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Study of AlN and Si_3N_4 powders synthesized by SHS reactions

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Abstract

The particular characteristics of aluminum nitride and silicon nitride powders obtained by SHS technology are reported. The synthesized powders showed high particle sizes that are not suitable for sintering. Consequently, the powders were subjected to an energetic milling process using an attritor with different milling media and times. Silicon nitride powders were milled with Si_3N_4 balls while for aluminum nitride powders different media (Si_3N_4, Al_2O_3, ZrO_2) were used. Particle size and specific surface area were determined in both powders as a function of the milling variables. The increase in the level of impurities associated with the milling procedure was measured. The morphology of each powder was analyzed before and after milling by scanning electron microscopy. The results were evaluated by comparing with characteristics of typical commercial powders of AlN and Si_3N_4, to establish the differences with the SHS powders. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved

Keywords: AlN powders; Si_3N_4 powders; SHS synthesis

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1. Introduction

Technical ceramic materials have slowly but progressively been introduced in applications where specific requirements, such as high temperature mechanical strength or higher thermal conductivities, are needed [1–4]. Silicon nitride and aluminum nitride are two important technical ceramic materials because of their intrinsic properties, mechanical strength and high thermal conductivity, respectively.

Silicon nitride materials have a high mechanical resistance at room and high temperature, excellent fracture toughness, low density and good fatigue behavior [5–8]. In fact, silicon nitride is nowadays one main candidate for the fabrication of gas turbine engines [1,2].

On the other hand, aluminum nitride materials have the following characteristics: high thermal conductivity, low density, high electrical resistivity and a thermal expansion coefficient close to silicon [9,10]. These properties have induced a tendency progressively to substitute alumina by aluminum nitride in the electronic industry [10].

A main disadvantage of both materials is their elevated production cost, when compared with metals or alumina, traditionally used for structural and electronic applications respectively. In this sense, interest for the Self-Propagating High-Temperature Synthesis method (SHS) has arisen because it takes advantage of the energy associated with high exothermic reactions to synthesize ceramic powders. The SHS technology uses initial reagents that once ignited spontaneously transform into products, due to the exothermic heat liberated [11–13].

Considering the respective fields of application of both materials, the control of impurities in the initial powders is an important factor to consider [14,15]. A general characteristic of the SHS powders is their elevated particle size consequence of the high temperatures generated during the synthesis [16]. Although SHS powders are reportedly of elevated purity [16], quantifying how the quality of the powders is affected by the required milling step is important [17]. In the present research, Si_3N_4 and AlN powders synthesized by SHS reactions and two commercial powders used as a reference have been studied. The effect of milling on the level of contaminants and morphology of the SHS powders has been analyzed.

2. Experimental

Powders from two different sources have been employed: AlN (grade B) and Si_3N_4 (LC12 SX) from Hermann Starck (Germany); AlN (S-14) and Si_3N_4, (II-SiN), SHS powders developed by SHS-España (Spain).

All the silicon nitride powders had a high α-phase content (Table 1). The SHS silicon nitride powder, II-SiN,

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was attrition milled to different periods of time using Si_3N_4 balls to reduce the impurity pick up [18] and isopropyl alcohol as grinding fluid. This powder was attrition milled for 29 h in a lab scale attritor with balls of 3.5 mm diameter ($\varnothing = 3.5$ mm). The average particle size (d_{50}) and specific surface area (S_{BET}) during milling was checked in the slurry at fixed periods. The specific surface area was measured at the liquid nitrogen temperature, using the BET method. The particle size distribution was determined by laser scattering with a particle size analyzer. The SHS aluminum nitride powder, AlN S-14, was milled in the same attritor. Here, three different milling media were used: Al_2O_3 ($\varnothing = 3$ mm), Si_3N_4 ($\varnothing = 0.5$ mm) and ZrO_2 ($\varnothing = 2$ mm). The ratio powder/balls used in all the milling tests was 30/120 by weight. Isopropyl alcohol was used as grinding fluid, since this solvent has been one of the most effective [19]. Milling times were dependant on the grinding media: up to 7 h for the Al_2O_3 and ZrO_2 balls, but 4 h for the Si_3N_4 media. The milled powders were labeled as: "Al/7h" for the milled 7 h with Al_2O_3 balls, "Zr/7h" for the milled 7 h with ZrO_2 and "Si/4h" for the milled 4 h with Si_3N_4. The removal of isopropyl was done by heating at 80°C for 24 h.

