

Cellular Ceramics in Combustion Environments

J. Adler, A. Fuessel, D. Boettge, F. Marschallek, M. Jahn, A. Michaelis,
Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Dresden, Germany

1 Introduction

Efficient conversion of chemical energy into heat by combustion processes is very important for modern civilization. The demand for higher radiant heating rates has to be compatible with the tightened environmental regulations, which require minimal pollutants emission. Recently, several investigations have shown the advantages of the porous burner technology [1]. The combustion takes place in a cellular material with a high thermal conductivity which transports the heat from the reaction zone upstream to the incoming gases. The preheating of the fuel/air mixture raises the flame temperature, reduces emissions and stabilizes the flame [2]. Porous burners offer low emissions of CO, NO_x and HC, high energy efficiency and high power density [3].

Therefore combustion in porous media is of growing interest. Both metal and ceramic concepts are used for several applications. As an alternative to metallic burners cellular ceramics permit higher operating temperatures, more efficient heat extraction through the radiating porous surface and/or volume and potentially better performance concerning flashback safety. As a result of the increase of power density up to some MWm⁻² caused by new designs, the requirements on the materials regarding thermal shock and operating temperature have also raised. But in spite of recent scientific and technical success in developing new or improved burner concepts, a lot of problems have remained to be solved for materials science. Most of these problems are connected with the long time stability of ceramics in high temperature combustion environments. This includes the special properties of cellular ceramics, e. g. microstructure, inner surface and mechanical strength.

2 Examples for different burner applications

Cellular ceramics for domestic gas heaters are of great economical and ecological interest [2]. They are also in use for afterburner in SOFC systems [4]. For starting-up the system, to ensure the afterburning of the anode offgas and for the improvement of the systems overall efficiency there is need for a burner component with special characteristics. The most wanted feature is the possibility to feed the burner with gas mixtures of different calorific value.

Many industrial processes containing drying steps use IR-emitters, e. g. in paper machines. Recently SiSiC foam plates 150x200x mm working as flat porous burners have been used for such driers [5], [6]. Another approach to enhance IR emission are emitter plates with very thin and long channels perpendicular to the surface of the plate acting like black holes ($\epsilon = 1$) [7].

Combustion in cellular structures can be improved by using catalysts. The catalysts can be placed on the porous burner as a thin layer in form of a washcoat or in the entire matrix of the

cellular structure. The presence of a catalyst stabilizes the flame even at very lean fuel/oxidant ratios and thus reduces the CO emission [8]. With or without catalytic coating cellular structures can be used for combustion of lean and ultra-lean fuel mixtures [9], [10].

3 Requirements on the material and potential candidates

Porous structures must resist thermo mechanical stress caused by the high gradients in temperature, especially during start and modulation of the burner [11]. This first feature already constrains the number of potential materials.

Depending on the fuel type, fuel/oxidant ratio and the pressure, very different corrosion effects can occur [12]. Materials for cellular burners need to resist harsh conditions for long time. Hot wet atmospheres up to 17% H₂O and velocities of 1 ms⁻¹ should be regarded at least. This entails very high requirements on the corrosion resistance, because most burners are used for long term applications, e. g. for more than 1000 h, in some cases up to 10000 h. However, for domestic or automotive mass application simple components made of cheap materials are needed.

According to the Stefan-Boltzmann-Law they should be characterized by high emissivity at highest operating temperatures (about 1200 °C) because of the enhancement of the heat radiation by the fourth power with the temperature and the linear dependence on material emissivity.

Considering the requirements mentioned above, only a few materials are suitable for the application in combustion environments. The materials listed in **Table 1** are characterized by outstanding properties making them very important for high temperature applications.

Furthermore parameters like peak temperature, gradients, atmosphere and velocity strongly depend on the geometry of the burner construction which must be taken into account in developing porous burners.

