

Study of the Sintering Kinetics of Silicon Nitride Containing Ceria and Alumina Additives

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Abstract: Sintering kinetics of silicon nitride based ceramics with CeO₂ and Al₂O₃ sintering aids was investigated. The total amount of oxides was kept constant at 10 weight %, while the ratio of Ce₂O₃ and Al₂O₃ was a variable parameter. Dilatometric experiments showed that the investigated materials in general densified readily. However, the increase of Ce₂O₃ contents hindered densification, shifting the maximum values of shrinkage to higher temperatures. The changes observed in the sintering kinetics behavior promote no variation in the final microstructure.

Introduction

The structural silicon nitride based ceramics are largely used in automotive engine components, cutting tools, refractories, and many other applications, mainly in the engineering area [1-4]. To achieve high density, oxide additives are usually used leading to a liquid phase formation during sintering [5-9]. The densification mechanism involves grains rearrangement and $\alpha \rightarrow \beta$ transformation of silicon nitride during solution-reprecipitation process [10-12]. The understanding of the relationships between processing, sintering, phase formation and final microstructure of the material is of fundamental importance, so that the properties can be appropriately adjusted, according to the materials final application [13-14].

The objective of this work is the study of sintering kinetics of silicon nitride using ceria and alumina as sintering aids, so that high-density materials can be obtained, with homogeneous microstructure.

Experimental Procedure

Si₃N₄ powders (H. C. Stark, grade M11, mean particle size of 0.51 μm , $\alpha = 92.7\%$), CeO₂ powders (Nuclemon, 97.2% pure, mean particle size of 1.64 μm after firing at 500 °C/1 h), and Al₂O₃ powders (Alcoa, grade A16-UG, mean particle size of 28.16 μm) were mixed in an attritor with silicon nitride milling media in isopropanol for 6 h. After the mixture was dried in a drying box at 100 °C for 24 h, it was milled in a porcelain mortar and passed through a 40 mm sieve to break soft agglomerates. Those mixtures were uniaxially pressed into cylindrical pellets, which were subsequently cold-isostatically pressed at 200 MPa for green density improvement.

Sintering experiments were carried out in a dilatometer (Netzsch, DIL 402 E/7) at a heating rate of 15 deg/min up to 1750 °C and holding for 1 h under flowing high purity nitrogen. Sintering was also accomplished in a graphite resistance furnace (Nukem). The samples were placed in a silicon nitride powder bed inside a graphite crucible lined with BN. Sintering was conducted according to the time-temperature schedule previously applied for dilatometric experiments.

Sintered samples were fully characterized. Density was determined geometrically and by Archimedes method. Crystalline phases were investigated by XRD (Phillips PW 1710), and the microstructures were observed on scanning electron microscope (Philips XL 30). Samples were prepared by a standard ceramographic procedure of multistep diamond grinding and polishing. For grain morphology observation polished samples were plasma etched using CF6. Analysis of β - Si_3N_4 grain morphology was further estimated by means of Quantikov image analyzer [15]. Grain size distribution, grain aspect ratio and other relevant morphological parameters were determined.

Results and Discussion

Nominal compositions of prepared mixtures, as well as the sintering aids ratio, are presented in Table 1. The theoretical densities were calculated using the rule of mixtures and are also shown. It was assumed that during sintering reduction of ceria ($2\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3 + 1/2 \text{O}_2$) and complete α to β transformation of silicon nitride occur.

Table 1: Mixture compositions

Composition	Si_3N_4 (wt %)	Ce_2O_3 (wt %)	Al_2O_3 (wt %)	$\text{Ce}_2\text{O}_3:\text{Al}_2\text{O}_3$ weight ratio	Theoretical density Td (g/cm^3)
90-4Ce	90	4	6	3: 4.5	3.29
90-6 Ce	90	6	4	3 : 2	3.31
90-7.5Ce	90	7.5	2.5	3 : 1	3.32

Results of dilatometric experiments are present in Table 2.

Table 2: Density values and temperatures of maximum shrinkage obtained for samples sintered in dilatometry.

Sample	weight loss (%)	green density (% Td)	Density of sintered samples		T1 ($^{\circ}\text{C}$) (see text)	T2 ($^{\circ}\text{C}$) (see text)
			geometrical (% Td)	apparent (% Td)		
90-4Ce	4.7	55.1	93.0	94.1	1120	1520
90-6Ce	6.3	56.2	93.6	95.4	1130	1600
90-7.5Ce	7.8	56.0	93.4	94.8	1160	1650

Two distinct peaks of linear shrinkage rate were present on all dilatometric curves (Fig. 1b), indicating the two stages of the densification process. The first one is attributed to the particle rearrangement, while the second corresponds to the solution-precipitation stage of the liquid phase sintering. The temperatures corresponding to the maximum shrinkage ratio for both stages, T1 and T2 respectively, are listed in Table 2.

