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Si_3N_4/SiC Nanocomposite Powder from a Preceramic Polymeric Network Based on Poly(methylsilane) as the SiC precursor

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Si_3N_4/SiC nanocomposite powders were obtained from a preceramic polymeric network based on poly(methylsilane) as the *in situ* quasi-stoichiometric SiC source. These powders were constituted of nanosized SiC particles homogeneously distributed in the Si_3N_4 particulate matrix. β-SiC whiskers were grown at 1400 °C in the pores of the matrix. At 1600 °C, the $\alpha \rightarrow \beta$ Si_3N_4 phase transition took place, but no elemental silicon from Si_3N_4 decomposition was detected, evidencing the protective effect of the SiC phase.

Keywords: *composite powders, silicon nitride, silicon carbide*

1. Introduction

Silicon nitride-silicon carbide (Si_3N_4/SiC) composites have received a great deal of attention in high temperature structural applications, such as turbine and automobile engine components and heat exchangers, due to their potentially high strength and toughness, and good creep resistance[1-6]. However, these good characteristics are difficult to achieve by the conventional mixture of SiC and Si_3N_4 commercial powders.

Several methods have been described to produce small-sized Si_3N_4 and/or SiC powders in a homogeneous mixture, such as: plasma synthesis, in which Si_3N_4 particles or Si-C-N powders are carbon-coated[2,3]; generation *in situ* of micrometer size β-Si_3N_4, from Si powder with flowing N_2/H_2 gas mixture reaction on SiC particles[7]; and polymeric precursors[1,8,9]. This last route offers the possibility of improving the compositional homogeneity and tailoring the composition and molecular structure of the ceramic powders. Furthermore, the solubility and the rheology of polymeric precursors provide potential processing routes to binders, to sintering aids and to the formation of thin films and fibers, which are often difficult or impossible to achieve by the more traditional ceramic processing techniques[10-12].

Small-sized Si_3N_4 and/or SiC powders can be processed by several methods, to produce ceramic composites with excellent mechanical properties, at ambient and high temperatures, and good oxidation resistance[2,3,13-16].

In a previous study, a polysilane network prepared from poly(methylsilane), PMS, and tetra-allylsilane, TAS, was used as a precursor of a quasi-stoichiometric SiC, in a reasonable yield (~60%)[17]. In this study, Si_3N_4/SiC nanocomposite powder was obtained from a mixture of PMS/TAS and Si_3N_4 powder, to investigate the evolution of the microstructure and crystalline phases of the composite powder, in relation to the temperature of pyrolysis. No attempts to obtain the composite in any pre-determined shape was made in the present investigation.

2. Experimental

2.1. Materials

Si_3N_4 powder (Hüls) (325 mesh) was used as received from the manufacturer. Poly(methylsilane) was synthesized by polycondensation of CH_3SiHCl_2 in the presence of Na, in toluene[18], and tetra-allylsilane was prepared through Grignard route[19]. Si_3N_4/SiC nanocomposite powder was prepared by the mixture of 4 g of Si_3N_4 powder, 1 g of PMS and 0.5 cm^3 of TAS, giving rise to a very viscous slurry, which was poured into an alumina crucible. This procedure was made in a glove box filled with dry argon. The pyrolysis was carried out in an EDG tube furnace (model EDGCON 5P) equipped with an internal alumina tube and a temperature controller, under an argon flow (Air Liquid, 50 mL/min, 99.9 %). The mixture was heated to 180 °C, at 5 °C/min, keeping the sample at this temperature for 60 min; then a second ramp to 350 °C, at 5 °C/min, remaining at this plateau for 90 min, and a third ramp to 1000 °C, at 2 °C/min, followed by holding at this temperature for 120 min. Finally, the sample was cooled

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down to room temperature, at 2 °C/min. Three fractions of the resulting powder received distinct thermal treatments in a Thermolyne tube furnace (model F59340-CM): the first one was heated up to 1200 °C, at 10 °C/min, under an argon flow, keeping at this temperature for 2 h; the second fraction received thermal treatment up to 1400 °C, and finally, the third fraction was heated up to 1600 °C, both keeping at the final temperature for 2 h, under the same condition. The ceramic yield was determined by thermogravimetric analysis (TGA), at 1000 °C.

