

Development and Characterization of Si-Al-O-N-C Ceramic Composites Obtained from Polysiloxane-Filler Mixtures

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Abstract : Manufacturing and microstructure of novel materials in the Si-Al-O-N-C system derived from polymer-filler mixtures were investigated. Silicon (Si) and aluminium (Al) were added to a poly(methyl and phenyl)siloxane matrix to react with the carbon-bearing products that result from the decomposition of the latter during pyrolysis. This was carried out in nitrogen atmosphere up to 1500 degrees for 2h. Silicon Carbide (SiC) particles were used as inert filler embedded in the polymer/active filler mixture. Green bodies of the metal/polysiloxane mixtures were pressed and cured at 170 °C for 30min. Microcrystalline composites, such as SiC, AlN and SiAlON, from the filler reaction products embedded in a silicon oxycarbide glass matrix could be formed with complex geometry through near-net-shape process of polymer/ceramic conversion.

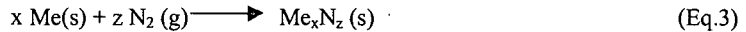
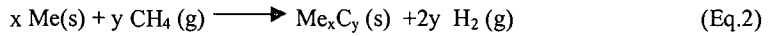
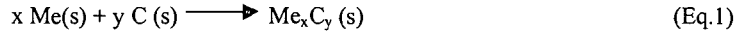
Introduction

The conventional preparation method of ceramic composites based on non-oxide powders, such as AlN, SiC, Si₃N₄, usually involves densification at very high temperatures (1700-2500 °C) and the use of pressure (hot pressing and hot isostatic pressing). Due to the extremely low self-diffusion constants of these materials, sintering aids are normally used to improve densification, when sintering is carried out without pressure [1]. Oxide-based sintering additives tend to form glass-like secondary phases at the grain boundaries, which due to their relatively low softening temperatures can be detrimental to the mechanical and physical properties of the material, especially at higher temperatures [2].

A low temperature process to manufacture ceramic composites from a preceramic polymer has been shown to be a promising technique. This method allows the preparation of monolithic ceramic blocks, via a process that excludes powder sintering phenomena [3-6]. The possibility to prepare polymers or polymer-like precursors containing at least one element other than carbon in the main chain, has been known for almost 100 years, with Kipping being the first to synthesize a simple silicone. The fact, that ceramic materials can be prepared from these precursors, however, has been attributed to Yajima et al and Veerbeek et al, which had the first initiatives in this field [7,8]. Later, a whole range of organosilicon polymers of high ceramic yield could be synthesized and the ceramic residue after pyrolysis could be investigated [9]. Attractive features of this route, compared to conventional methods, are low temperature processing methods, the possibility to synthesize novel non-oxide compounds and the use of high-purity starting materials.

The major drawback that until recently hindered the production of components from preceramic polymers rather than thin films or fibers is the enormous shrinkage (up to 60 vol%) and density increase (from ~ 1 g.cm⁻³ for the polymer to 2-3 g.cm⁻³ for the ceramic) that occur during the polymer-to-ceramic conversion. These behaviors usually lead to highly porous and cracked products.

An alternative route to avoid these problems may be through the dispersion of filler powders in the polymer precursor, which gives the possibility to reduce shrinkage and porosity. Active fillers (Me) can lower the shrinkage during polymer-to-ceramic conversion by reacting either with carbon-containing solid (Eq. 1) and gaseous (Eq. 2) decomposition products of the polymer phase or, with a reactive gas atmosphere (N₂) (Eq. 3) to form carbides, nitrides, oxides or mixtures [10,11]. The following equations illustrate the type of reactions that may take place:



These reactions can in fact occur with an expansion of the filler particles. Polysiloxane (RSiO_{1.5})_n, where R=H, CH₃, C₆H₅, C₂H₅, and so forth, is a relatively inexpensive polymer precursor produced in an industrial scale and provide an easy route to Si-O-C ceramic phase [12]. The microstructure of the resulting ceramic composites consists of the filler reaction product embedded in the polymer-derived Si-O-C matrix [13]. When polysiloxanes are used as preceramic polymers, an amorphous silicon oxycarbide glass is formed above 800 °C which crystallizes into SiC, SiO₂ and C at temperatures above 1200 °C [3].

