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Alkali-bonded SiC based foams

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Abstract

Silicon carbide (SiC) foams were developed by using a low temperature process such as chemical consolidation that is suitable to replace the sintering step. An alkali aluminosilicates binder, also known as geopolymer, was used. It was prepared from metakaolin, as aluminosilicatic raw powder, and KOH/K_2SiO_3 aqueous solution. The foaming agent was the metallic silicon present as impurity in SiC powders. Different grades of SiC were used as the main component (90 wt%) of the foams and the micro and macrostructures varied with the morphologies of the SiC raw powders. The surface of SiC grains participates to the geopolymeric process because of the dissolution of the silica layer into the alkaline solution. SiC foams were tested and characterized under oxidative atmospheres up to 1200 °C.

Keywords: Geopolymers; B. Porosity; C. Corrosion; D. SiC; D. Silicate

1. Introduction

Reticulated porous ceramics characterized by high porosity (70–95%), are expected to be used in many different technological applications because of their high gas permeability and large surface area as well as for the high temperature stability and thermal shock resistance.[1–3] Industrial uses include structural lightened parts, insulator panels, filters and membranes (for micro- and ultrafiltration, separation, particulate environmental clean-up and reuse, molten metal filters), radiant burners, gas or chemical sensors, support materials for catalysis or adsorbents. For all the mentioned applications, it is mandatory to control the pore structure (shape, morphology, orientation, surface properties) as well as the texture, porosity and pore size distribution.

Several ways to produce porous ceramics have been reported, such as: burnout of fugitive additives,[3,4] alginate gelation process,[5–7] replica method of 3D templates,[8] foaming agents added to the ceramic suspension.[9] Regardless of the technique used, ceramics foams are usually sinterized at high temperature to reach specific mechanical and functional properties.

Consolidation by using chemically activated inorganic binders is suitable to replace the sintering step. Among inorganic binders, alkali alumino silicate binders behave as inorganic polymers, the so-called geopolymers, and they were developed as an alternative to organic matrices for composites.[10,11]

Geopolymers are alkali bonded ceramics (ABC),[12] i.e. they belong to the class of the chemically bonded ceramics (CBCs) meaning that ceramics can be produced at low temperatures using chemical reactions. Actually, the reaction of an aluminosilicate powder with a highly concentrated aqueous alkali hydroxide (KOH, NaOH) and/or silicate (potassium or sodium silicates) solution produces a synthetic amorphous to semi-crystalline alkali aluminosilicate material which is X-ray amorphous analogues of zeolites. Among the aluminosilicatic raw powders, metakaolin is the most reactive in alkaline conditions.[13] The metakaolin reactivity is not uniform and depends on both its morphology and degree of dehydroxylation, and may result in the different degree of its geopolymerization.[14] During geopolymerization a gel network is formed, consisting of SiO_4 and AlO^{4-} tetrahedra linked in an alternating sequence. The geopolymeric resin consists of nanoprecipitates[15,16] that act like a glue sticking together the fillers (powders or fibres, glass, ceramic, metal or organics) forming the geopolymeric composite materials. Different fillers are used to tailor specific physical and mechanical properties of the geopolymers in dependence of the applications.[17–21]

Hydrogen peroxide it is a well know blowing agent,[22] in geopolymeric gels however it induces closed porosity, while the redox reaction of Al in alkaline solution induces open porosity by H_2 evolution.[23] Also redox reaction of metallic Si impurities

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in silica fume could be used to prepare geopolymeric foams.[24,25] Actually, the Pourbaix diagram of silicon indicates that in alkaline conditions hydrogen evolution is always favoured.[26] The reaction responsible for gas evolution is[25]:

$$4H_2O + Si^0 \rightarrow 2H_2\uparrow + Si(OH)_4, \Delta H = -314\,kJ \qquad (1)$$

In this feasibility study, the possibility to develop silicon carbide foams with a low temperature process such as chemically bonding was investigated. The foaming agent was metallic silicon that is always present as impurity in SiC powders because of the synthesis process. Two grades of SiC powder with very different morphologies were used as the main component. The binder for the chemical bonding was a geopolymeric resin with atomic ratio Si/Al = 2 and potassium as alkaline cation, classified as (K)poly(silalate-siloxo).[10,11] The binder was prepared using metakaolin as aluminosilicatic raw powder, while the alkali aqueous solution was KOH/K_2SiO_3.[27]

SiC foams were tested and characterized in oxidative atmospheres up to 1200 °C.

