Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 29 (2009) 843–849

www.elsevier.com/locate/jeurceramsoc

Advanced ceramics from a preceramic polymer and nano-fillers

E. Bernardo[a,*], P. Colombo[a], S. Hampshire[b]

[a] Dipartimento di Ingegneria Meccanica, Settore Materiali, Università di Padova, via Marzolo 9, 35131 Padova, Italy
[b] Materials and Surface Science Institute, University of Limerick, Limerick, Ireland

Abstract

A commercial silicone resin ("silicone") filled with ceramic nanoparticles has been employed for the preparation of mullite and β-SiAlON ceramics. Dense, pure, crack free mullite were prepared by the heating in air of a mixture of silicone resin and alumina nanoparticles in the temperature range 1200–1550 °C. The high reactivity of Al_2O_3 towards silica, coupled with nanometric size, led to a large volume fraction of mullite crystals even at low firing temperatures (1250 °C). β-SiAlON ceramics were prepared by the heating of a mixture of silicone resin and fillers consisting of Al_2O_3 nanoparticles and Si_3N_4 and AlN microparticles, in the temperature range 1450–1550 °C in nitrogen atmosphere. The formation of SiAlON was found to be preceded by the formation of intermediate alumino-silicate phases like mullite and sillimanite, successively reduced (due to the carbon content of the ceramic residue of silicone resins) and nitrided. Although some oxide contamination was still present after the high temperature treatment, a high β-SiAlON yield (about 80%) was achieved. The use of nano-filled silicones provides a promising route for the fabrication of advanced ceramic components by exploiting polymer processing techniques, with the achievement of complex shapes.

Keywords: Nano-sized fillers; Preceramic precursors

1. Introduction

Mullite and SiAlON ceramics are of considerable technological interest because of their combined thermal and mechanical properties. Mullite ($3Al_2O_3{\cdot}2SiO_2$) is widely employed for high temperature structural applications for its remarkable creep resistance and good mechanical strength,[1] coupled with a relatively low thermal expansion coefficient ($\alpha_{20/200} = 4 \times 10^{-6}\,K^{-1}$), a high thermal shock resistance and a low thermal conductivity ($k = 2.0\,W\,m^{-1}\,K^{-1}$).[2,3] In addition, mullite ceramics are employed as substrates for electronic devices, especially in the field of high density packaging, due to its low electric conductivity and low dielectric constant ($\varepsilon = 6.5$ at 1 MHz).[2] β-phase SiAlON ceramics correspond to a solid solution of Al and O atoms in the β-Si_3N_4 structure, summarized by the formula $Si_{6-z}Al_zO_zN_{8-z}$ (z varying from 0 to 4.2) and they are well known for their excellent mechanical and thermal properties, exploited in various engineering applications.[4,5]

Mullite synthesis is mostly based on heating alumina/silica mixtures in stoichiometric proportions. Different processes are related to the particular sources for the two oxides (including the use of metallic Al) and include sol–gel processing,[6–8] co-precipitation,[9] hydrothermal synthesis,[10] chemical vapour deposition,[11] sintering of silica-coated alumina micropowders,[3,12] and, above all, reaction sintering of natural alumino-silicates (derived from clay) and reactive alumina mixtures.[2,13,14]

The usual preparation of SiAlON ceramics[15] is based on sintering mixtures of Si_3N_4, Al_2O_3, AlN and SiO_2, but a cheaper processing may come from the usage, like in the case of mullite synthesis, of alumina/silica mixtures or natural alumino-silicates,[16,17] subjected to carbothermal reduction and nitridation.

In this paper we present the usage of a variously filled silicone resin ("silicone") as the raw material for the obtainment of both mullite and β-SiAlON, after treatments in oxidative or reducing (nitrogen) atmosphere, respectively. General advantages of preceramic polymers like silicone resins are mainly the low processing temperatures and the possibility of using polymer-processing techniques, useful for achieving complex shapes. However, the thermal treatment of pure silicone resins generally leads to the formation of cracks and pores in the products, due to the release of a great amount of gases (mainly hydrocarbons) [18] during the polymer-to-ceramic conversion (occurring

---

[*] Corresponding author. Tel.: +39 049 8275510; fax: +39 049 8275505.
E-mail address: enrico.bernardo@unipd.it (E. Bernardo).

0955-2219/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2008.07.011

above 500 °C), coupled with a significant volume contraction of up to 60%.[19] The addition of secondary, filler materials (reactive with the preceramic precursor or inert during firing), allows the production of monolithic ceramics with a good structural integrity upon heat treatment.[19]

In the present investigation, in oxidative atmosphere, the nanometric size of fillers (Al_2O_3 nanopowders and calcined clay) pure mullite ceramics were effectively achieved at relatively low temperatures (1350 °C) and with a remarkable density (in the case of filling of silicone with only Al_2O_3). In nitrogen atmosphere, the formation of alumino-silicates phases (sillimanite and mullite) constituted a key point for structural evolution, which provided a high β-SiAlON yield (about 80%) at 1550 °C. Although some oxide contaminations are present, the usage of filled preceramic polymers appears promising for the fabrication of advanced ceramic components.

