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Effect of the additive content on the sintering of pre-sintered Si_3N_4 composite.

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Abstract

Sintering of Si_3N_4 compounds requires additives that promote densification through the dissolution-precipitation mechanism in liquid phase sintering. The sintering of the Si_3N_4 with the SiO_2-Y_2O_3-Al_2O_3 system has been extensively studied. Nevertheless, because SiO_2 depends on the natural amount on the Si_3N_4 surface, little has been studied about SiO_2 control. A pre-sintering treatment can increase the content of SiO_2 through controlled oxidation of Si_3N_4. In this work the effect of the additive content on the densification of Si_3N_4 composite ceramics was evaluated. For this purpose, powder mixtures of Si_3N_4, Y_2O_3 and Al_2O_3 were prepared. The Y_2O_3 and Al_2O_3 ratio were modified in percentages of 4, 8 and 12% by weight. The mixtures were compacted and pre-sintered at 1300°C for 1 hour. Then, these were sintered at 1450°C for two hours. The samples were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Results showed that during pre-sintering, the $Y_5(SiO_4)_3N$ phase is formed; then, it's subsequently oxidized at the sintering stage. A second phase identified as $Y_3Al_5O_{12}$ was found in samples with higher proportions of Al_2O_3. Composition and quantity of the observed phases depend of Y_2O_3 and Al_2O_3 proportion in the added additive.

INTRODUCTION

Silicon nitride composites are important materials for engineering applications because their high temperature resistance, high strength, oxidation and wear resistance [1, 2]. Sintering of Si_3N_4 composites requires the use of additives like metal oxides (Al_2O_3, MgO) and rare earth oxides (La_2O_3, Yb_2O_3, Y_2O_3) in order to generate high-density ceramics [3,4]. Those additives react with the SiO_2 that lies on the surface of the Si_3N_4 particle to form a liquid phase at the sintering temperature [5]. Then, the formed liquid phase promote densification by the liquid-phase sintering process [4]. The use of Y_2O_3 and Al_2O_3 powders as additives of sintering produces dense materials with good mechanical properties [6,7]. The melt temperature , densification and phase transformations depend on the content of constituents in raw materials [6]. Moreover, the kinetics of sintering, microstructure and properties depend of the composition of liquid phase obtained during the densification process [6]. There are works about the sintering of Si_3N_4 with different content of Al_2O_3 and Y_2O_3 [6-8]. Nevertheless, the control of the content of SiO_2 has been little studied. It’s because the SiO_2 is an inherent component on the surface of Si_3N_4 powder particles [5,9]. The Si_3N_4 is easily oxidized in air above 1027°C [10]. Therefore, an oxidation treatment can increase the SiO_2 content in the material before the sintering process. An oxygen atmosphere is necessary for the sintering of Si_3N_4. However, its excess promote the degradation of the material [8.9]. Oxygen needs to be decreased in a nitrogen atmosphere.

The present work was focus on the study of the effect of the additive content on the composition of the liquid phase obtained during the sintering of Si_3N_4 compounds. Samples were heated at 1300°C as pre-sintering process in order to increase the amount of SiO_2 through controlled oxidation of Si_3N_4. Then, they were sintered at 1450°C during 2 hours. Samples were characterized by X ray diffraction (RDX) and Scanning electronic microscopy (SEM) in order to observe microstructural changes and chemical composition in each process.

METODOLOGY

Ceramic compacts were manufactured from Si_3N_4, Y_2O_3 and Al_2O_3 powder mixtures. Y_2O_3 and Al_2O_3 powders were mixed in proportions of 75-25% and vice versa. These mixtures were added as additive to the Si_3N_4 in amounts of 4, 8 and 12% by weight. The proportion of powders in each mixture is shown in table 1. Compacts were obtained by uni-axial pressing using a steel die and a hydraulic press. Consequently, compacts of 6.35 mm in diameter and five mm of length were obtained.

Table 1. Proportions of powder mixtures for each sample.

Sample	**Content of Si_3N_4 (%)**	**Content of additive (%)**	**Composition of additive (%)**	
			Al_2O_3	Y_2O_3
4a	96	4	75	25
4y			25	75
8a	92	8	75	25
8y			25	75
12a	88	12	75	25
12y			25	75

Ceramic compacts were pre-sintered in a tubular electric furnace (carbolite brand). The compact pieces were heated at 1300 °C for one hour. A constant flow of nitrogen (purity 99%) was supplied during the process to avoid an excessive oxidation. The pre-sintering process was carried out in order to hold time for promote the oxidation the Si_3N_4 particles and increase the SiO_2 content.