2. Experimental

2.1. SiC foam preparation

A calcined kaolin (metakaolin) with high specific surface ($30\,m^2/g$) was used to prepare the alkali aluminosilicate binder. The powder was prepared from a commercial kaolin (grade BS4, AGS Mineraux, Clèrac, France) by calcination in electric kiln (750 °C for 15 h). Details about this raw powder are reported elsewhere.[27]

Potassium silicate solutions with molar ratios of $SiO_2:K_2O = 2$ and $H_2O:K_2O = 23$ were prepared by dissolving KOH pellets (purity > 99%, Merck, Darmstadt, Germany) into potassium silicate aqueous solution with molar ratio $SiO_2:K_2O = 3.57$ (KSil 35Bè R3.5, Ingessil srl, Montorio, Italy) under magnetic stirring.

Two grades of SiC powder were used as main components of the foams:

- β-SiC grade BF 12 (H.C., Starck, Germany), specific surface area: $11.6\,m^2/g$, D10 = 0.30 μm, D50 = 1.10, D90 = 2.07 μm; Si content: 0.1 vol%.
- R-SiC, grade 100F, re-crystallized silicon carbide (SIKA TECH, Saint-Gobain Ceramic Materials GmbH, Germany), specific surface area: $0.58\,m^2/g$, bi-modal distribution centred at 150 μm (20%) and 45 μm (80%); Si content: 0.9 vol%.

Foams were prepared by eccentric mixing of the R-SiC (65 mass%) with metakaolins (7 mass%) and then by mechanical mixing (Yellow line OST 20 basic, IKA-WERKE GmbH & Co., Staufen, Germany) at 100 rpm the powder mixtures with the KOH/K_2SiO_3 solution (14 mass%) and distilled water (14 mass%). Additional water was added to the slurries when β-SiC grade BF 12 was used, reaching a molar ratio $H_2O:K_2O = 106$, because of the high specific surface of the β-SiC powders. After setting and water removal, the mass fraction of SiC corresponded to 90% of the foam.

The slurries (20 ml) were cast in open plastic cylindrical moulds with a diameter of 40 mm and maturated at room temperature or cured at 80 °C for 24 h. The foam expansion occurred in the axial direction of the cylindrical mould. After setting, the foams were let at 80 °C for other 24 h.

2.2. Structural and mechanical characterization

The bulk density and porosity of the sponges were determined by weight-to-volume ratio. The morphological and microstructural features were observed by SEM-EDS (SEM, Cambridge S360, Cambridge, UK; EDS, INCA Energy 300, Oxford Instruments, Oxford, UK). Ultra-macro-porosity was investigated by image analysis (Image Pro Plus 6.0., Media Cybernetics, Inc. Bethesda, MD, USA) of high resolution photos (scanner Sharp JX330, Japan) and of scanning electron micrographs of the cross sections.

Preliminary compressive strength tests on SiC foams were carried out on 20 mm cubic samples using a Zwick Z050 testing machine (Zwick GmbH, Ulm, Germany). The compressive load was applied parallelly to the foam expansion direction. The crosshead speed was set at 1 mm/min.

2.3. Oxidation behaviour

Oxidation tests were performed on R-SiC foams and powder with a non-isothermal simultaneous thermal analysis (Polymer Thermal Science STA 1500, UK) in static air with a heating rate of 10 °C/min. Long term oxidation tests were performed on R-SiC foams and green body (relative density of 45%) for 100 h at 1200 °C using a laboratory kiln and operating in static air. The dimensional changes were measured with a calliper (accuracy ±0.01 mm).

3. Results and discussion

3.1. Foaming mechanism and macro- and micro-structure development

Figs. 1–3 show the macro- and micro-structural features of the developed alkali bonded SiC based foams. Curing temperature enhancement favoured the foaming process having clear effects on volume expansion of the slurries (Table 1). Actually, reaction (1) is favoured by temperature increase ($\Delta G = -359.4$ kJ at 25 °C and $\Delta G = -366.6$ kJ at 80 °C[28]).

During maturation at room temperature or curing at 80 °C of the slurries, Si impurities in the SiC powders induce H_2 evolution as a consequence of the redox reaction (1) occurring in alkaline aqueous solution. The anodic reaction is:

$$Si^0 \rightarrow Si^{4+} + 4e^- \qquad (2)$$

while the cathodic reaction concerning di-hidrogen formation is[24]:

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \qquad (3)$$

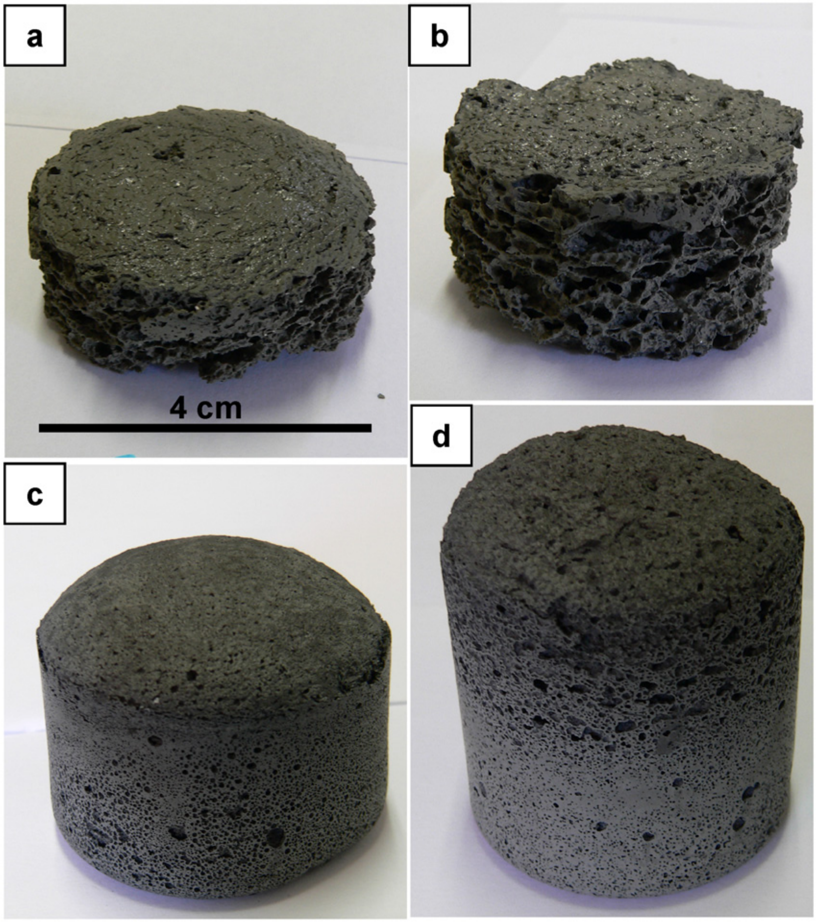

Fig. 1. Photos of the alkali-bonded β-SiC foams prepared at RT (a) and 80 °C (b) and of the alkali-bonded R-SiC foams prepared at RT (c) and 80 °C (d).

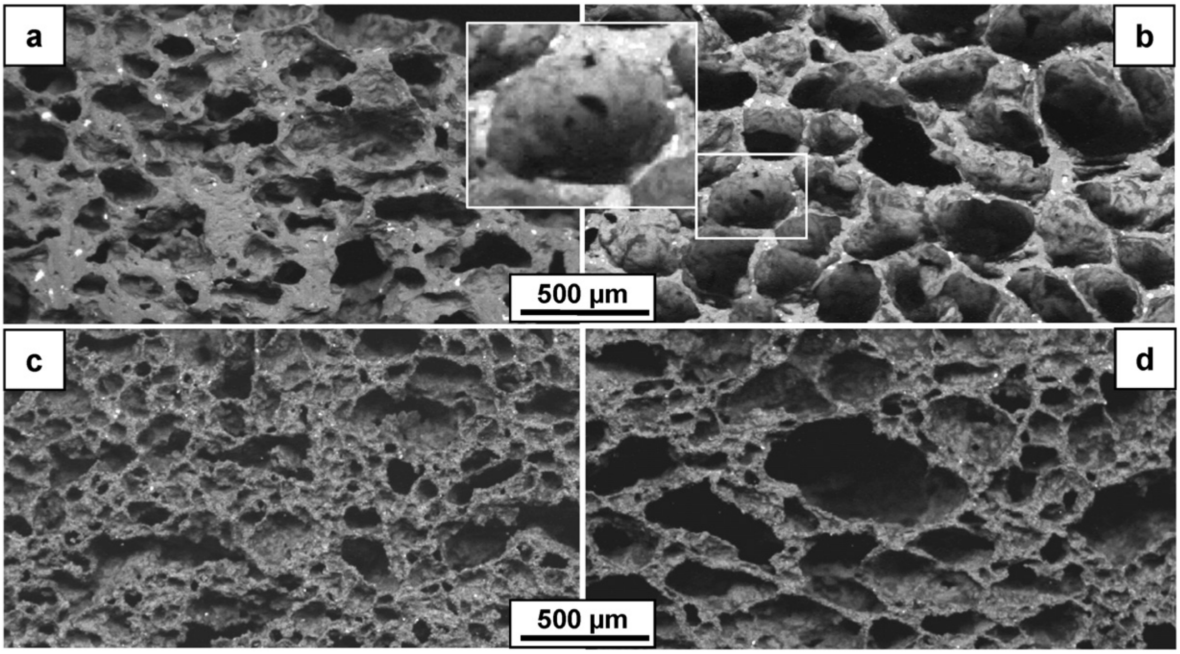

Fig. 2. High resolution photos of the β-SiC foams prepared at RT (a) and 80 °C (b) and of the R-SiC foams prepared at RT (c) and 80 °C (d).

