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Sintering of Dense Silicon Nitride Ceramics at Low Temperature

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Abstract. Densification curves of silicon nitride specimens with varying composition were determined with the aid of a dilatometer and these curves are presented in this paper. A novel procedure has been used to determine the densification curves as well as the temperature at which the rate of densification was highest. From these data, sintering profiles have been proposed to produce silicon nitride based ceramics with high apparent density (above 96% of theoretical density) at temperatures as low as 1520º C, with incipient grain growth. This procedure also enabled efficient separation of the densification and grain growth phenomena and it can be used in other two-step sintering studies.

Introduction

The properties of silicon nitride ceramics are extremely sensitive to its microstructural characteristics, and the development of methods to control these characteristics has been the focus of many studies. One of the most interesting and versatile ways to affect the microstructure of silicon nitride is through modification of its sintering profile. Sintering of silicon nitride follows the classical Kingery's model for liquid phase sintering (rearrangement of particles, re-precipitation of solution and grain growth).

The microstructure of Si_3N_4 can be modified by interfering with the three phenomena that happen during sintering: phase transformation, densification and grain growth. These phenomena happen simultaneously, especially during the second stage, as described by the Kingery's model. Based on the understanding that the sintering profile is affected by temperature, time and atmosphere (specimen and gas pressure), several studies have demonstrated the possibility of controlling the final microstructure of silicon nitride by interfering with the occurrence of these phenomena; i.e. by varying the sintering profile. For instance, hot isostatic pressing results in extremely dense Si_3N_4 at relatively low temperatures. This creates a microstructure with very small and spherical grains, and consequently a material with high mechanical strength, but with very low fracture toughness. On the other hand, to obtain a dense material and with abnormal grain growth, it is essential to use high temperatures for long periods, and this can be obtained by using the gas-pressure-sintering technique.

Progress in microstructure-properties correlations has also lead to new proposals involving complex sintering profiles. Presently, the objective has been to obtain very dense silicon nitride with a bi-modal microstructure, with controlled grain size distribution, and with a specific volume fraction of highly anisotropic grains in a fine matrix. Several authors [1-7] have proposed the two-step sintering method in which the material is maintained initially at a certain intermediate temperature T1 for time t', followed by treatment at the final temperature T2 for time t''. The characteristics of the atmosphere used depend on the choice of sintering method. The specified temperatures and times of this process do not follow clear criteria, and depend on the objectives. Some authors [1] seek homogenization of the liquid phase with the first step, while others try to achieve complete phase transformation with the first step and grain growth with the second step. In the latter, densification is not considered [2,3]. Other authors [4] suggest that to obtain a microstructure with a bi-modal grain size distribution, the necessary first step is high densification followed by complete phase transformation and grain growth during the second step. They achieved this by not only manipulating the sintering profile, but with additives.

In this study, with the aid of a dilatometer, densification curves of Si_3N_4 with different compositions were obtained along with their respective densification rates. Identification of the temperature at which densification rate was maximum, for the Si_3N_4 with different compositions, enabled sintering profiles to be defined. This in turn permitted us to obtain dense Si_3N_4 (with above 96% of the theoretical density) at relatively low temperatures and avoided grain growth. This method allowed efficient separation of the densification and grain growth phenomena, and it can be used in other studies involving two-step-sintering.

Materials and methods

Commercially available α-Si_3N_4 powder (M11, H.C.Starck, Germany), Al_2O_3 powder (Baikalox CR-10, Baikowski Chimie, France), Y_2O_3, La_2O_3 and Yb_2O_3 powder (with purity higher than 99.9 %, Aldrich Chemical Co, USA) were used in this study. Samples, with compositions as shown in Table 1, were mixed in an attritor mill for 4 hours and at 400 rpm. The balls and the jar were of silicon nitride, and the milling was carried out with isopropyl alcohol. The slurries obtained after milling were separated from the milling media by sieving (325 mesh) and subsequently dried in a rotary vacuum evaporator.