The impurity concentration before and after the milling step was determined in each powder by inductively coupled plasma spectroscopy and atomic emission spectrometry. For the oxygen and carbon contents, a hot gas extraction equipment was used. The morphology of the commercial and SHS powders were studied by scanning electron microscopy (SEM). The α-Si_3N_4 phase content was determined in each powder by X-ray diffraction techniques [20].

3. Results and discussion

3.1. Si_3N_4 powders: milling procedure

The evolution of the particle size with the milling time in the II-SiN powder is shown in Fig. 1. Initial average particle size was reduced from 10 to 1 μm after 1 h of milling, which probably corresponded to the breaking of agglomerates. Between 1 and 5 h of milling the change in the particle size was less significant, reaching an average size < 1 μm after 5 h. From hour 5 to 29, the grain size practically remained constant. That is, the particle size was drastically reduced during the initial 5 hours and afterwards the grain size reduction was asymptotic. Correspondingly, evolution of the specific surface area (S_{BET}) showed an inverse trend. It increased from 3.5 to 9.5 m^2/g for the initial 10 h of milling. After this point, S_{BET} rose slowly up to 11.3 m^2/g for the 29 h of milling. Although the specific surface area increased progressively, the grain size was not reduced for milling times longer than 10 h. Therefore, this increment in the specific surface area could be linked with changes in the shape factor [21] during the milling.

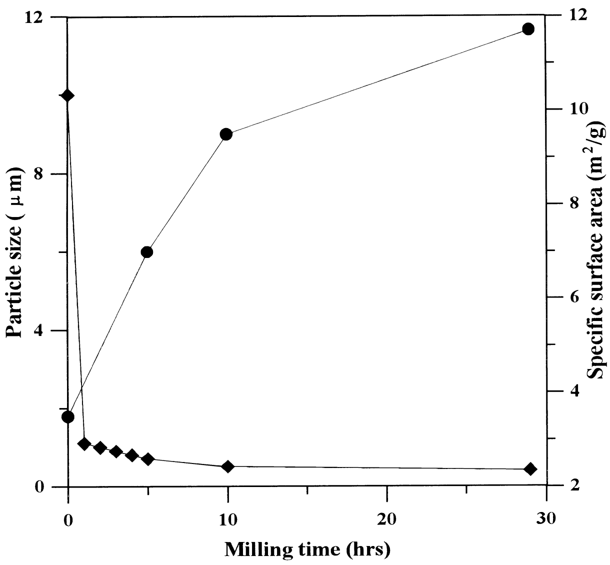

Fig. 1. Particle size (◆) and specific surface area (●) in the powder II-SiN vs milling time.

Table 1
Average grain size (d_{50}), specific surface area (S_{BET}), percentage of α-phase and impurities in the Si_3N_4 powders

	LC 12-SX[a]	II-SiN[a]	II-SiN[b]
d_{50} (μm)	0.7	10	0.4
S_{BET} (m^2/g)	21	3.5	11.7
α-phase (%)	93	89	89
O_2 (wt%)	2	1.2	2.4
C (wt%)	0.1	0.1	0.99
Al (wt%)	0.05	0.02	0.14
Fe (wt%)	0.02	0.1	0.1
Cr (wt%)	0.002	0.01	0.01

[a] As-received powders.
[b] Milled powders.

