Sintering Behavior of Si$_3$N$_4$-TaC based composites

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Abstract: Silicon nitride was the first nitride developed for engineering applications. The excellent combination of thermomechanical properties makes silicon nitride a good candidate for applications where high hardness and mechanical properties are fundamental. However, the low fracture toughness of this material limits its use as structural material. The improve of mechanical properties of silicon nitride comes from many factors, like refined microstructure by restraining grain growth, localized stress, crack tip bridging, etc. Within these factors, microstructure formation of the silicon nitride is critically important for the final properties. The design of silicon nitride based composite materials is of particular interest because of their improved high temperature strength and fracture toughness. In this work, Si$_3$N$_4$-TaC particulate composite was investigated. For this study was prepared a basis composition (CB) with 90%wt α-Si$_3$N$_4$, 6%wt and 4%wt Y$_2$O$_3$ and Al$_2$O$_3$, respectively. TaC (20%vol) was added into CB and after mixture, in high-energy milling, the powder was compacted into pellets. The kinetics of sintering was studied by means of dilatometry. The shrinkage rate versus time and temperature curves exhibit two well-defined peaks. The first peak refers to the particle rearrangement process and the second, more pronounced, to solution-reprecipitation process. It is quite clear that the presence of TaC particles has small influence on sintering kinetics of silicon nitride. It was observed the complete α→β-Si$_3$N$_4$ phase transformation. The microstructure shows good homogeneity both in regard of grain size and secondary phase distribution.

Introduction

In the last 20 years has been given increasing importance to ceramic materials for engineering applications, despite their inherent brittleness. Because of their high strength, hardness and thermal stability, silicon nitride ceramics are among the most important materials for structural applications. The need for further improvement in the mechanical reability of silicon nitride has recently led to the development of high-strength and high toughness ceramics, such as fiber-, whisker- or particulate-reinforced silicon nitride ceramics [1].

Silicon Carbide was used as an addition to silicon nitride more than 20 years ago. Although silicon nitride monolithic ceramics exhibit very attractive properties, the design of silicon nitride based composite materials is of particular interest because of their improved high temperature strength and fracture toughness[2, [3, [4, [5, [6].

The improve of mechanical properties of silicon nitride based composites comes from many factors, like refined microstructure by restraining grain growth, localized stress, crack tip bridging, etc. Within these factors, microstructure formation of the silicon nitride matrix is critically important for the final properties [7].

There are three stages for the microstructure formation in silicon nitride ceramics: β-Si$_3$N$_4$ nucleation, α→β-Si$_3$N$_4$ phase transformation and rod like β-Si$_3$N$_4$ grain growth (Ostwald

Ripening)[8]. The addition of a second phase, both the $\alpha \rightarrow \beta$-Si_3N_4 phase transformation and grain growth are generally restrained [8, [9, [10].

The effect of grain boundary *"pinning"* by small inclusions is described by Zener [15], and the relationship between grain size and inclusions can be given as following:

$$\overline{D} \propto \frac{r}{V_1}$$

where Đ is the average matrix grain diameter, r and V_1 are the radius and volume fraction of spherical inclusions. Zener's model is applied to a system that contains monosized, spherical, insoluble, immobile particles and considers the retarding force exerted by these particles on rigidly moving boundauries. This retarding force is derived from a reduction in grain boundary area and, thus, grain boundary energy, which results from the presence of a particle on a boundary [15].

The purpose of this work is study the sintering behavior of Si_3N_4/TaC based composites.

Experimetal Procedure

Mixtures were prepared from high-purity powders of α-Si_3N_4 (H.C.Starck – M11 with 92,7% of α-Si_3N_4), TaC (H.C.Starck – HGS), Al_2O_3 (A16/SG Alcoa) and Y_2O_3 (99,98% purity, Aldrich Chemical Company).

For this study was prepared a composition containing 90wt% of α-Si_3N_4, 6wt% of Y_2O_3 and 4wt% of Al_2O_3 as sintering additives. This composition was named CB. The CB was mixed in an attrition mill with Si_3N_4 milling media, in isopropanol alcohol for 4 hours at 300rpm. The slurry obtained was separated from the milling media by passing through a ASTM 325 sieve and subsequently dried in a rotary evaporator.10 and 20 vol% of TaC powder was added into CB and the composition was prepared using the same conditions described before. The powder was passed through a ASTM 100 sieve to crush soft agglomerate. The powder was compacted by uniaxial pressing (50MPa) and cold isostatic pressing (200MPa) into cylindrical specimens with 7 and 14 mm in diameter.

