The importance of Si_3N_4 characterization by SEM at the different sintering stages

C. Santos[1]; S.Ribeiro[1]; K.Strecker[1] and L.E.G.da Silva[1]
[1] *FAENQUIL – Faculdade de Engenharia Química de Lorena - Departamento de Engenharia de Materiais. Address: Polo Urbo-Industrial, Gleba Al-6, cep 12600-000, Lorena-SP, Brazil. Phone: +55 (012)31599900, FAX +55 (012) 31533006 – e-mail: claudinei@ppgem.faenquil.br*

Abstract

Silicon nitride (Si_3N_4) is a very important ceramic material for structural applications because its corrosion and good thermal shock resistance and high mechanical resistances at high temperatures. The best properties are related with the sucess of the sintering process, producing sintered samples with low porosity. Furthermore, efficient sintering programs must be elaborated to optimize the sintering parameters (such as heating rate and isothermal holding times) for better the microsctructural control. The present work shows the microstructural changes on Si_3N_4 at the differents sintering temperatures. Microstructural evaluation, examined using backscattered electrons (BSE) and secondary electrons (SE) in a LEO 1450VP Scanning Electron Microscope, was utilized for the characterization of the sintering stages.

Keywords: silicon nitride, characterization, scanning electron microscopy (SEM), densification, microstructural evaluation.

Introduction

Silicon nitride (Si_3N_4) has unique properties compared with other structural ceramics. Si_3N_4 exists in two crystallographic modification: α–Si_3N_4 and β-Si_3N_4. The α-Si_3N_4 is unstable at high temperatures and will transform into β-Si_3N_4, over 1400 °C [9,11].

The combination of properties such as high mechanical resistance at room and high temperature, low coefficient of thermal expansion and good wear resistance has made the Si_3N_4 one of the most studied ceramic structural materials in the last 20 years [1,5-9,11]. However, the correlation between Si_3N_4 powder properties, sintering mechanisms and characteristics of the resulting ceramic product is not well established.

The best mechanical properties of Si_3N_4 are obtained when it is sintered by liquid phase sintering (LPS). This properties depends on, mainly, of the sintering conditions, microstructure and intergranular phases obtained after sintering [6,11]. Si_3N_4 ceramics sintered by liquid phase sintering (LPS) present three sintering stages: (1) particles rearrangement stage; (2) solution-reprecipitation and (3) final densification stage [2,5,7,9]. In this work, the relative density and microstructural evaluation of Si_3N_4 were examined as a function of sintering temperature and, the microstructural aspects in each sintering stage, were analysed using Scanning electronic Microscopy (SEM).

Materials and Methods

Materials

The following powders were used as starting materials: α– Si_3N_4 (SN-10-UBE Industries, Japan), α–Al_2O_3 (CR-6 – BAIKALOX) and Y_2O_3 (H.C.Starck-Germany). The characteristics of the powders (Table 1) were taken from the manufacturers specifications.

Table I – Characteristics of the starting powders.

Materials	Si_3N_4	Al_2O_3	Y_2O_3
Purity (%)	92% α-phase	99.99	99.98
Specific Area (m^2/g)	11.2	6.0	12.76
Average particle size (μm)	0.99	0.98	0.80

Processing

Silicon nitride (α–Si_3N_4) was mixed with 14 vol% of Al_2O_3/Y_2O_3 in the stoichiometry to form YAG "$Y_3Al_5O_{12}$" as intergranular phase, because it has good mechanical properties [4].

The starting powders were mixed for 6 hours (1000 rpm) in an attritor milling using an organic solvent (isopropyl alcohol). The resultant homogeneized mixtures were then dried at 80 °C for 6 hours.

Powder mixture was compacted by uniaxial pressing using 30 MPa and subsequently isostatic pressing (300 MPa). After this step the compacts were sintered in 1.5 MPa N_2 atmosphere at a heating rate of 15 °C/minute up to differents temperatures ranged on: 1500, 1600, 1700, 1800, 1900 °C without isotermal and 1900°C with isothermal of 2 hours.

After the sintering the samples were submitted at heat treatment for intergranular phase devitrification (1400 °C - 24h, in 0.1 MPa N_2 atmosphere) [1,4]. After the heat treatment, the samples were immediatelly coolled down to room temperature.

The characterization of the different sintering stages was obtained using the densification analysis and microstructural characterization of the sintered samples in the different conditions. The density of the sintered samples (ρ_{sint}) was obtained by Archimedis Method [9]. This results were correlated by theoretical density, obtaining then the relative density (%) of the sintered samples. The fracture surface of the samples was observed by SEM with mixed emission of backscattered electrons (BSE) and secondary electrons (SE) [3].

Results and Discussion

Relative Density

Table 2 presents the relative densities results to the differents sintering temperatures.