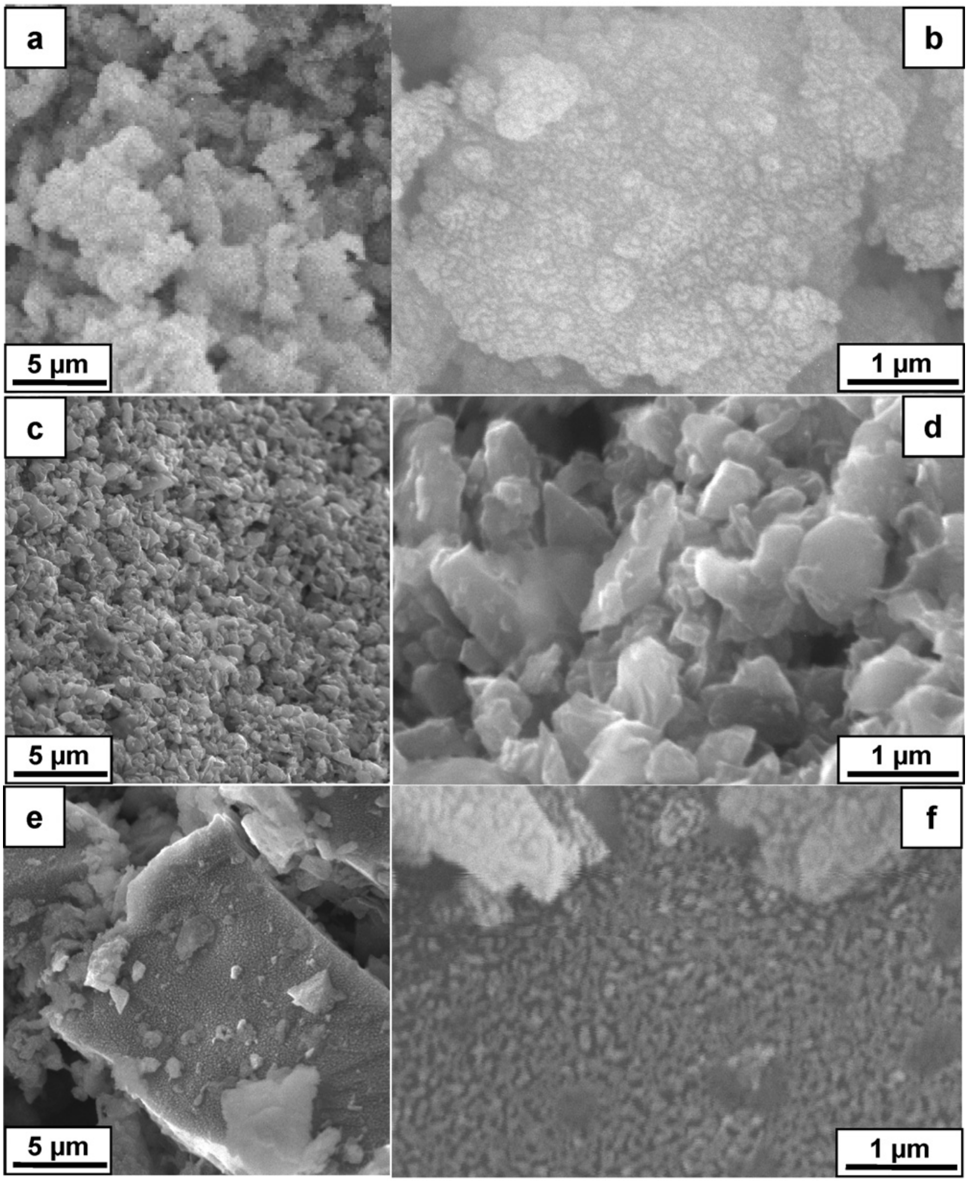

Fig. 3. Scanning electron micrographs of the geopolymeric resin without SiC addition (a and b), β-SiC foam (c and d) and of the R-SiC foam (e and f) prepared 80 °C.

