SILICON NITRIDE/NIOBIUM CARBIDE PARTICULATE COMPOSITES

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ABSTRACT

Ceramics are promising materials having rather good mechanical strength characteristics but quite low crack resistance properties at the same time. This is one of the major factors hindering the wide scale applications of these materials in various fields. To allow their use, it is necessary to improve their reliability. One of the most attractive ways to achieve this goal consists of strengthening and toughening them through composite development. Among ceramics composites, silicon nitride based composites are regarded as some of the most important high temperature structural materials. The addition of a second phase influences the sintering process and in case of Si_3N_4, the liquid phase process is very complex. In this work, the sintering behavior of Si_3N_4-NbC particulate composite was investigated. For this study a basis composition (CB) with 90%wt α-Si_3N_4, 6%wt and 4%wt Y_2O_3 and Al_2O_3, respectively, was prepared. NbC (10 and 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 an alteration on sintering kinetics, due to the presence of NbC second particulate phase. It was observed the complete $\alpha \rightarrow \beta$-Si_3N_4 phase transformation. The microstructure shows good homogeneity concerning grain size and secondary phase distribution.

1. INTRODUCTION

Silicon nitride ceramics are, among ceramics materials, some of the most important materials for structural applications [1]. However, due to their inherent brittleness, their use in new areas such as engines and turbines is limited [2]. The need for further improvement in mechanical reliability 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 [2,3].

Among ceramics composites, silicon nitride based composites are regarded as some of the most important high temperature structural materials. The most commonso silicon nitride based composites are Si_3N_4-TiC, Si_3N_4-SiC and Si_3N_4-TiN [1].

The addition of a second phase influences the sintering process and in case of Si_3N_4, the liquid phase process is very complex. Owing to the covalent bonding of Si-N, Si_3N_4 is difficult to densify without sintering additives such as Al_2O_3, MgO, Y_2O_3 and rare earth oxides. These sintering additives promote sinterization by solution-diffusion-reprecipitation mechanism, during which densification, phase transformation and grain growth take place simultaneously [4].

The dispersion of particles into a Si_3N_4 matrix can lead to a considerable improvement in composite strength but the addition of a second phase restrains the $\alpha \rightarrow \beta$-Si_3N_4 phase transformation and grain growth [5,6,7]. In case of Si_3N_4/SiC composites, the effect of SiC second phase particles was studied. Yang and co-authors [8] observed that the SiC particles decreases the sinterability of composite, which causes the lowering density and limit the silicon nitride grain growth by *"pinning"* and slowing down the grain boundary movement.

Zener described the effect of grain boundary "pinning" by small inclusions in 1948. Zener's model applies to a system that contains monosized, spherical, insoluble, immobile particles and considers the retarding force exerted by these particles on rigidly moving boundaries. The retarding force is derived from a reduction in grain-boundary area and, thus, grain boundary energy, which results from the presence of particles on boundary [9].

With nanosized SiC addition, the $\alpha \rightarrow \beta$-Si_3N_4 phase transformation and grain growth of β-Si_3N_4 are generally restrained. This effect can be explained by the suppression of mass transport and inhibition of Si_3N_4 grain boundary migration by intergranular SiC particles. E a ref?

The development of a new composite, Si_3N_4/NbC, was studied in this work. The sintering kinetics of Si_3N_4 with addition of 10 and 20 vol % of NbC, as a second phase, was studied. The microstructure and related phases was also evaluated.

2. EXPERIMENTAL 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), α-SiC (H.C.Starck), Al_2O_3 (A16/SG Alcoa) and Y_2O_3 (99.98% purity, Aldrich Chemical Company).

For this study a composition containing 90wt% of α-Si_3N_4, 6wt% of Y_2O_3 and 4wt% of Al_2O_3 as sintering additives, was prepared. This composition was named CB. The CB was mixed in an attrition mill with Si_3N_4 milling medium, in isopropanol alcohol for 4 hours at 300rpm. The slurry obtained was separated from the milling medium by passing through a 325 mesh sieve and subsequently dried in a rotary evaporator. In the CB, 10 and 20vol% of NbC was added and the composition was prepared under the same conditions described before. The powder was passed through an ASTM 100 sieve to crush soft agglomerates and 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 Technology, 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 by weight loss, density (Archimedes Method), microstructure (SEM – Phillips XL30), and present phase (XRD). Samples for microstructure investigation were prepared by standard ceramographic procedure of multistep diamond polishing with subsequent plasma etching (CF_4).

