RSiC- and the liquid phase sintered SiC-materials a growing of an oxidation layer takes place. An example is shown in figure 3 for material R3. Material B3 has shown a significant formation of bubbles, whereas this could not be observed for the similar material B4 (figure 4, top). As it was expected no changes in structure or surface of the grains was observed for the oxide based materials.

Exposure No. 6* with soaked specimen was performed at the same temperature and pressure as exposure No. 6. The soaking has led to a strengthened effect of bubble formation for material B3. Material B4 has shown no bubbles or other changes as it was measured after exposure No. 6 (see figure 4, bottom). Most of the materials have shown only minor changes in the skeleton density (see table 3). A significant effect of the soaking was measured for material L1. The skeleton density and the amount of porosity were decreased and the FE-SEM investigation of the grain surface has revealed a rough and tumid surface (see figure 5). Due to this it can be assumed that mechanical properties are influenced drastically. However, this was not confirmed in the experimental data.

Mechanical properties
- Reducing atmospheres
The results of strength measurement can be correlated to the results of investigation of the microstructure for most of the materials. The exposure at 400°C without alkali load has no influence to the mechanical properties. An exposure at 650°C without alkali load has led to minor decrease of strength for L1 and B3. No decrease was measured for all other materials (see table 4), when the specimen were not soaked before exposition. However, a strong increase of strength up to 39 MPa was measured for B2. The reason for this behavior could not be explained yet.

The operation temperature will be up to 1000°C in the future. At these temperatures the binder of clay bonded silicon carbide materials often begins to soften. This can result in an elongation of the materials, can lead to crack formation and can result in the failure of the whole element. Hence it is necessary to achieve a creep rate as small as possible. The resistance against deformation was measured at temperatures from 850°C to 1000°C. The spinel as well as the RSiC materials have shown no change in the deformation behavior caused by the exposures 1 to 3. In figure 6 the results for some clay bonded silicon carbides B1, B3 and

B4 are shown with significant decreases in the deformation resistance after exposure for B4. B1 has also shown an increase of deformation. However, for material B3 no change of deformation resistance could be measured. Compared to the decrease in strength there seem to be no correlation with the deformation resistance. This can be explained by the mechanisms of degradation. While the strength can be influenced by geometric alterations of the necks between the grains in the material and by the accumulation of flaws, the deformation resistance will be mainly influenced by chemical variation in the siliceous binder. The measurements for the deformation resistance of the soaked specimen are not yet accomplished.

The soaking in salt solutions and the further increase of temperature up to 750°C affects the strength of the materials. The strength of R3 was increased significantly. This is correlated to the decrease of porosity by surface reactions. L1 was not affected by the soaking. The strength of the Spinel was decreased to 18 MPa as well as the strength of the siliceous bonded silicon carbide materials were decreased to 50%-80% of their initial strength (table 4).

- Oxidizing atmospheres
Exposures under oxidizing atmospheres are leading to the formation of oxide layers for RSiC as it was shown in figure 3 for R3. The oxide layer provokes a strong increase in bending strength. A similar behavior was observed for L1. Only minor effects to the strength were measured for all other materials. However a slight decrease was measured for B3. If the exposure is with or without alkali load seems to be not of importance, but surprisingly the strength values measured at room temperature after exposure for the highest temperature (850°C) with alkali load were higher compared to those after exposure at 750°C or at 850°C without alkali load (table 4).

The soaking has resulted in similar materials properties as measured after the exposition in alkali loaded gas streams. However, further strength degradations and further degradations in deformation resistance were measured (table 4 and figures 7 to 9).

The RSiC-materials has a very high deformation resistance. After exposure in oxidizing atmospheres no changes could be observed. The same was measured for the Spinel (figure 7). A reduction in deformation resistance was observed for all siliceous bonded SiC-materials. An increase in exposition temperature as well as the addition of alkali to the gas stream leads to an increase in strain during creep experiments (see examples in figures 8 and 9 for materials B3 and B4). The investigation of microstructure has shown the formation of bubbles for material B3. However, this was not observed for material B4. Therefore the reason for the decrease of deformation resistance for material B4 can only be explained by alteration of the secondary phase, i.e. by crystallization or incorporation of impurities from the alkali loading.