Table 1. Properties of important technical materials (bulk)

		Al ₂ O ₃	Cordierite	ZrO ₂	SiC	Fe-Cr-Al
Density	gcm ⁻³	3.98	2	6.1	3.1–3.2	7.3
TC ^I	Wm ⁻¹ K ⁻¹	5–30	1–3	2–5	80–160	13.5–17.7
Specific heat capacity	Jg ⁻¹ K ⁻¹	0.9–1.0	0.8–1.2	0.5–0.6	0.7–0.8	0.5–0.8
CTE ^{II}	10 ⁻⁶ K ⁻¹	8	2–6	10–13	4.7–5.2	10.1–13.2
TSP ^{III} R1 $\sigma/E*\alpha$	K	100	650	400	230	
TSP ^{III} R2 $\sigma*\lambda/E*\alpha$	10 ⁻³ Wm ⁻¹	3	2	1.5	28	
TAL ^{IV}	°C	1900	1300	1800	1600	1330
Corrosion resistance		+	-	o	++	+
Price		o	+	--	-	-

^I thermal conductivity 20–1000 °C, ^{II} linear coefficient of thermal expansion 20–1000 °C, ^{III} thermal shock parameter, ^{IV} thermal application limit (in air, short time)

For the high application temperatures up to 1900 °C Al₂O₃ has been used in porous burners [13], [14], [15] restricted by the low thermal shock resistance. In contrast due to the excellent thermal shock resistance, cordierite has been used in spite of the application temperature being limited at 1300 °C [16], [17]. Several investigations have been done on ZrO₂ [18], [19],

[20], [21]. The properties of pure ZrO_2 are very interesting, but the phase change from tetragonal to monoclinic at 1170 °C is connected with a change in volume (5–8%). To prevent this the tetragonal phase ZrO_2 has to be stabilized by sintering additives like yttrium, for example, accepting a lowering of the bearable temperature.

For applications requiring high thermal shock resistance and lower temperatures (up to 1330 °C) FeCrAl alloys are very interesting [22], [23]. Composite materials and mullite have also been investigated as candidates for porous burners [24], [25].

However, with the specified requirements silicon carbide is the best compromise between application temperature, corrosion resistance, thermal conductivity and thermal shock resistance. Furthermore the low CTE and the high emissivity and strength at high temperatures are reasons for the usage of SiC for burner applications.

5 Cellular ceramics made of silicon carbide for combustion environments

5.1 Types of cellular silicon carbide

As mentioned above SiC is the most promising material, whereas the properties strongly depend on the type of SiC ceramics. For high temperature applications pressure-less sintered (SSiC), reaction-bonded silicon infiltrated (SiSiC) and recrystallized (RSiC) silicon carbide are typical representatives. All materials have been tested for porous burner application [26], [27], [28]. Bulk ceramics made of SSiC are nearly pure and dense. They are sintered from submicron and pure active powders, using small amounts of sintering aids (boron). They have a linear shrinkage of 16–22%. In contrast SiSiC is a shrinkage-free but dense material where the coarse primary particles are bonded by the reaction of silicon metal melt with carbon to secondary β -SiC. Remaining pores are filled by silicon. RSiC consists of a mixture of coarse and very fine powder and is sintered between 2300 °C and 2500 °C. A pure SiC matrix is formed with a porosity of 11–15%, lowering the mechanical strength but enhancing the thermal shock resistance.

Cellular ceramics can be realized by replication techniques. Foams, for example, are created by coating polymeric templates with ceramic slurry, drying, pyrolysing and afterwards sintering or siliconizing. Non-isotropic components can also be manufactured with technical textiles, e. g. woven and knitted structures. Different structures have been investigated for burner application, but in most cases open celled ceramic foams have been used.

The properties of bulk ceramics may vary from that of ceramic foams, according to a different microstructure. **Figure 1** shows the cross-sections of foam struts from the mentioned SiC-types. The nearly pure SSiC material (left) has a very high chemical corrosion resistance. For short time the application limit in air is about 1600 °C. The porosity of the microstructure (up to 30%) causes inner oxidation of the ceramic which limits the long term stability. The picture in the middle shows a strut of SiSiC almost filled with Si. The metallic Si causes very high mechanical strength but low corrosion resistance. The application limit is about 1350 °C (short time). RSiC foams (right picture) show enhanced porosity up to 37% compared to the bulk material with mostly 11% to 15% porosity.

