GAS PRESSURE SINTERIZATION OF SILICON NITRIDE BASED CERAMICS USING RARE EARTH OXIDES AS SINTERING ADDITIVES

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ABSTRACT: Silicon nitride ceramics with additions of 3wt.% of yttria together with 2wt% of rare earth and transition metals oxides, were gas pressure sintered using multiple steps of temperature and pressure. Compositions containing La_2O_3, Nd_2O_3 and Sm_2O_3, and the transition metals oxides, Cr_2O_3, and TiO_2, were tested. The results showed that gas pressure sintering (GPS) is a possible way to process these ceramics to high density. Also, the final density and aspect ratio of β-Si_3N_4 grains are strong dependent of soaking time in the last step of temperature and pressure.

Key Words: Silicon Nitride, Gas Pressure Sintering

1. Introduction

Structural ceramics based on the silicon nitride have been explored for more than four decades for applications as structural components in engines and turbines. Despite several excellent properties of these materials and demonstrated clear advantages, a wide range of applications is still not realized[1]. A breakthrough in their use was not only inhibited by the high cost of the components. It was also inhibited by a large scatter of the property data such as strength, fracture toughness and reliability plus insufficient reproducibility [2]. This can be attributed to the relativity complex microstructure developed during densification. At the end of densification process, the microstructure of silicon nitride based ceramics is constituted of an amorphous intergranular phase distributed by the β-Si_3N_4 grain boundaries resulting from the cooling of the liquid phase formed by the melting of sintering additives. This intergranular phase is responsible by the high temperature mechanical properties and by the aspect ratio of β-Si_3N_4 grains[3]**.** Among the methods to produce silicon nitride based ceramics, gas pressure sintering (GPS) show economic advantages as well as the possibility to obtain products with very high quality. In the GPS process, moderated N_2 pressures between 1 and 10 MPa, are usually applied in a second sintering stage on normal sintered products[4-6] . This nitrogen pressure levels in GPS is enough to depresses thermal decomposition of Si_3N_4 at temperatures greater than 1800^{o}C allowing the use of more refractory sintering additives that improve the high temperature mechanical properties of this material. Besides the advantages already mentioned, the GPS process has been shown to be an effective way to get *in situ* reinforcement . During gas pressure sintering at elevated temperatures, silicon nitride grains are allow to grow, promoting the development of microstructure where β-Si_3N_4 grains exhibit a high aspect ratio, which leads to materials with high fracture toughness. In previous works[7] it was verified that it is possible to use gas pressure sintering to sinter silicon nitride closed to theoretical density using between 4,5 wt.% and 5wt.% of yttria – alumina as sintering adds. The aim of this work was to study the densification, fracture toughness, densification kinetic and microstructure of silicon nitride ceramics employing 3wt.% of yttria together with 2wt% of rare earth oxides, La_2O_3, Nd_2O_3 and Sm_2O_3, and 2wt% of transition metals oxides, Cr_2O_3, CdO and TiO_2, sintered by GPS using multiple steps of temperature and pressure.

2 . Material and Methods

High purity Si_3N_4, Y_2O_3, Nd_2O_3, Sm_2O_3, Cr_2O_3, and TiO_2 were used for the preparation of compositions, as shown in Tab. I.

All compositions were milled during 6 hours in an attrition mill using ethyl alcohol P.A. as a fluid. After drying, the mixtures were sieved through a 65 mesh screen to eliminate large agglomerates and, then, uniaxialy pressed at 60 MPa.