Remarkable is the softening of material B4 after exposure No. 6* in deformation experiments at 900°C. This behavior can not be explained yet, because there was no degradation in strength and no significant alteration of microstructure after exposure observed.

Summary
Three different types of materials have been investigated: oxides, self-bonded silicon carbide and silicon carbide with siliceous binder. After exposure to reducing atmospheres at 650 °C no significant changes with respect to texture, micro- and pore structure could be observed. The mechanical properties, however, show particularly an obvious deterioration of strength and softening behavior. Especially the strength of silicate bonded silicon carbide is decreased

significantly after exposure to an alkali containing gas stream. The soaking of specimen in alkali solutions before exposure leads to a further decrease in mechanical properties.

As a result spinel as an oxide ceramic was identified to be a favorable material with respect to mechanical properties and resistance towards reducing atmospheres until 650°C. However the soaking has also for the spinel material led to a strong decrease of strength. Nevertheless the spinel and some siliceous bonded silicon carbides should be considered for filter applications in reducing atmospheres even though some improvements have to be done with these materials.

When exposed to an oxidizing atmosphere the formation of oxide layers for some types of SiC is observed. At SiC with a siliceous binder, however, no oxidation products could be detected. So the binder is thought to be a protective phase against oxidation. Thus only minor changes of the mechanical properties were expected. The assumption could be verified by measuring the strength of the materials after exposure. In some cases an increase of strength compared to the as sintered state was measured. Also the soaking before exposure has minor influence on the strength of the materials. But there were significant changes in deformation behavior after exposure measured. For some siliceous bonded materials the maximum application temperature was decreased to 850°C or lower.

This study shows that an oxide ceramic (spinel), could be a favorable material in hot gas cleaning under reducing conditions up to 650°C and in oxidizing atmospheres up to 850°C. However the amount of pores and the pore structure of these materials have to be optimized. The porous Al_2O_3 can only be investigated in further experiments when the strength and the porosity is optimized first.

Despite of the general expectation the evaluation of silicate bonded and self bonded silicon carbide materials reveals a considerable potential for these materials in long-term applications particularly under oxidizing conditions.

Future Activities
In this project mainly a screening of some new and some commercially available materials was performed. At the moment a first optimization of some materials takes place. Afterwards a second step of screening is necessary to confirm the expected results of optimization.

Even if a lot of different exposure conditions were used in this project, the influence of humid air on the lifetime of the ceramic support materials is not yet investigated. This should be a topic of future activities.

References
Alvin, M. A. 1999. Hot Gas Filter Development and Performance. In *High Temperature Gas Cleaning, Vol.2*, Edited by A. Dittler et al., Karlsruhe, 455-467.

Alvin, M.A. et al. 1998. Advanced Hot Gas Filter Performance and Characterization. Published via Internet at: http://www.fetc.doe.gov/publications/proceedings/98/98ps/ps3a-7.pdf

Angermann, J. et al., 2002. Investigation of Chemical Resistance of Ceramic Filter Materials for Hot-Gas Cleaning. The same proceedings as this publication.

Eggerstedt, P. and Zievers, J., 1999. High Temperature Particulate Removal Using Recrystallized Silicon Carbide Candle Filters. In *High Temperature Gas Cleaning, Vol.2*, Edited by A. Dittler et al., Karlsruhe, 375-383.

Grannell, S.K. et al., 1996. Investigation into the Behaviour of Particle Compacts and Comparison with Industrial Experience. In *High Temperature Gas Cleaning, Vol.1*, Edited by E. Schmidt et al., Karlsruhe, 145-156

Montanaro, L. et al., 2000. Corrosion of Ceramic Filters For Hot Gas Cleaning in Thermal Power Plants. *Proc. of the 24th Annual Conference on Composites, Advanced Ceramics, Materials, and Structures: B*. Edited by T. Jessen, E. Ustundag, Cocoa Beach, 561-568

Pastila, P. et al., 2001. Environmental effects on microstructure and strength of SiC-based hot gas filters. *Journal Europ. Cer. Soc.* (21) 1261-1268