The control of temperature as a function of time can be observed in figure 1a. The heating rate, holding time and cooling were controlled up to a temperature of 800 °C.

The pre-sintered samples were sintered at 1450 °C for 2 hours with a constant flow of nitrogen; A graphite sample holder coated with boron nitride was used to transport the samples into the furnace and remain during the sintering process. The sintering treatment heating graph is shown in Figure 1b.

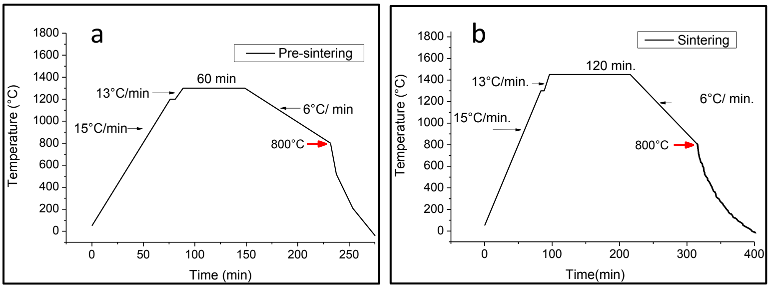

Figure 1. a) Heating graph of pre-sintering process; b) Heating graph of sintering process.

Pre-sintered and sintered samples were ground on their surface with a 1000 grit diamond plate and polished with diamond compound 1 um. Then, samples were cleaned with ultrasonic-cleaner in ethanol, rinsed with deionized water and stored in a desiccator jar until its analysis. The samples were analyzed by scanning electron microscopy using a Jeol Scanning Microscope JSM-6400 electron microscope, coupled with an energy dispersive detector (EDS). The XRD analysis was performed with a Bruker D8 advance X-ray diffractometer; the analysis mode was Bragg-Brentano, measured in a 2θ range of 10-70, step time of of 0.6 s and step size of 0.02 degrees.

RESULTS

X ray diffraction

Figure 2 shows XRD patterns of pre-sintered samples. Figure 2a are samples of the group a, whereas figure 2b are samples of the group y. In both groups were identified α-Si_3N_4, β-Si_3N_4 and yttrium oxynitride ($Y_5(SiO_4)_3N$) phases. Alpha and beta Si_3N_4 are the raw material and there aren't changes in their intensities. It's because the temperature of a→b phase transformation begins above 1500°C [11,12]. Moreover, Al_2O_3 and Y_2O_3 phases were not observed. The intensity of reflections associated with the $Y_5(SiO_4)_3N$ phase increases in figure 2b. Therefore, the increment is proportional to the content of Y_2O_3 on the additive added in the mixture. According to R.R. Wills, Vuckovic and Bertaut [13-15], $Y_5(SiO_4)_3N$ is formed from the reaction between Y_2O_3, Si_3N_4 and SiO_2. That phase was not found in samples 4a and 8a in figure 2a because they have low content of Y_2O_3. The amount of $Y_5(SiO_4)_3N$ on those samples could be too small, hence its diffraction peaks might not be observed on the diffraction pattern. On the other hand, no phase associated with the Al_2O_3-SiO_2 reaction product was identified.

Figure 3 shows XRD patterns for sintered samples. The sintered samples from the group *a* in figure 3a, revealed the formation of the $Y_{4.67}(SiO_4)_3O$ phase, whereas the group *y* in figure 3b have the $Y_3Al_5O_{12}$ phase. R.R. Wills [13] showed that $Y_{4.67}(SiO_4)_3O$ can be obtained by oxidation from $Y_5(SiO_4)_3N$ in Si-Y-O-N compound since 1000 ° C. By comparison with $Y_5(SiO_4)_3N$, the XRD pattern of $Y_{4.67}(SiO_4)_3O$ is quite similar. However, they differs on its interplanar spacings. On the other hand, Nathan [16] briefly describe that $Y_3Al_5O_{12}$ is produced from the vitreous Al-Si-Y-N-O; he also reported this phase is common in materials with high Al_2O_3 content. That is in accordance with the composition of the samples of the group *a*.