2. Experimental

The preceramic polymer consisted of a polymethylsiloxane (MK, Wacker-Chemie GmbH, München, Germany). This material is known to be converted, after pyrolysis in inert atmosphere, into a silicon oxycarbide (SiOC) residue, corresponding to the atomic proportions 31.6% Si–48.1% O–20.2% C (later indicated with $Si_3O_{4.56}C_{1.92}$).[20] The ceramic yield, i.e. the weight ratio between the mass of the starting polymer and the mass of SiOC, is about 0.84. In oxidative atmosphere, the residue is expected to be oxidized to amorphous silica. The silica yield may be calculated to be again about 0.84 (the weight loss due to the burn-out of C is compensated by the intake of oxygen).

The silicone resin, in powder form, was dissolved in acetone under magnetic stirring for 15 min, thus producing solutions with 2% solid content (1 g silicone for 50 ml acetone). For mullite synthesis, γ-Al_2O_3 nanopowders (aluminium oxide C′, Degussa, 15 nm mean particle size, specific surface area of $100\,m^2\,g^{-1}$) were added, in the weight ratio silicone/γ-Al_2O_3 = 1/2.125, again under magnetic stirring. As an alternative, also mixtures with calcined kaolin clay (metakaolinite, $Al_2O_3{\cdot}2SiO_2$), corresponding to the weight proportions silicone/clay/γ-Al_2O_3 = 1/1/3, were produced.

For β-SiAlON synthesis, γ-Al_2O_3 nanopowders and AlN micropowders (Denka, Tokyo, Japan, 4 μm mean particle size) were added to the silicone solution, in the proportions suggested by the following idealized reaction:

$$Si_3O_{4.56}C_{1.92} + 0.12Al_2O_3 + 2.76AlN + 1.12N_2 \rightarrow Si_3Al_3O_3N_5 + 1.92CO \quad (1)$$

Two additional mixtures were tested, corresponding to the following reactions:

$$Si_3O_{4.56}C_{1.92} + 0.4Al_2O_3 + 3.763AlN + 0.4N_2 \rightarrow 1.14Si_2Al_4O_4N_4 + 1.20CO + 0.72SiC \quad (2)$$

$$Si_3O_{4.56}C_{1.92} + 3AlN + 0.3Si_3N_4 + 1N_2 \rightarrow 1.15Si_{3.39}Al_{2.61}O_{2.61}N_{5.39} + 1.56CO + 0.36C \quad (3)$$

For the last composition, also Si_3N_4 micropowders (Denka, Tokyo, Japan, 95% α-phase, 4 μm mean particle size) were employed. All the mixtures were ultrasonicated for 10 min, thus producing homogeneous dispersions of fillers, then poured in a glass container and dried at 60 °C overnight. After evaporation of the solvent, the mixtures were finely ground (particles size <10 μm) and cold pressed at 40 MPa in a cylindrical steel die. For mullite preparation, the pressed samples (diameter ∼31 mm, height ∼1 mm) were heat treated in air at various temperatures ranging from 1200 to 1550 °C, with a heating rate of 10 °C/min and a holding time of 2.5 h. For SiAlON preparation, the pressed samples were fired under flowing nitrogen (2 l/min) at 1450 and 1550 °C, with a heating rate of 10 °C/min and a holding time of 2 h.

Morphological information on the samples after thermal transformation were obtained by using scanning electron microscopy (SEM, Philips XL 30 ESEM, Eindhoven, The Netherlands). Samples in powder form were investigated by X-ray diffraction (Philips PW 3710, Eindhoven, The Netherlands), using Cu Kα radiation (0.15418 nm). Selected XRD patterns were refined, according to the Rietveld's method, by employing the material analysis using diffraction (MAUD) program package.[21]

3. Results and discussion

According to Schneider's definition,[6] mullite may be formed by three types of precursors. The first corresponds to single-phase systems featuring an atomic or near atomic homogeneity in the Al–Si mixing, capable of transforming into mullite at about 980 °C, like in the case of sol–gel systems. The second type is represented by diphasic systems consisting of amorphous silica and reactive alumina (γ-Al_2O_3, transforming into δ-Al_2O_3), capable of mullitization above 1250 °C. Finally, the third type is due to diphasic systems, non-crystalline up to about 980 °C, in which mullite formation is favoured by the formation of weakly crystalline transient phases (such as Al–Si spinel or γ-Al_2O_3), capable of mullitization at temperatures lower than 1250 °C.

Silicone filled with only γ-Al_2O_3 and heated in air, as recently evidenced by Bernardo et al.[22] assumes the behaviour of the second type of precursors. The XRD patterns (Fig. 1a) reveal the formation of mullite at 1250 °C, with no presence of other crystal phases. Below this temperature (at 1200 °C), only peaks corresponding to γ-Al_2O_3 are visible. This result is comparable to those for reaction sintering of amorphous SiO_2-coated γ-Al_2O_3 particle nanocomposites, as reported by Bartsch et al.[3] but in this case the silica coating is not due to a complex sol–gel procedure; on the contrary, the processing of a meltable polymer is very simple and could be exploited for manufacturing articles with complex shapes (via extrusion, spinning, cold or warm pressing).