Table 2 – Relative Densities at the differents sintering conditions.

Sintering Condition	Relative Density(%)
1500°C	49.4
1600°C	52.2
1700°C	92.1
1800°C	96.3
1900°C	97.1
1900°C – 2 hours	99.5

Fig.1 shows the densification behaviour of the Si_3N_4 ceramics as a function of sintering temperature.

The results have showed that between 1500 and 1600°C have only a little rearregement of the particles, without considerable alterations. The liquid phase was formed between 1600 and 1700 °C, promoting an increase in the relative density of compact. Densification results have demonstrated that the *rearrangement stage* (first sintering stage) has occured in this temperature range promoting a high increase in relative density. However, the next sintering stages needed microstructural analysis for best characterization, because in this stages a little deference in the relative density is showed.

Microstructural Evaluation

The Si_3N_4 microstructural evaluation is shown in Fig. 2.a-f for samples sintered at 1500, 1600, 1700, 1800 and 1900 °C without isothermal and 1900 °C during 2 hours. The samples were characterized by SEM using fracture surface analysis.

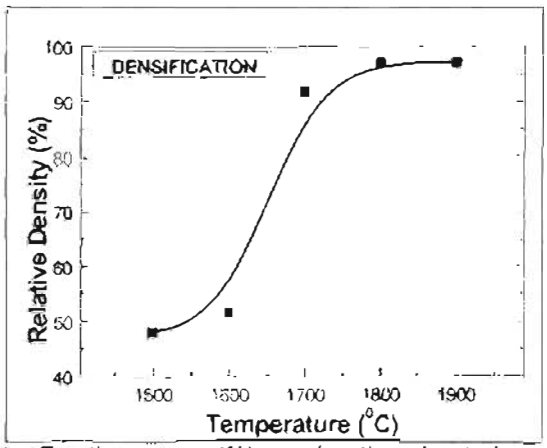

Fig.1 – Relative density (%) as a function of sintering temperature

Between 1500°C and 1600°C (Fig.2.a-b), a little aproximation of the α–Si_3N_4 particles is observed. In these temperatures, no liquid phase is detected. The liquid phase is necessary to start the particles rearrangement [2,5].

Fig. 2.c shows the particles rearrangement at 1700 °C caused by the liquid phase formation. In this temperature, α–β Si_3N_4 transformation wasn't detected and the porosity is uniformelly distributed in the microstructure.

Fig. 2.d (1800°C) shows precipited β–Si_3N_4 grains covered by the glassy intergranular phase, characterizing the *solution-reprecipitation stage* [2,3].

Fig. 2.e (1900 °C) shows the microstructure with intergranular phase more uniformly distributed and a small presence of porosity in the microstructure.

After 2 hours, at 1900°C (Fig. 2.f), an homogeneous microstructure with low porosity was observed. This behavior characterize the final sintering stage (*final densification*) [2,5].

Conclusions

For $Si_3N_4/Y_3Al_5O_{12}$ system, temperatures higher than 1700 °C are necessary to reach the of complete rearrangement of the and, to obtain high densification.

temperatures around 1900 ^{0}C added to isothermal times are required. The microstructural study using Scanning Electron Microscopy as a characterization technique, is very important to auxiliary in the elaboration of the efficient sintering programs, to obtaining of dense ceramics with homogeneous microstructure and, consequently, best mechanical properties.