2.2. Instrumentation

The composition of the powders was determined by crossing the results obtained by elemental analysis, ^{29}Si MAS NMR spectrum and X-ray fluorescence data. Carbon and nitrogen elemental analysis were performed in an elemental analyser (Perkin Elmer 2400) according to the procedure suggested by Ref. 20. Solid-state ^{29}Si magic-angle spinning nuclear magnetic resonance (^{29}Si MAS NMR) spectrum was acquired using a pulse angle of 75° and a delay of 1 h, on a Bruker AC300P instrument at 59.6 MHz, with spinning frequency of ~5 kHz. Silicon and metal traces in the samples were estimated by X-ray fluorescence, applying the fundamental parameters method, in a spectrometer Spectrace 5000 Tracor X-ray, using cellulose filter. The crystalline phases of the samples were investigated by X-ray diffractometry (XRD) using a diffractometer Schimadzu, model XD3A, with the CuKα radiation. The grain size values of the β-SiC, were calculated through the full width of half height measures of the XRD patterns, using the reflection centered at 35.6° (2θ) <111>. Transmission electron microscopy observations (TEM), were performed on a Zeiss CEM 902 microscope, with 80 eV. The samples were grounded to a very fine powder, which was then dispersed in isopropanol and transferred onto a 100 mesh copper grid (parlodium coated) using an eye dropper. Some observations were done in a field emission scanning electron microscope (FESEM) JEOL JSM-6340F. For these investigations, a thin layer of gold previously coated the samples.

3. Results and Discussion

A highly crosslinked polymeric network prepared from the mixture of PMS and TAS was based in a hydrosilylation reaction between SiH bonds, from PMS, and C=C bonds, from TAS, at around 200 °C[21]. The use of a polymeric network generated *in situ* as a ceramic precursor hinders the splitting of volatile organosilicon compounds during the pyrolysis process, increasing the ceramic yield[12]. At around 350 °C, the so-called Kumada's rearrangement took place, when Si-Si groups were converted into Si-CH_2-Si groups by the insertion of methyl side groups in the main chain of silicon[22]. The mineralization process (loss of organic and hydrogen groups) gradually occurred at temperatures above that, and finally, at around 800 °C, the crystallization of β-SiC took place[21]. A typical XRD pattern of the ceramic product obtained at 1000 °C is shown in Fig. 1, where the mean grain size of the crystal, estimated by the Scherrer's equation, was around 4 nm.

Si_3N_4 powder used in this work was present in the α and β crystalline forms. In addition, a certain amount of crystalline Si was found in this powder. From the XRD pattern of this sample, the following crystalline composition was estimated[23]: α-Si_3N_4 52%, β-Si_3N_4 40% and Si 8%. The total weight composition of this powder was estimated crossing data from X-ray fluorescence, ^{29}Si MAS NMR and elemental analysis (taking the amorphous fraction into account): Si_3N_4 82%, Si 7%, SiO_2 5%, free carbon 5%, and metals (mostly Fe, Ni and Cu) 1%.

Besides being the SiC precursor, the PMS/TAS mixture had also a binder role in the preceramic slurry. Conveniently, after pyrolysis it did not leave any undesirable residue in the final product, as other well-known binders do[24]. Interesting to note that usually oily or waxy binders perform better than powders[25].

The PMS/TAS reactive mixture presented an oily consistency. When its proportion was high in the preceramic slurry (PMS/TAS + Si_3N_4), sedimentation of the nitride powder occurred, and the fired material was heterogeneous (composition-wise). The Si_3N_4/PMS/TAS composition used in this work (see experimental section for details) was adjusted in order to avoid the mentioned sedimentation, and to guarantee the homogeneity of the ceramic powder composite.