Dilatometric experiments were accomplished in a high temperature dilatometer (DIL 402 E/7, Netzsch, Germany) with a graphite resistance furnace in a flowing nitrogen atmosphere. The heating rate, pattern and cooling rate were 20°C/min, 1750°C/1h and 30°C/min, respectively. Sintering of the samples with 14mm was accomplished in a gas pressure furnace (Thermal Technologies, Santa Barbara, USA) with a graphite heating element, at 1750°C and 1800°C for 1 hour, in nitrogen atmosphere under 1,5 MPa pressure.

Sintered samples were characterized for weight loss, density (Archimedes method), phase composition, by X-ray diffraction (XRD) and microstructure (SEM – Phillips XL30). Samples for microstrucure investigation were prepared by standard ceramographic procedure of multistep diamond polishing with subsequent plasma etching (CF_4).

Results and Discussion

The nominal formulation of the prepared mixtures, together with some of their granulometric characteristics are presented in Table 1.

The results of dilatometric investigations, linear shrinkage and shrinkage rate as function of temperature, of the sample with 20vol% TaC and CB are presented in Fig. 1. The behavior observed for the CB+20vol% TaC is quite similar of that observed for the CB. The begging of shrinkage and the maximum shrinkage rate are similar for both samples (Table 2).

The shrinkage rate *vs.* temperature, of the CB, exhibit two peaks of maximum shrinkage rate. The first peak observed, in lower temperature, refers to the liquid formation and rearrangement of the particles. The second peak, observed in higher temperature, refers to the solution-reprecipitation process. When 20vol%TaC is added into CB, it was observed that the peak of liquid

formation and solution-reprecipitation occurs in lower temperature. So, the evolution of the composite is the similar as observed in CB, but the shrinkage occurs faster in composite than in the CB. The lower temperature, of liquid formation and solution-reprecipitation, observed in the sample with 20vol%TaC (Table 2) was expected due to the lower total amount of additives.What should be specifically emphasized is that the presence of a second phase do not interfer on solution-reprecipitation process of silicon nitride.

Table 1 – Characteristics of the starting and mixtures powders

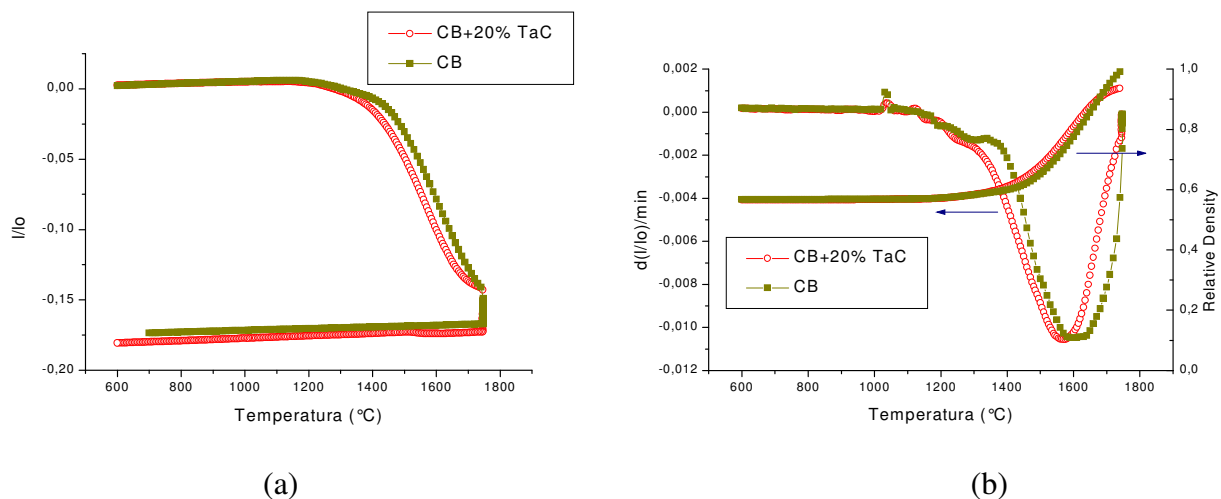| Material	CB (g)	TaC (g)	Grain size distribution (µm)			Specific Surface Area (m^2/g)
			d_{10}	d_{50}	d_{90}	
CB	100	0	0.12	0.44	1.03	15.5
TaC	0	100	0.54	2.11	11.6	1.0
CB+10vol% TaC	68.10	31.90	0.10	0.43	1.11	10.6
CB+20vol%TaC	48.69	51.31	0.09	0.42	1.22	9.7