The aim of this work is to process and characterize monolithic ceramic composites bodies in the system Si-Al-O-N-C, using silicon (Si) and aluminum (Al) as reactive fillers dispersed in poly(methylsiloxane) and poly(phenylsiloxane). Homogeneous powder mixtures of 40 vol% of the filler powder (a mixture of 1:1 of Al and Si in volume) in the polymeric matrix (previously dissolved in suitable solvents) were obtained and used for consolidating the samples. Fired in nitrogen atmosphere, the materials could be used either as ceramic composite themselves, or could have the function of ceramic matrix for particle reinforced ceramic composites. In this last approach, large particles of SiC were surrounded by the matrix formed from the polymer precursor/(Al-Si) mixture to work as inert fillers.

Experimental Procedure

This work focuses on filled silicones, also known as polysiloxanes. Two types of commercially available polysiloxanes were chosen as preceramic precursors. Poly(methylsiloxane), PMS, (Mk, Wacher Chemie, Germany) of low carbon content (17 wt%) and a phenyl-containing poly(siloxane), PPS, (H62, Wacher Chemie, Germany), of high carbon content (45.5 wt%). Table 1 summarizes the raw material data, as provided by suppliers. The PMS contains silanol groups which undergo a condensation reaction upon heating above 150 °C, resulting in the release of H₂O. Curing reaction of PPS is governed by hydrosilation via vinyl groups at similar temperatures.

Table 1: Characteristics of the poly(siloxanes) PMS and PPS used as raw materials.

Polymer	Poly(phenylmethylhydrogensiloxane)-PPS	Poly(methylhydrogensiloxane)-PMS
Composition	RSiO _{1.5} ; R= [(C ₆ H ₅) _{2.8} (CH ₃) _{1.5} , (CH ₂ =CH), (H)] liquid	RSiO _{1.5} ; R= [(CH ₃)] ; powder
Polymerisation mechanism	Polyaddition	Polycondensation
Solvent	Isopropanol, Aceton	Isopropanol, Aceton
Density (23 °C) (kg m ⁻³)	1,1-1,5	1,1-1,31
Melting point (°C)	RT liquid	≥ 45
Viscosity (23 °C) (m ² s ⁻¹)	1.4 x 10 ⁻³ ± 4 x 10 ⁻⁴	powder

Aluminum (Al) and silicon (Si) used as active fillers and silicon carbide (SiC) as an inert filler (SiC), were mixed with the polymer. The samples were named as follows:

- (I) 60MS(20Al20Si)
- (II) 30MS30PS(20Al20Si)
- (III) 60MS(20Al20Si):30vol%SiC.

The composition of samples (I) and (II) was fixed at 60 vol% polymer phase (where MS is poly(methyl)siloxane) and PS is poly(phenyl)siloxane) and 40 vol% active filler Al and Si (in a 1:1 ratio). Sample (III) corresponds to 30 vol% of SiC particles involved by 70 vol% by the matrix formed from the same composition of sample (I).

Polymer and fillers were mixed with help of a solvent (acetone) and homogenized by mechanical and ultrasonic stirring. After removing the solvent using hot plate with magnetic stirring, the mixtures were dried at 45 °C for 12h and then milled and sieved (150 μm) to obtain a fine powder. Cylindrical specimens with diameters of 30 mm were formed by uniaxial warm pressing with a pressure of 40 MPa and 170 °C for 30 min. During warm pressing, poly(methylsiloxane) curing via polycondensation of Si:OH groups takes place resulting in an unmeltable thermoset. Aluminum acetylacetonate ($\text{AlO}_6\text{C}_{15}\text{H}_{21}$) was added as the curing catalyst (0.1 wt%). The specimens were cut and pyrolysed in an electrically heated tube furnace, in nitrogen atmosphere. A typical heating cycle involved heating up to 500 °C at 5 °C/min, holding this temperature for 4h, a second ramp at 3 °C/min up to the final temperature of 1450 / 1500 °C with 2h dwell time, and a final cooling ramp at 10 °C/min.