Silicone filled with γ-Al_2O_3 and calcined clay (metakaolinite) exhibited a remarkably different behaviour (Fig. 1b). Mullite was developed even at 1200 °C. In addition, a peak corresponding to crystalline silica, i.e. cristobalite, is clearly visible in the XRD patterns of samples treated below 1450 °C. The processing of silicone with only Al_2O_3 nano-filler revealed that

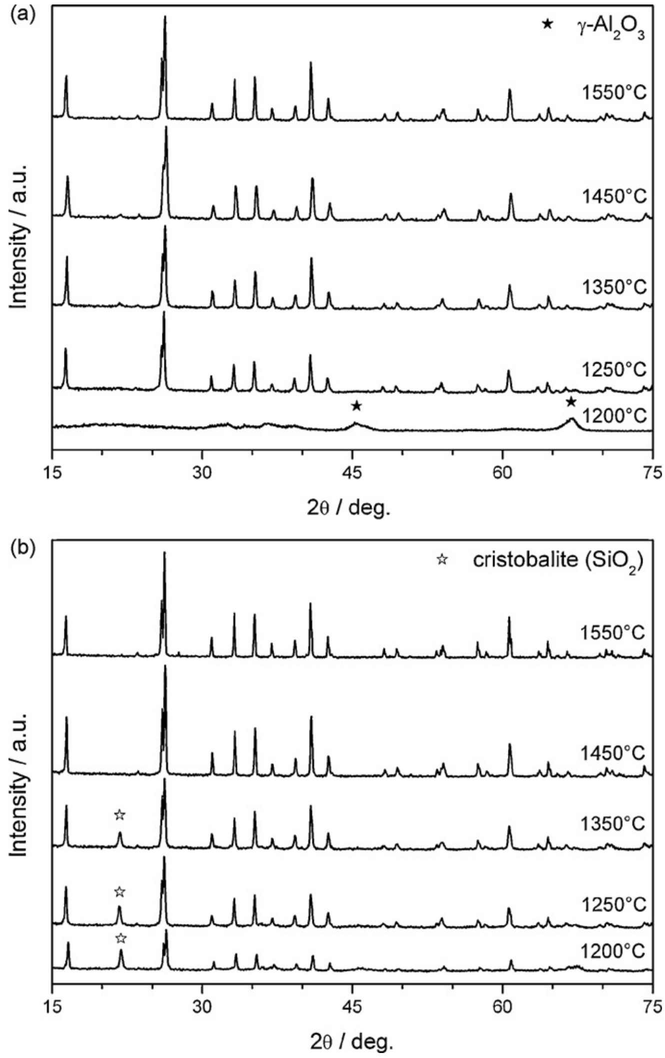

Fig. 1. XRD patterns of samples from (a) silicone/Al_2O_3 mixtures and (b) silicone/Al_2O_3/calcined clay mixtures (the not indexed peaks correspond to mullite).

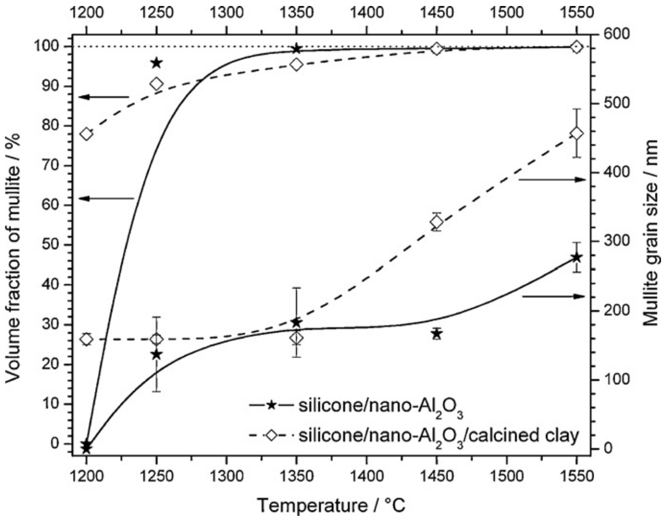

Fig. 2. Volume fraction and grain size of mullite as functions of the processing temperature.

no crystal phase can be attributed to the ceramic residue of the preceramic polymer. As a consequence, the new crystal phase should be due to the presence of calcined clay, which is well known to decompose in mullite and silica at about 980 °C.[13] It must be noted, however, that this silica usually crystallizes as cristobalite at about 1350 °C (at lower temperatures the silica from metakaolinite is reported to be amorphous).[13] Cristobalite may be seen as the result of a particular interaction silicone/clay, to be investigated in the future.

The Rietveld refinements of XRD patterns, allowing a quantification of the phases, provided an interesting comparison between the two formulations for mullite synthesis. As shown by Fig. 2, the processing of silicone with only alumina nano-filler leads to almost complete conversion at 1250 °C, corresponding to a volume fraction of mullite of about 95%. The new phase features a grain size of 150–160 nm, kept almost constant at 1350 and 1450 °C, when the conversion reaches 100%. Only at 1550 °C a certain grain coarsening is observed, leading to a grain size of about 280 nm. In the case of the processing with clay, the mullite conversion approaches 80% even at 1200 °C and corresponds to a grain size again of 150–160 nm. The grain size is stationary when passing from 1200 to 1350 °C, but remarkably increases with a further increase of processing temperature, with the elimination of the silica contamination. The grain size, at 1450 and 1550 °C, is much greater than in the case of silicone/alumina mixtures, being about 320 and 460 nm, respectively.