Figures and Tables

|	Materials type	Porosity in %	Mean pore size in µm	Strength in MPa (4-Point bending)	
				σ_0	m
R1	RSiC, new developed	~20	100	12	2
R2	RSiC, new developed	20	30		
R3	RSiC, established	22	74	24	25
S	Spinell, new devel.	28	18	39	20
A	Alumina, new devel.	46	54	4	8
L1	LP-SiC, new devel.	43	4	22	9
B1	sil. bonded SiC, new d.	30	43	29	20
B2	sil. bonded SiC, new d.	32	43	22	15
B3	sil. bonded SiC, establ.	37	60	25	31
B4	sil. bonded SiC, establ.	33	60	21	30

Table 1: Basic properties of the investigated materials.
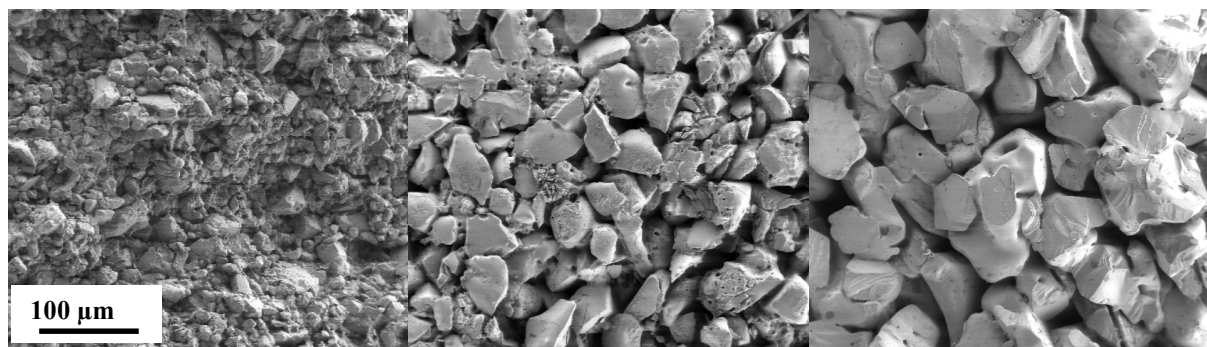
Figure 1: Microstructure of Material S (left), B2 (middle) and R3 (right).

No.	Atmosphere	Temperature in °C	pressure in MPa	Time in h	Alkali load
1	Reducing	400	1	100	No
2		650	1	100	No
3		650	1	100	Yes
3*		750	0.5	100	Yes
4	Oxidizing	850	0.5	100	No
5		750	0.5	100	Yes
6		850	0.5	100	Yes
6*		850	0.5	100	Yes

*additionally performed with soaked specimen

Table 2: Process conditions during thermochemical loading

Skeleton density	R1	R2	R3	L1	B1	B2	B3	B4	A	S
as sintered	3.18	3.2	3.12	3.23	3.02	2.97	2.95	2.91	3.94	3.56
after expos. 3*			3.04	2.66	2.79	2.78	2.95	2.76	n.d.	3.52
after expos. 4			3.14	2.99	3	2.96	3.05	3	3.91	3.55
after expos. 5			3.17	3.11	3	2.97	3.04	3	3.93	3.54
after expos. 6	3.17	3.14	3.16	3.03	2.98	2.96	3.01	2.97	3.93	3.55
after expos. 6*			3.11	2.6	2.88	2.87	2.97	2.85	n.d.	3.54

Porosity as sintered	17-27%	20.2%	22.0%	43.3%	32.2%	30.2%	37.2%	32.5%	46.0%	27.5%
after expos. 3*			14.7%	29.9%	32.2%	29.8%	36.4%	33.6%	n.d.	27.0%
after expos. 4			22.2%	37.5%	32.5%	29.8%	39.2%	33.3%	46.3%	27.7%
after expos. 5			22.8%	40.6%	32.1%	29.9%	38.8%	33.4%	46.6%	27.0%
after expos. 6	27.7%	18.3%	23.1%	38.2%	31.6%	30.0%	37.6%	33.9%	46.7%	27.4%
after expos. 6*			18.6%	31.6%	30.9%	27.8%	34.9%	31.3%	n.d.	26.7%