Samples were initially heated at 600°C for 2 hours to eliminate the binder added during the milling (PEG). After that, they were placed in a graphite crucible coated with boron nitride and gas pressure sintered in a high pure nitrogen atmosphere, according to two sintering conditions, as follows:

1 - Multiple step sintering, with the first step similar to the normal sintering at 1750°C, with soaking time of 40 min. At the end of this step the pressure was increased to 40 bar and temperature simultaneously increased to 1950°C with a heating rate of 10°C/min. After 15 min. at 1950°C, the pressure was raised to 100 bar, with a 15 min. soaking time at 1950°C. (1950°C/30min)

2 – The same condition of cycle 1 except for the soaking time of the last step, which were 4h.(1950°C/4h)

Using a dilatometer coupled in the GPS furnace, it was determined the densification curve and the densification rate along the process of some compositions**.** The samples density were determined by Archimedes method and compared with theoretical density of each composition investigated and calculated from the density values of each component according to the phase rule. Fracture toughness was measured by Vickers indentation method using a load of 10N.

Table I. Compositions and Theoretical Density (d_t)

CODE	COMPOSITION	d_t (g/cm^3)
3Y2S	95% Si_3N_4 - 3% Y_2O_3 - 2% Sm_2O_3	3,254
3Y2N	95% Si_3N_4 - 3% Y_2O_3 - 2% Nd_2O_3	3,250
3Y2L	95% Si_3N_4 - 3% Y_2O_3 - 2% La_2O_3	3,247
3Y2Cr	95% Si_3N_4 - 3% Y_2O_3 - 2% Cr_2O_3	3,239
3Y2T	95% Si_3N_4 - 3% Y_2O_3 - 2% TiO_2	3,225
3Y2A	95% Si_3N_4 - 3% Y_2O_3 - 2% Al_2O_3	3,226

3. Results and Discussion

3.1 Densification of Studied Compositions

The Table II shows the final densities for each composition sintered according to the cycles 1 and 2.

Table II. Relative density in percentage of theoretical density (%d_t)

COMPOSITION	1750 °C/40min. – 1950 °C/30min.	1750 °C/40min. – 1950 °C/4h
3Y2L	99.4	99,7
3Y2T	92.9	97,7
3Y2S	89.9	97,2
3Y2N	90.8	96,5
3Y2Cr	90.3	93,5
3Y2A	99,6	99,7

Although the conditions employed in cycle 1 were enough to promote densification closed to theoretical density in silicon nitride ceramics doped with yttria and alumina[4], those conditions were unsuitable to achieve high density values, except for the composition 3Y2L, with lanthanum oxide. The results also showed that 5 wt.% of these additive systems are insufficient to achieve density greater than 99% even in this condition. The four hour soaking time employed in cycle 2, shows that to obtain silicon nitride ceramics with high density it is necessary longer soaking times at high temperatures. The reason to the lowest density values of composition 3Y2Cr is due to the high melting point of chromium silicides formed during the sintering.

Analysis of densification rate curve for the composition 3Y2T show that the increase of pressure in the last stage of sintering doesn't have a perceptive effect on densification. It could explain the lower density of composition with titanium oxide than ones obtained when more refractory oxides were used.

3.2. Densification Kinetic

The Tables III and IV show the maximum rate of densification for studied compositions and the temperatures where the maximum rate was observed in each stage of densification. In both tables the composition 3Y2A is also included for comparison.

Table III - Maximum rate densification for compositions 3Y2L, 3Y2S and 3Y2N

Composition	Rearrangement		Solution-reprecipitation	
	ds/dt(máx)µm/min	Temp.°C	ds/dt(máx)µm/min	Temp.°C
3Y2A	310	1210	807	1650
3Y2L	78	1210	650	1710
3Y2S	92	1210	720	1740
3Y2N	84	1210	630	1745

Table IV - Maximum rate densification for compositions 3Y2Cr and 3Y2T

Composition	Rearrangement		Solution-reprecipitation	
	ds/dt(máx)µm/min	Temp.°C	ds/dt(máx)µm/min	Temp.°C
3Y2A	310	1210	807	1650
3Y2Cr	93	1210	625	1763
3Y2T	57	1210	634	1745

As can be observed, the change of sintering additive did not have influence on the temperature where was observed the maximum rate of densification in the rearrangement stage. However, in the solution-reprecipitation stage, the temperature where the maximum rate was observed was growing as the more refractory sintering additive was employed. Also was observed that the maximum value rate was lowering as far as the refractory character of sintering additive was growing. The exception seemed to be the composition 3Y2T for which was expected an upper densification rate. The microstructure of composition 3Y2T shows that the addition of TiO_2 seems to promote a refinement in the microstructure influencing the α-β transformation and lowering the densification rate by excessive nucleation of β grains, what cause a steric hindrance.

