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Manufacturing of cellular β-SiAlON/β-SiC composite ceramics from cardboard

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Light-weight, cellular β-SiAlON/SiC ceramics were produced via dip-coating of an Al/Si-powder containing preceramic polymer slurry into corrugated cardboard. The coated cardboard preforms were pyrolyzed in Ar-atmosphere at 1200°C, where the cellulose fibres decomposed into carbon. Simultaneously the Al/Si melt infiltrated into the porous carbon and formed β-SiC. Subsequent nitridation at temperatures between 1200–1530°C resulted in the formation of a β-SiC-containing β-$Si_{6-z}Al_zO_zN_{8-z}$ composite. Different pre-oxidation treatment resulted in a variation of the oxygen content in the solid solution phase ($z = 0.6$–1.2).

1. Introduction

SiAlONs denote a wide range of silicon nitride solid solution ceramics [1–3]. Either reactive sintering of mixtures of Al_2O_3, Si_3N_4 and AlN powders or liquid phase sintering of SiAlON-powders is commonly applied to manufacture dense components [4, 5]. SiAlON-based ceramics and ceramic composites are potential candidates for high-temperature engineering applications, due to excellent high-temperature strength and thermal shock resistance [6, 7]. The mechanical properties of SiAlON's are similar to Si_3N_4 but with a superior oxidation and creep resistance. Table I summarizes some characteristic properties of SiAlON ceramics compared to Al_2O_3 and Si_3N_4. A low density and low coefficient of thermal expansion [6], are highly attractive for packaging materials in microelectronics or components for aeronautics [4].

Two types of SiAlON's are of special interest for engineering applications: β-SiAlON (β') and α-SiAlON (α'). The term α/β-SiAlON denotes solid solutions of Si_3N_4 in the β-type modification, β-$Si_{6-z}Al_zO_zN_{8-z}$, ($z = 0$–4.2) in the α-type modification, α-$M_xSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$ where x is the amount of stabilizing cation M ($M = Li^+, Mg^{2+}, Ca^{2+}, Y^{3+}$ and lanthanides with $Z \geq 60$), x may vary from 0.3–0.5 with $n = 0.75$–1.26 and $m = 1$–1.5, respectively or mixtures thereof [2, 4]. The structure of β-SiAlON (β') can be described as SiN_4 tetrahedral units, which are joined by nitrogen sharing atoms. The unit cell of the β' crystal lattice contains two Si_3N_4 molecules. The cell parameters (a_0 and c_0) of the hexagonal β' lattice varies with z according to the 3 M/4X lines ($M = Si + Al$, $X = N + O$)-obtained from the equations [3]:

$$a_0 = 7.603 + 0.02967z \qquad (1)$$

and

$$c_0 = 2.907 + 0.02554\,z \qquad (2)$$

Since the last two decades a large variety of raw materials and synthesis routes were reported for the preparation of β-SiAlON ceramics [8–12]. A single β-SiAlON phase was obtained by Peelamedu *et al.* [13] by nitridation of a powder mixture of Si and AlN. The oxygen necessary for the β-SiAlON formation was provided by the N_2 gas supply (O_2 impurity of 10^{-4} atm partial pressure). Davies *et al.* [14] prepared β-SiAlON powder by carbothermal reduction and simultaneous nitridation of ultrafine powder in the Al_2O_3-SiO_2 system. Several investigations were carried out to improve the sinterability and strength of pure β-SiAlON phases, e.g. by metallic Al [15] or by fine grained alumina [16]. Ruiz *et al.* [17] showed the use of rare earths as sintering additives for β-SiAlON. Kishi *et al.* [18] fabricated β-$Si_{6-z}Al_zO_zN_{8-z}$ with $z = 0.5$ by using a fine grain size Al_2O_3 and Si_3N_4 powders and obtained a high strength β-SiAlON. Beyond the studies of pure solid solution β' phase, β-SiAlON-SiC composite ceramics were investigated, in order to improve the

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TABLE I Physical properties of Al_2O_3, Si_3N_4 (RSBN-reaction bonded silicon nitride) and SiAlON [5]

	Al_2O_3	Si_3N_4	SiAlON
Density (g/cm^3)	3.96	3.2	3.08–3.18
Elastic modulus (GPa)	386	250–320	300
Coefficient of Thermal Expansion ($\times 10^{-8}/°C$)	7.4	3.0	1.9–3.3

mechanical properties of the composites [19]. Makuntuala *et al.* [20] studied the synthesis of a SiC-SiAlON composite by nitridation of a SiC-AlSi powder mixture. Changming *et al.* [21] obtained SiAlON bonded SiC with low porosity and very low linear shrinkage on densification using yttria as sintering additive.