Even for the longest milling times, the value of the specific surface of the SHS powder remained lower than that of the commercial powder (Table 1). Due to oxidation of the new surfaces formed during milling [22,23], oxygen content increased two times (see Table 1). Neverthelss, it was very close to the level of commercial Si_3N_4.

The impurity content in the initial and milled powders are shown in Table 1. The carbon content increased ten times because the erosion by the powder of the inner polymeric coating of the attritor [24]. Besides, the aluminum content was 7 times higher in the milled powder, and this unexpected increase can only be attributed to the wearing of the milling media: commercial Si_3N_4 balls that probably were sintered with Al_2O_3 additives. The level of other contaminants was not affected by the milling procedure. Finally, the high Fe content in the synthesized SHS powder is noticeable when compared with the commercial powder, although unchanged by the milling step.

3.2. AlN powders: milling procedure

The evolution of the average particle size (d_{50}) with milling time and media for the AlN SHS powder is shown in Fig. 2. As can be observed, d_{50} was drastically reduced during the first hour, independently of the milling media used as occurred for the SHS Si_3N_4 powders. The reduction of size after the first hour is very slow and asymptotic from the fifth hour. The final size reached after the milling process was ≈ 1 μm, when Si_3N_4 (Si/4h) and Al_2O_3 (Al/7h) balls were used, but 1.8 μm when ZrO_2 (Zr/7h) balls were employed as milling media. Consequently, the grain sizes reached in the AlN SHS milled powders (Table 2) were 2–3 times higher than in the commercial AlN. Maximum effectiveness was reached by milling with Si_3N_4 balls, probably due to their smaller diameter ($\varnothing = 0.5$ mm), which allowed more impacts.

As can be observed in Table 2, the initial particle size in the SHS AlN was 36 times bigger than in the commercial powder. Although it was reduced after milling to the 1–2 μm range, particle size is more than two times that of the commercial powder (0.5 μm). The specific surface area for the powders Zr/7h and Si/4h were closer to that measured in the commercial powder (3.6 m^2/g) although, that obtained in the Al/7h was almost double (7 m^2/g).

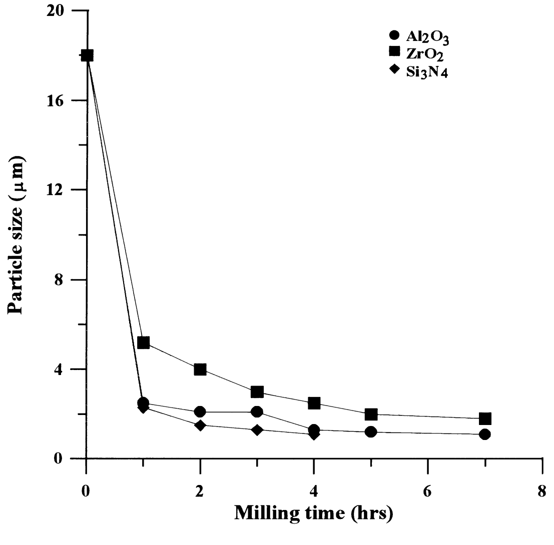

Fig. 2. Particle size of the powder AlN S-14 vs milling time. Different milling media are shown (Al_2O_3, Si_3N_4, ZrO_2).

Table 2
Average grain size (d_{50}), specific surface area (S_{BET}) and main impurities in the AlN powders

	B[a]	S-14[a]	S-14 Zr/7h[b]	S-14 Al/7h[b]	S-14 Si/4h[b]
d_{50} (μm)	0.5	18	1.8	1.1	1.1
S_{BET} (m^2/g)	3.6	0.5	3.4	7	4
O_2 (wt%)	1.7	0.5	1.4	4.3	1.5
Si (wt%)	0.26	0.21	0.21	0.21	0.56
Fe (wt%)	0.04	0.01	0.014	0.01	0.017
Ti (wt%)	0.033	nd	0.02	0.002	0.003
Ca (wt%)	0.01	0.01	0.02	0.001	0.028
Zr (wt%)	0.07	0.04	1.15	0.04	0.069

[a] As-received powders.
[b] Milled SHS powders indicating milling time and media.
nd — not determined.