As reported by Prud'homme et al.,[25] gas evolution leads to foamed macro-structures, i.e. inorganic *in situ* foam formation, when the viscosity of the composite slurries increases contemporary and the material consequently consolidates. On the contrary, structure collapses when the gas pressure exceeds the strength of the pore walls. Generally, the viscosity of a slurry decreases with the rise of the process temperature, while H_2 pressure is enhanced as H_2 formation in reaction (1) is favoured by temperature increase. However, at 80 °C the hardening due to the setting of the alkali alluminosilicate binder takes place faster than at room temperature. The hardening is also favoured by viscosity increase due to partial water evaporation occurring at

Table 1
Characteristics of the alkali-bonded SiC based foams prepared at different setting temperatures.

SiC powder	β-SiC		R-SiC	
Setting temperature	RT	80 °C	RT	80 °C
Slurry volume expansion, %	50	100	100	150
Final density, g/cm^3	0.49 ± 0.02	0.40 ± 0.02	0.63 ± 0.02	0.50 ± 0.01
Total porosity, %	84	87	78	83

80 °C and tight pore walls are formed. It follows that at 80 °C highly porous materials are developed without any structural collapse.

When fast setting (hardening) takes place, reaction (1) does not occur because the alkaline aqueous solution is the medium for the silicon anodic corrosion. This is the case of previously developed SiC-based paints prepared with alkali aluminosilicate binders,[27] as the 200 μm thick coatings deposited by brushing quickly set and harden.

Although β-SiC and R-SiC foams share the same foaming mechanism, the developed micro and macrostructure are very different because of the very different morphologies of the raw powders.

β-SiC foams undergo lower volume expansions than R-SiC foams (Table 1) since the solid content of the slurry is lower because of the very high dilution. Moreover the final foamed structures are fragile and they tend to broken during demoulding (Fig. 1a and b). The relative densities of β-SiC foams are lower than those of R-SiC foams (Table 1) as β-SiC particles are very fine and thus lightweight, while the R-SiC powder is constituted by big and consequently heavy particles.

The pore shapes of the β-SiC foams maturated at room temperature are flattened with thick pore struts ranging from 0.2 to 2 mm in length (Fig. 2a). With curing at 80 °C, macro-pores are rounded and range from 0.15 to 0.3 mm (Fig. 2b), with few pores up to 0.5 mm. Pore walls present gas escaping windows in the range of micrometers while the struts are 0.25–0.35 mm thick. The dilution decreases the alkalinity of a system where the amount of Si is very low and consequently the foaming at RT is scarce. On the contrary, the narrow particle size distribution and the rounded shape of β-SiC favours the developing at 80 °C of almost mono-modal macro-porosity.

This feature is not observed in R-SiC foams, since the starting powder has bimodal size distribution, centred at 150 μm (20%) and 45 μm (80%), and the grains have an acicular shape. In this case, the pore size is very broadened, ranging from 50 μm to about 0.5–0.6 mm, with thin pore walls.

The microstructures of the geopolymeric resin without SiC addition and of the β-SiC and R-SiC foams are compared in Fig. 3. The geopolymeric resin is formed by nanoprecipitates of 60 nm agglomerated in flake structures with an average pore diameter of less than 1 μm (Fig. 3a and b). In β-SiC foams, small grains constitute uniform and compact pore walls, where the binder is almost not visible (Fig. 3d). In R-SiC foams, the pore walls are not compact but formed by big acicular grains where the binder is not homogenously distributed (Fig. 3e).

Moreover, the surface of the R-SiC particles is covered by geopolymeric nanoprecipitate of 60 nm and almost fully geopolymerized metakaolin particles (Fig. 3f) similarly to the as-prepared geopolymeric resin (Fig. 3b). During the first step of geopolymerization, the aluminosilicate source is dissolved by alkaline hydrolysis, giving aluminate and silicate species. In the mild corrosion conditions of the geopolymerization ($T \leq 80\,^{\circ}$C and pH = 12) the bulk of the SiC powder particles is inert. However, the surface of silicon carbide grains is always covered by an oxygen rich layer. As reported for silicon,[29] the oxidized layer is chemically similar to the surface of silica. The hydroxyl anion (OH^-) is considered to be a catalyst for the dissolution reaction of silica.[30] As such, silica readily dissolves in highly alkaline media (pH > 11) in the form of monomeric $Si(OH)_4$ until the equilibrium concentration is reached.[31] Moreover, silica solubility increases with temperature.[32] It follows that due to the presence of silica, the surface of SiC particles participates to the geopolymeric process and geopolymeric nano-precipitates easily forms on SiC surface.