The processing of light-weight, porous ceramics and ceramic composites from natural cellulose fibre preforms such as papers and corrugated cardboards has attained increasing attention in the recent years. Low cost raw materials as well as the availability of well established paper processing technologies offer an economic way for manufacturing of lightweight ceramic composites with complex geometries [22, 23]. Ohzawa *et al.* [24] and Almeida Streitwieser *et al.* [25] prepared highly-porous fibrous SiC-ceramics from different cellulose paper preforms by pressure-pulsed or conventional chemical vapour infiltration (CVI) techniques. The reactive conversion of Si-powder filled cellulose papers made by low-viscous slurry infiltration [26] or incorporated in the paper making process [27] was used for manufacturing of pre-shaped, highly-porous SiC-ceramics.

Previous work was also performed on the conversion of preformed corrugated cardboard structures into cellular Si-Al-C-O ceramic composites [28, 29]. Dip-coating with Al/Si-containing slurries followed by reaction of the molten Al/Si-alloy with the carbonized cellulose fibre paper preform and subsequent oxidation resulted in cellular SiC-Al_2O_3-mullite ceramic composites. In contrast to the sintering of porous powder preforms, reactive processing of cardboard preforms showed only minor shrinkage during processing, which facilitates near-net shape manufacturing [30].

The aim of the present work was to examine the manufacturing of light-weight β-SiAlON/β-SiC ceramic composites with an unidirected pore structure from preformed corrugated cardboard templates. A Si/Al powder based slurry was deposited on the cardboard preform by dip coating. Upon heating above the melting temperature of the Al/Si-alloy composition, local infiltration into the carbonised porous preform with the formation of β-SiC took place. Subsequent annealing in N_2 atmosphere finally resulted in the formation of a cellular β-SiAlON/β-SiC composites.

2. Experimental

Preforms of corrugated cardboard made of secondary cellulose fibres (fibres obtained from recovered paper) were used as templates (corrugation area weight of about 125 g/m^2 and top layer area weight of about 165 g/m^2, cell diameters between 2–6 mm and a cell wall thickness of about 100 μm, *190TL*, *Wellpappenwerk*, *Bruchsal/Germany*) were dried at 70°C and infiltrated by dip-coating with a metal powder/preceramic polymer slurry. The slurry was prepared with isopropyl alcohol containing 40 vol.% Si-powder (>98%), 40 vol.% Al-powder (>99%) and 20 vol.% of a preceramic polymer (Polymethylsilsesquioxane – PMS, MK, *Wacker AG, Burghausen/Germany*). The PMS has an average molecular composition corresponding to $[CH_3SiO_{1.5}]_n$ ($n \approx 130$–150). It is characterized by a high ceramic yield (Si-C-O) of more than 75 wt.% of SiO_2, SiC and C in the inorganic residue upon pyrolysis in Ar-atmosphere [31–36]. The mean particle size of the metallic powders was below 10 μm for Si and 20 μm for Al. The Al/Si ratio corresponds to a weight fraction of 53.8 wt.% Al and 46.2 wt% Si, which exhibits a melting temperature of 1012°C.

After dip-coating, the specimens were pyrolyzed in Ar atmosphere at 1200°C for 1 h in a comercial tubular furnace. During pyrolysis the cellulose based fibres of the cardboard decomposed into carbon and the preceramic polymer into an amorphous Si-O-C residue [32, 35].

At temperatures above 1012°C the Si/Al powder mixture melts, which infiltrates the porous carbon. Subsequently, the samples were nitrided in N_2 atmosphere at 1200–1530°C. Alternatively, the samples were oxidized in air at 800°C for 1 h before nitridation to increase the amount of oxygen, which is necessary for the β solid solution formation. Fig. 1 shows the schematic processing route for manufacturing of cellular β-SiAlON/SiC ceramics from corrugated cardboard.

The crystalline reaction products were analysed by X-ray diffractometry of powdered specimens using monochromated Cu K_α radiation (XRD) (*D 500, Siemens, Karlsruhe/Germany*). The z values of the β-$Si_{6-z}Al_zO_zN_{8-z}$ phase were calculated using the relationships between z and the unit-cell dimensions a_0 and c_0 of the β-Si_3N_4 (hexagonal, space group P63) according to K. H. Jack [4]. The microstructures of the cellular ceramic composites were characterized by scanning electron microscopy (SEM) (*Phillips XL 30*, *Netherlands*). The skeleton density was measured by He-pycnometry (*Accu Pyk 1330*, *Micromeritics*, *Düsseldorf/Germany)*. Thermogravimetric analysis (TGA) (*Du Pont Instruments*, *951 Termogr. Analyze*, *Wilmington/USA)* was applied in order to evaluate the weight change during oxidation.