TEM investigations of several fractions of the composite powder were undertaken. In all of them, a micro/nanomicrostructure was observed, with nanosized SiC particles dispersed in the surroundings of the α and β-Si_3N_4 crystals (crystalline arrangements were checked by XRD). Figure 2 shows a TEM micrograph of the Si_3N_4/SiC composite powder.

Some reports on the mechanical properties of processed Si_3N_4/SiC composite powders have shown that this intimate and uniform arrangement can lead to a material with excellent mechanical properties[1-3,11].

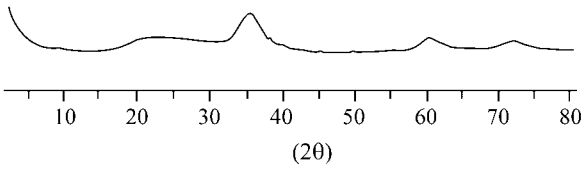

Figure 1. XRD of the ceramic powder obtained from the pyrolysis of the PMS/TAS, at 1000 °C, under argon flux.

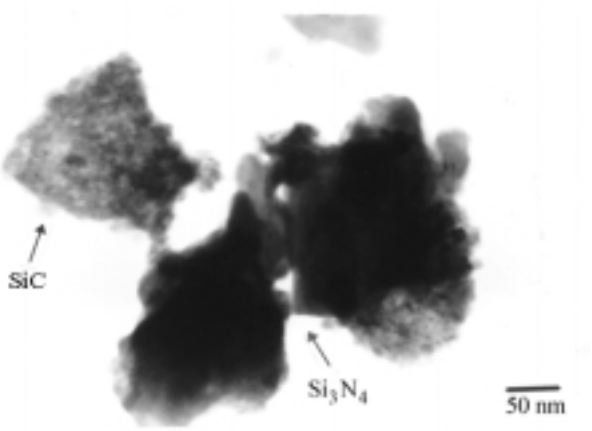

Figure 2. TEM micrograph of the Si_3N_4/SiC nanocomposite powder.

The evolution of the microstructure and crystalline phases of the Si_3N_4/SiC powder, was monitored after heating up to 1200 °C, 1400 °C and 1600 °C, for 2 h at each final temperature, under argon atmosphere. Figure 3 shows FESEM micrographs and XRD patterns of the products.

At 1200 °C, the composite powder showed a homogeneous nature, with no evidence of phase segregation at this amplification. In the respective XRD pattern, phases of β-SiC, Si, α- and β-Si_3N_4 could be observed. The estimation of the mean grain size of β-SiC crystals by the Scherrer's equation, was not possible, since the peak used for this calculation at 35.77° (2θ) was overlapped by the peak at 35.24° (2θ), assigned to α-Si_3N_4.[26] However, this peak was thinner than the analogous diffraction of the ceramic obtained from PMS/TAS, pyrolysed at 1000 °C, as it was shown in Fig. 1.

At 1400 °C, the SiC phase bridges neighbor Si_3N_4 grains at their interfaces, and a pronounced formation of β-SiC whiskers was observed. The estimated mean size of these whiskers (by FESEM) was 730 nm long and 26 nm wide. Also noticeable was the disappearance of Si signals in the X-ray pattern, suggesting that it was consumed at this temperature. The reaction between the Si impurity, which was present originally in the Si_3N_4 powder, and carbon was commonly thought to occur in the liquid phase[27], or even on the Si activated surface, as:

$$Si_{(s,l)} + C_{(s)} \rightarrow SiC_{(s)} \quad (1)$$

It is also well known that Si_3N_4 decomposes into liquid Si when heated at around 1450 °C, under inert atmosphere[28]. The result described above suggested that this decomposition became less significant in the presence of SiC phase.