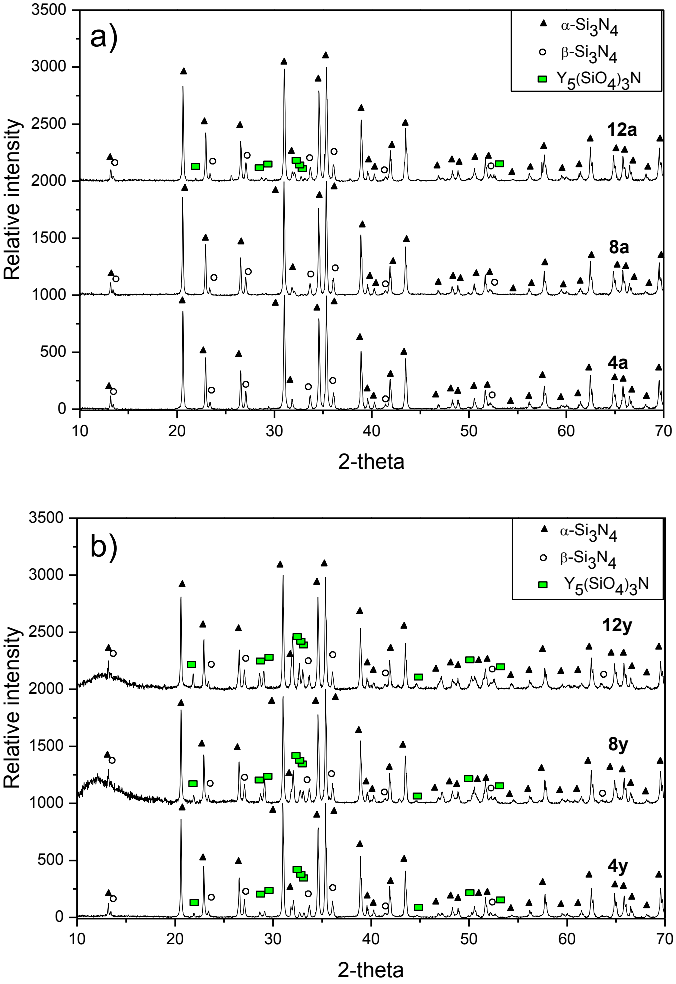

Figure 2. XRD patterns of samples pre-sintered at 1300°C for 1 hour. A) samples of group *a*; b) samples of group *y*.

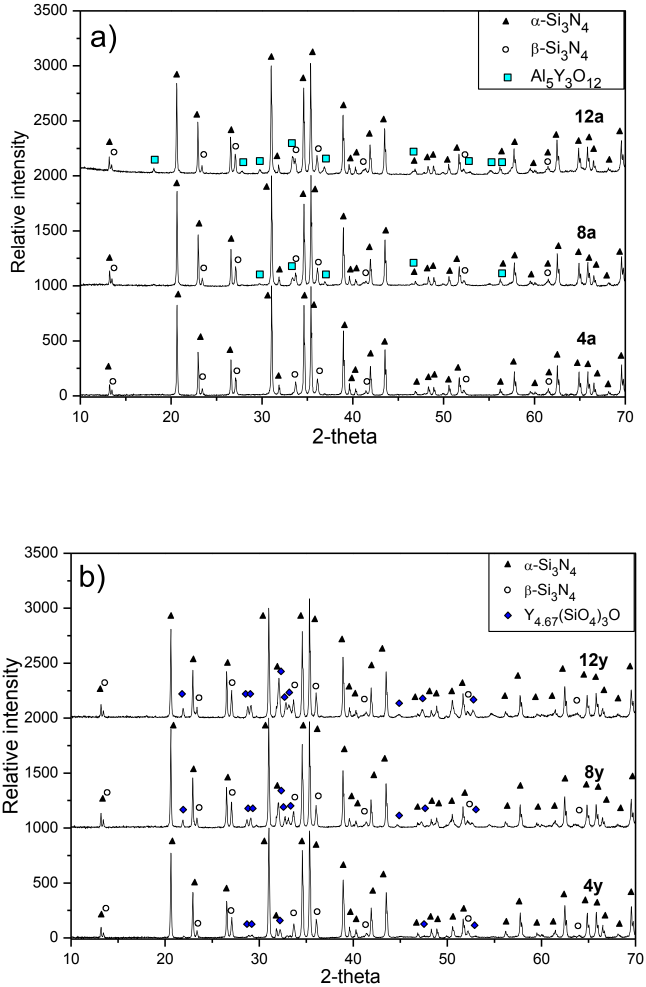

Figure 3. XRD patterns of samples sintered at 1450°C for 2 hours. A) samples of group *a*; b) samples of group *y*.