3. Results and discussion

3.1. Phase evolution

After pyrolysis at 1200°C the Si/Al slurry dip-coated cardboard specimens were converted into β-SiC-Si/Al composites. SiC was formed by the reaction of the Si from the Si/Al melt with carbon from the cellulose fibres. A linear shrinkage of about 3% in the direction parallel and perpendicular to the pore channel elongation was

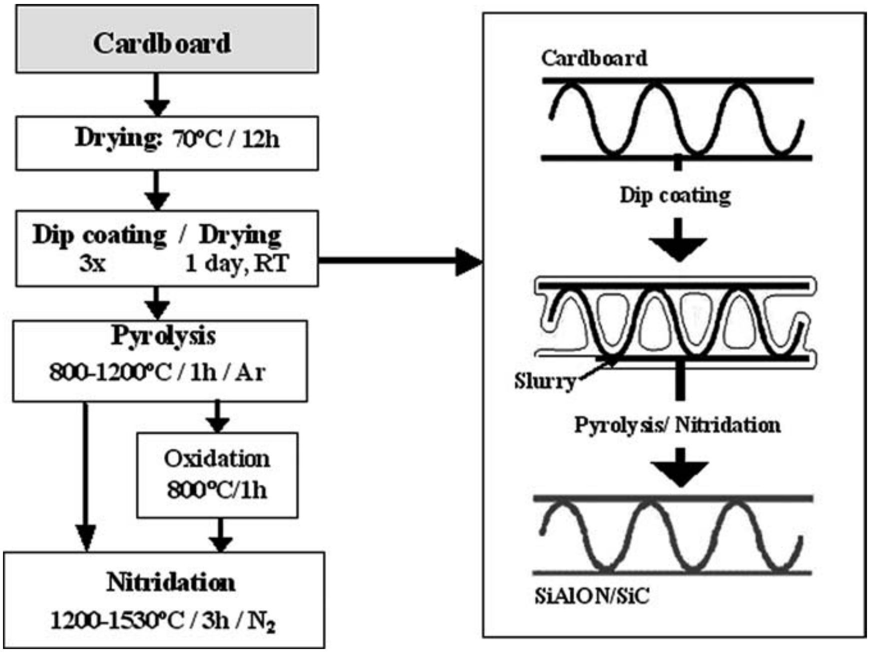

Figure 1 Schematic processing diagram for manufacturing of cellular β-SiAlON/SiC ceramics from corrugated cardboard.