Cylindrical green bodies (7 and 12 mm in diameter and about 12 mm high) were prepared by uniaxial compaction at 50 MPa and cold isostatic pressing at 200 MPa. Sintering was carried out in a gas pressurized furnace (Thermal Technologies, Santa Barbara, USA) with graphite heating elements in nitrogen atmosphere at 1580°C for 60 to 360 minutes. The density of the sintered samples was determined by the Archimedes method. The sample surfaces were diamond-polished to 1 μm and then plasma etched in a RF Plasma Barrel Etcher (Polaron PT7160) in a mixture of CF_4 and O_2 (2:1 ratio) to reveal structural details. The specimens were then examined in a scanning electron microscope (SEM) (Phillips XL-30 scanning electron microscope). The micrographs were subsequently used for quantitative microstructure analysis.

Table 1. Starting composition of mixtures

Sample (*)	Si_3N_4 [wt%]	Si_3N_4 corrected [wt%] (**)	Al_2O_3 [wt%]	Y_2O_3 [wt%]	La_2O_3 [wt%]	Yb_2O_3 [wt%]	NbC [wt%]
Y7	89.39	92.34	4.56	6.05	-	-	
L7	87.05	89.93	4.44	-	8.51	-	
Yb7	85.51	88.34	4.36	-	-	10.13	
Y3	95.16	98.31	2.08	2.76	-	-	
L3	94.01	97.12	2.06	-	3.93	-	
Yb3	93.23	96.31	2.04	-	-	4.73	
N1(***)	71.05	73.40	3.51	4.65			20.79

(*) – the codes of samples X7 or X3 refer to compositions with 7 mol% and 3 mol% of additives respectively.

(**) – corrected considering 1.668% as the amount of O_2 in the form of SiO_2

(***) – composition Y7 with addition of 10 vol.% NbC

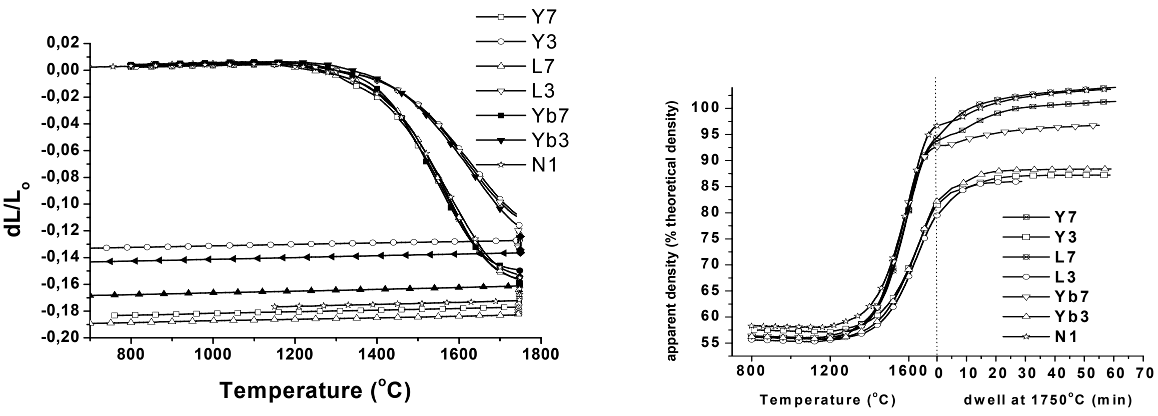
Results and discussion

Cylindrical specimens (7mmφ x 12mm) with the various compositions were prepared and sintered in the high temperature dilatometer (DIL402 E/7, Netzsch Thermal Analysis), in flowing N_2 at temperatures up to 1750º C and heating rate of 20 º C / minute. From these measurements the densification parameters were determined. Subsequently the heat treatment of silicon nitride was altered using the two stage method. This enabled high density bodies to be obtained at relatively lower temperatures.