For a full explanation of the mullite synthesis new experiments are undoubtedly needed, especially for silicone/clay/Al_2O_3 mixtures, mostly below 1200 °C. In any case, we can observe that employing only Al_2O_3 nano-filler corresponds to the formation of mullite grains embedded in a matrix of amorphous silica, which is highly reactive at every temperature. The beginning of conversion at 1250 °C is likely due to homogeneous nucleation of mullite (active only above 1250 °C, as observed in the literature).[8]

In the system with clay, heterogeneous nucleation reasonably occurred at the mullite crystals developed upon the transformation of clay, and amorphous silica reacted with the Al_2O_3 nano-filler even below 1200 °C. In fact, the conversion at 1200 °C cannot be attributed only to mullite from clay ("primary mullite", or mullite I, see Table 1). To our calculations, this contribution is very limited, being about 13 wt%; if we consider the amorphous silica from silicone to be fully active with nano-Al_2O_3 (yielding "secondary mullite ", or mullite II), the mullite conversion reaches about 75 wt% corresponding to about 76 vol.%, very close to the conversion calculated from the fitting of XRD patterns (78 vol.%).

The cristobalite by-product of the decomposition of clay limits the full exploitment of Al_2O_3 nano-filler at low temperatures and the completion of mullitization (crystalline silica is reasonably less reactive than amorphous silica, since chemical interaction with alumina must be preceded by structural rearrangements). In any case it is evident that the mixture silicone/Al_2O_3 nano-filler may act like precursors of the third type (capable of mullitization below 1250 °C) in the presence

Table 1
Scheme of reaction of the mixture silicone /clay/Al_2O_3 at 1200 °C

		1) Before mullitization		
Raw materials	Nano-Al_2O_3	Silicone*	Calcined clay**	
Components	Al_2O_3	SiO_2	Mullite I	SiO_2
Weight proportions	3	0.84	0.64	0.36
Weight %	62	17.5	13	7.5
	2) After mullitization of silica from silicone and nano-Al_2O_3 (weight ratio 1/2.54)			
Components	Residual Al_2O_3	Mullite II	Mullite I	SiO_2
Weight %	18	61.5	13	7.5
		3) Summary of products		
Components	Residual Al_2O_3	Total Mullite (Mullite I+ Mullite II)		SiO_2
Weight %	18	74.5		7.5
Vol.%	14	76		10
Vol.% from Rietveld analysis	16	78		6

[*] 1 silicone resin = 0.84 amorphous silica (0.84 = ceramic yield)

[**] 1 calcined kaolin clay = 0.64 mullite + 0.36 silica, owing to the reaction: 3 $(Al_2O_3{\cdot}2SiO_2) \rightarrow 3Al_2O_3{\cdot}2SiO_2 + 4SiO_2$

of mullite “seeds”, like those provided by the decomposition of clay. As a consequence, mixtures silicone/Al_2O_3 nanofiller/mullite seeds could be very attractive for low temperature mullitization, without silica impurity, and will be the object of future experiences.

The SEM observations evidenced a different microstructure for mullite samples from silicone/Al_2O_3 and silicone/Al_2O_3/calcined clay mixtures. Samples from the usage of alumina nano-filler are crack free (Fig. 3a) and contain only isolated micropores (Fig. 3b). The residual porosity, from gas pycnometry, was measured to be about 2.6% at 1550 °C. The roughness of the fracture surface of Fig. 3b is also consistent with the fine mullite grain size from XRD refinements. Samples from the usage of alumina nano-filler coupled with metakaolinite featured a complex microstructure, composed of “islands” of homogeneous, dense mullite, surrounded by a number of micropores. The final porosity was measured to be about 13%. This relevant porosity might be due both to a difficult homogenisation of metakaolinite (compared to alumina nano-filler) and to the complex interaction between silicone and the two types of fillers, which led to the formation of cristobalite and mullite even below 1200 °C. This behaviour