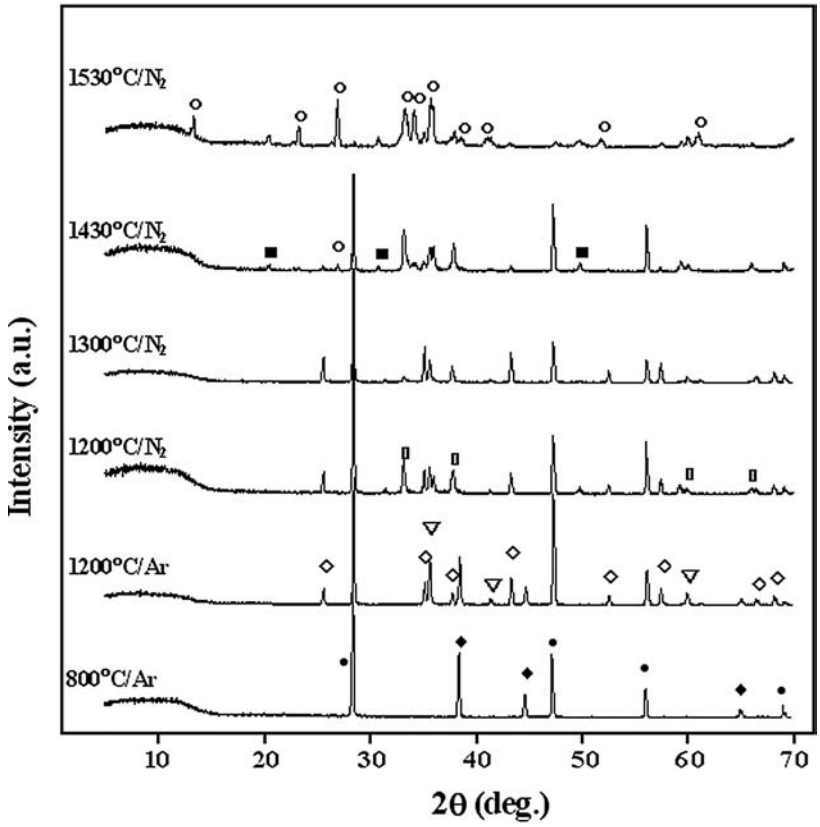

Figure 2 XRD spectra of the specimens after pyrolysis up to 1200°C for 1 h in Ar and nitridation at different temperatures for 3 h ((○), β-SiAlON; (▽), β-SiC; (■), β-Si_3N_4; (□), AlN; (◇), α-Al_2O_3; (◆), Al; (●) Si).

observed. The shrinkage is related to the decomposition of the cellulose fibres (weight loss about 80 wt.%) into carbon fibres during pyrolysis [28]. Upon nitridation no further shrinkage could be measured. Similar results were observed in previous work from Si/Al dip-coated cardboard preforms after oxidation and formation of cellular mullite/alumina/SiC ceramic composites [29].

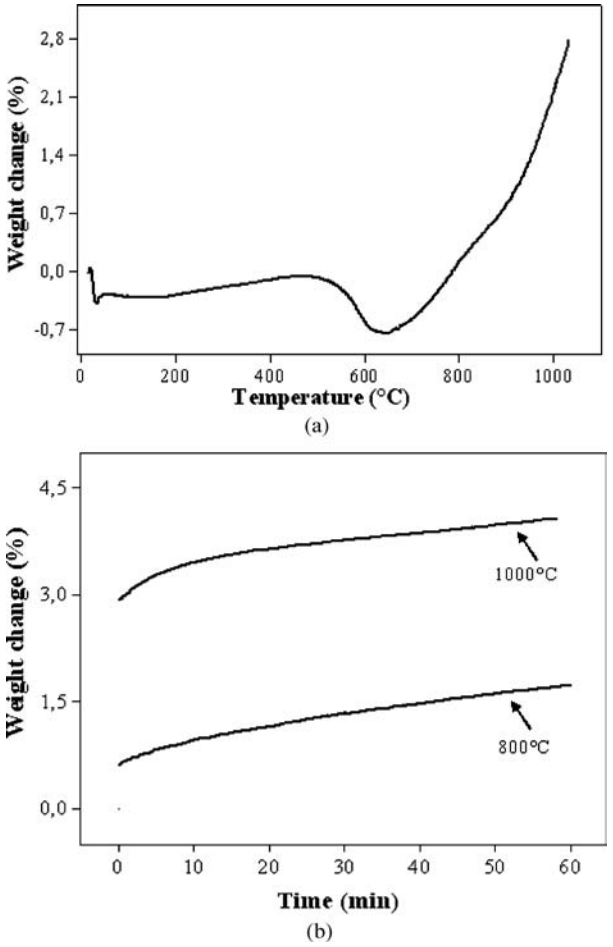

Figure 3 (a) TGA and (b) isothermal curve at 800°C for 1 h in air.

Fig. 2 shows the XRD spectra of the specimens after processing at different temperatures. A temperature of 1200°C in Ar-atmosphere was found as the minimum temperature to achieve effective wetting and infiltration of the Al/Si-alloy melt ($T_M = 1012°C$) into the carbon template fibres. After pyrolysis and reactive infiltration at 1200°C β-SiC but also small amounts of α-Al_2O_3 were detected. The oxygen necessary for the oxidation of the Al was provided by the preceramic polymer, which decomposed into an amorphous or partially crystallized Si-O-C network [33] after pyrolysis at 1200°C. The polysiloxane starts to decompose at around 400–500°C. During the infiltration process, the Al/Si-melt partially reduces the decomposition products leading to free Si and Al_2O_3. The Al/Si-melt front reacts with carbon to form SiC as shown in Equations 3 and 4:

$$3SiO_2(s) + 4Al(l) \rightarrow 3Si(s) + 2Al_2O_3(s) \qquad (3)$$

$$(Si + Al)(l) + C \rightarrow SiC(s) + Al(l) \qquad (4)$$

An amorphous Si-O-C phase normally forms above 1000°C with a general composition range represented by