Scanning electron microscopy.

Figure 4 shows the chemical composition of green bodies samples and after being pre-sintered. An increase in the amount of silicon can be observed in the pre-sintered samples. This result is in agreement with that reported by S. Wada [17] that predicts the passive oxidation of Si_3N_4 according to equation 1.

$$Si_3N_4(s) + 3O_2(g) \xrightleftharpoons{\Delta\ 1027°C} 3SiO_2(l) + 2N_2(g)$$

The presence of SiO_2 in the liquid state allows it to migrate across the grain boundaries of the Si_3N_4 particles and additives. This helps contribute at the increase in the density of the samples through the mechanism of sliding and reordering of the particles. That process form part of the early stage of the liquid phase sintering mechanism [18, 19].

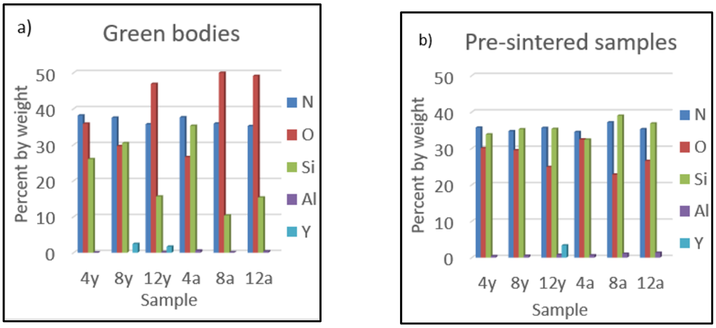

Figure 4. Chemical composition. a) Green bodies; b) pre-sintered samples.

Samples pre-sintered were observed by mapping at 500X in order to locate the particles of additive. Then, these particles were analyzed by EDS to determine its chemical composition and to evaluate changes after the pre-sintering treatment. Figure 5 shows the chemical composition of sites with high content of yttrium, aluminum and matrix of Si_3N_4 that were found in the samples. Figure 5a shows the chemical composition in sites with high yttrium content. Only sample 4a didn't have sites associated with yttrium particle. Chemical composition revealed that sites contain yttrium, oxygen, nitrogen and silicon. This is because some Si_3N_4 particles were added to surface of Y_2O_3. Moreover, according to XRD results, there is evidence that Y_2O_3 reacted with Si_3N_4. The chemical composition determined on sites with high yttrium content in agree with the $Y_5(SiO_4)_3N$ phase. The presence of $Y_5(SiO_4)_3N$ in Si_3N_4 compounds has already been observed by other researchers [14,15]. However, that phase has not been reported at temperature below 1400°C. Figure 5b shows the chemical composition of sites with high aluminium content. In these sites were observed particles of alumina. In exception to samples 12y and 4a, the Al_2O_3 particles only presented oxygen and aluminum as elements in their composition. Nevertheless by observing the Al_2O_3 particles in 4a and 12y, were identified Si_3N_4 particles adhered to its surface. Figure 5c shows the chemical composition of the Si_3N_4 matrix. The analysis revealed the presence of aluminum on the matrix. It suggests that the Al_2O_3 particles were partially dissolved by the SiO_2. The dissolution of Al^{3+} in the Si_3N_4 matrix was also observed by Jack and H. Mao et al. [20,21].

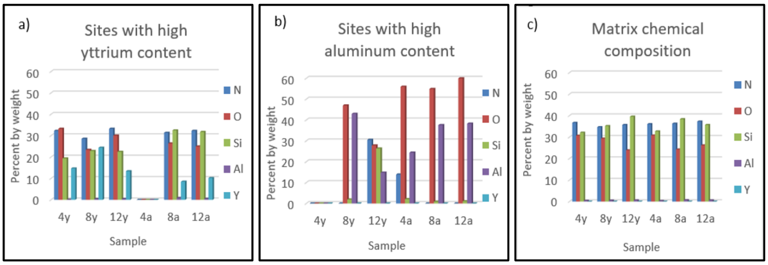

Figure 5.Chemical composition of the most relevant sites in pre-sintered samples.