The analysis of the shrinkage curves presented in Fig. 1a shows that the shrinkage continues during the isothermal part of heat treatment. From Fig. 1b, where linear shrinkage rate versus sintering time curves are presented, it can be seen that the higher amounts of ceria sintering aid causes the shift of both stages of shrinkage to higher temperatures. This fact can be explained by the lower amount of alumina in these samples, which is the main glass former in the system under investigation. The high alumina amount also act on the liquid formed, decreasing the viscosity. The effect of $\text{Ce}_2\text{O}_3:\text{Al}_2\text{O}_3$ ratio variation become clear if the data from Table 2 and Fig. 1b are considered together.

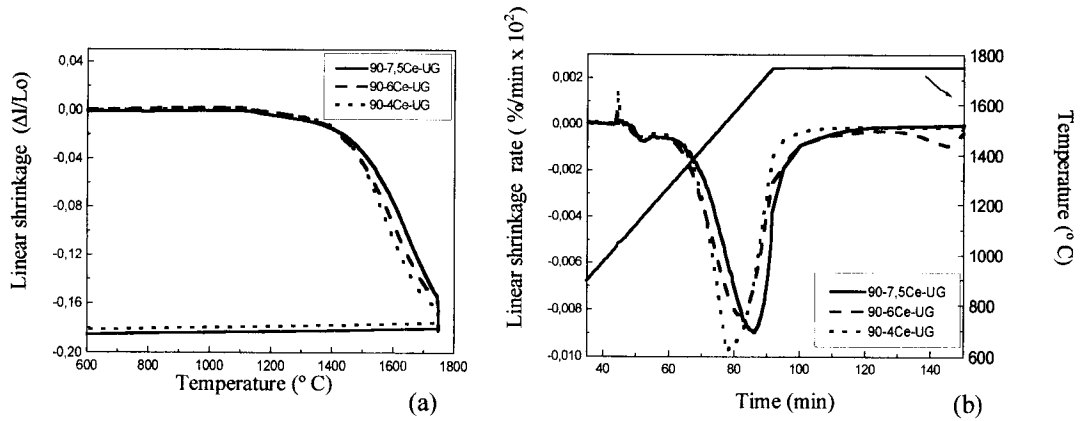


Fig. 1: Dilatometric curves obtained for silicon nitride samples
 (a): Linear shrinkage versus sintering temperature
 (b): Linear shrinkage rate versus sintering time

Curves of linear shrinkage versus the relative density of the samples are presented in Fig. 2. It is observed that all samples reached high densities. However, the maximum shrinkage rate shifts to higher relative densities with the decrease of Al₂O₃ content.

The results of sintering performed in the graphite resistance furnace are presented in Table 3. All the relevant characteristics of the samples after furnace sintering are similar to the ones after sintering in dilatometer [16-18]. The same trends in regard of densities are observed.

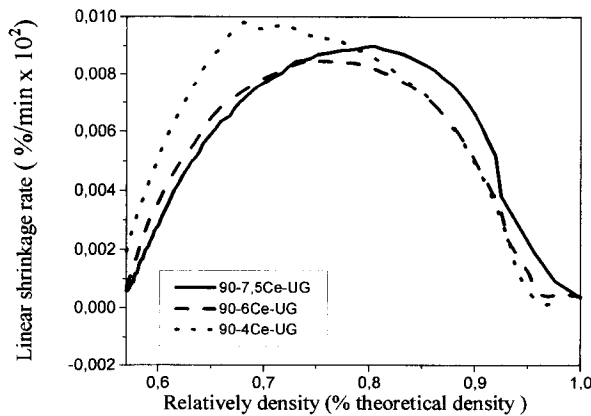


Fig. 2: Linear shrinkage ratio versus samples relative density

Table 3: Sintering results obtained in a graphite resistance furnace

Sample	weight loss (%)	green density (% Td)	Density of sintered samples	
			Geometrical (% Td)	apparent (% Td)
90-4Ce	4.7 ± 1.9	56.8 ± 0.1	94.5 ± 0.4	96.1 ± 0.2
90-6Ce	6.1 ± 1.8	56.9 ± 0.3	95.7 ± 0.4	96.1 ± 0.1
90-7.5Ce	7.5 ± 0.7	56.9 ± 0.2	95.4 ± 0.3	97.1 ± 0.1

The results of XRD analysis of the bulk of the sintered samples are presented in Fig. 3. The main crystalline phase that was present in all sintered materials was β - Si_3N_4 . Secondary phases composition changes as a function of the sintering aids ratio. Silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$), CeSiO_2N and one of the cerium silicates - $\text{Ce}_{4,667}(\text{SiO}_4)_3$; $\text{Ce}_5\text{Si}_3\text{O}_{12}\text{N}$ or $\text{Ce}_{10}(\text{Si}_{3,61}\text{N}_{0,39})_6\text{O}_{1,83}$ - were identified as secondary phases, but in a random way. A more precise definition of cerium silicates presented a problem due to the low amounts of the phase present in the sample, and to structural parameters similarity of the silicates in question.