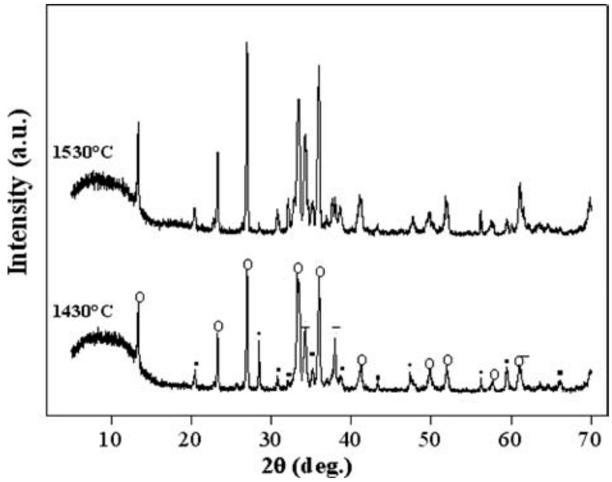

Figure 4 XRD spectra of the specimens nitrided for 3 h after pre-oxidation ((○), β-SiAlON; (△), α-SiC; (▽), β-SiC; (■), β-Si_3N; (◇), α-Al_2O_{34}; (●), Si).

SiC_xO_y [34]. The amorphous oxycarbide phase consists of a network of C, Si and O, where C is bonded to C (free carbon) and Si [35]. This phase is normally stable up to 1200°C, when cristobalite and SiC starts to form [36]. Al partially reduced the Si-O-C phases, which was confirmed by the observation of free Si and Al_2O_3 after processing [29, 37]. The polyaromatic carbon [36] reacts with Si from the melt, which increases the SiC yield in the composite.

After nitridation at 1000°C AlN was formed whereas at 1200°C Al_2O_3 and AlN were found. At 1430°C a substantial amount of β-Si_3N_4 was formed. The formation of the β′ phase occurs via solution and precipitation in a transient liquid phase [2, 15]. β-$Si_{6-z}Al_zO_zN_{8-z}$ formation was found in literature to require temperatures exceeding 1250°C with the maximum reaction rate occurring between 1450°C and 1550°C, depending on the starting fraction of AlN, Al_2O_3 and Si_3N_4 [10]. Accelerated formation of the β′ solid solution was found to

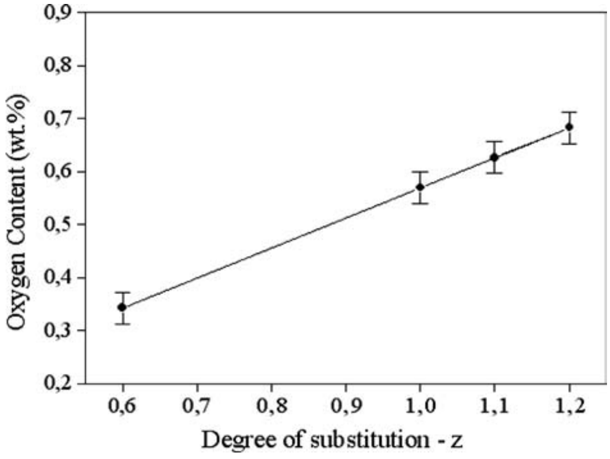

Figure 5 Oxygen content in the specimens as a function of the degree of substitution *z*.