3. RESULTS & DISCUSSION

The formulations of the prepared mixtures, together with some of their granulometric characteristics are presented in Table1.

"**Table 1** - Characteristics of the starting and mixture powders"

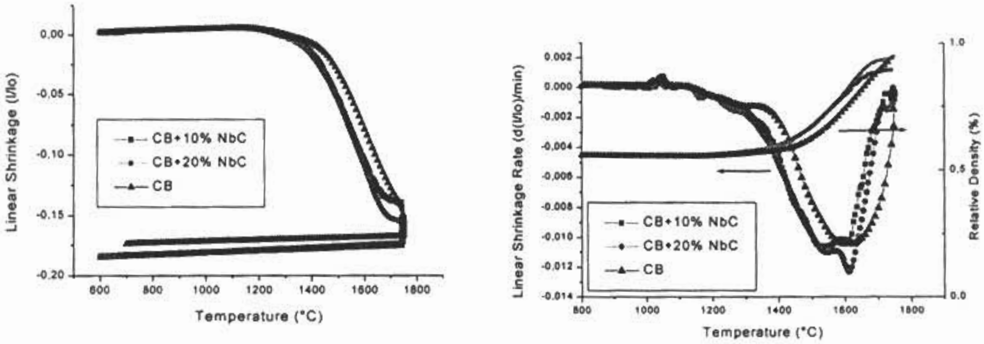
Material	CB (g)	NbC (g)	Grain size distribution (μm)			Specific Surface Area (m^2/g)
			d_{10}	d_{50}	d_{90}	
CB	100	0	0.12	0.44	1.03	15.5
NbC	0	100	0.69	1.48	3.39	1.8
CB+10vol% NbC	79.6	20.4	0.10	0.42	1.12	12.4
CB+20vol%NbC	63.4	36.6	0.09	0.45	1.34	10.1

The results of dilatometric investigations, linear shrinkage, shrinkage rate and relative density as function of temperature of the studied samples are presented in Fig.1.

In Fig.1a it can be observed that the shrinkage starts, approximately, at the same temperature for CB and composites, and during pattern, the shrinkage still occurs.

The shrinkage rate *vs.* temperature, (Fig 1 b) exhibits two steps of maximum shrinkage rate. The first step observed, in lower temperature, refers to the liquid formation and rearrangement of the particles. The liquid formation temperature is quite similar for CB and composites (~1280°C); no reaction between NbC and sintering aids occurs due to the refractory properties of the materials.

The second step, observed at ~1600°C in CB, refers to the solution-reprecipitation process, characteristic of the liquid phase sintering process of silicon nitride based ceramics. In the composites, the step related to the solution-reprecipitation process exhibits an alteration on the shrinkage behavior. This alteration on the shrinkage rate is more pronounced when 20vol% of NbC was added, so it is concluded that the presence of NbC as second phase influences the sintering kinetics. The presence of NbC may influence the particle rearrangement of α-Si_3N_4 and the solution reprecipitation process of silicon nitride, analogous to the effect observed in Si_3N_4/SiC compositesas ref. Ainda vão ser colocadas?. In Si_3N_4/SiC composites, the presence of SiC particles restrains the $\alpha \rightarrow \beta$-Si_3N_4 phase transformation and grain growth, due to the suppression on mass transport [8]. When more energy, i.e. higher temperature, is given to the system, the shrinkage rate increases again. The evolution of shrinkage rate *vs.* temperature of the composites occurs fasters than in CB.



(a)

(b)

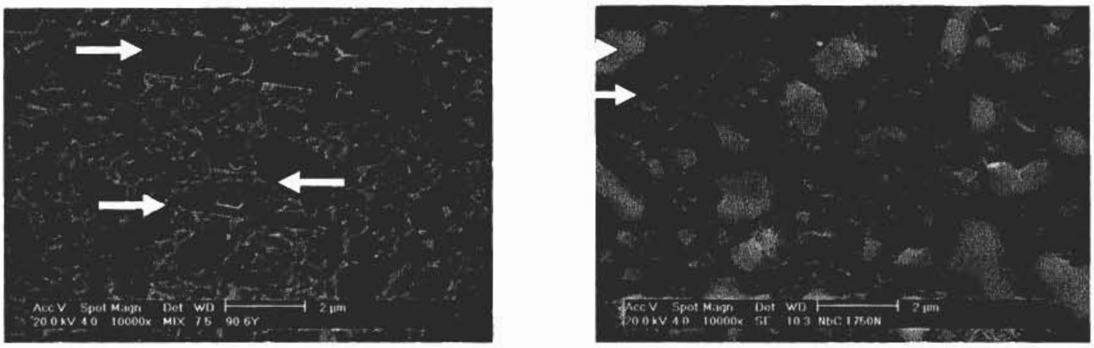
" **Fig. 1.** Results of dilatometric experiments: (a) linear shrinkage *vs* temperature; (b) shrinkage rate and relative density *vs.* temperature."

