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Fabrication of porous silicon nitride by sacrificing template method

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Abstract: High performance porous structural ceramics have been widely studied. Silicon nitride is an interesting material for this application because bodies with high mechanical strength, achieved as a result of "in situ" anisotropic grain grown, can be obtained. In this study, Si_3N_4 bodies with different porosity related aspects (percentage, morphology, etc.) are made using the sacrificing template method, by changing the percentage (vol%) and the drying method of the mixture as well as the sintering time. The porosity, apparent density (Archimedes method), microstructure (SEM) and the mechanical strength (in compression) of these bodies were determined. It was thus possible to relate the type and amount of starch with the porosity and mechanical properties of the bodies.

Introduction

Dense silicon nitride is used to produce cutting tools and others high-temperature structural applications due its mechanical performance. In certain level of porosity the silicon nitride offers an interesting combination of strength and stiffness. [1-7]

In a study [6], the authors made a comparison between different fabrication routes to produce porous silicon nitride, like the methods of partial sintering, sacrificial template and partial hot pressing. The main difference between the methods was porous size, the partial hot pressing had the smallest porous size (~1μm) and the sample prepared by sacrificial template had the biggest porous size (~40μm). The strain to failure does not significantly change with the porosity by samples made with of partial sintering and sacrificial template methods, but for the samples made with partial hot pressing method the strain to failure increases quick for porosities up to ~25% volume, the high strength for this material is thought to be associated with β-Si_3N_4 grains and pores alignment effects.[6]

Macro porous ceramics are made by many methods like gel-casting of foams, sacrificial template, starch consolidation and others. In recent works starch showed important as a pore-forming agent, for environmental friendly issues, easy processing, burnout without the generation of toxins and commercial availability. The control of the process make possible to choose the size, shape and fraction of porous in the material. [8-16]

Studies with the starch consolidation method had started with potato starch, they made porous ceramics with alumina [8], cordierite [9], calcium carbonate[10] and mullite[12]. The newest studies made the method became more feasibly [13, 14]. In a recent study had related the last advances in the use of starch and the problems that remains unsolved, like the porosity control above 50%, this problem was caused by agglomeration of the starch, that consequently decreases the homogeneity of the samples.[15]

The main study about porous silicon nitride using starch in the sacrificial template method was made by varying the starch in volume (2% to 20%). After measuring the mechanical properties they found a proportional relationship between porosity and mechanical strength. The best fit for the Young´s modulus-porosity relation was obtained for the equation form: $E=E_0(1-aP)^n$. The zero porosity modulus values were between 327 and 332 GPa with had a very good agreement with those related in the literature.[11]

In the current work the corn starch was used as pore agent; the samples were densified in two conditions to provide a difference in the "*in situ*" reinforcement; density and porosity are

measured by Archimedes method, mechanical strength by compressive test and microstructure with Scanning Electronic Microscope (SEM) were valuated.

Experimental Procedure

In this study a powder containing 92% Si_3N_4 (M11 – HC Starck), 6% Y_2O_3 (Aldrich 99.99 purity) and 2% Al_2O_3 (A16 Alcoa) was milled with attritor milling (4 hours at 300rpm). And dried in a rotoevaporator, the obtained powder was sieved through a 40 MESH sieve. This mixture was called BC (basic composition). Before mixture with BC powder corn starch has been characterized by laser scattering.

The suspensions were prepared with 50% of solid contend (a mix of 20-40% in volume of corn starch related to BC) and distilled water or isopropyl alcohol. After mixing, they were drying by 3 different methods (kiln-drying, rotoevaporator, using water or alcohol, and freeze-drying). The samples obtained are summarized in table 1.

Samples was conformed in cylindrical form with dimension of approximately d=10mm, h=10mm. Removal of starch was performed using a furnace with air atmosphere, with a rate of 1ºC/min until 200ºC, 300ºC and 400ºC steps and held for 1 hour. The sintering was performed using a graphite resistance furnace (**Astro** 1000, 4560,FP 20, Thermal Technology Inc.) and a sintering profile of 1800ºC, by 1 and 3 hours, in nitrogen as atmosphere. Porosity was measured using Archimedes method, with distilled water. The mechanical properties were measured with a compressive strength test using an insertion with a strain rate of 0,5mm/min in an Instron 4400R.