The bulk density of the pyrolysed samples was measured by the Archimedes method, using distilled water. The open porosity was determined by measuring the absorbed water volume. Weight and dimension variation were examined by weighting and measuring the thickness of the samples before and after pyrolysis. Phase analysis of the crystalline constituents was examined by X-ray diffraction using monochromated $\text{CuK}\alpha$ -radiation. Microstructure of the pyrolysed material was analyzed by scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) for element mapping.

Results and Discussion

Fig. 1 shows the particle size distribution of the three different fillers Al, Si and SiC measured by laser scattering.

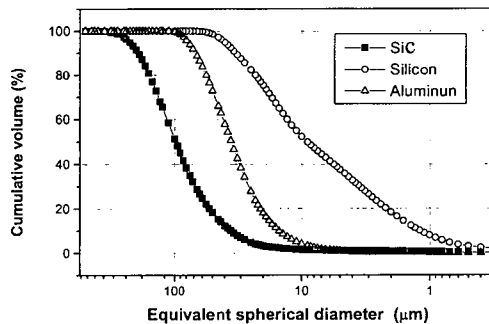


Fig. 1-Particle size distribution curves of the filler powders Al, Si (reactive) and SiC (inert).

The green bodies produced from the mixture of polysiloxane and the metal powders were compact and withstood to machining and drilling, without change in shape after pyrolysis and visually crack free (Fig. 2).

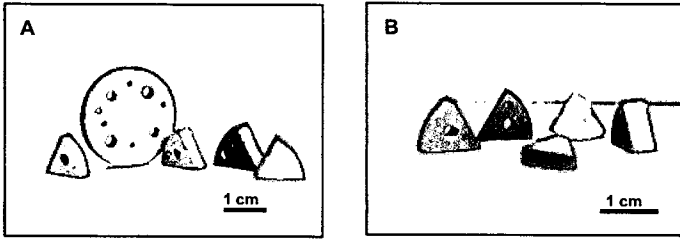


Fig. 2- Cut and drilled samples obtained from the active filler polymer pyrolysis process. (a) Green samples and (b) samples pyrolysed at 1450 °C and 1500 °C for 2h in N₂.

Fig. 3 shows SEM micrographs of polished surfaces of the sample (II) before and after pyrolysis. Metal phase distribution in the polymeric matrix could be observed in the green samples using back-scattering electrons. In the same way, white spots surrounded by the Si-Al-O-C matrix were observed in polished samples after pyrolysis, for both 1450 and 1500 °C. Using the energy dispersive spectroscopy (EDS) in the reacted samples (Fig 3b), these light gray spots were identified as silicon, which have not reacted during pyrolysis. Fig. 4 shows a micrograph of the silicon spot at higher magnification and the EDS of three different chosen regions.

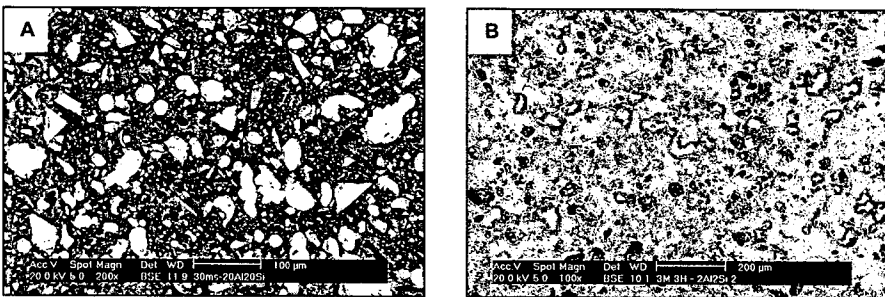


Fig. 3- SEM micrographs of polished surface of the specimen 30MS30PS(20Al20Si). (a) before pyrolysis and (b) after pyrolysis at 1450 °C/2h.