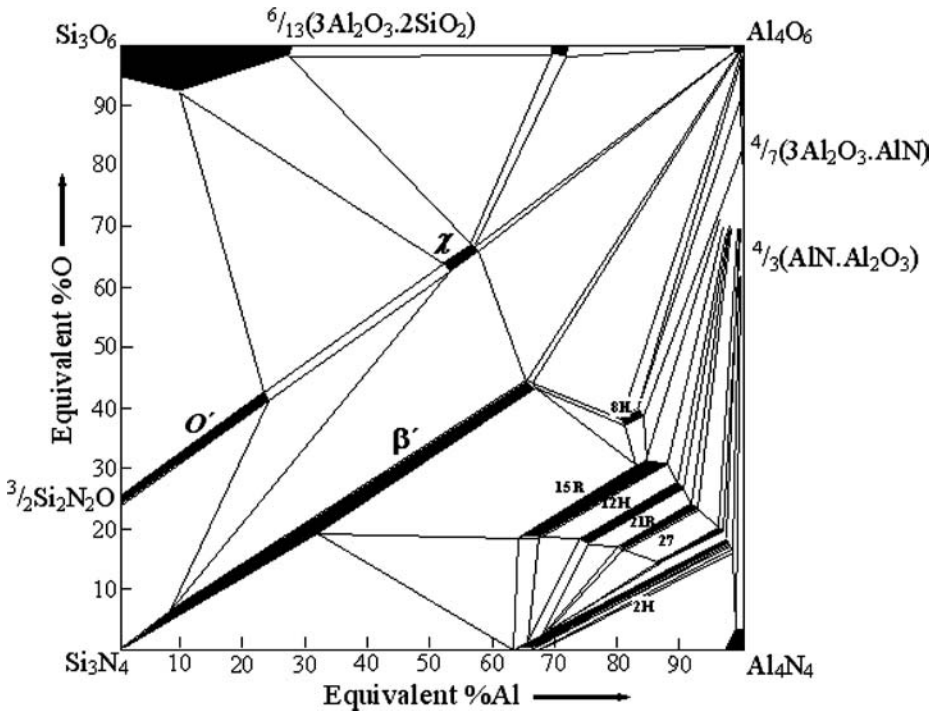

Figure 6 Quaternary phase diagram of the system Si_3N_4-Al_2O_3-SiO_2-AlN [2].

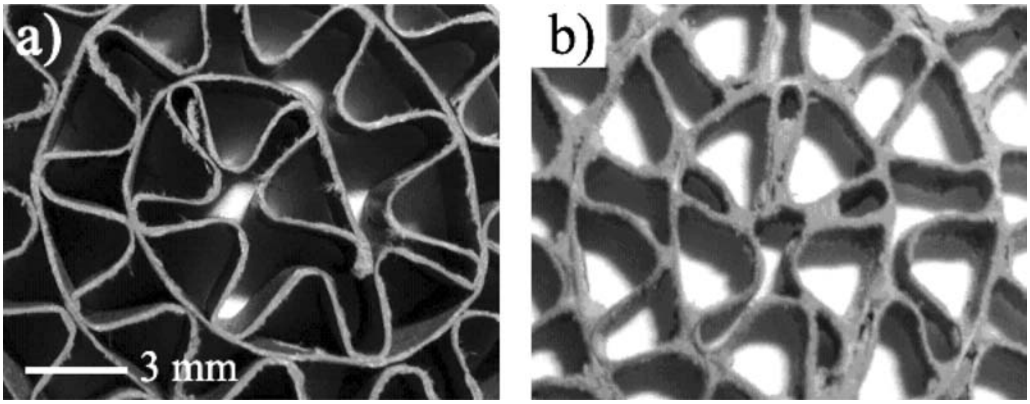

Figure 7 Optical photographs of: (a) corrugated cardboard and (b) cellular SiAlON/SiC-ceramic composite.

occur at 1530°C. With increasing temperature the degree of substitution, z, increased from 0.6 at 1430°C up to 1.0 at 1530°C. The amount of SiC increased slightly during processing due to the decomposition of the Si-O-C into β-SiC, SiO_2 and carbon above 1300°C [31].

A second set of specimens was exposed to a pre-oxidation treatment in air after pyrolysis. Fig. 3 shows the weight change versus temperature (Fig. 3a) and time (Fig. 3b). After oxidation a total weight increase of approximately 2.8% was measured at 1000°C, which further increased to 4.1% after oxidation for 1 h (Fig. 4b). After oxidation at 800°C for 1 h, a weight increase of 1.7% was measured. A more pronounced oxidation treatment yields a higher amount of oxygen in the specimen and may lead to the formation of mullite or other oxide species (Al_2O_3, Si_2N_2O) prior to the formation of SiAlON [10]. For the further investigations, a pre-oxidation temperature of 800°C for 1 h was used.

During nitridation of the pre-oxidized specimen, the major amount of β-SiAlON was formed already at 1430°C after 3 h, as shown in the XRD spectra of Fig. 4. As in the non-oxidizes specimen, the Al was completely reacted after processing at a temperature of 1430°C. However, the amount of Si and AlN was decreased drastically in the pre-oxidized specimen after nitridation at 1430°C compared to the non-oxidized sample. After nitridation at 1430°C a small amount of α-Al_2O_3 was detected that vanished at 1530°C.