3.2. Compressive strength

R-SiC-based foams maturated at room temperature were tested under a compressive load applied parallelly to the foam expansion direction. The compressive strength is 0.9 ± 0.2 MPa with a dispersion of about 20% in the data. In all the compression tests, the specimens fail showing a jagged load–displacement curve, which is a typical feature of porous ceramics in compression.[33]

3.3. Oxidation behaviour

Non-isothermal simultaneous thermal analyses in air of R-SiC powder and powdered R-SiC-based foams are reported in Fig. 4. No weight change has been registered for R-SiC starting powder up to 600 °C, where a weight loss of 1% may be related to residual carbon combustion, as suggested by the exothermic peak in the DTA analysis.[27] The apparent weight gain due to R-SiC oxidation to form silica and gaseous carbon oxides starts at 760 °C, following reaction (4):

$$SiC + 2O_2(g) \rightarrow SiO_2 + CO_2(g) \tag{4}$$

R-SiC-based foam shows a weight loss due to water vaporization, as suggested by the endothermic peak around 100 °C. The weight losses at about 600 °C are related to the oxidation of carbon as in R-SiC powder, too. The stating oxidation temperature is about 700 °C, i.e. 80 °C lower than in pure R-SiC, while the oxidation rate remains the same, i.e. ∼4 °C/min.[27] The oxidation starts at lower temperature because the protective silica layer, that is usually present on the R-SiC surface, is involved in the geopolymerization process and then it is replaced by a nano-porous geopolymeric layer.

Similarly to what previously observed for an alkali bonded SiC paint[27] after long term oxidation at 1200 °C, the weight gain related to the oxidation of R-SiC in R-SiC-based foam is 7%, i.e. half of the R-SiC powder green compact. As shown in Fig. 5, after the oxidation test the macrostructure of the R-SiC foam remains almost the same and the dimensional change is close to zero. On the contrary, the microstructure of the R-SiC foam changes, as micro and nano-porosity disappear because of glass formation due to SiC oxidation and melting of the geopolymeric binder. Geopolymers with molar ratio $SiO_2{:}Al_2O_3 = 4$ have been shown to crystallize into leucite, $K_2O{\cdot}Al_2O_3{\cdot}4SiO_2$, by heating.[34] Moreover, compositional heterogeneities, together with the presence of free alkali ions in the geopolymer structure, favour the formation of a glassy phase.[34,35]

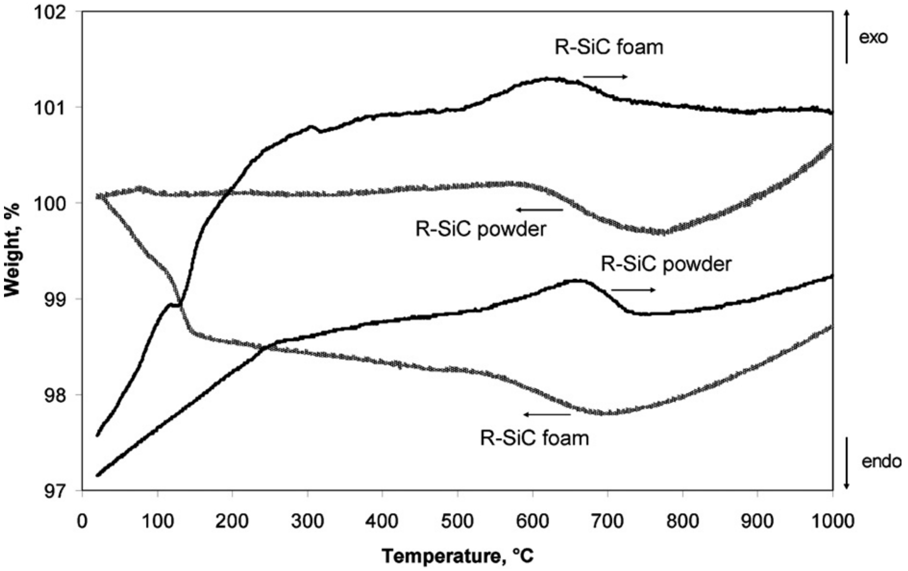

Fig. 4. Non-isothermal simultaneous thermal analysis in air of R-SiC powder and powdered R-SiC-based foam prepared at 80 °C.