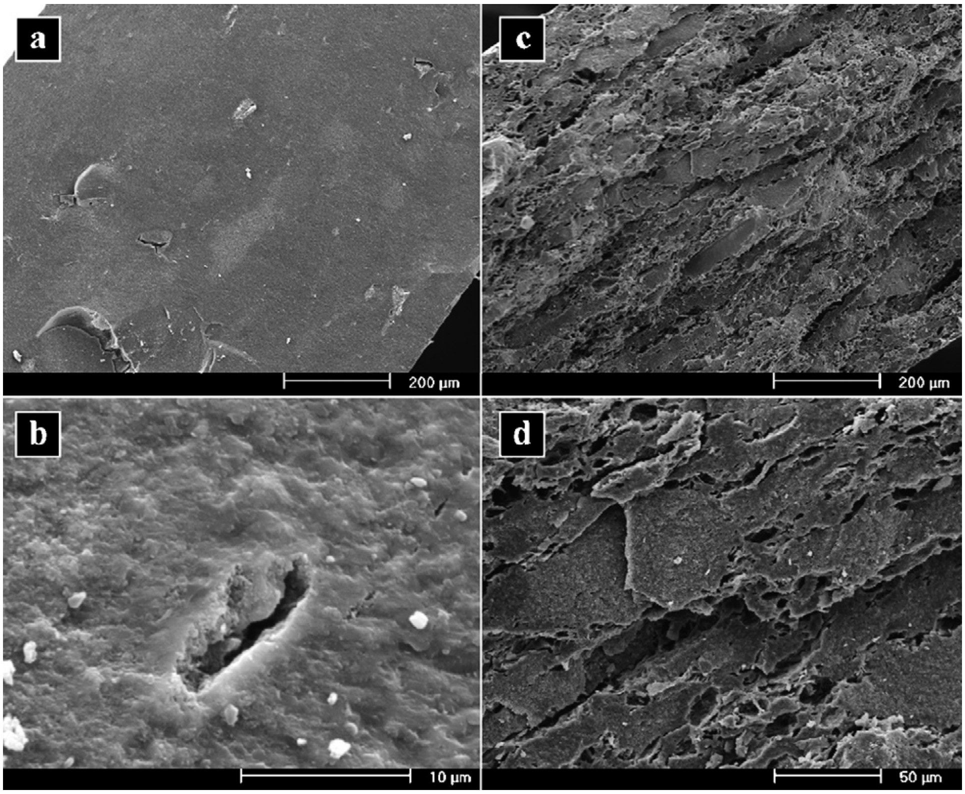

Fig. 3. SEM micrographs of selected mullite samples, after firing at 1450 °C: (a and b) silicone/Al_2O_3 and (c and d) silicone/Al_2O_3/calcined clay.

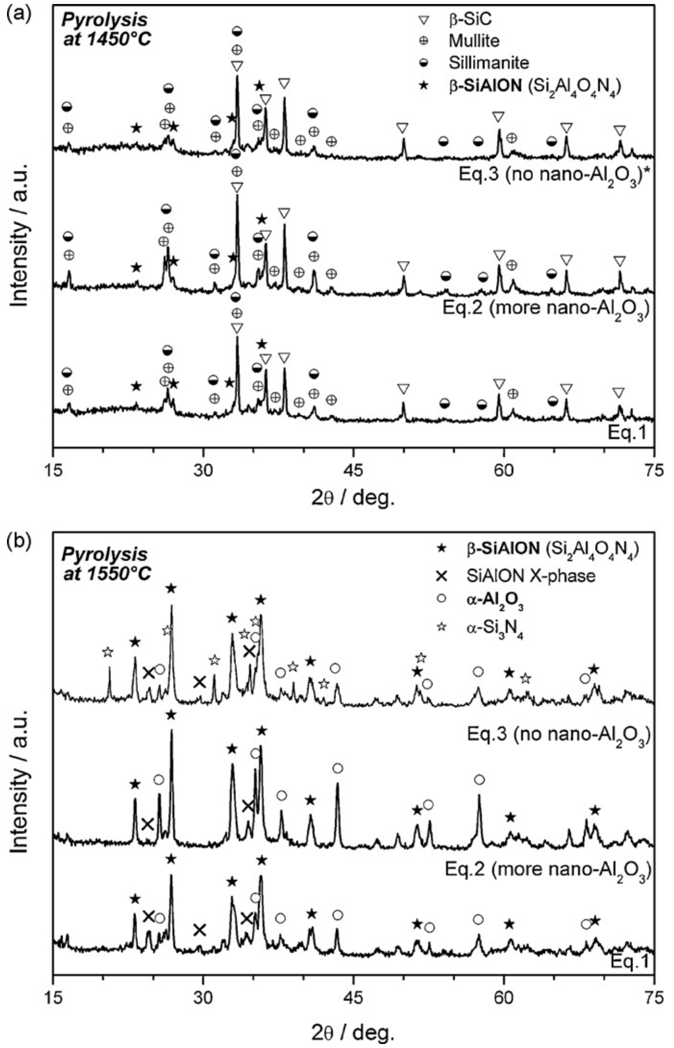

Fig. 4. Evolution of phases for the compositions intended for SiAlON synthesis: (a) treatments at 1450 °C and (b) treatments at 1550 °C. *The mixture of Eq. (3) was tested at 1450 °C without Si_3N_4.

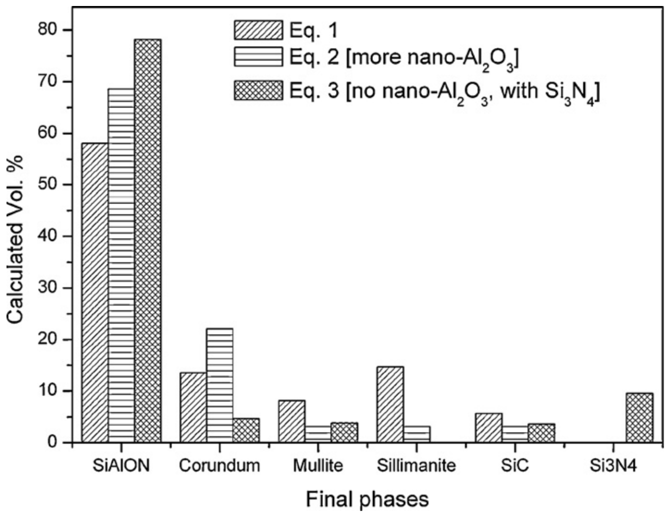

Fig. 5. Balance of the phases (deriving from Rietveld's analysis of XRD patterns) for SiAlON-based ceramics treated at 1550 °C.

will be probably clarified by substituting, as reported previously, metakaolinite with pure mullite "seeds".