Analysis of samples sintered by mapping revealed the presence of sites with high yttrium and aluminum content. Figure 6 shows the chemical composition of sites with high content of yttrium, aluminum and matrix of Si_3N_4 that were found in the samples sintered. At the figure 6a were observed two kind of chemical compositions on sites with high yttrium content. These are: 1. Sites with Si, O, Y that were observed in 4y and 8y samples, 2. Sites with N, O, Si, Al, Y that were observed in 12y and 12a samples. The first one agrees with the $Y_{4.67}$ (SiO_4) 3O phase identified in XRD. The oxidation of Y5 (SiO4) 3N were reported by R. Wills and it's represented by ecuation 2 [13].

$$Y_5(SiO_4)_3N + 0.75O_2 \rightleftharpoons Y_{4.67}(SiO_4)3O + 0.165Y_2O_3 + 0.5N_2$$

The second type of chemical composition agrees with the $Y_3Al_5O_{12}$ phase identified in XRD. The Y_2O_3-Al_2O_3-SiO_2 ternary system predicts an amorphous liquid phase above 1371°C [4,6]. According to Nathan [16], $Y_3Al_5O_{12}$ is generate by the Al-Si-Y-N-O vitreous liquid. 4a and 8a samples didn't have sites with high yttrium content because all Y_2O_3 particles reacted to form an amorphous liquid phase. Based on DRX results in figure 3a, only sample 8a have the $Y_3Al_5O_{12}$ phase because the alumina content is higher.

Figure 6b shows sites with high aluminum content. The chemical composition in samples 8y and 12y were type 2. That suggest the presence of $Y_3Al_5O_{12}$ phase in these samples. So, both $Y_{4.67}(SiO_4)_3O$ and $Y_3Al_5O_{12}$ can exist in samples of group *y*. Particles of Al_2O_3 with Si_3N_4 adhered on their surface were observed in samples 4a, 8a and 12a. That suggests there are an excess of alumina and the dissolution reaction was incomplete due to the depletion of SiO_2. Alumina particles only were seen in samples of group *a* because they contain a higher proportion of Al_2O_3 in the additive mixture. The increase of oxygen amount in the matrix indicates that the oxidation reaction of Si_3N_4 remained during the sintering process. Since $Y_5(SiO_4)_3N$ was oxidized to form $Y_{4.67}(SiO_4)_3O$, the presence of new SiO_2 allowed the formation of $Y_3Al_5O_{12}$ from free Y_2O_3 and Al_2O_3.

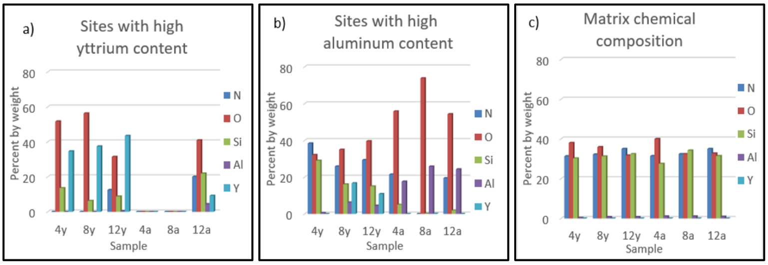

Figure 6. Chemical composition of the most relevant sites in sintered samples.

CONCLUSIONS

The pre-sintering treatment increases the percentage of SiO_2 in the samples as a result the oxidation of Si_3N_4. SiO_2 in liquid state interacts with Y_2O_3 and Al_2O_3 particles that compete to form a primary phase of Y5 (SiO4) 3N and a matrix of Si_3N_4 with low amount of dissolved aluminum.

The $Y_5(SiO_4)_3N$ phase oxidized to form $Y_{4.67}(SiO_4)_3O$ phase during the sintering process. The excess of Al_2O_3 in samples in group *a*, in addition with the continuous oxidation of Si_3N_4 allowed the formation of the $Y_3Al_5O_{12}$ phase.

The composition of sintered samples depends of the composition of the additive added. It was observed that the reaction between SiO_2 with Y_2O_3 and Al_2O_3 particles begins at temperature lower than expected.

Phases generated during pre-sintering process participate in subsequent reactions at the sintering process. The SiO_2 was sufficient to dissolve all Y_2O_3 particles in samples 4a and 8a. However, a greater quantity of SiO_2 is required to dissolve samples with higher additive content.

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