(not listed for exposures 1 to 3 due to no changes compared to the as sintered state)
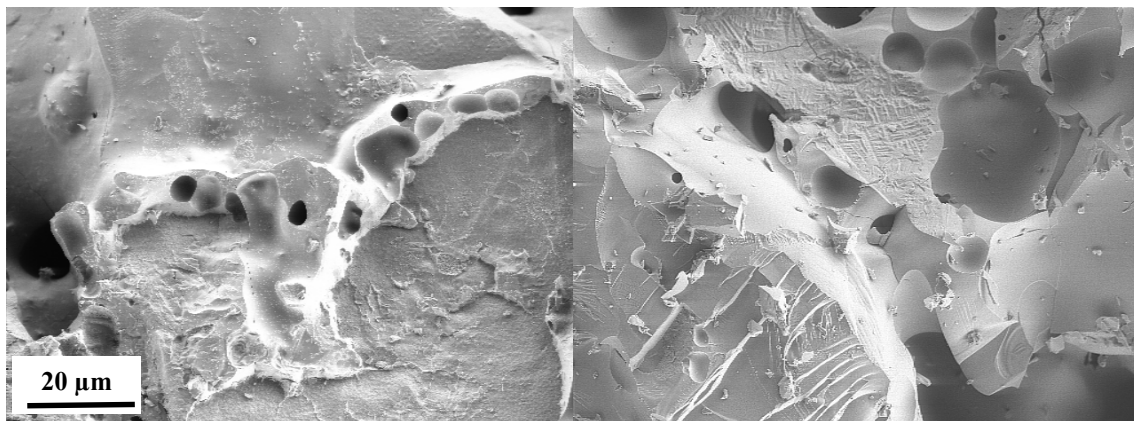
Table 3: Skeleton density and porosity

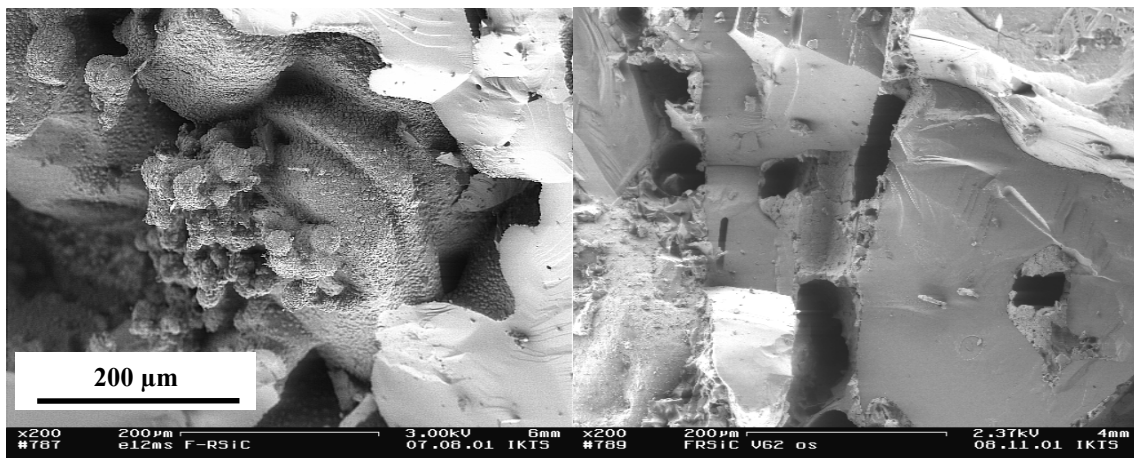Figure 2: Bubble formation in the binder of SiC-materials B3 (left) and B4 (right) after 3*.