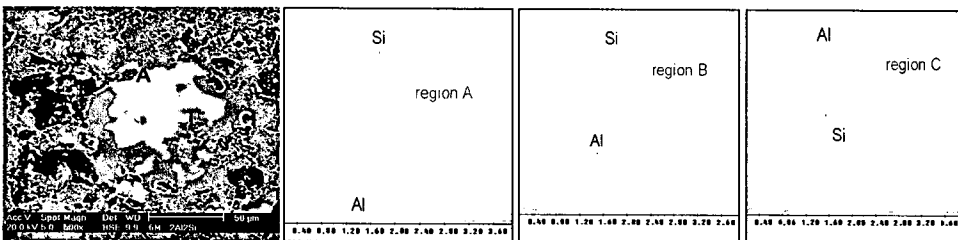


Fig. 4 – SEM micrograph using back-scattering electrons showing Si particles embedded in a Si-Al based matrix, as determined by EDS spectra.

Fig. 5 gives X-ray spectrum of the specimens 60MS(20Al20Si), 30MS30PS(20Al20Si) and 60MS(20Al20Si) 30vol%SiC, pyrolysed in 1450 °C and 1500 °C for 2h. Silicon was also identified in the X-ray diffraction patterns for in all samples. However the peak intensity for residual Si (111) decreased with increasing temperature. Crystalline phases, such as β -SiC, α -SiC AlN and SiAlON, were also identified.

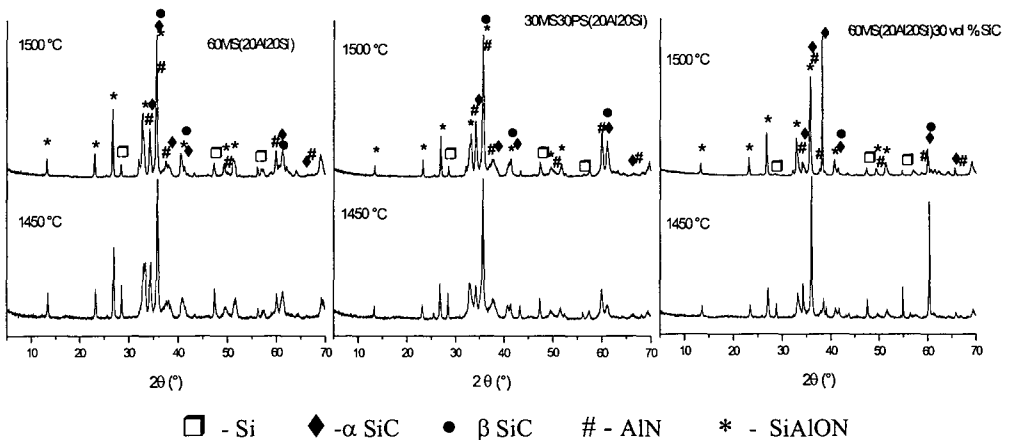


Fig. 5-X-ray diffraction patterns of specimens: (a) 60MS(20Al20Si); (b) 30MS30PS(20Al20Si); (c) 60MS(20Al20Si):30vol%SiC.

Table 2 displays the data of density, porosity, weight and dimensional variation of the bodies pyrolysed at 1450 °C and 1500 °C for 2 h. All samples showed an increase in their weight, owing to nitrogen consumption during pyrolysis, for both treatment temperatures. The little change in shape was demonstrated by the much smaller linear variation after pyrolysis (0.5 – 2.1%) than those typically found in the conventional sintering processes (15 to 20%)[1,2]. The observed linear variation was isotropic for all compositions, though samples with PMS showed a positive variation, and samples with PPS showed a negative one.

Table 2. Data of apparent densities, porosity, weight and linear variation for the prepared composites.