The densification curves of specimens sintered at 1750º C with heating rate of 20º C /minute are shown in Fig. 1. The effect of the amount of additive on densification can be clearly seen. The specimen with a composition that contained 7 mol% of additives revealed highest shrinkage and attained apparent density values higher than 96% of the theoretical density. The apparent density of the specimens with 3 mol% of additives did not go beyond 90% of its theoretical density. As for the effect of the composition of the sintering additive, no significant differences in the shapes of the densification curves were observed during the whole heating stage up to 1700º C. However, beyond this temperature, a clear difference was observed in the plateau at 1750º C. The specimen Yb7 revealed slight densification at the plateau (at 4%), followed by Y7 (at 6%) and L7 (at 9.5%). The specimens with lower amounts of additives, such as L3, revealed least densification. The beneficial effect of adding NbC on the densification of specimens with composition corresponding toY7 was significant. The apparent density values as a function of temperature ρ(T) were calculated using equation 1 and the theoretical density values (table II) were obtained using the rule of mixtures.

$$\rho(T) = \rho_0 \left(\frac{L_0}{L(T)} \right)^3 \quad . \tag{1}$$

where ρ_0 is green density, L_0, the initial length of the specimen and L(T), the length at temperature T.



(a) (b)

Figure 1. Densification curves of Si_3N_4 specimens, with varying compositions, treated in a dilatometer at 1750 º C for 60 minutes.

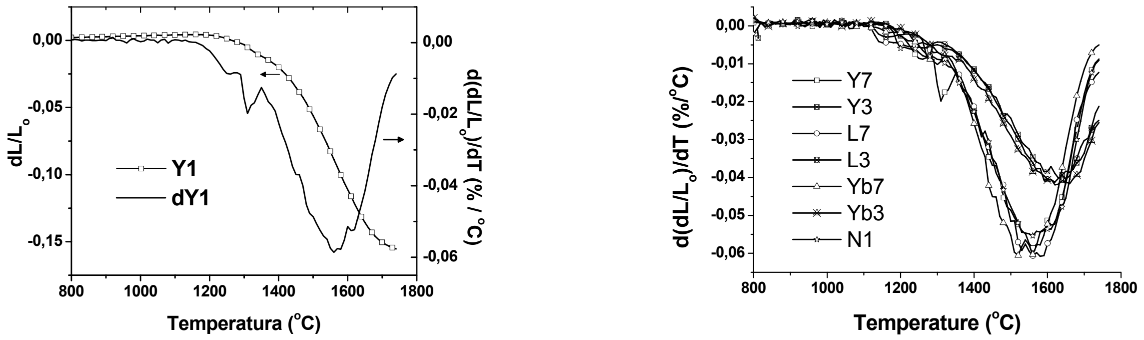
Linear shrinkage rate versus temperature curves were constructed for Si_3N_4 specimens with the different compositions from the derived linear shrinkage versus temperature curves in Fig. 1(a). Figure 2(a) presents, as an example, the linear shrinkage curve for Y7 with the corresponding derivative that gives the linear shrinkage rate. Figure 2(b) shows the shrinkage rate versus temperature curves for the different compositions and enables comparison of the influence of composition and the amount of sintering additives on their profiles. These curves are shown separately in Fig. 3 to observe other details. The temperatures for shrinkage rates are indicated.

Besides the peaks of maximum shrinkage rate, other smaller secondary peaks can be observed between 1100º C and 1300º C, and these can be related to the start of liquid phase formation, and to other phenomena related to the start of sintering. Occurrence of the first peak and the start of liquid phase formation are related, and consequently, the start of densification by rearrangement. In Ln-Si-Al-O-N [8] type glasses and lanthanide containing alumino-silicates [9], the softening temperature is inversely proportional to the ionic radius of the lanthanide. Hence, the first peaks were observed at 1145º C for the composition containing La, at 1257º C for the composition containing Y, and at 1300º C for the composition containing Yb.

The maximum shrinkage rates for compositions containing 7 mol% of additive, occur at temperatures between 1520º C and 1580º C, and for the compositions containing 3 mol% additive, at temperatures between 1620º C and 1630º C. It can be seen that the quantity of additive, and therefore the liquid phase, affect the magnitude of the shrinkage rate. The compositions with higher amounts of additives undergo higher rates of shrinkage at lower temperatures. Table 2 presents the maximum shrinkage rate values, and the temperatures at which these occur for all the compositions.