Table 1: Studied Compositions:

Sample	Drying Method	Starch contents (%volume)
BC	kiln-drying	0
20K	kiln-drying	20
30K	kiln-drying	30
40K	kiln-drying	40
20RW	Rotoevaporator+ water	20
20RA	Rotoevaporator+ alcohol	20
20FD	freeze-drying	20

Results and discussion

The fig. 1 is presented particle size distribution of corn starch evaluated by laser scattering. Where can be observed that, corn starch powder presented a narrow distribution of mean particle size, with particles mean size about 12μm.

Porosity values of the samples are presented in Table 2. Samples without addition of starch presented porosity about 2% and can be observe in Table 2 that the increase of sintering time did not promote reduction in these porosity. These results are related with a residual porosity of β-Si_3N_4 matrix. In table 2 can be observed too that, the sample containing 20% of starch sintered at1800ºC /1 hour, dried using different methods presented no significant change in porosity (about 6%). When the sintering time was increased to 3 hours the difference of the final porosity obtained varies about 10% depending on the drying method used. This study shows that the increase in starch quantity did not significantly promote the increase in sample porosity.

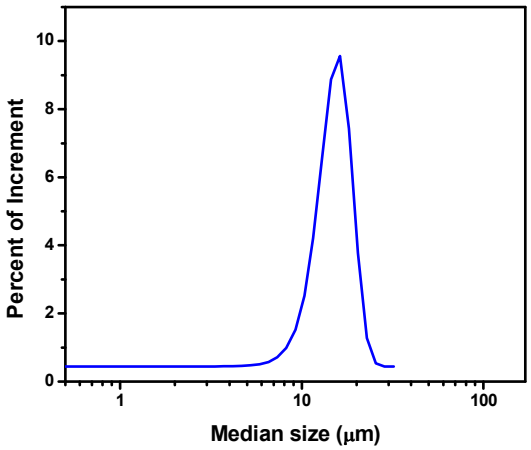

Fig.1: Particle distribution for corn starch.

Table 2: Porosity of the samples

Sample	Porosity (%)
BC/1800ºC/1h	2±1
BC/1800ºC/3h	2±1
20K/1800ºC/1h	25±1
30K/1800ºC/1h	29±1
40K/1800ºC/1h	34±1
20RW/1800ºC/1h	25±1
20RW/1800ºC/3h	5±1
20RA/1800ºC/1h	29±1
20RA/1800ºC/3h	15±1
20FD/1800ºC/1h	31±1
20FD/1800ºC/3h	15±1

In fig. 2 (a), is possible to observe the porous and the cracks created by compressive test, the cracks had started in the porous and spread through the sample. The porous morphology is showed in the fig. 2(b), the mean size of porous was about 10μm. These values were close of starch particle size and agree with reports in the literature [14]. In fig. 2(c) are showed the fracture surface of the sample 30K/1800ºC/1h, where can be found some anisotropic grains in the ceramic matrix. At least in fig. 2(d) are showed the fracture surface of sample 40K/1800ºC/1h.

The fig. 3 shows the results of the compressive strength test. In this figure were showed two different behaviors. The first behavior was for samples sintered by 1 hour with difference in drying methods. Rotoevaporation and freeze-drying methods improves the mechanical properties by a better particles packing because the powder was less agglomerated than the kiln-dried powder, what reduces the number of defects in the ceramic matrix. The samples produced by kiln-dried powder, showed the lowest values of rupture modulus, so the research with them are discontinued. The amount of starch was fixed at 20% because in the region between 20% and 40% the mechanical properties presented no significant variation. The second behavior observed was the increase in the rupture module by increase in sintering time to 3 hours. This behavior is expected due porosity decreases allied with "*in situ*" reinforcement of the silicon nitride ceramics. Through a linear fit of the data of sample sintered during 1 hour is possible note a strong relationship between the rupture module and the porosity. When the sintering time was increased to 3 hours the phenomenon of "*in situ"* reinforcement, promoted by the anisotropic grain growth of silicon nitride become more evident.