Unlike mullite synthesis, SiAlON preparation from a filled preceramic polymer was very complex. The basic mixture proposed for SiAlON synthesis, corresponding to Eq. (1), led to foamed samples. The heating temperature, 1450 or 1550 °C, had a remarkable effect on the phase assemblage in the ceramic products, as shown by Fig. 4a. At 1450 °C, only mullite, sillimanite ($Al_2O_3\cdot SiO_2$) and β-SiC are clearly visible in the diffraction pattern. Some traces of β-SiAlON are also present. A significant β-SiAlON formation was achieved upon heat treatment at 1550 °C for 2h; corundum (α-Al_2O_3) and SiAlON X-phase ($Si_3Al_6O_{12}N_2$) are also visible. It must be noted that the closest fitting of XRD peaks is given by $Si_2Al_4O_4N_4$ instead of $Si_3Al_3O_3N_5$ (i.e. the degree of solid solution of Al and O atoms in the β-Si_3N_4 structure is higher than expected).

Eq. (1) was formulated in the hypothesis of a direct reaction between Si and O atoms from SiOC and the fillers. The full carbon content of SiOC was supposed to favour carbothermal reduction and nitridation. Aluminium nitride was intended to adjust the Si/Al balance and introduce more nitrogen, in addition to that from the atmosphere. The evidences of the XRD patterns undoubtedly contradicted this scheme.

A phase separation within the SiOC residue reasonably occurred, so that three different species, i.e. SiO_2, SiC and some "free" C, should be considered to react independently. The formation of alumino-silicate phases represents a fundamental example of this phenomenon. Mullite and sillimanite may be attributed only to the reaction of the silica fraction of SiOC with both nano-Al_2O_3 (the previous experiences about mullite show that this filler is highly reactive) and AlN (since the Al_2O_3 content of all composition is too low for extensive mullitization). If we consider the mullite formation from the oxidation of AlN, N_2 gas should be released and this may cause the foaming, effectively observed. Mullite is reported to be actually a source for the corundum contamination, also revealed in the XRD, due to its reduction/nitridation to SiAlON, as follows[17]:

$$3Al_2O_3\cdot 2SiO_2 + 6C + 2N_2 \rightarrow Si_2Al_4O_4N_4 + 6CO + Al_2O_3$$

X-phase SiAlON can be seen as intermediate stage of nitridation, due to its similarity to mullite (a quarter of silica units of mullite is replaced by silicon nitride units [$Si_3Al_6O_{12}N_2 = 3Al_2O_3\cdot 1.5SiO_2\cdot 0.5Si_3N_4$]).[4]

The presence of SiC, at 1450 °C, lowered both the amount of carbon for nitridation and the amount of Si in the final ceramic product, and this is consistent with the formation of $Si_2Al_4O_4N_4$ instead of $Si_3Al_3O_3N_5$.

Eqs. (2) and (3) were hypothesized in order to confirm the already reported observations. In Eq. (2) the SiC fraction in the SiOC, estimated in the order of 16 wt%,[20] was considered to act as a separate species, so that only the "free" carbon was expected to be active for nitridation. Eq. (3) refers to the absence of nano-Al_2O_3, the most probable origin for alumino-silicates, and the expected solid substitution degree of SiAlON was lowered by the introduction of Si_3N_4; in addition, some carbon excess was intended to favour nitridation.

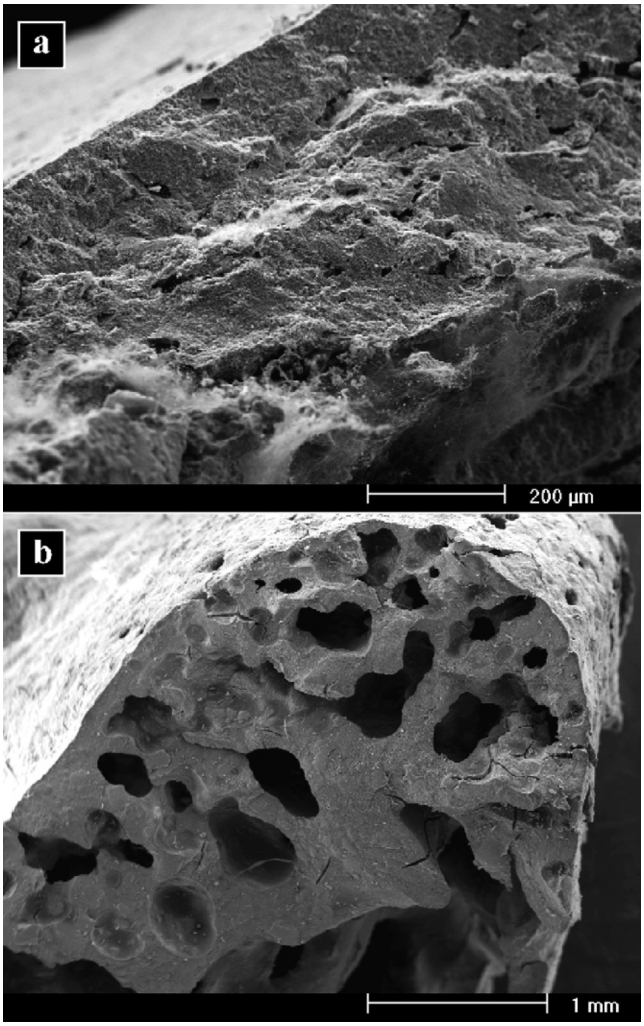

Fig. 6. SEM micrographs of SiAlON-based ceramics from silicone/filler mixtures based on Eq. (2) (a) and Eq. (3) (b).