(a)   (b)

Fig. 1 – Results of dilatometric experiments: (a) linear shrinkage *vs* temperature and (b) shrinkage rate *vs.* temperature

Based on the results of dilatometric investigations, the time-temperature schedule for furnace sintering was determined. The sintering temperature was 1750°C and 1800°C due to the fact that the shrinkage still occurs at 1750°C (dilatometer result).

Table 2 – Maximum retraction temperature of the CB and composite

Sample	Begging of retraction (°C)	Maximum Retraction Temperature	
		Peak 1 (°C)	Solution-Reprecipitation (°C)
CB	1170	1300	1650
CB+20wt% TaC	1170	1220	1590

The density and relationship between TaC content and relative density, of the samples sintered in graphite resistance furnace, are shown on Fig. 2 and Table 3. When the composite was sintered at 1750°C, the relative density decrease with the increase of TaC content. However, the relative density of the composites, sintered at 1800 °C is the same. For the monolithic Si_3N_4, the relative density is higher than those observed for the composites. This observation suggests that a large amount of TaC particles inhibit the densification of the material. Many authors show that the densification is substantially retarded by the addition of a second phase [11, [12, [13]. In the case of

Si_3N_4/SiC composites, some theories about the effect of SiC second phase particles were demonstrated. Yang et al[14] observed that the SiC particles decreases the sinterability of composite, which causes the lowering density and limit the Si_3N_4 grain growth by *"pinning"* and slowing down the grain boundary movement.

Thus, the final density of the composite, residual porosity and microstructure are closely related with the amount and size of second phase particles.

Table 3 – Apparent density of the materials

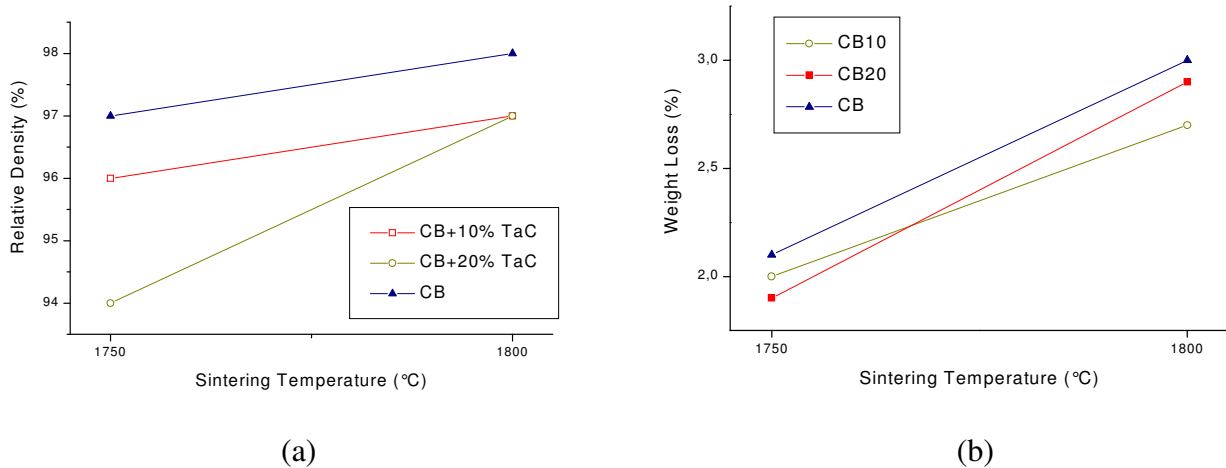| Samples | Dt (g/cm³) | SINTERIZATION | | | |
| | | 1750°C/1h | | 1800°C/1h | |
		%Dt	%weight loss	%Dt	%weight loss
CB	3.30	97	2.1	98	3.0
CB+10vol%TaC	4.36	96	1.7	97	2.7
CB+20vol%TaC	5.42	94	1.9	97	2.9