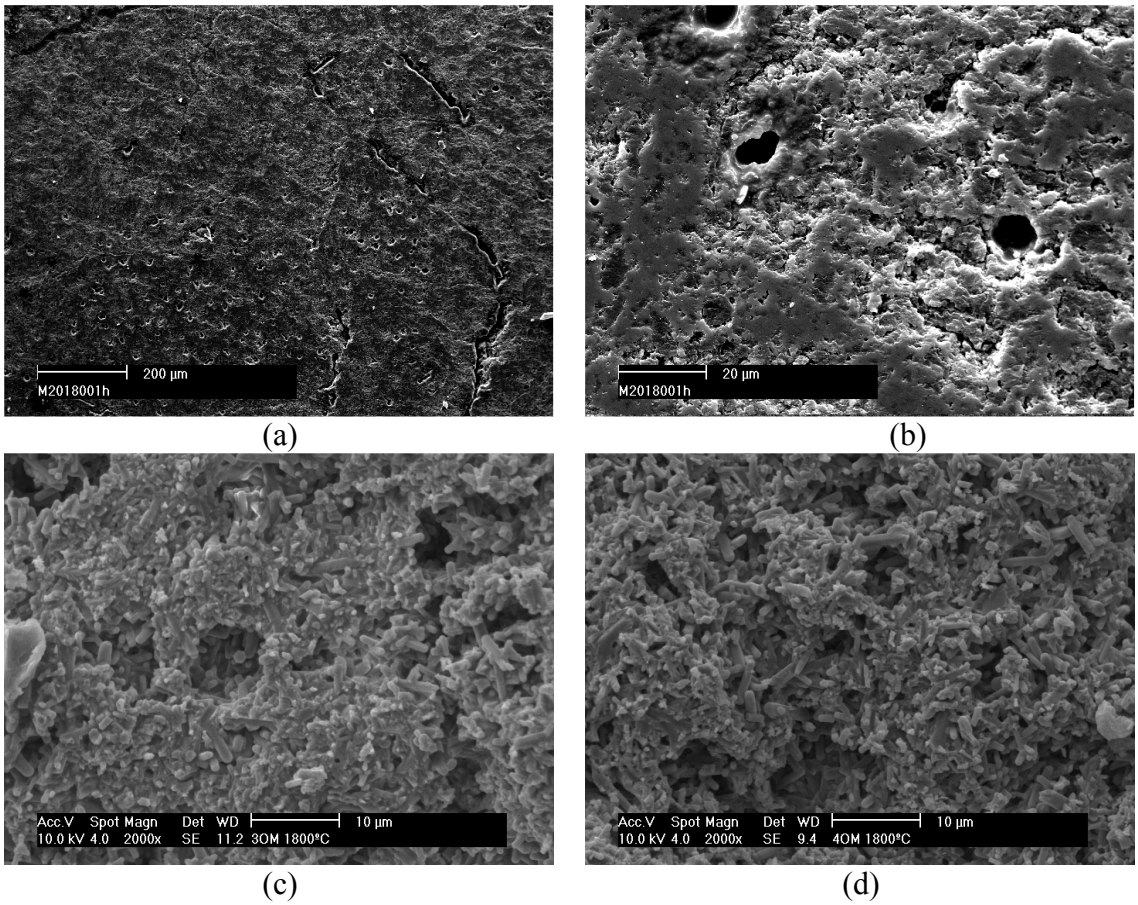

Fig. 2: Micrograph of the sample 20K/1800ºC by 1 hour (a), (b), the fracture surface of the sample 30K/1800ºC by 1 hour (c) and the start of anisotropic grain growth, sample 40K/1800ºC by 1 hour (d).

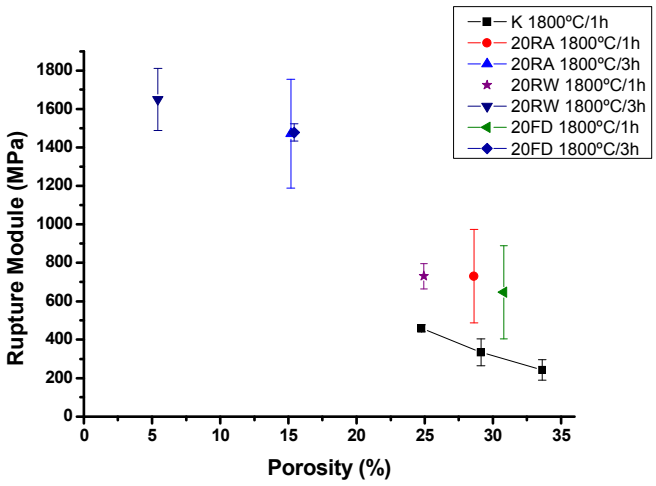

Fig. 3: Average rupture modules of the samples dried in different conditions.

Conclusion

Studied samples presented porosity range of 5% to 35% and a rupture module of 200 MPa to 1800 MPa. Results of mechanical strength presented strong relation with de porosity and “in situ” reinforcement promoted by the anisotropic grains of silicon nitride. These effects promote an

increase in mechanical properties on a higher level compared to the samples submitted to a shorter sintering time.

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