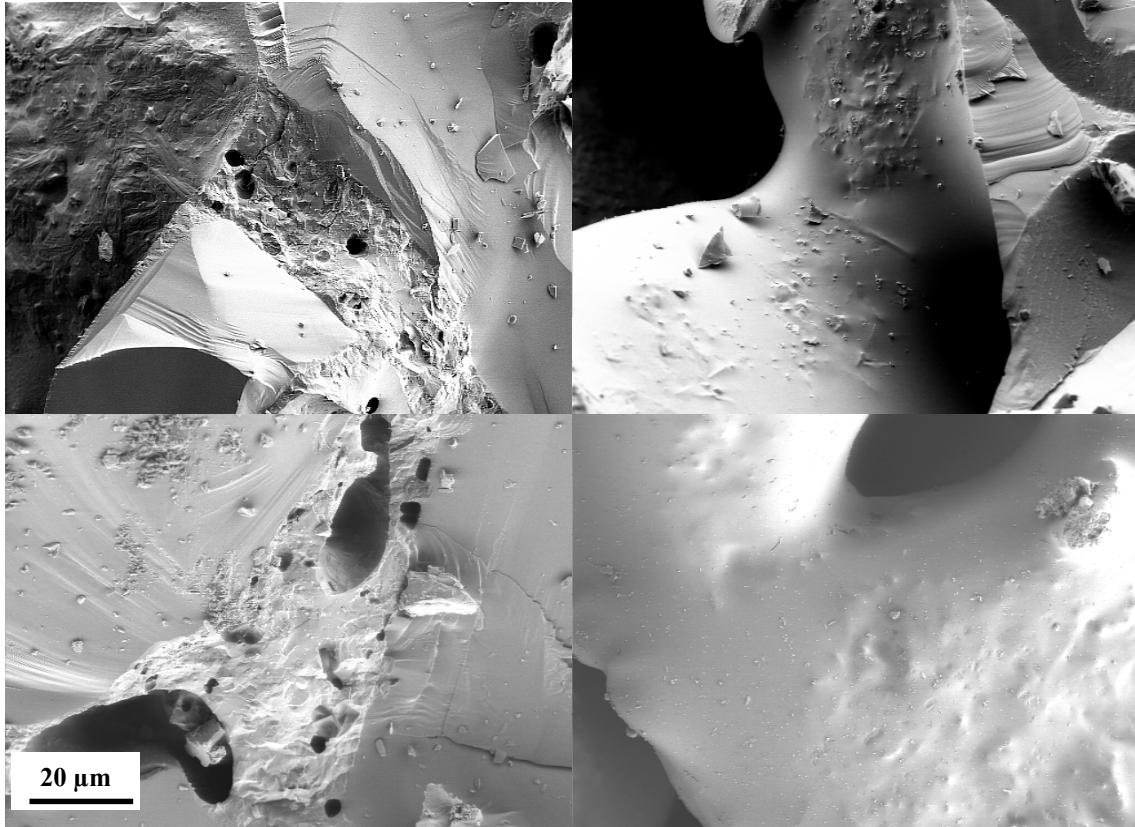Figure 3: Oxide layer after exposure 3 (left) and 3* (right) for material R3.

Figure 4: Bubble formation after exposure under oxidizing conditions for material B3 (left). No bubbles observed for material B4 (right). Top: after exp. 6; Bottom: after exp. 6*.
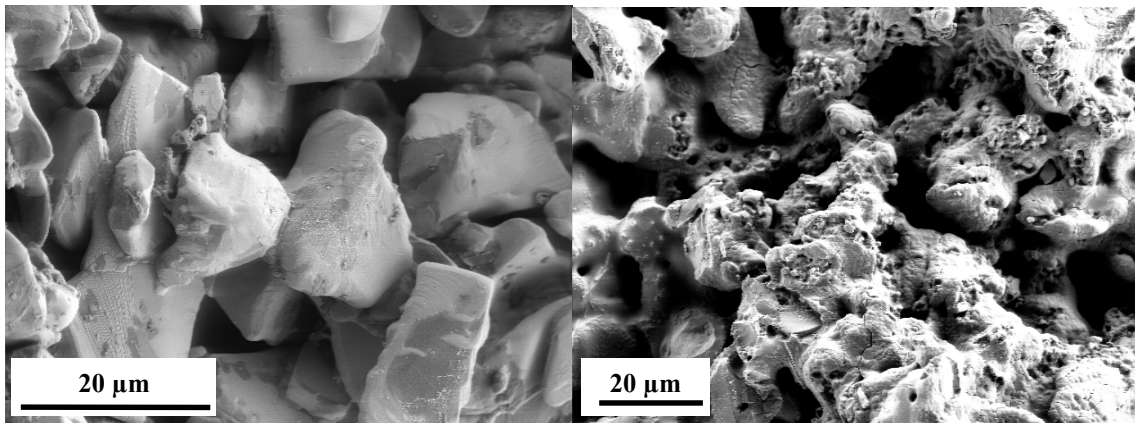

Figure 5: Rough surface of L1 after exposure of soaked specimens under oxidizing atmosphere. Left: as sintered; right: after exp. 6*.