The mechanism of the whisker formation is related to a process in which materials are transported to the vapor phase during the heating process. It has already been reported in the literature, that to grow SiC in whisker morphology, the presence of reactants in a vapor phase during the final stage of the reaction is necessary. Otherwise, particulate SiC would result[29,30]. The reactions involved can be summarized as:

$$SiO_{2(s)} + C_{(s)} \rightarrow SiO_{(g)} + CO_{(g)} \quad (2)$$

$$SiO_{(g)} + 2C_{(s)} \rightarrow SiC_{(s)} + CO_{(g)} \quad (3)$$

Hence, the overall reaction is:

$$SiO_{2(s)} + 3C_{(s)} \rightarrow SiC_{(s)} + 2CO_{(g)} \quad (4)$$

Distributing SiC whiskers uniformly in the ceramic matrixes is not an easy task. However, when it is done, the potential benefit of the whisker reinforcement is possible to achieve[31]. Considering the homogeneous nature of the Si_3N_4/SiC nanocomposite powder prepared in this work, it is reasonable to believe that β-SiC whiskers were uniformly distributed in the porous structure of Si_3N_4 grains.

At 1600 °C, a completely different microstructure was observed. SiC whiskers were no longer detectable. It seemed they were embedded in the Si_3N_4 matrix. The α-Si_3N_4 crystals underwent a phase transformation to β-Si_3N_4 [32]. The $\alpha \rightarrow \beta$ phase transformation occurs via a solution-precipitation process, and can be hindered by nanosized SiC particles. This effect appears to increase with increasing SiC content[33]. The transition observed suggested that probably there were not enough nanosized SiC particles in the powder composite, to hinder the $\alpha \rightarrow \beta$ Si_3N_4 phase transformation. This also explains the microstructure observed. The XRD pattern of this composite powder suggests a certain consumption of the Si_3N_4 phase, once the peak-height ratio of β-SiC to Si_3N_4 became greater. At this point, the mean size of the β-SiC crystals could easily be estimated as being approximately 83 nm.

It is interesting to observe that pure Si_3N_4 presents a distinct degradation process compared to the powder reinforced by SiC. While pure Si_3N_4 at 1600 °C under argon atmosphere is decomposed producing Si, there was no evidence of this element in the Si_3N_4/SiC composite powder, treated at the same condition. It is very reasonable to suppose that in the reaction of the SiO_2 impurity with carbon (reaction (2)), the $CO_{(g)}$ produced on the Si_3N_4 particle surface, altered the degradation process of the silicon nitride, to form SiC[34]:

$$3CO_{(g)} + Si_3N_{4(s)} \rightarrow 2SiC_{(s)} + 2N_{2(g)} + CO_{2(g)} + SiO_{(g)} \quad (5)$$

4. Conclusion

The pyrolysis of the PMS/TAS polymer as the *in situ* SiC source, in the presence of Si_3N_4 powder, gave rise to Si_3N_4/SiC nanocomposite powder with β-SiC uniformly distributed in the matrix of Si_3N_4 particles.

Growth of β-SiC whiskers was observed when the composite was heated at 1400 °C, under argon atmosphere. At 1600 °C, these SiC whiskers were embedded in the matrix, and the $\alpha \rightarrow \beta$ Si_3N_4 phase transformation took place. There was no evidence of Si formation, opposite to the behavior of pure Si_3N_4.