(a)   (b)

Fig. 2 – Effect of sintering temperature on density (a) and weight loss (b) of the studied composites

X-ray diffraction patterns of sintered composites and CB are shown in Fig. 3. Major phases in the composites were β-Si_3N_4 and TaC. There was not identified any secondary phase resulting from crystallization of the additives and reaction of TaC with the additives or N_2 atmosphere.
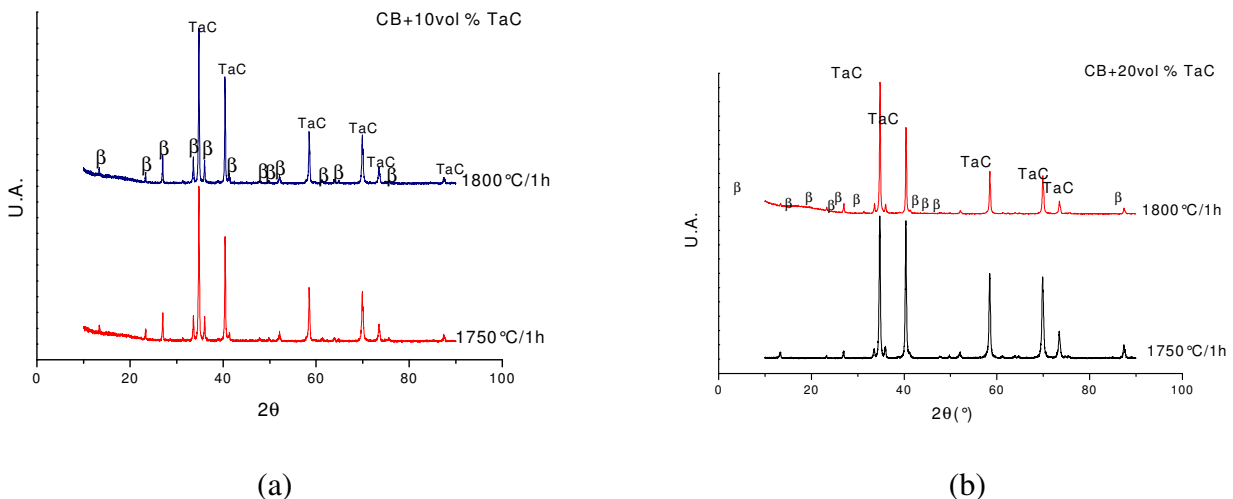

(a)   (b)

Fig. 3 – X-ray diffractograms of sintered samples: (a) CB+10vol%TaC and (b) CB+20vol%TaC

The microstructures of the monolithic Si_3N_4 and of the composites before and after plasma etching are presented in Fig. 4. The microstructure of the monolithic Si_3N_4 is a typical one of a liquid phase sintered silicon nitride, consisting of elongated β-Si_3N_4 grains of prismatic shape embedded into a secondary phase formed by the oxide sintering aids. The composites have elongated grains, similar to the monolithic Si_3N_4. The TaC particles are uniformly distributed in the materials, among the grains. Some grains of β-Si_3N_4 exhibit an internal structure indicated by arrows, with a core in the middle visible after plasma etching. This kind of microstructure occurs due to the β-Si_3N_4 grains, in the starting powder, act as nucleation sites for new β-Si_3N_4 grains. During densification of silicon nitride based ceramics, can be distinguished two differents mechanisms of nucleation: homogeneous or heterogeneous nucleation. In both cases, nucleation occurs from the supersaturated oxinitride glass, but in case of heterogeneous nucleation the β-Si_3N_4, present at starting powder, act as a nucleation sites. So, the core observed in β-Si_3N_4 grains pre-existant grains in starting powder.