The degree of substitution z was evaluated in terms of the oxygen content in the final composition after nitridation. With increasing degree of substitution z the hexagonal unit cell lattice parameters a_0 and c_0

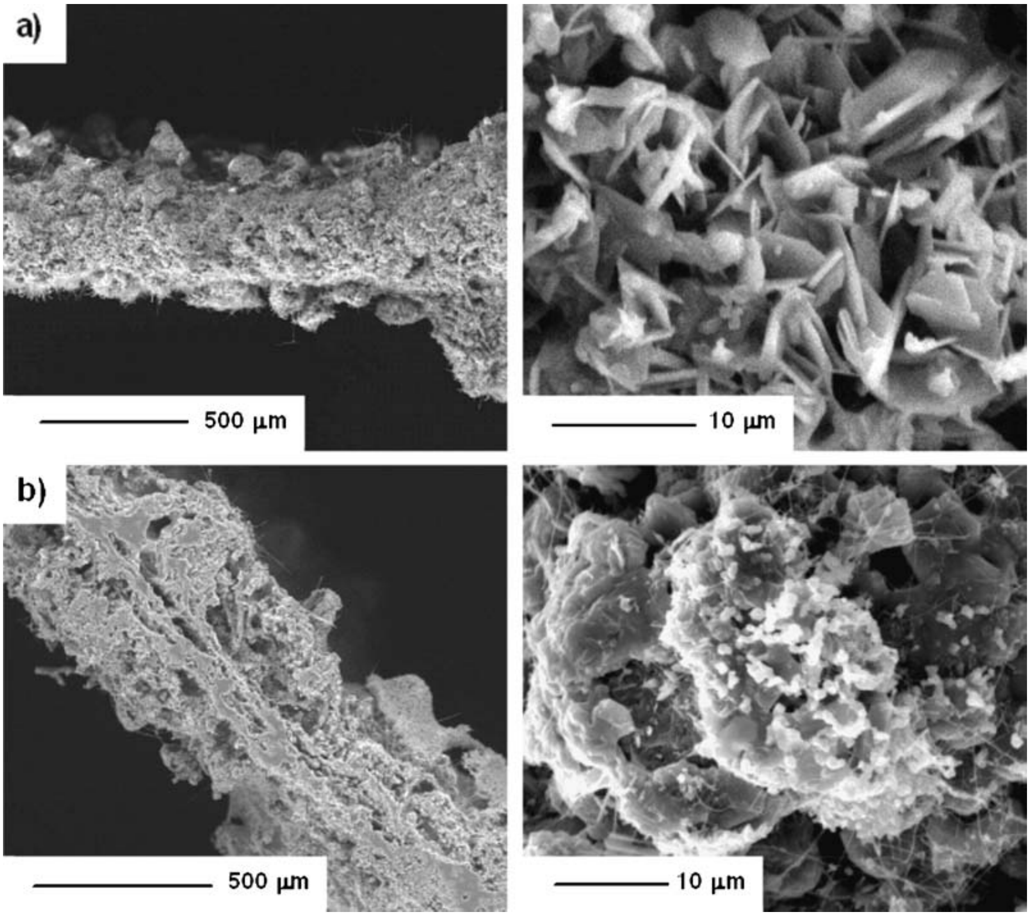

Figure 8 SEM micrographs of the non-oxidized corrugated cardboard specimens after nitridation for 3 h at: (a) 1530°C; (b) 1530°C after pre-oxidation.

change according to Equations 1 and 2. Fig. 5 shows the oxygen content in the samples *versus* degree of substitution z.

Since no other oxide phases, with exception of alumina (e.g. cristobalite or mullite) were detected by XRD, the overall oxygen content in the sample–less the oxygen in Al_2O_3-could be directly related to the degree of oxygen substitution in the β' solid solution phase, leading to a linear z increase.

Table II summarizes the results of the XRD measurements. The degree of oxygen substitution z in the β-SiAlON phase is higher in the samples with a higher oxygen content (provided by the pre-oxidation step). However, after nitridation at 1530°C for 3 h the z is only slightly different in both specimens (1.0 in the non-oxidized and 1.1 in the pre-oxidized sample). According to the quaternary phase diagram of the system Si_3N_4-Al_2O_3-SiO_2-AlN (Fig. 6) [2] the obtained stoichiometry range for the formed β-solid solution lies at the beginning of the β' line with low degree of oxygen substitution.

TABLE II Semiquantitative analysis of the phase fractions and respective z-value of the obtained SiAlON's determined from powder XRD measurements ($\beta = \beta$-Si_3N_4, $\beta' = \beta$-SiAlON; $A = Al_2O_3$)

	Non- oxidized	Pre-oxidized
Nitridation at 1430°C	Si > SiC ≈ AlN > A > $\beta' \approx \beta$ ($z = 0.6$)	$\beta' >$ SiC $> A \approx \beta >$ Si > AlN ($z = 1.2$)
Nitridation at 1530°C	$\beta' >$ SiC $> \beta \approx$ AlN ($z = 1.0$)	$\beta' > \beta >$ AlN ≈ SiC ($z = 1.1$)

The use of a metallic Al powder as a precursor for the synthesis of β-SiAlON showed two additional advantages: first, the Al lowers the melting temperature of the Si-Al alloy, favouring the reactive Si-Al infiltration into the porous carbon template at lower temperatures. Secondly, it may also improve the sintering behaviour of SiAlON due to the formation of nanosized Al_2O_3 by Al-oxidation as shown by Zhang *et al*. [15].