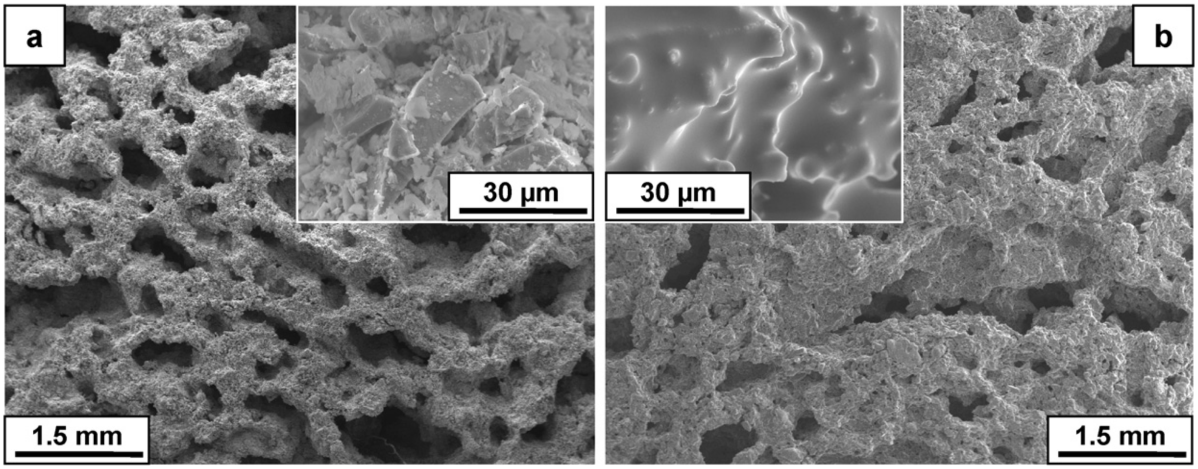

Fig. 5. Scanning electron micrographs of the R-SiC foams prepared 80 °C before (a) and after long term oxidation at 1200 °C for 100 h (b).

4. Conclusion

SiC based foams were successfully prepared by using alkali activated inorganic binders (the so-called geopolymers) to cause *in situ* foam formation with contemporary consolidation to replace the sintering step.

The foaming agent is Si^0 that is always present in SiC powders as synthesis process impurity. The rising of the foaming temperature enhances the volume expansion, while the use of fine SiC powder with narrow particle size distribution allows the formation of SiC based foams with almost monomodal macropores.

The amorphous silica layer covering the surface of SiC particles participates to geopolymerization so that nano-precipitates easily forms on SiC surface.

Consequently, the oxidation of the geopolymerized (alkali bonded) SiC based foams starts at lower temperature compared to SiC green body, because SiC surface is depleted of the protective silica layer.

Dimensional change is close to zero after long term oxidation at 1200 °C and micro- and nano-porosity disappears because of glassy phase formation.

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References

1. Colombo P. Conventional and novel processing methods for cellular ceramics. *Philosophical Transactions of the Royal Society A* 2006;**364**:109–24.
2. Innocentini MDM, Salvini VR, Pandolfelli VC, Coury JR. The permeability of ceramic foams. *American Ceramic Society Bulletin* 1999;**78**(9):78–84.
3. Pu X, Liu X, Qui X, Huang L. Novel method to optimize the structure of reticolate porous ceramics. *Journal of the American Ceramic Society* 2004;**87**:1392–4.