The relationship between the particle size (D) and the specific surface area (S) of powders [19] can be expressed like:

$$S = \frac{\alpha}{\rho D}$$

where ρ is the density of the powder, and α is a coefficient affected by the shape, particle size distribution and surface state of the powders.

The increase in S_{BET} observed for Al/7h powders can only be related to changes in the surface state (α) associated to the milling media. Actually, the oxygen proportion in this powder, 4.3 wt%, was almost three times higher than in the other two milled powders (≈ 1.5 wt%) (Table 2). This extra oxygen content probably comes from a higher wearing of the Al_2O_3 balls, and it seems that this alumina contaminant changes the surface state of the AlN powders [23].

Observing Table 2, the increment of Si is specially remarkable in the powder Si/4h, due to the wearing of the Si_3N_4 balls. A similar situation is observed in the powder Zr/7h, where the Zr content increased after milling with zirconia balls. Other main impurities in the initial powders did not change during milling, being the titanium content one order of magnitude higher in the commercial powder while the Fe and Ca are in the same range for the SHS and commercial powders (Table 2).

3.3. Morphology of the powders

Micrographs of the SHS and commercial silicon nitride powders are shown in Fig. 3. Commercial powder [Fig. 3(A)] showed the presence of soft agglomerates of 1–2 μm diameter, formed by spherical homogeneous smaller particles (≈ 0.3 μm). The powder II-SiN [Fig. 3(B)] was quite inhomogeneous formed by elongated grains of 1–2 μm length and rounded particles of variable size. The milled II-SiN powder [Fig. 3(C)] was still quite inhomogeneous showing rounded and columnar particles.