The results confirmed the basic concept that the thermal stability behavior of Si_3N_4/SiC composite powders can be

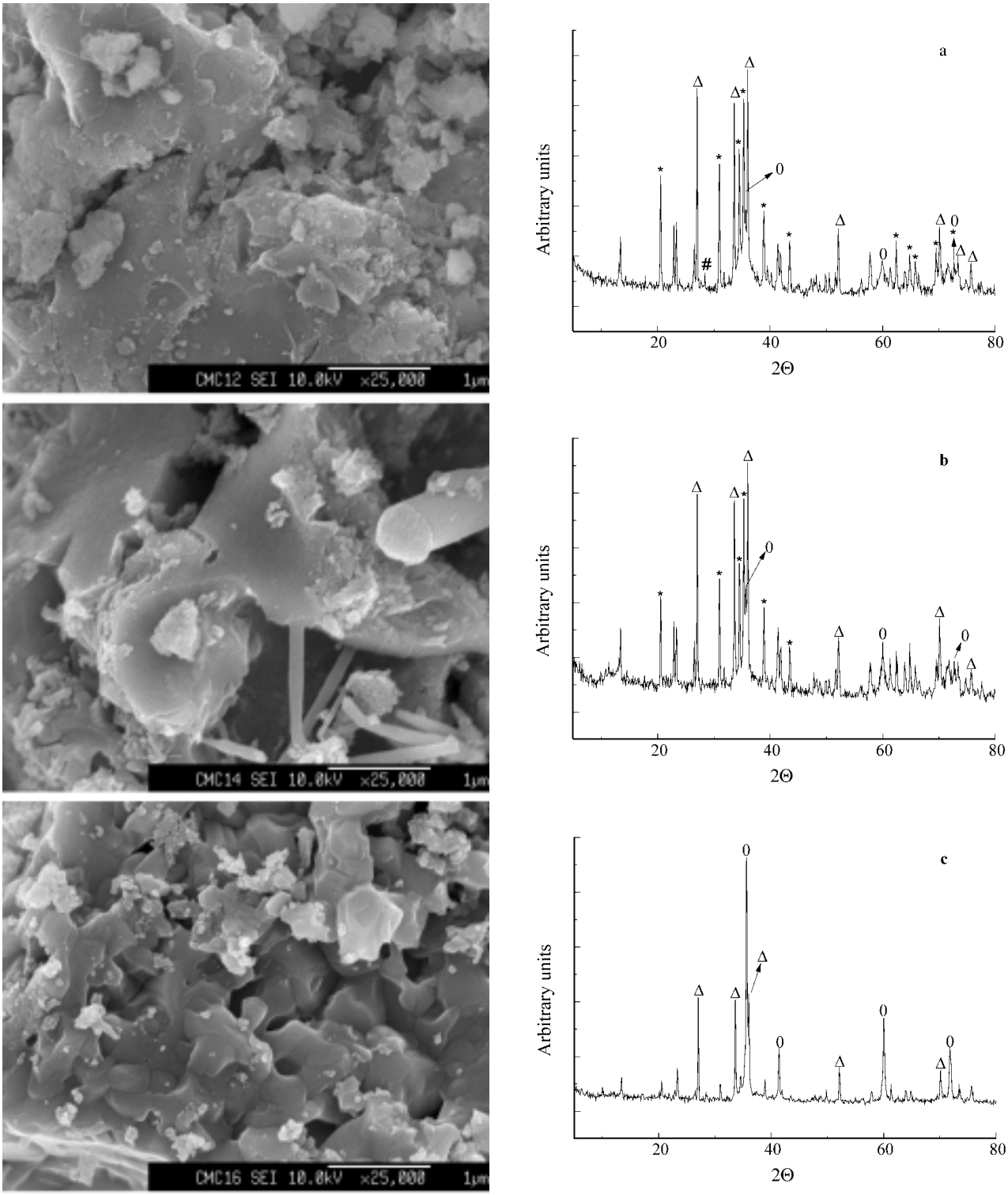

Figure 3. FESEM micrographs and XRD patterns of Si_3N_4/SiC heated for 2 h at (a) 1200 °C; (b) 1400 °C; and (c) 1600 °C. XRD peaks legend: *: α-Si_3N_4;Δ: β-Si_3N_4; #: Si and 0: β-SiC. Not marked peaks: SiO_2.

remarkably improved via the incorporation of nanosized SiC, obtained from polymeric precursor.

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