3.3. Microstructure

The figures 1 and 2 show the microstructure of composition 3Y2L in both conditions of sinterization. As can be seen the permanence during four hours at 1950ºC promoted the growth of β-Si_3N_4 grains leading a strong improve in fracture toughness (Table V) despite of no changes in final density. The same effect was observed for composition 3Y2Cr but in this case a small growth of final density has occurred. The change in microstructure of this composition can be seen in figure 3 and 4.

The figures 5 and 6 show the microstructure of compositions 3Y2N and 3Y2S sintered for 1950ºC and 4 hour. The figure 5 show that the conditions employed were not enough to obtain a microstructure made of elongated β-Si_3N_4 grain with a high aspect ratio. Probably, the amount of 2wt% of neodymium oxide needs to be improved to promote the growth of silicon nitride grains and the final density. The same observation can be applied to the compositon 3Y2S. The figures 7 and 8 show the composition 3Y2T for the conditions 1950°C/30min and 1950°C/4h respectively. As was sad before seems there were a steric hidance resulting in formation of a lot of β-Si_3N_4 grais with a small aspect ratio.

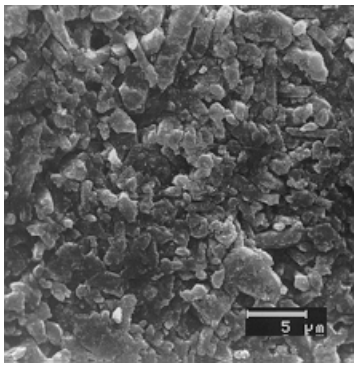

Figure 1 – 3Y2L (1950°C/30min)

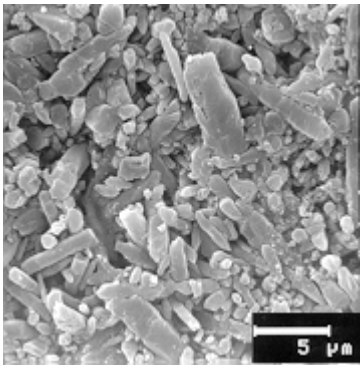

Figure 2 – 3Y2L(1950ºC/4h)

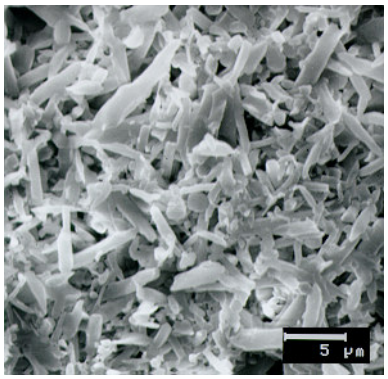

Figure 3 – 3Y2Cr(1950°C/30min)

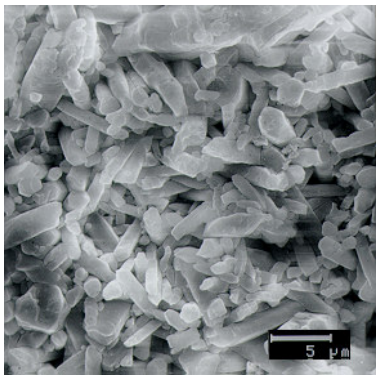

Figure 4 – 3Y2Cr(1950°C/4h)