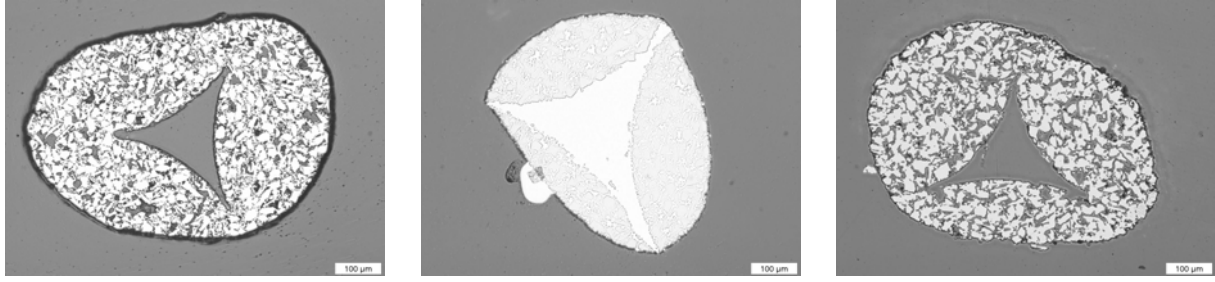


Figure 1. Cross-sections of ceramic foam struts; left SSiC, middle SiSiC, right RSiC

5.2 Cellular ceramics at high temperatures

The stability of high temperature materials has to be proved with different methods, characterizing the oxidation behavior under several conditions. Because of the high amount of inner porosity RSiC is excluded from the investigations listed in Table 2. The cell amount of the samples was about 90%. To improve the oxidation resistance of the SSiC foams new slurries have been developed. Porosities less than 12% were achieved, reducing the effect of inner oxidation.

Table 2. Parameters which were used to investigate the oxidation resistance

	Temp. (°C)	Power density (kWm ⁻²)	Time (h)	Material	ppi	Geometry (mm)
muffle furnace	1265–1415		100	SSiC	20	Ø = 60; h = 40
				SiSiC	10	40x40x25
burner rig	1000–1300	1050–1216	100	SSiC	10	Ø = 135; h = 15
				SiSiC	10	Ø = 135; h = 15
lifetime test rig	600–1350	602–1055	100–1000	SSiC	10	Ø = 65; h = 40
				SiSiC	10	Ø = 65; h = 40

5.3 Comparison of parabolic oxidation rates

Figure 2 shows some parabolic rate constants determined during the investigations. Basically SSiC foams with a low amount of inner porosity have the smallest oxidation rates, even at high amounts of water vapor and temperature. The results of the oxidation at dry air point out that SSiC has a better resistance than SiSiC when the amount of inner porosity is fewer than 12%. The comparison between the foam and a nearly dense SiC oxidized in dry air at 1400 °C, reported by Costello [30], shows that currently developed foams are close to the bulk material.

A sample of FeCrAl-alloy, oxidized in dry air at 1200 °C over 600 h, showed an oxidation rate of $88,2 \cdot 10^{-12} \text{ kg}^2\text{m}^{-4}\text{s}^{-1}$ [29]. Though 200 K colder this is about the same magnitude as SSiC-foams oxidized in dry air at 1415 °C.

5.4 Influences on the oxidation behavior

Many environmental and intrinsic specifics affect the oxidation behavior of high temperature materials. In case of silicon carbide the creation of a protective silica layer is the reason for

the high temperature corrosion resistance of SiC. The less sintering additives are in the material, the better the stability is. The dependencies of the rates and ambient conditions are very complex. The most important factor is the temperature accelerating the transport of the oxidants to the interface of SiC and SiO₂ and the reaction products outwards to the surface. Impurities in the ceramic material or from the combustion environment can cause bubbles in the oxide layer or accelerate the transport of oxidants by the decrease of the viscosity, too. The formation of volatile silicon hydroxides at high water vapor and low oxygen partial pressure can change the oxidation kinetic from parabolic to para-linear [26]. At very high velocities (100 ms⁻¹) even a linear weight loss is possible. The inner porosity of the samples influences the long term stability of the cellular structure, too. Inner oxidation of the foam struts causes cracks and decreases the mechanical strength of the cellular structure.