4. Lyckfeldt O, Ferreira JMF. Processing of porous ceramics by starch consolidation. *Journal of the European Ceramic Society* 1998;**18**:131–40.
5. Fukasawa T, Deng ZY, Ando M, Ohji T, Kanzaki S. Synthesis of porous silicon nitride with unidirectionally aligned channels using freeze drying process. *Journal of the American Ceramic Society* 1992;**85**:2151–5.
6. Fukasawa T, Ando M, Ohji T, Kanzaki S. Synthesis of porous ceramics with complex pore structure by freeze drying processing. *Journal of the American Ceramic Society* 2001;**84**:230–2.
7. Smidsrod O, Draget KI. Alginate gelation technology. *Special Publication – Royal Society Chemistry* 1997;**192**:279–93.
8. Weber K, Tomandl G. Porous Al_2O_3-ceramics with uniform capillaries. *Ceramic Forum International* 1988;**75**:22–4.
9. Woyansky JS, Scott CE, Minneay WP. Processing of porous ceramics. *American Ceramic Society Bulletin* 1992;**71**:1674–82.
10. Davidovits J. 30 years of successes and failures in geopolymer applications. Market trends and potential breakthroughs. In: Lukey G, editor. *Proceedings of geopolymer 2002 3rd international conference*. 2002. p. 1–16.
11. Davidovits J. Geopolymer: inorganic polymeric new materials. *Journal of Thermal Analysis* 1991;**37**:1633–56.
12. Gordon M, Bell J, Kriven WM. Geopolymers: alkali bonded ceramics (ABCs) for high-tech applications. *Ceramic Transaction* 2006;**175**:215–24.
13. Panagiotopoulou Ch, Kontori E, Perraki Th, Kakali G. Dissolution of aluminosilicate minerals and by-products in alkaline media. *Journal of Material Science* 2007;**42**:2967.
14. Medri V, Fabbri S, Dedecek J, Sobalik Z, Tvaruzkova Z, Vaccari A. Role of the morphology and the dehydroxylation of metakaolins on geopolymerization. *Applied Clay Science* 2010;**50**:538–45.
15. Kriven WM, Bell JL, Gordon M. Microstructure and microchemistry of fully-reacted geopolymers and geopolymer matrix composites. *Ceramic Transactions* 2003;**153**:227.
16. Kriven WM, Gordon M, Bell J. Geopolymers: nanoparticulate, nanoporous ceramics made under ambient conditions. In: Anderson IM, Price R, Hall E, Clark E, McKernan S, editors. *Proceedings of the 62nd annual meeting of Microscopy Society of America, vol. 10*. Savannah: University of Cambridge; 2004. p. 404–5.
17. Buchwald A, Vicent M, Kriegel R, Kaps C, Monzó M, Barba A. Geopolymeric binders with different fine fillers – phase transformations at high temperatures. *Applied Clay Science* 2009;**46**:190–5.
18. Comrie DC, Kriven WM. Composite cold ceramic geopolymer in a refractory application. *Ceramic Transactions* 2003;**153**:211–25.
19. Zhao Q, Nair B, Rahimian T, Balaguru P. Novel geopolymer based composites with enhanced ductility. *Journal of Materials Science* 2007;**42**:3131–7.
20. Zhang Y, Sun W, Li Z, Zhou X, Eddie, Chau C. Impact properties of geopolymer based extrudates incorporated with fly ash and PVA short fiber. *Construction and Building Materials* 2008;**22**:370–83.
21. Lin T, Jia D, He P, Wang M, Liang D. Effects of fiber length on mechanical properties and fracture behaviour of short carbon fiber reinforced geopolymer matrix composites. *Materials Science and Engineering A* 2008;**497**:181–5.
22. Hydrogen peroxides blowing agent for silicate foams. US Patent 3,864,137; 1975.
23. Bell JL, Kriven WM. Preparation of ceramic foams from metakaolin-based geopolymer gels. In: Lin HT, Koumoto K, Kriven WM, Garcia E, Reimanis IE, Norton DP, editors. *Developments in strategic materials: ceramic engineering and science proceedings*, vol. 29, no. 10. 2009. p. 97–111.
24. Prud'homme E, Michaud P, Joussein E, Peyratout C, Smith A, Rossignol S. In situ inorganic foams prepared from various clays at low temperature. *Applied Clay Science* 2010, doi:10.1016/j.clay.2010.10.016.
25. Prud'homme E, Michaud P, Joussein E, Peyratout C, Smith A, Arrii-Clacens S, et al. Silica fume as porogent agent in geo-materials at low temperature. *Journal of the European Ceramic Society* 2010;**30**:1641–8.
26. Zhang XG. *Electrochemistry of silicon and its oxide*. New York: Kluwer Academic/Plenum Publishers; 2001.
27. Medri V, Fabbri S, Ruffini A, Dedecek J, Vaccari A. SiC-based refractory paints prepared with alkali aluminosilicate binders. *Journal of the European Ceramic Society* 2011;**31**:2155–65.
28. Roine A. HSC chemistry 5.1. Outukumpu Research Oy, Finland.
29. Hackly VA, Paik U, Kim BH, Malghan SG. Aqueous processing of sintered reaction-bonded silicon carbide: 1, dispersion of silicon powder. *Journal of the American Ceramic Society* 1997;**80**(8):1781–8.
30. Iler RK. *The chemistry of silica*. New York: John Wiley and Sons; 1979.
31. Wijnen PWJG, Beelen TPM, de Haan JW, Rummens CPJ, van de Ven LJM, van Santen RA. Silica gel dissolution in aqueous alkali metal hydroxides studied by ^{29}Si-NMR. *Journal of Non-Crystalline Solids* 1989;**109**: 85–94.
32. Vogelsberger W, Mittlebach T, Seidel A. A contribution to the solubility of oxidic solid in water. The dissolution kinetics of silica gel and its interpretation. *Ber Bunsenges Phys Chem* 1996;**100**:1118–27.
33. Gibson LJ, Ashby MF. *Cellular solids: structure and properties*. 2nd ed. Cambridge, UK: Cambridge University Press; 1997.
34. Bell JL, Driemeyer PE, Kriven WM. Formation of ceramics from metakaolin-based geopolymers. Part II: K-based geopolymer. *Journal of the American Ceramic Society* 2009;**92**(3):607–15.
35. Kingery WD, Bowden HK, Uhlmann DR. *Introduction to ceramics*. 2nd ed. New York: Wiley; 1976.