σ_0 [MPa] / m	R1	R2	R3	L1	B1	B2	B3	B4	A	S
as sintered σ_0 / m	12.4 / 1.8		24.1 / 25.3	21.9 / 8.6	21.9 / 14.8	29.4 / 19.8	24.9 / 30.6	20.6 / 29.3	3.4 / 7.7	38.9 / 20.1
after exp. 2 σ_0 / m			20.2 / 7.9	14.8 / 5.3	21.0 / 6.2	26.8 / 10.2	22.3 / 13.6	17.9 / 5.8	2.1 / 4.3	36.9 / 7.1
after exp. 3 σ_0 / m		11.7 / 3.9	23.1 / 17.5		15.1 / 3.5	39.4 / 3.2	10.6 / 10.8	14.5 / 4.1	0.6 / -	39.3 / 5.3
after exp. 3* σ_0 / m			43.4 / 8.8	22.9 / 2.1	17.6 / 2.7	25.8 / 5.1	13.0 / 6.8	14.0 / 3.9		18.0 / 5.8
after exp. 4 σ_0 / m			31.4 / 6.1	31.3 / 3.3	20.2 / 4.7	28.7 / 10.7	19.6 / 10.9	19.0 / 9.5		33.7 / 5.0
after exp. 5 σ_0 / m			36.7 / 8.1	37.7 / 6.5	23.0 / 3.1	32.0 / 25.9	22.6 / 33.3	21.3 / 17.5		36.8 / 13.0
after exp. 6 σ_0 / m	13.5 / 6.1	103.9 / 10.6	32.1 / 2.6	30.5 / 3.5	24.3 / 4.5	27.9 / 18.2	19.7 / 8.9	19.9 / 11.0		34.9 / 7.6
after exp. 6* σ_0 / m			31.6 / 7.1	27.3 / 2.7	24.3 / 5.7	29.0 / 16.9	18.2 / 6.6	24.7 / 7.9		31.5 / 9.2

Not listed for exposure 1 due to no changes compared to the as sintered state. Due to the low strength of material A no further investigations were made.