Composites	Density (g/cm ³)		Porosity (%)		Weight change (%)		Linear change (%)	
	1450 °C	1500 °C	1450 °C	1500 °C	1450 °C	1500 °C	1450 °C	1500 °C
60MS(20Al20Si)	2.28	2.21	21.5	22.4	10.9	11.7	1.6	2.1
30MS30PS(20Al20Si)	2.30	2.28	19.5	20.2	14.0	14.1	-2.4	-0.2
[60MS(20Al20Si)]-30SiC	2.25	2.13	26.6	28.1	11.1	11.8	0.5	1.3

Regardless of the carbon content or the presence of SiC particles the porosity for all samples (19.5 – 28.1 %), was relatively high compared to ceramics obtained by conventional sintering of non-oxide powders at elevated temperatures. The samples exhibited a slight increment in porosity with the increase in temperature. Samples with SiC particles showed the highest porosity, probably owing to the low adhesion between the reacted matrix and the large SiC particles during pyrolysis.

Fig. 6 shows micrographs of the fracture surface of each composition after pyrolysis at 1500 °C/2h. These micrographs give clear evidence of the large porosity volumes in the samples. At higher magnification, different structures could be observed inside the large pores and channels, such as whisker and platelet formation. The mechanism of the whisker formation is related to a process in which material is transported through vapour phase during the heating process [14].

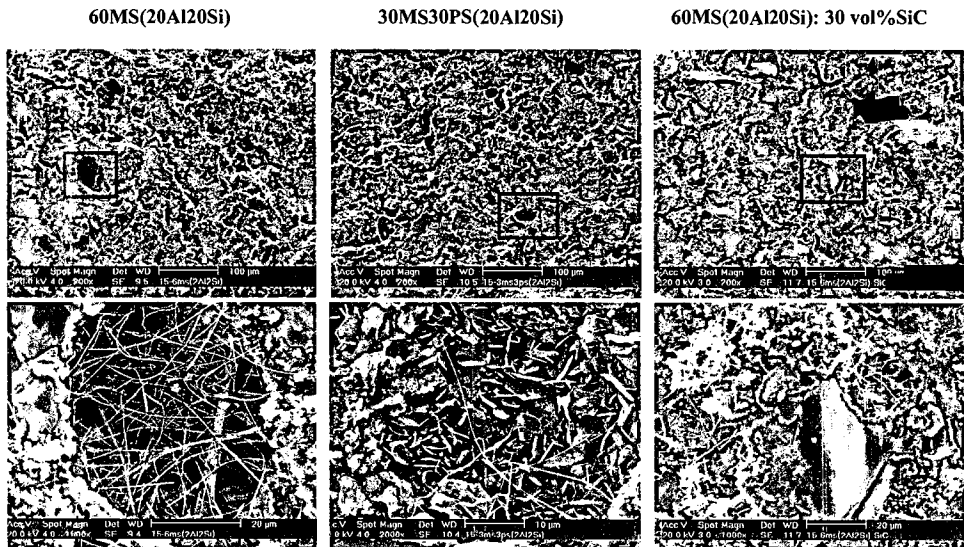


Fig. 6- SEM micrographs of the surfaces fracture of all samples pyrolysed at 1500 °C/2h and at higher magnification the corresponding micrographs showing details of the microstructure.

Conclusions

Ceramic composites based on non-oxide materials can be easily manufactured, from a preceramic polymer and a mixture of Al/Si active filler, under nitrogen atmosphere. The bodies maintained their shape and showed very low dimensional change after pyrolysis, compared with powder sintering techniques. Using Si and Al powders as active fillers, even for samples pyrolysed at 1500 °C/2h, the metallic phase still remained unreacted. Interesting crystalline phases that originated during pyrolysis are AlN, SiC, Si₃N₄ and SiAlON. Despite the relative high content of porosity, these materials seem promising for application as matrix in ceramic matrix composites, or as refractories.

Acknowledgements

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