Fig. 4b (see the typical peaks of $Si_2Al_4O_4N_4$) evidences that some improvements in the SiAlON yield, at 1550 °C, were achieved with Eqs. (2) and (3). This is substantially confirmed by the refinements of XRD patterns, whose results are illustrated by Fig. 5. Even if there are some uncertainties in the balance of the phases, due to the lacking of crystallographic information about X-phase SiAlON, the yield of β-phase passed from 58 vol.% Eq. (1) to 69 vol.% Eq. (2) and 78 vol.% Eq. (3).

Eq. (2) led to porous monoliths (Fig. 6a). Eq. (3) led to foams (Fig. 6b), like those related to Eq. (1), containing mullite and sillimanite, at 1450 °C, and some corundum contamination, at 1550 °C, even without nano-Al_2O_3 in the raw materials. As a consequence, alumino-silicates may be effectively produced by the oxidation of AlN, with the effect of foaming. The high reactivity of nano-Al_2O_3, more abundant for the formulation of Eq. (2), reasonably caused a lower oxidation of AlN and prevented from extensive foaming.

The remarkable corundum presence for samples related to Eq. (2) may be correlated to the formation of SiC, which may lead to volatile SiO interacting with silica ($2SiO_2 + SiC \rightarrow 3SiO + CO$)[23]: the lowering of the Si/Al ratio causes the impossibility of incorporating all Al and O atoms in the SiAlON structure.

The samples related to Eq. (3), besides a much lowered oxide contamination, exhibited the presence of residual Si_3N_4. Si_3N_4 was attractive for the possibility of interacting with corundum by-product (thus providing "secondary SiAlON"). This reaction is likely the reason for the improved SiAlON yield, but it was not complete. This may be due both to the lower reactivity of microsized powders compared to nano-powders (owing to the much lower specific surface area) and to the dominant content of α-phase, having a different structure to that of β-phase and no tendency to accommodate Al and O in the structure as in β-SiAlON, except in the presence of other modifying cations.[24] Amorphous and nano-sized Si_3N_4, in the formulations related to both Eqs. (2) and (3), is expected to react more properly with corundum and will be tested in future experiences.

Although the products are impure, the formulations for β-SiAlON may have application in the preparation of nanocomposite foams (for the compositions leading to highly porous bodies) or in the joining of SiAlON articles (for the composition leading to less porous ceramics).

4. Conclusions

A variously filled silicone resin has been successfully employed for mullite and SiAlON synthesis, in oxidative or reducing atmosphere, respectively. Some key points, useful for the actual exploitment of the proposed processing have been evidenced, as follows:

- The processing of silicone/Al_2O_3 nano-filler mixtures allows the obtainment of chemically pure, fine grained, crack free and dense mullite ceramics at a relatively low temperature of 1250 °C; mullitization is practically complete for treatments at 1350 °C;
- The processing of silicone/Al_2O_3 nano-filler/calcined clay mixtures allows the obtainment of pure mullite ceramics at 1450 °C; the presence of mullite "seeds" from the decomposition of clay allows mullitization of silica (from silicone) and Al_2O_3 nano-filler even below 1250 °C. Silicone/Al_2O_3 nano-filler/mullite seeds mixtures are reasonably attractive for further experiments;
- The processing of silicone/AlN/Al_2O_3 nano-filler mixtures allows the formation of β-SiAlON based ceramics upon pyrolysis at 1550 °C;
- Alumino-silicate phases, like mullite and sillimanite, are key intermediates in the synthesis of β-SiAlON and mullite is the most probable source for the observed corundum contaminations. Mullite formation from AlN filler is likely the origin for the high porosity of the produced SiAlON based ceramics;
- The phase separation within the SiOC residue of the silicone resin, upon pyrolysis, must be taken into account in future formulations; moreover, the SiAlON yield may be improved by adding nano-sized Si_3N_4 filler, reacting with the corundum contaminations.