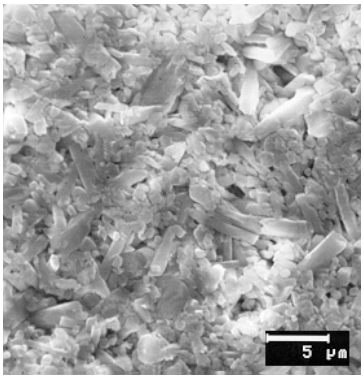

Figure 5 – 3Y2N – 1950°C/4h

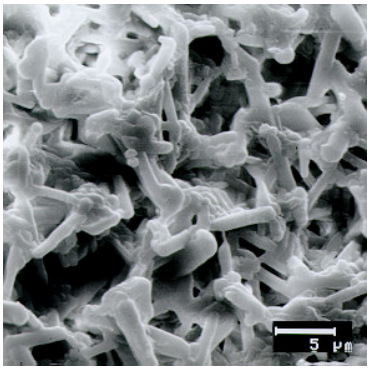

Figure 6 – 3Y2S (1950°C/4h)

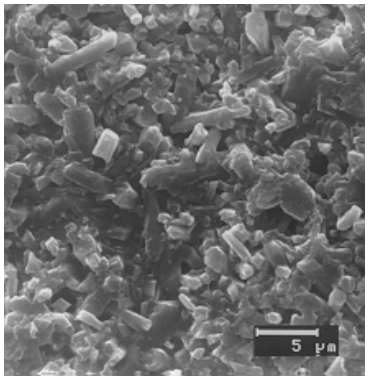

Figure 7 – 3Y2T(1950°C/30min)

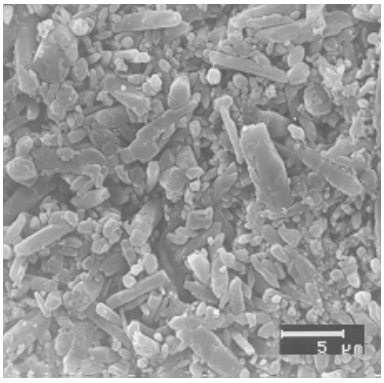

Figure 8 – 3Y2T(1950°C/4h)

3.4. Fracture Toughness

The Table V shows the fracture toughness of composition 3Y2L sintered according cycles 1 and 2 and compositions 3Y2N, 3Y2S and 3S2A sintered according cycle 2.

Table V - Fracture Toughness K_{IC} ($MPa.m^{-1/2}$)

COMPOSITION	1750 °C/40min. – 1950 °C/30min.	1750 °C/40min. – 1950 °C/4h
3Y2L	2.0 ± 0.4	6.3 ± 0.4
3Y2N	-	3.6 ± 0.3
3Y2S	-	5.1± 0.4
3Y2A	5,3 ± 0,2	4,5 ± 0,1

As it can be seen in Table II, the better value of fracture toughness was achieved by the composition 3Y2L, reflecting its density and aspect ratio of β-Si_3N_4 grain dependence.

In spite of good densification obtained for the composition 3Y2L sintered according cycle 1 (30 min. Soaking time at 1950°C), the fracture toughness was very low. The increase of soaking time in cycle 2 led to a better aspect ratio and, consequently, improved the fracture toughness, although some abnormal grain growth were observed. The fracture toughness was not measured to compositions 3Y2Cr due to the low density obtained.

4. Conclusions

Density around 99,5% of the theoretical density and K_{IC} of 6,3 $MPa.m^{-1/2}$ for the composition containing 3wt% of yttria and 2wt% of lanthanum oxide as sintering adds, shows that the gas pressuring sintering is a feasible way to obtain high density silicon nitride ceramics with low quantities of sintering adds and more refractory grain boundary phase. The substitution o lanthanum oxide by the same amount of neodymium, samarium, chromium and titanium oxides, has shown to be insufficient to obtain silicon nitride ceramics with densities closed to theoretical density, using the same gas pressure sintering conditions. However, the results obtained allow us to suppose that a small increase in the total amount of sintering adds will lead high density bodies.

The intense nucleation of β-Si_3N_4 grains observed in composition 3Y2T suggest that TiO_2 could be employed together otrer more refractory sintering additives to promote a microstructural refinament leading to better mechanical properties of silicon nitride based ceramics.

5- REFERENCES

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