The XRD results indicate the formation of the β' solid solution at temperatures below 1430°C. First Al_2O_3 and AlN are formed as intermediary phases at temperatures below 1200°C. Above 1300°C, β-Si_3N_4 is formed leading to the initial composition for the reaction into β-SiAlON. No mullite, cristobalite or other nitride crystalline phases such as silicon oxynitride (Si_2N_2O) were observed in the XRD investigations. During nitridation between 1200°C and 1300°C, Al_2O_3 is reduced to AlN, which will be dissolved in the β-Si_3N_4 lattice, leading to the formation of the solid solution β' phase according to the Equation 5

[2]:

$$0.5z\mathrm{Al_2O_3} + (2 - 0.25z)\mathrm{Si_3N_4} \Leftrightarrow \mathrm{Si}_{6-z}\mathrm{Al}_z\mathrm{O}_z\mathrm{N}_{8-z} + 0.25z\mathrm{SiO_2} \quad (5)$$

As the carbon was consumed for the formation of β-SiC or oxidized at temperatures below 1300°C, it is reasonable to state that no other significant reaction mechanism occurred simultaneously with the β' phase formation, e.g. carbothermal reduction/nitridation of $\mathrm{SiO_2}$.

3.2. Microstructure

Fig. 7 shows optical photographs of the corrugated cardboard (Fig. 7a) and of the cellular SiAlON/SiC-ceramic composite (Fig. 7b). The original corrugated cellular structure of the cardboard was well reproduced in the ceramic composite.

Fig. 8 shows SEM-micrographs of the specimens after nitridation at 1530°C. In the case of non-oxidized specimen, (Fig. 8a) the surface is covered by hexagonal plate-like grains of the β-SiAlON phase with a mean thickness of 0.5–2 μm and a diameter of about 3–7 μm. The pre-oxidized samples (Fig. 8b) exhibits an inhomogeneous grain morphology, with SiC whiskers and hexagonal equiaxed β-SiAlON grains. The SEM results suggest, that only a minor amount of liquid phase was present during processing, otherwise it would favor the growth of elongated grains of β-SiAlON [7, 13, 37]. Similarly, the grain size and grain morphology of β-SiAlON phase significantly depend on the composition (z-value) [38]. Hexagonal equiaxial grains were found by Petterson *et al.* [7] for z of 1.5 and the grain size increases as z increases.

The measured skeleton (strut) density of the non-oxidized SiAlON/SiC composites achieved 2.9 g/cm^3 when nitrided at 1430°C and 3.12 g/cm^3 at 1530°C, respectively. An open porosity of 84% and 85% was measured for the specimens nitrided at 1430°C and 1530°C, respectively. The skeleton density after nitridation at 1530°C is slightly lower than the theoretical density of β-SiAlON (3.15 g/cm^3 for $z = 1.7$) and SiC (3.2 g/cm^3) indicating only a low amount of residual porosity in the strut material of the final SiAlON/SiC-ceramic composites. In the pre-oxidized samples a skeleton density of 3.10 g/cm^3 was measured for the samples after nitridation at both temperatures. The slightly larger amount of closed porosity in the struts of these samples may be attributed to the oxidation of unreacted carbon after pyrolysis.

4. Conclusions

β-SiAlON/β-SiC-ceramic composites were manufactured from corrugated cardboard preforms. Dip-coating of the cardboard preforms with a slurry containing Al/Si powder mixture and polymethylsilsesquioxane and subsequent heat treatment up to 1530°C resulted in the formation of a macrocellular ceramic composite. Depending on oxidation treatments before nitridation the starting temperature for the β-SiAlON formation and degree of oxygen substitution z for the β-$\mathrm{Si}_{6-z}\mathrm{Al}_z\mathrm{O}_z\mathrm{N}_{8-z}$ varied between $z = 0.6$–1.2. The conversion of preformed cardboard structures into light-weight ceramic composites offers an interesting potential for the low-cost manufacturing of uni- or multidirectional, macrocellular silicon nitride based components.

Acknowledgments

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