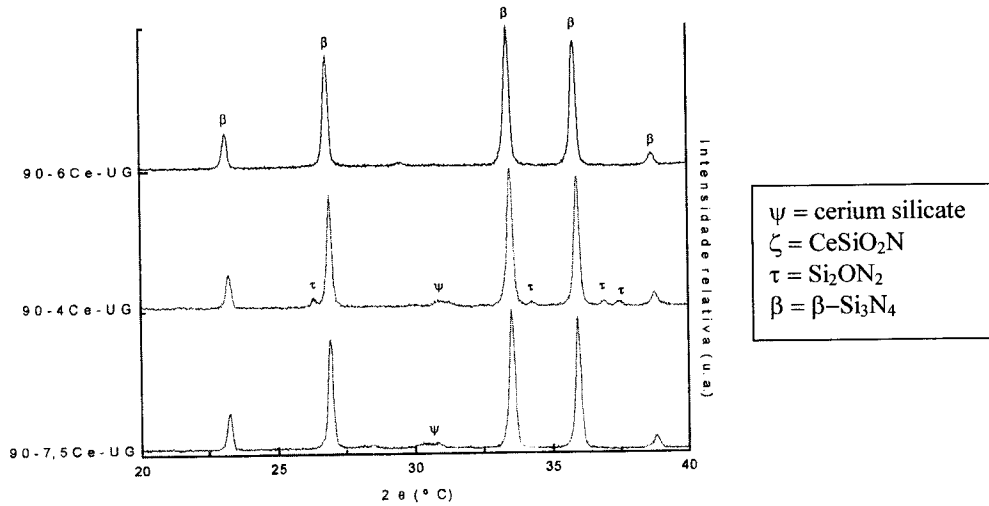


Fig. 3: X-ray diffratograms of sintered samples.

The sintering kinetics behavior (Figs. 1 and 2) could suggest a microstructural variation among the several compositions studied. However, as investigated by scanning electron microscopy (SEM) on the polished surfaces, the microstructure of the sintered samples displays no composition dependence. The back-scattered electron images presented in Fig. 4 show that the secondary phase is homogeneously distributed, indicating the high homogeneity of the mixtures.

In order to evaluate the grain morphology of β - Si_3N_4 polished samples were plasma etched. The micrographs obtained as a secondary electron image (Fig. 5) reveals the rod-like morphology of the β - Si_3N_4 grains. From these images, the mean grain size, the aspect ratio, the shape factor, and the specific surface area of the β - Si_3N_4 grains were determined using the Saltykov method [15]. The results are presented in Table 4. The mean grain size of the β - Si_3N_4 grains, as well as the others parameters, did not vary with the different compositions, keeping the processing conditions.

Table 4: Parameters determined by Quantikov program

Sample	mean grain size (μm)	aspect ratio	shape factor	Sv ($1/\mu\text{m}$)	mean intercept (μm)
90-4Ce	0.2 ± 0.5	1.9 ± 0.9	0.74	0.8	1.1
90-6Ce	0.3 ± 0.2	2.0 ± 0.9	0.73	2.3	0.9
90-7.5Ce	0.3 ± 0.5	2.1 ± 0.9	0.72	5.1	0.9