(a)   (b)
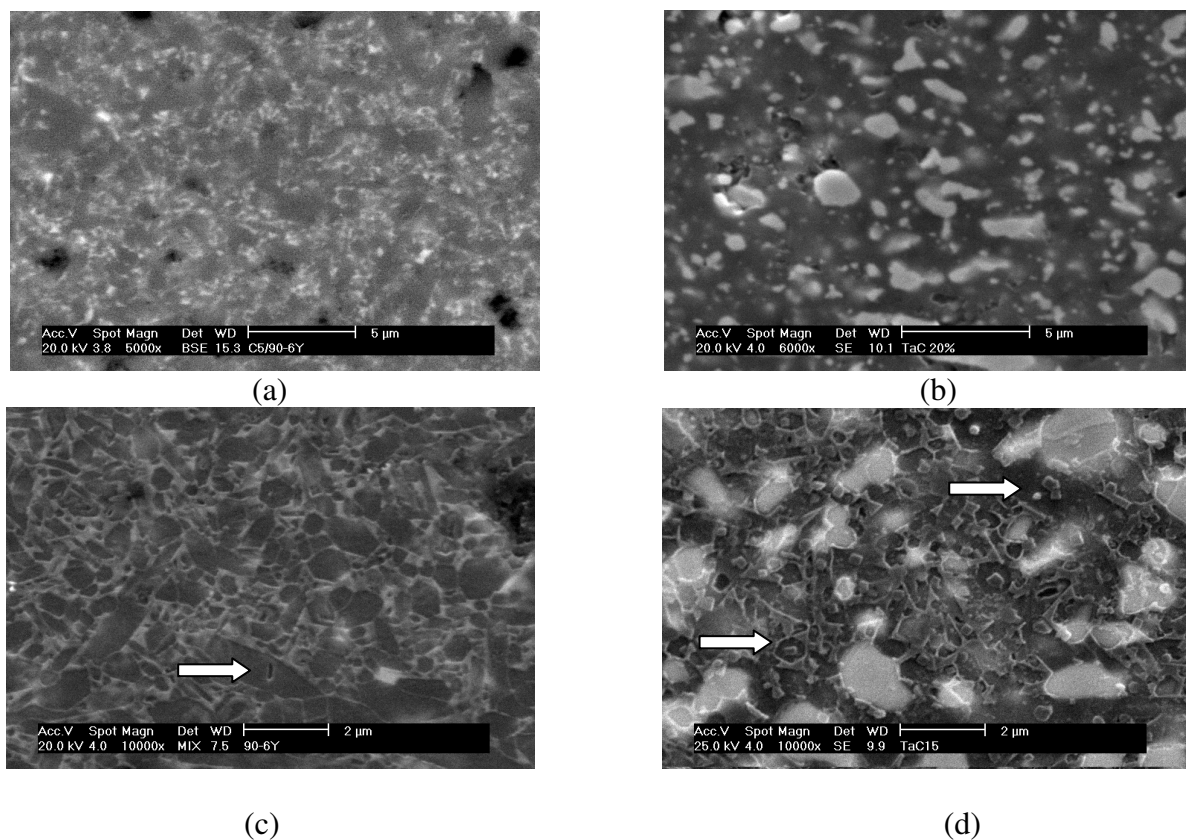
(c)   (d)

Fig. 4 – Microstructure of (a) CB before plasma etching; (b) CB+20vol%TaC before plasma etching; (c) CB after plasma etching and (d) CB+20vol%TaC after plasma etching, sintered at 1750°C/1h

Conclusions

The influence on sintering behavior of TaC in a Si_3N_4 matrix was investigated by dilatometric experiments and pressureless sintering.

The addition of TaC into Si_3N_4 don't have a prononceous effect on the sintering behavior. Only the temperature of solution-repreciptation of Si_3N_4 was affected with the addition of TaC, but densification was similar for monolithic Si_3N_4 and composite.

Apparent density of the composites is quite similar to the ones observed in monolithic Si_3N_4, after sintering at 1800°C/1h.

It was observed the complete $\alpha \rightarrow \beta$-Si_3N_4 phase transformation and the TaC particles remained as a inert phase.

The microstructure exhibit good homogeneity and phase distribution. It was observed intergranular second phase, TaC, and amorphous phase formed from the reaction of sintering additives and SiO_2 presented on the surface of silicon nitride starting powder.

Acknowledgements

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