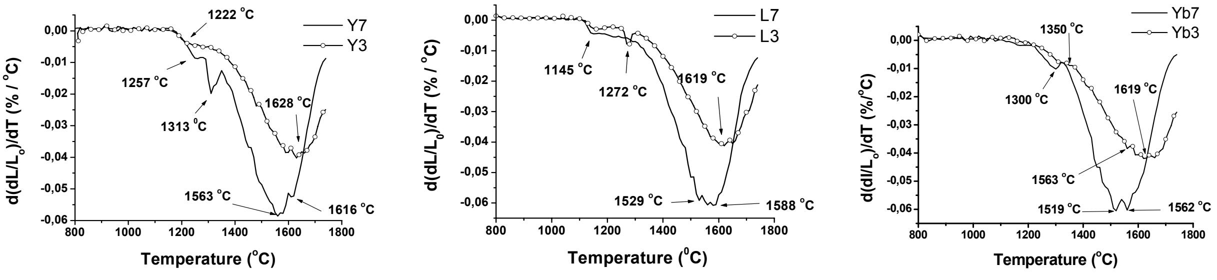
Table 2 – Theoretical density values (obtained using the rule of mixtures) and maximum shrinkage rates for the various compositions.

composition	Theoretical density [g/cm^3]	Maximum shrinkage rate temperature [ºC]	Maximum shrinkage rate x10^{-2} [% / ºC]
Y7	3.254	1563	-5,84
Y3	3.199	1628	-4,02
L7	3.323	1580	-6,08
L3	3.230	1619	-4,13
Yb7	3.404	1519	-6,06
Yb3	3.266	1621	-4,19
N1	3.702	1560	-5,54



(a) (b)

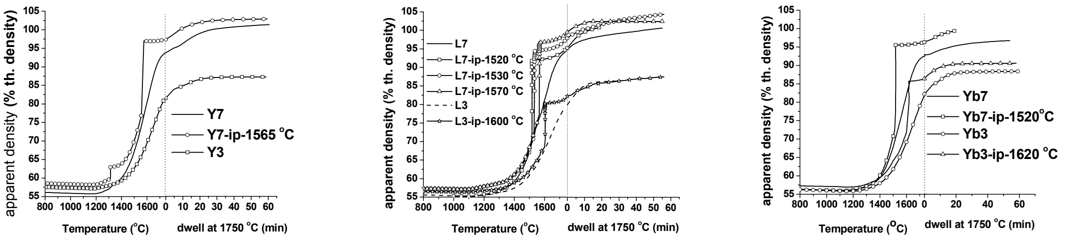
Figure 2 Linear shrinkage curves and corresponding derivatives, as a function of temperature.



(a) (b) (c)

Figure 3. Maximum shrinkage rate versus temperature curves for compositions: (a) Y7 and Y3, (b) L7 and L3 and (c) Yb7 and Yb3.

On the basis of data obtained so far, specimens with the various compositions were sintered in the dilatometer, at 1750º C with an intermediate plateau for 60 minutes at their respective maximum shrinkage rate temperatures. Further experiments were carried out in which the intermediate plateau temperature of composition L7 was varied (1520, 1530 and 1560º C), and a second intermediate plateau (1313º C/60 min), related to the second observed peak, was introduced during the heat treatment of compositionY7. Figure 4 shows the densification curves that were obtained for the different compositions, and permits evaluation of the effect of introducing the intermediate plateaus during heat treatment. On the basis of these curves one may conclude that introduction of intermediate plateaus at temperatures related to the maximum shrinkage rates, leads to improvement in the final density of the materials that have been studied here. From Fig. 4-b it can be seen that for composition L7, even with change in the intermediate plateau temperature (between 1520º C and 1570º C), the beneficial effect on densification is maintained. It shifts from 72% to 92% of theoretical density with a plateau of 60 minutes at 1520º C, from 72% to 94.5% with the plateau at 1530º C, and from 72% to 97% with the plateau at 157º C. In this temperature range the shrinkage rate is high for all compositions containing 7 mol% of additive (see Fig. 3). Hence, with the temperature plateau related to the maximum shrinkage rate, for silicon nitride with 7 mol% additive, densities higher than 96 % of theoretical density can be attained even at temperatures as low a 1520º C.