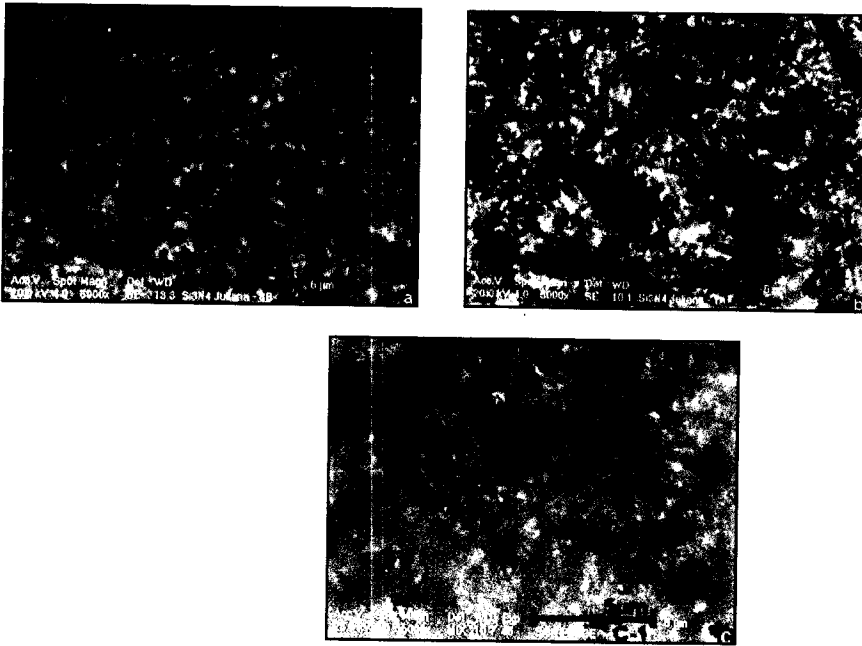


Fig. 4: Scanning electron micrographs of polished samples
(a): 90-4Ce; (b): 90-6Ce; (c): 90-7.5Ce

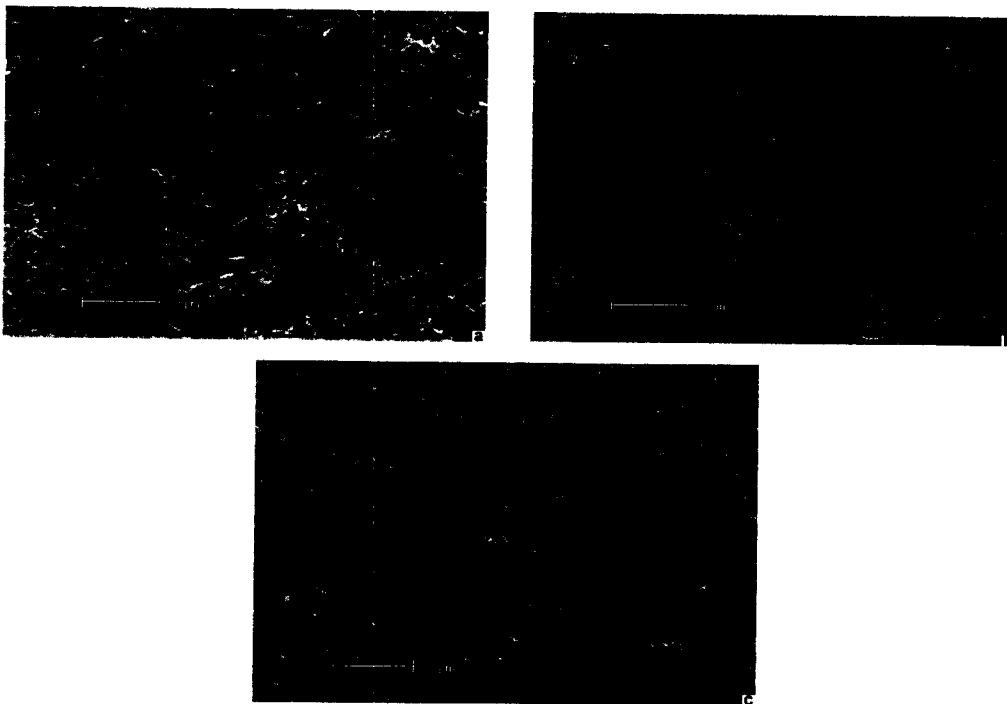


Fig. 5: Scanning electron micrographs of polished and plasma etched samples.
(a): 90-4Ce; (b): 90-6Ce; (c): 90-7.5Ce

Conclusions

For the silicon nitride based ceramics doped with ceria and alumina, the total amount of 10 wt % of sintering aids was sufficient for densification to achieve 95% of the theoretical density under conditions of pressureless sintering.

Higher alumina content promoted densification, by two mechanisms (particle rearrangement and solution-precipitation), shifting the maximum of the shrinkage rate towards lower temperature, due to the intrinsic characteristic of alumina as a glass former. Therefore, higher rates of shrinkage were observed at higher relative densities. The changes observed in sintering kinetics behavior promoted no variation in the final microstructure. All materials presented good homogeneity of secondary phases distributions. Typical rod-like β - Si_3N_4 grain morphology was observed.

β - Si_3N_4 shows to be a predominant crystalline phase in all sintered materials thus confirming the α - β transformation to be complete during sintering. Minor amounts of Ce-rich secondary phases were also identified.

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