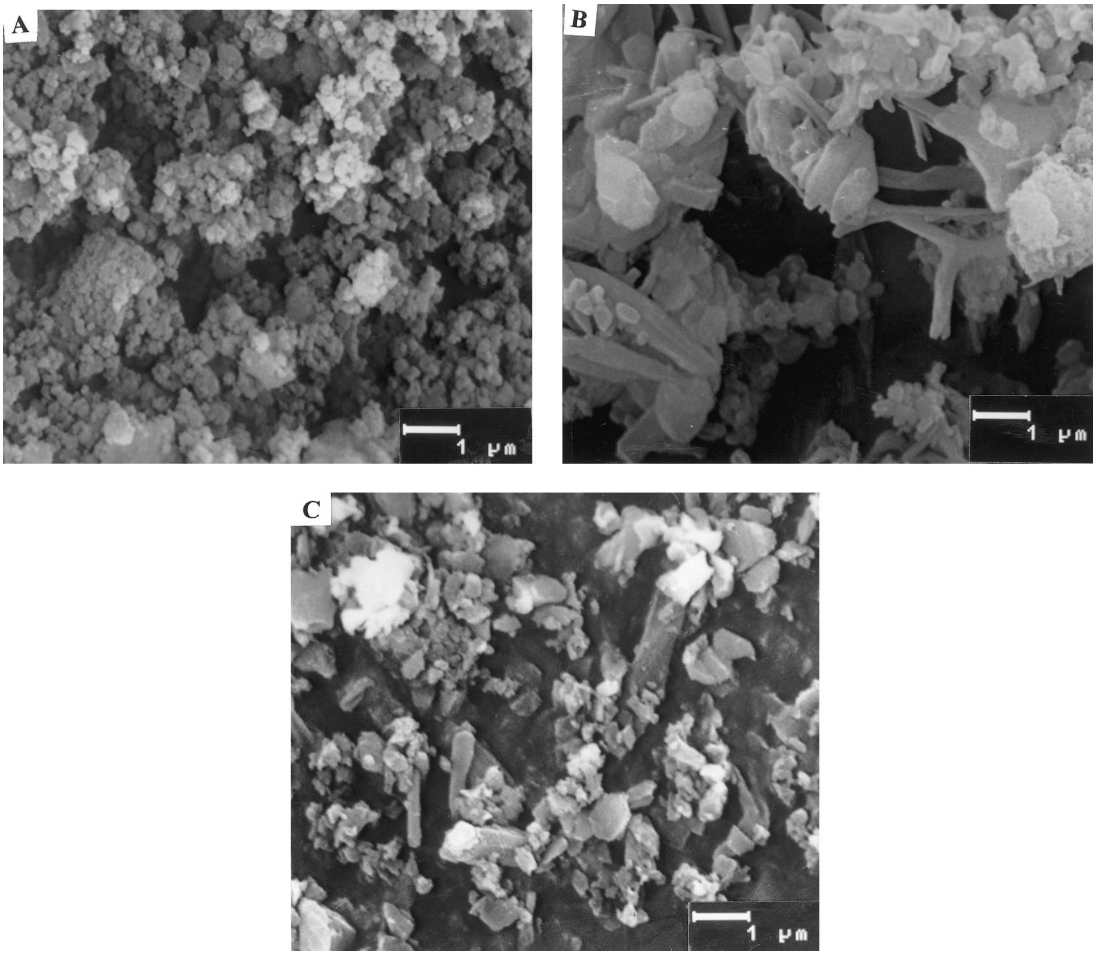

Fig. 3. SEM micrographs of the silicon nitride powders: (A) LC 12-SX, (B) II-SiN, and (C) II-SiN milled.

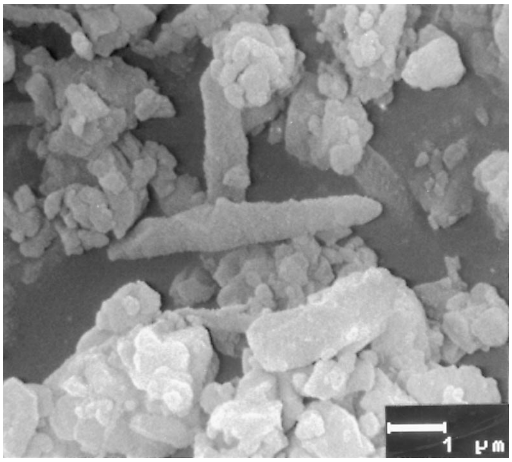

Fig. 4. SEM micrograph of the AlN commercial powders.

In relation to the AlN powders, a representative micrograph of the commercial powder showing presence of rounded and elongated agglomerates of 1–2 μm size is illustrated in Fig. 4. Comparable micrographs of the as received and milled SHS AlN powders (Al/7h, Zr/7h, Si/4h) are shown in Fig. 5. As received AlN S-14 [Fig. 5(A)] showed big spherical agglomerates (> 20 μm diameter) formed by spherical particles (1–10 μm diameter). These particles seemed to be partially bonded, due to the high adiabatic temperature developed in the SHS synthesis [16]. The Al/7h [Fig. 5(B)] milled powder presented irregular particles of 1–1.5 μm diameter and some large particles of 2–3 μm size. The Zr/7h milled powder [Fig. 5(D)] showed also a range of sizes: big particles (2–3 μm) and smaller ones (0.2–0.5 μm). Bigger particles presented a marked angular morphology, due to the fracture of the initial agglomerates under the action of the ZrO_2 balls. This powder had the highest particle size (Table 2) as it can be also observed in the micrographs. The Si/4h milled powder [Fig. 5(C)] seemed to have a narrower size distribution, the morphology of this powder was also very angular. Summarizing, the milled powders presented similar features independently of the milling media: angular shapeless particles and a range of sizes.