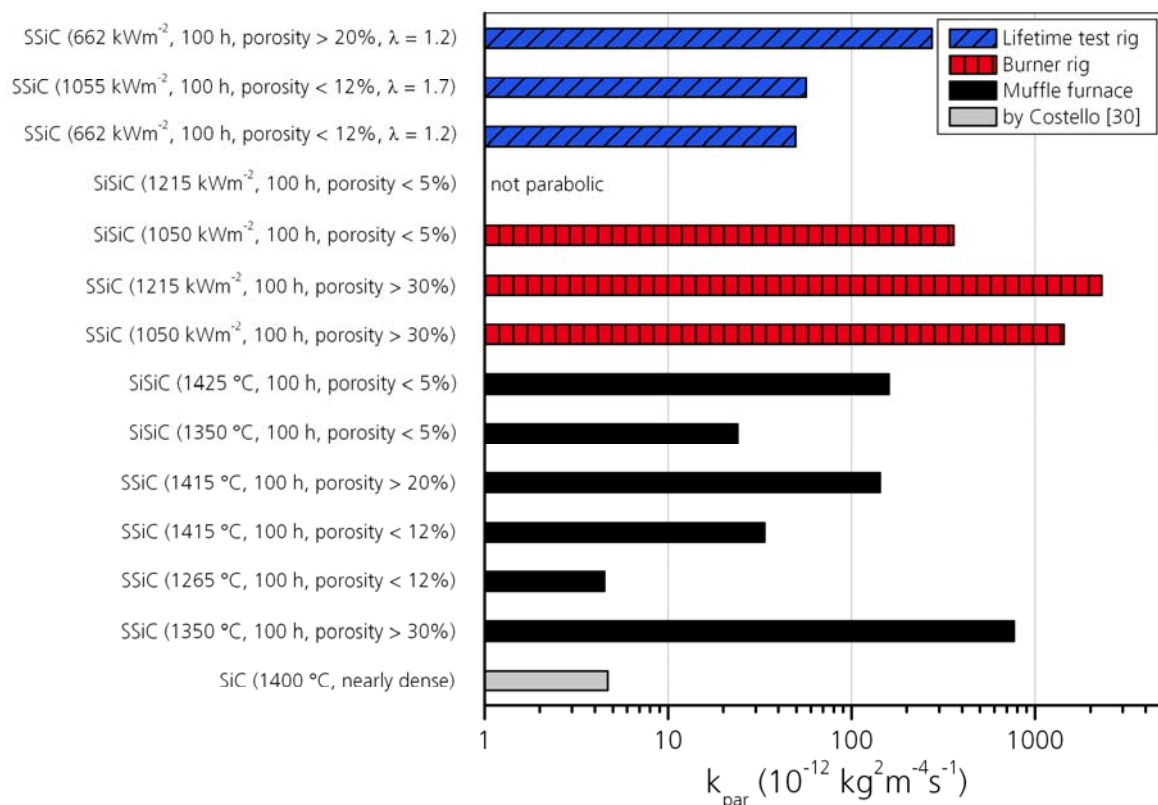


Figure 2. Oxidation rates of open celled SiC foams in different environments

6 Summary and conclusion

Porous burners made of silicon carbide are currently under development for different applications. Although the oxidation rates of foams are higher than those for bulk materials, SSiC is the most promising material. By lowering the inner porosity a significant decrease of the oxidation rate has been achieved. The task for future work is the advancement of microstructure to reduce inner porosity further. This allows the use of SSiC in long term applications such as afterburner in the SOFC system.