References

1. Schneider, H., Okada, K. and Pask, J., *Mullite and Mullite Ceramics*. John Wiley and Sons Ltd., Chichester, UK, 1994, pp. 1–251.
2. Viswabaskaran, V., Gnanam, F. D. and Balasubramanian, M., Mullitisation behaviour of calcined clay–alumina mixtures. *Ceram. Int.*, 2003, **29**, 561–571.
3. Bartsch, M., Saruhan, B., Schmucker, M. and Schneider, H., Novel low-temperature processing route of dense mullite ceramics by reaction sintering of amorphous SiO_2-coated γ-alumina particle nanocomposites. *J. Am. Ceram. Soc.*, 1999, **74**, 2448–2452.
4. Jack, K. H., The crystal chemistry of the sialons and related sialon ceramics. In *Nitrogen Ceramics*, ed. F. L. Riley. Noord-hoff International, Leyden, The Netherlands, 1976, pp. 109–126.
5. Gauckler, L. J., Prietzel, S., Bodemer, G. and Petzow, G., Some properties of β-Si6-*x*Al*x*O*x*N8-*x*. In *Nitrogen Ceramics*, ed. F. L. Riley. Noord-hoff International, Leyden, The Netherlands, 1976, pp. 529–535.
6. Schneider, H., Voll, D., Saruhan, B., Sanz, J., Schrader, G., Ruscher, C. and Mosset, A., Synthesis and structural characterization of non-crystalline mulliteprecursors. *J. Non-Cryst. Solids*, 1994, **178**, 262–271.
7. Soraru, G. D., Kleebe, H.-J., Ceccato, R. and Pederiva, L., Development of mullite-SiC nanocomposites by pyrolysis of filled polymethylsiloxane gels. *J. Eur. Ceram. Soc.*, 2000, **20**, 2509–2517.
8. Ivankovic, H., Tkalcec, E., Nass, R. and Schmidt, H., Correlation of the precursor type with densification behavior and microstructure of sintered mullite ceramics. *J. Eur. Ceram. Soc.*, 2003, **23**, 283–292.
9. Chaudhuri, S. P. and Patra, S. K., Preparation and characterization of transition metal ion doped mullite. *Trans. Br. Ceram. Soc.*, 1997, **97**, 105–111.
10. Kaya, C., Gu, X., Al-Dawery, I. and Butler, E. G., Microstructural development of woven mullite fibre-reinforced mullite ceramic matrix composites by infiltration processing. *Sci. Technol. Adv. Mater.*, 2002, **3**, 35–44.
11. Hirata, Y., Aksay, I. A., Kurita, R., Hori, S. and Kaji, H., Processing of mullite powders processed by CVD. In *Ceramic Transactions Mullite and Mullite Matrix Composites*, *vol. 6*, ed. S. Somiya, R. F. Davies and J. A. Pask. American Ceramic Society, Westerville, OH, 1990, pp. 119–126.
12. Sacks, M. D., Wang, K., Scheiffele, G. W. and Bozkurt, N., Effect of composition on mullitization behavior of α-alumina/silica microcomposite powders. *J. Am. Ceram. Soc.*, 1997, **80**, 663–672.
13. Liu, K. G. and Thomas, G., Time-temperature transformation curves for kaolinite-α-alumina. *J. Am. Ceram. Soc.*, 1994, **77**, 1545–1552.
14. Sainz, M. A., Serrano, F. J., Amigo, J. M., Bastida, J. and Caballero, A., XRD microstructural analysis of mullites obtained from caolinite-alumina mixtures. *J. Eur. Ceram. Soc.*, 2000, **20**, 403–412.
15. Dutta, S., Fabrication, microstructure, and strength of sintered β'-Si_3N_4 solid solution. *Am. Ceram. Bull.*, 1980, **59**, 623–625.
16. Lee, J.-G. and Cutler, I., Sinterable sialon powder by reaction of clay with carbon and nitrogen. *Am. Ceram. Bull.*, 1979, **58**, 869–871.
17. Liu, X.-J., Sun, X. W., Zhang, J. J., Pu, X. P., Ge, Q. M. and Huang, L. P., Fabrication of β-SiAlON Powder from Kaolin. *Mater. Res. Bull.*, 2003, **38**, 1939–1948.
18. Renlund, G. M., Prochazka, S. and Doremus, R. H., Silicon oxycarbide glasses. Part I. Preparation and chemistry. *J. Mater. Res.*, 1991, **6**, 2716–2722;
    Renlund, G. M., Prochazka, S. and Doremus, R. H., Silicon oxycarbide glasses. Part II. Structure and properties. *J. Mater. Res.*, 1991, **6**, 2723–2734.
19. Greil, P., Active-filler-controlled pyrolysis of preceramic polymers. *J. Am. Ceram. Soc.*, 1995, **78**, 835–848.
20. Scheffler, M., Takahashi, T., Kaschta, J., Muensted, H., Buhler, P. and Greil, P., Pyrolytic decomposition of preceramic organo polysiloxanes. In *Innovative Processing and Synthesis of Ceramics, Glasses, and Composites IV: Ceramic Transactions, vol. 115*, 2000, pp. 239–250.
21. http://www.ing.unitn.it/~luttero/maud/.
22. Bernardo, E., Colombo, P., Pippel, E. and Woltersdorf, J., Novel mullite synthesis based on alumina nanoparticles and a preceramic polymer. *J. Am. Ceram. Soc.*, 2006, **89**, 1577–1583.
23. Ewing, H., Vital, A., Vogt, U. and Hendry, A., The nucleation and growth mechanism of Si–N–O fibres. *Mater. Sci. Forum*, 2000, 325–326, 37–42.
24. Hampshire, S., Park, H. K., Thompson, D. P. and Jack, K. H., α-Sialon ceramics. *Nature*, 1978, **274**, 880–883.