(a) (b) (c)

Figure 4- Effect of intermediate temperature on densification of compositions: a) Y7, b) L3 and L7, c) Yb3 and Yb7.

Figure 5 shows that sintering at 1580º C brought about densification of specimens with 7 mol% additives, attaining apparent densities higher than 96% of theoretical densities. In specimens with compositions containing 3 mol % of additives, densification did not occur to the same extent and the apparent density remained around 83% of the theoretical density, even after 360 minutes at the plateau. These results are in agreement with data obtained from the dilatometer measurements. The latter revealed that high density specimens could be obtained, with compositions containing 7 mol% of additives, after treatment at the relatively low temperature plateaus and which correspond to low shrinkage rates.

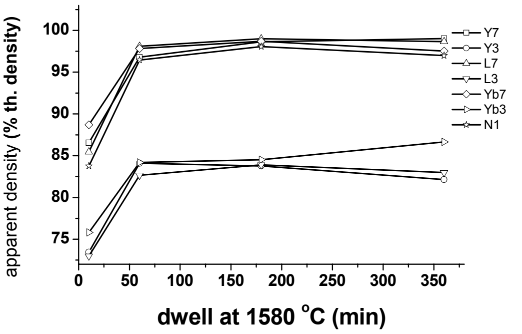
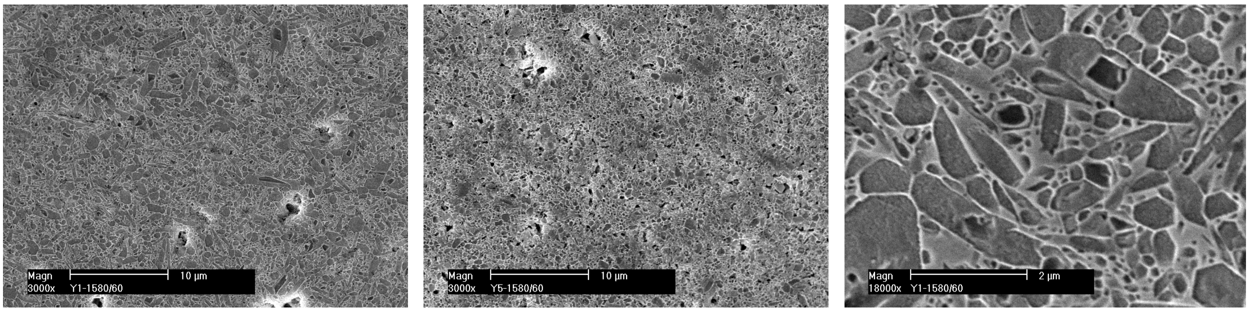


Figure 5 – Apparent density with sintering at 1580º C for different durations.

Figure 6 shows micrographs of specimens Y7 and Y3 sintered at 1580º C for 60 minutes. Densification of these specimens can be observed and in specimen Y3, as one would expect, high residual porosity. At the maximum shrinkage rate temperature, it can also be observed that in spite of initiation of grain growth (Fig. 6-c), there is a clear separation between the densification phenomenon (almost total) and grain growth (incipient) phenomenon. This fact will be used in future two-stage sintering studies.



(a) Y7- 60 min. (b) Y3 – 60 min. (c) Y7 – 60 min.

Figure 6 – Micrographs of specimens sintered at 1580º C, revealing very few pores.

Conclusions

Determination of the maximum densification rate temperature enabled silicon nitride bodies with very high densities (>96% of theoretical density) to be obtained at relatively low temperatures. This temperature also permitted separation of the phenomena, densification and grain growth. This in turn enabled tailoring of the microstructure and consequently, the properties of silicon nitride. Finally, introduction of an intermediate plateau at this temperature brought about improvements in final densification of silicon nitride obtained by two-stage sintering.

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