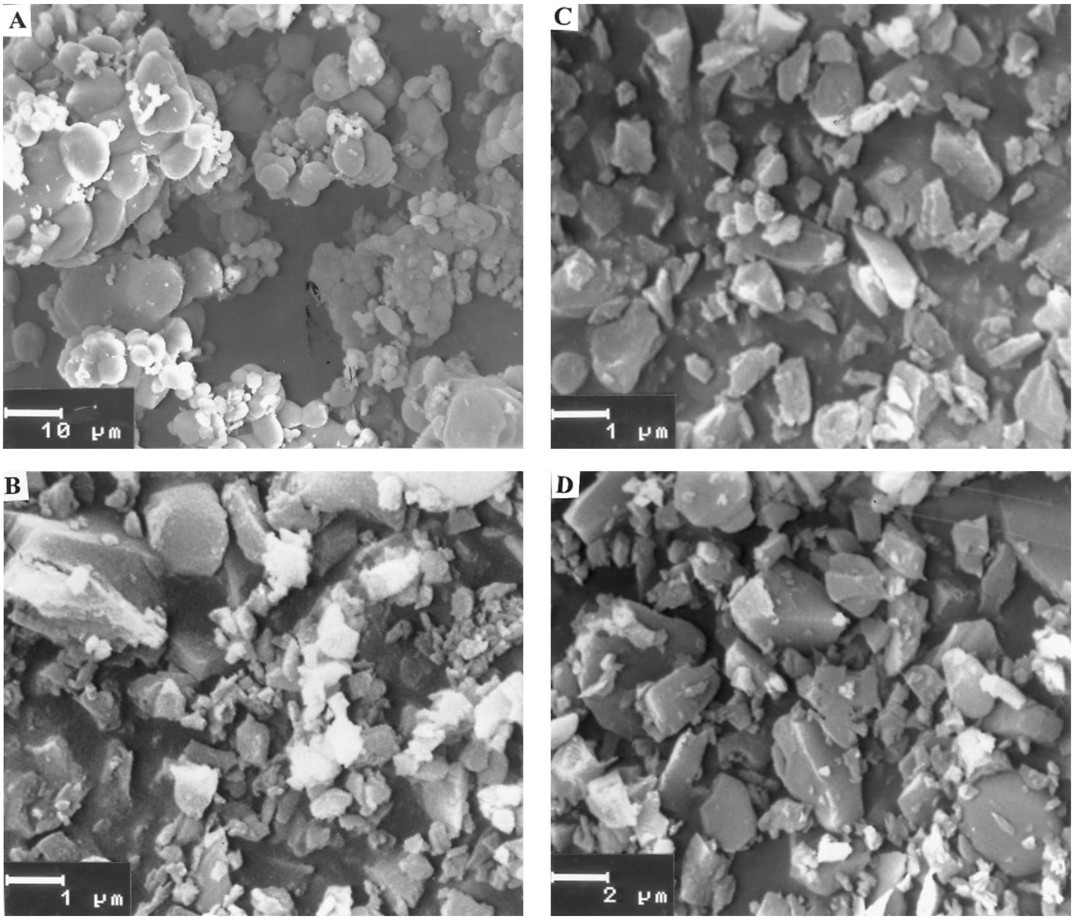

Fig. 5. SEM micrograph of the SHS AlN S-14 powders: (A) as-received, (B) milled Al/7h, (C) milled Si/4h and (D) milled Zr/7h.

4. Conclusions

The high particle size of the SHS powders (AlN, Si_3N_4) makes unavoidable a milling step to reduce conveniently the size and enable sintering.

The attrition milling of the SHS Si_3N_4 powders with silicon nitride balls reduced particle size significantly, without increasing the amount of contaminants except the oxygen that, nevertheless, remained similar to the level of commercial powder. Furthermore, reactivity of the SHS powders increased markedly after milling.

Different milling media yielded SHS AlN powders with different particle sizes and specific surface area, some of them about the same size as the commercial one. The morphology of the powders was mostly prismatic for any of the milling media. Oxygen and other contaminants depended on the kind of media used. The type of milling media should be an essential factor that may affect importantly the properties of the sintered materials.

Acknowledgements

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