Table 4: Strength and Weibull modulus measured at room temperature in 4 point bending mode with 20/40 mm inner/outer span.
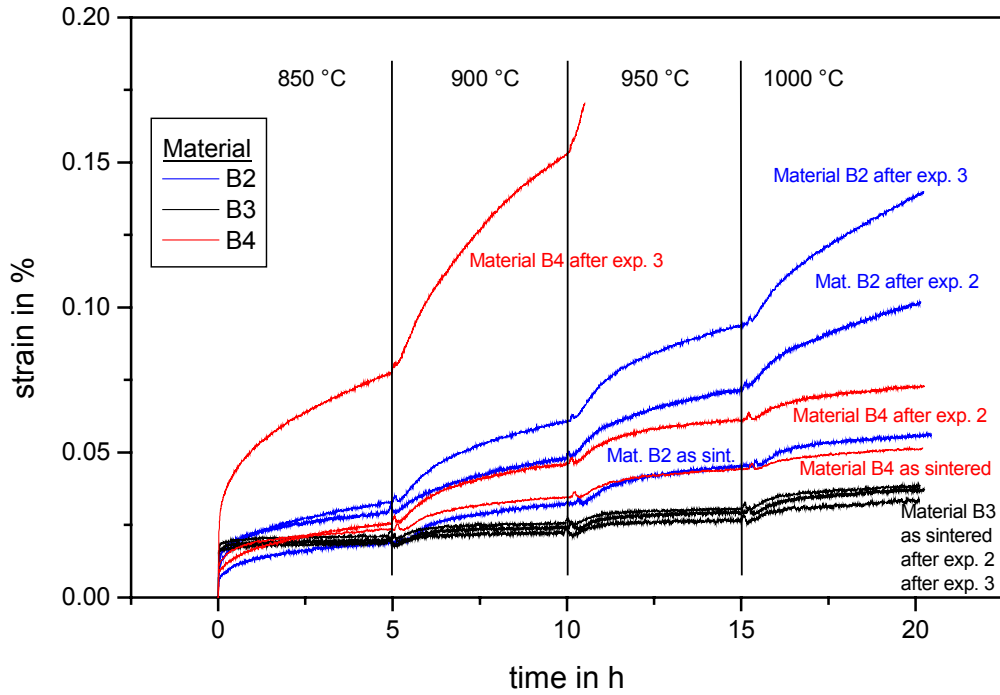
Figure 6: Deformation behavior in creep investigations before and after exposure under reduzing atmospheres for siliceous bonded silicon carbides.
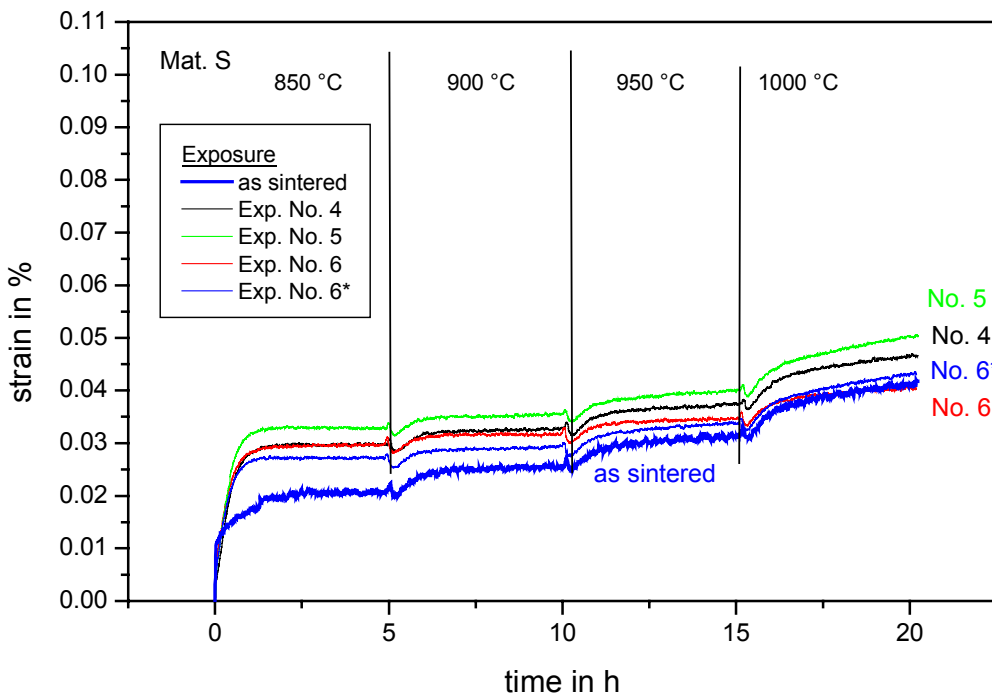