7 References

- [1] D. Trimis, O. Pickenäcker, K. Wawrzinek in *Cellulare Ceramics* (Ed.: M. Scheffler, P. Colombo), Wiley-VCH, Weinheim, 2005, Chapter 5.5.
- [2] S. Wood, A. T. Harris, *Progr. Energ. Combust. Sci.* 2008, 34, 667–684.
- [3] G. J. Rørtveit, K. Zepter, Ø. Skreiberg, M. Fossum, J. E. Hustad, *Proc. Combust. Inst.* 2002, 29, 1123–1129.
- [4] F. Marschallek, J. Adler, R. Belitz, D. Böttge, M. Heddrich, M. Jahn. *Chem. Ing. Tech.* 2008, 80(9), 1266–1266.
- [5] D. Gruchot, R. Krieger, *Gaswärme International* 2002, 51, 388–390.
- [6] J. Schmidt, M. Scheiffle, A. Mach, F. v. Issendorff, *Adv. in Sci. and Tech.* 2006, 45, 2316–2322.
- [7] Aust, R. US Patent 6 575 736, 2001.
- [8] I. Cerri, G. Saracco, V. Specchia, *Catalysis Today* 2000, 60, 21–32.
- [9] C. Tierney, A. T. Harris, *J. Aust. Ceram. Soc.* 2008, 45, 20-29.
- [10] D. Böttge, M. Endisch, J. Adler, Th. Kuchling, *Schriftenreihe WAR* 2008, 166, 63–72.
- [11] R. Brezny, D. J. Green, C. Q. Dam, *J. Am. Ceram. Soc.* 1989, 72, 885–889.
- [12] V. Presser, K. G. Nickel in *Technische Keramische Werkstoffe* (Ed.: J. Kriegesmann), HvB Verlag, 2010, Chapter 5.4.1.1
- [13] O. Pickenäcker, K. Pickenäcker, *Keramische Zeitschrift* 2001, 9, 780–787.
- [14] N. Delalic, Dz. Mulahasanovic, E. N. Ganic, *Exp. Therm. Fluid Sci.* 2004, 28, 185–192.
- [15] Z. AL-Hamamre, S. Diezinger, P. Talukdar, F. v. Issendorff, D. Trimis, *Proc. Saf. Environ. Protec.* 2006, 84, 297–308.
- [16] R. Mital, J. P. Gore, R. Viskanta, *Combustion and Flame* 1997, 111, 175–184.
- [17] E. Garcia, M. I. Osendi, P. Miranzo, *J. Appl. Phys.* 2002, 92, 2346–2349.
- [18] P-F. Hsu, W. D. Evans, J. R. Howell, *Combust. Sci. Technol.* 1993, 90, 149–172.
- [19] V. Khanna, R. Goel, J. L. Ellzey, *Combust. Sci. Technol.* 1994, 99, 133–142.
- [20] W. Acchar, E. Ramalho, F. Souza, W. Torquato, V. Rodrigues, M. Innocentini, *J. Mater. Sci.* 2008, 43, 6556–6561.
- [21] P. J. Elverum, J. L. Ellzey, D. Kovar, *J. Mater. Sci.* 2005, 40, 155–164.
- [22] O. Kawaguchi, T. Otoh, S. Nakamura, A. Todoroki, Y. Murayama, *Symp. (Internat.) on Combustion* 1991, 23, 1019–1024.
- [23] B. J. Vogel, J. L. Ellzey, *Combust. Sci. Technol.* 2005, 177, 1323–1338.
- [24] T. L. Marbach, A. K. Agrawal, *J. Eng. Gas Turbines Power* 2005, 127, 307-313.
- [25] W. M. Mathis, J. L. Ellzey, *Combustion Scientific and Technique* 2003, 175, 825-839
- [26] J. Adler, G. Standke, M. Jahn, F. Marschallek in *Advances in Bioceramics and Porous Ceramics* (Ed.: P. C. Narayan), Wiley, 2009, 271–286
- [27] A. Mach in *Technische Keramische Werkstoffe* (Ed.: J. Kriegesmann), HvB Verlag, 2008, Chapter 5.4.1.6
- [28] A. Herzog, U. Vogt, *International Conference Porous Ceramic Materials* 2005, p. 10-20
- [29] W. J. Quadackers, D. Naumenko, E. Wessel, V. Kochubey, *Oxidation of Metals* 2004, 61, 17-37
- [30] J. A. Costello, R. E. Tressler. *J. Am. Ceram. Soc.* 1986, 69(9), 674–681.