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/1h due to the fact that shrinkage still occurs at 1750°C (dilatometer result), Fig 1a.

The density and relationship between NbC content and relative density of the samples sintered in graphite resistance furnace are shown on Table 2.

in the starting powder, and acts as nucleation sites for new β-Si_3N_4 grains [10]. During densification of silicon nitride based ceramics, two different mechanisms of nucleation can be distinguished: homogeneous or heterogeneous nucleation. In both cases, nucleation occurs from the supersaturated oxinitride glass, but in the case of heterogeneous nucleation, the β-Si_3N_4, present at the starting powder acts as nucleation sites. So, the cores observed are β-Si_3N_4 pre-existent grains in starting powder [10].

In the case of Si_3N_4/SiC composite, it was observed the presence of intragranular SiC. Yang et al [8] have proposed that the SiC particles can be nucleation sites for β-Si_3N_4 in Si_3N_4/SiC nanocomposites. In this case, the intragranular structure was identified as of Si_3N_4.



(a) (b)

"**Fig. 3**. Microstructure of (a) CB (b) CB+20vol%TaC after plasma etching, sintered at 1750°C/1h"

4. CONCLUSIONS

The influence on the sintering behavior of NbC, in a Si_3N_4 matrix, was investigated by dilatometry experiments and pressureless sintering.resumo ou conclusão?

The addition of NbC into Si_3N_4 has a pronounced effect on the sintering kinetics of the Si_3N_4. The temperature of solution-repreciptation and the shrinkage rate of Si_3N_4 were affected by the addition of NbC, but densification was similar for monolithic Si_3N_4 and composite.

The apparent density of the composites is quite similar to that 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 NbC particles remained as an inert phase.

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

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References

1. **Pellon, F.C.** and **Thevenot, F.T.**, "Microstructure designing of silicon nitride relate toghness", J.Euro.Ceram.Soc., **22**/3 (2002), 271-278.
2. **Poorteman, M., Descamps, P., Cambier, F., Plisnier, M., Canonne, V., Descamps, J.C.**, "Silicon nitride/silicon carbide nanocomposites obtained by nitridation of SiC: fabrication and high temperature mechanical properties", J.Euro.Ceram.Soc., **23**/13 (2003), 2361-2366.
3. **Gogotsi, Y.**, "Particulate silicon nitride-based composites", J.Mater.Scie., **29**/10 (1994), 2541-2556.
4. **Chiang, Y.M., Birnie III, D., Kingery, W.D.**, "Physical Ceramics Principles", 1st edition (1997), John Wiley & Sons, New York, USA.
5. **Kitayama, M., Hirao, K., Toriyama, M., Kansak, S.**, "Modelling and simulation of grain growth in Si_3N_4 – I – Anisotropic Ostwald Ripening", Acta Mater., **46**/18 (1998) 6541-6550.
6. **Hirano, T., Niihara, K.**, ""Microstructure and mechanical properties of Si_3N_4/SiC composites", Mater. Lett., **22**/5-6 (1995), 249-254.
7. **Cheong, D.S., Hwang, K.T., Kim, C.S.**, "High-temperature strength and microstructural analysis in Si_3N_4/20-vol%-SiC nanocompósitos", J.Am.Ceram.Soc., **82**/4 (1999), 981-986.
8. **Yang, J.F., Ohji, T., Niihara, K.**, "Role of sintering aids in phase transformation, microstructure and mechanical properties of Si_3N_4/SiC nanocompósitos", J.Ceram.Soc.Japan, **109**/11, (2001), 920-923.
9. **Stearns, L.C., Harmer, M.P.**, "Particle –inhibited grain growth in Al_2O_3-SiC: II, Equilibrium and kinetic analyses", J.Am.Ceram.Soc., **79**/12 (1996), 3020-3028.
10. **Petzow, G., Hoffmann, M.J.**, "Grain growth studies in Si_3N_4 Ceramics", Mater. Sci. Forum **113-115**/2 (1993), 91-102.