Figure 7: Deformation behavior in creep investigations before and after exposure under oxidizing atmospheres for spinel.
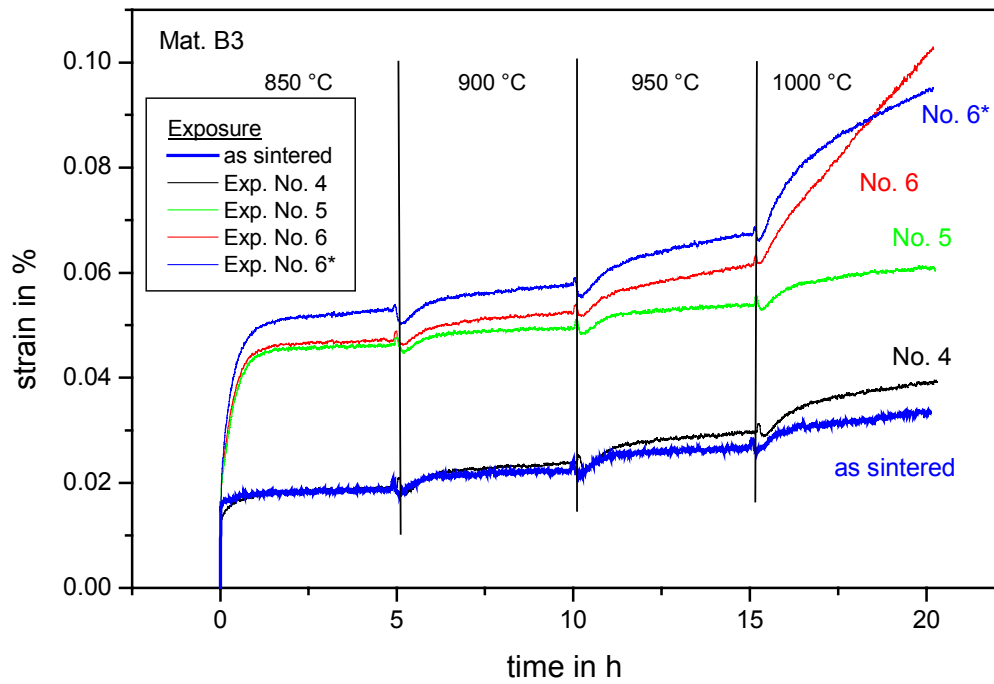
Figure 8: Deformation behavior in creep investigations before and after exposure under oxidizing atmospheres for material B3.
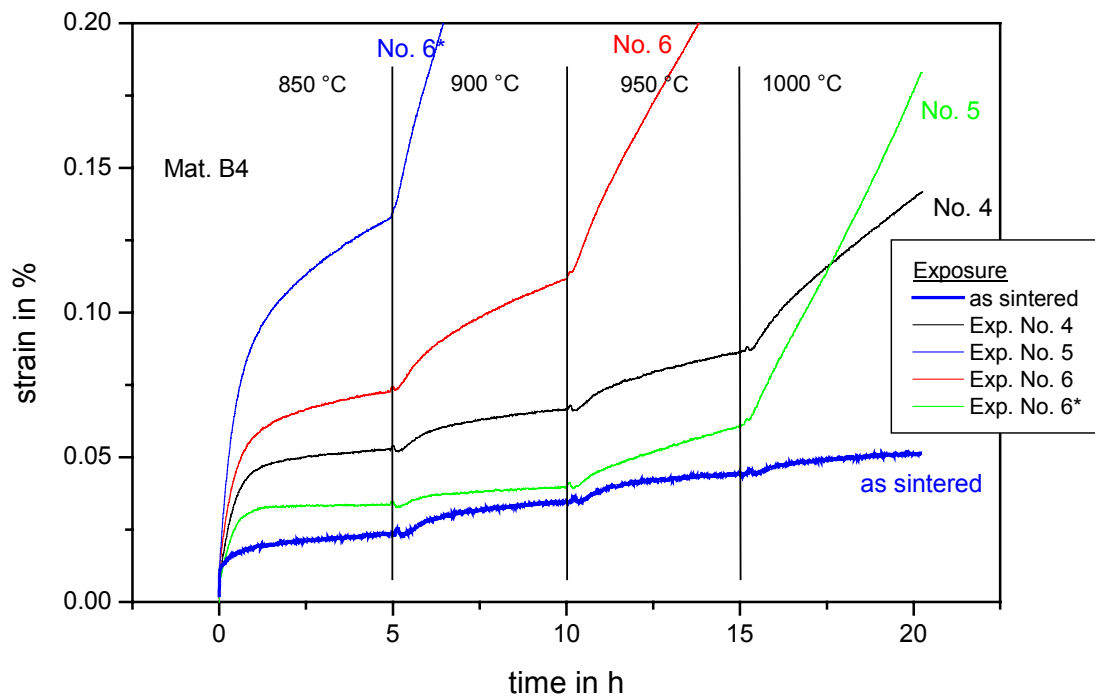

Figure 9: Deformation behavior in creep investigations before and after exposure under oxidizing atmospheres for material B4.