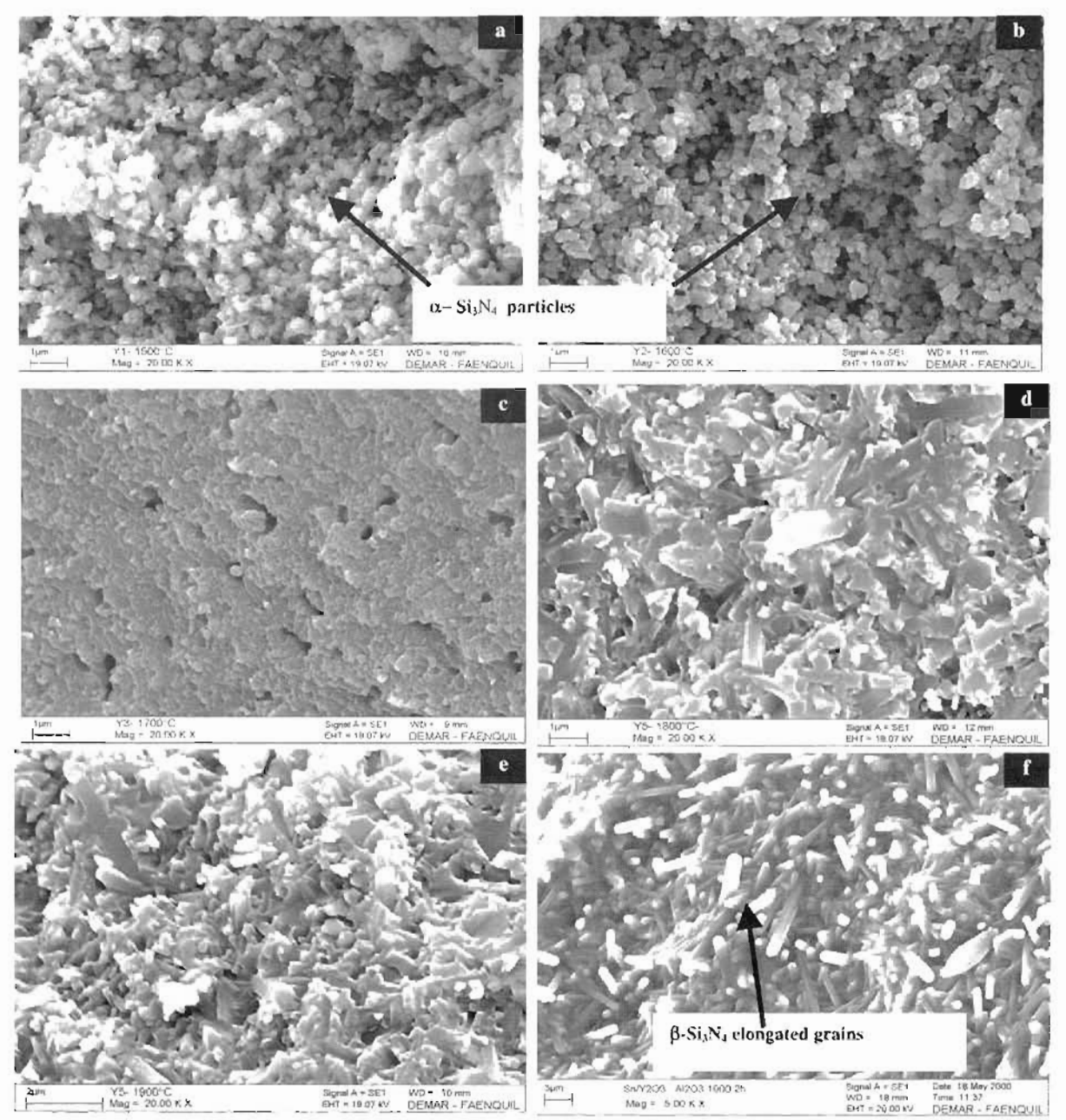

Fig.2 – Micrographs of Si_3N_4 fracture surface samples sintered at:
(a)1500^{0}C: (b) 1600^{0}C; (c) 1700^{0}C: (d) 1800^{0}C; (e) 1900^{0}C and (f) 1900 ^{0}C during 2 hours.

Acknowledgments

The authors would like to thank to FAPESP (Processes n° 99/08976-8 and 00/11204-6), for financial support.

References

1. Alper, A.M. Ed by, (1995), *Phase Diagrams in Advanced Ceramics*, academic Press Inc., USA, 227p.

2. German, R.M., (1996), *Sintering Theory and Practice*, John Wiley and Sons, New York, 550p.

3. Goldstein, J.I., Newbury, D.E., Joy, D.C., (1987), *Advanced Scanning Electron Microscopy and X-Ray Microanalysis*, Plenum Press-USA, 454p.

4. Keller, K., Mah, T., Parthasarathy, T.A., (1990), *Ceramic Eng, Sci. Proc.*, 11:7-8, pp 1122-1133.

5. Kingery,W.D., Bowen,H.K., Uhlmann, D.R., (1976), *Introduction to Ceramics*, 2nd ed. J. Wiley., 1032 p

6. Mörgenthaler, K.D.; Bühl, H.; in "*Tailoring of Mechanical Properties of Si_3N_4 Ceramics*"; (1994) (ed. Hoffmann, M.J. et al.) p429-41, Dordrecht, NATO ASI Series.

7. Rahaman, M.N.; (1995), *Ceramic Processing and Sintering*; Marcel Dekker. 770p.

8. Schwartz, H., *Application for Ceramic Materials and Processes*, (1992), *Struct. Cer.*, n.8, p.8.1 – 8.85.

9. Strecker, K., Gonzaga, R., Ribeiro, S., Hoffmann, M. J., (2000), *J. Mat.Lett*, 45:.39-42.

10. Reed, J.S., (1995), *Principles of Ceramics Processing - 2nd edition*, John Wiley & Sons, 658p.

11. Ziegler, G., Heinrich, J; Wotting,G.; (1987), *J.Mat.Sci.*,.22:3041-86.