

INFLUENCE of ADDITION of POLYSILOXANE on SINTERING of Al₂O₃

Ana Lúcia Exner Godoy, José Carlos Bressiani,
Ana Helena de Almeida Bressiani

Instituto de Pesquisas Energéticas e Nucleares

Av. Prof. Lineu Prestes, 2242, Cidade Universitária, 05508-000, São Paulo, SP, Brazil

analucia@ipen.br

Keywords: sintering; polysiloxane; microstructure; alumina

Abstract: The effects of adding polysiloxane (polymethylsilsesquioxane) on the sintering behavior, microstructure and hardness of alumina ceramics have been studied. The sintering kinetics of cold-pressed specimens was studied by dilatometry. Polymer sintering aid was used for alumina based ceramics sintered at 1650° C. The sintered materials were characterized using helium pycnometry, x-ray diffraction analysis, scanning electron microscopy, transmission electron microscopy, energy dispersive x-ray spectrometry and Vickers indentation. The addition of polymethylsilsesquioxane yielded alumina/Si₂Al₄O₄N₄ composites. The sintering studies in nitrogen atmosphere (1650 °C/1h) revealed that the highest densities were obtained for specimens with 1wt% PMS. The materials prepared with ceramic polymer precursors had higher hardness than the standard specimen. The preparation of ceramic composites using small amounts of polymer precursors is suited for alumina based ceramics. The processing route being simple, it has the potential to enable the manufacture of complex shaped pieces.

Introduction

Inorganic polymers have attracted interest as precursors for advanced ceramics, mainly due to the processing opportunities given by viscous flow in the polymeric state, e.g. in the realization of complex shapes or in the manufacturing of ceramic matrix composites. However, in the pyrolysis of preceramic polymers the significant shrinkage (about 60 vol%) and the formation of cracks deriving from the gas release occurring during the polymer-to-ceramic conversion are poorly controllable [1]. Unmodified polymers are most suited for thin-walled components, like fibres, microtubes or foams. Monolithic samples may be achieved only by the introduction of appropriate fillers, following the pioneering research carried by Greil [1,2].

The development of new inorganic polymers or organo-metallics has enabled new ceramic materials to be produced and these have found applications in many areas, especially in high temperature chemically aggressive environments [3-6].

The synthesis of Si based ceramics using polymeric precursors and in the form of fibres, thin films, foams, nanocomposites, nanofibers, coatings, glasses and compacted materials has received much attention [7-13].

The structure of the materials produced from polymer precursors can vary from amorphous to nanocrystalline, depending on the raw materials and the heat treatment temperatures during processing. Both, the chemical composition and the microstructure of the final product are dictated by the composition of the polymer used, by the heat treatment environment and by the temperature [14,15].

In this research, alumina was the material under study. Alumina is extensively used as a ceramic material due to an excellent combination of physical and chemical properties such as high heat, wear and oxidation resistance. Alumina has high chemical stability and is therefore used as a refractory oxide because of its capacity to resist heat without undergoing any significant change in its chemical nature [16]. Besides these properties, alumina has a low thermal expansion coefficient and therefore, high thermal shock resistance [17-19]. Alumina has been widely used as ceramic

coatings, a grinding agent, for furnace parts, as cutting tools, in medical and dental components, besides its use as a biomaterial [20].

This paper presents the effects of adding polymethylsilsesquioxane on microstructure, hardness and fracture toughness of Al_2O_3 .

Materials And Methods

The raw materials used were: aluminium oxide – Al_2O_3 -A16 SG-Alcoa; polymethylsilsesquioxane (PMS) -MK-Wacker Chemie; resin MK, in the form of powder at room temperature, general formula $(\text{CH}_3\text{SiO}_{1.5})_n$, with n varying from 130 to 150; catalyst with platinum - Hüll. The polymer additions to Al_2O_3 were 1, 5 and 10 wt%. Specimen processing consisted of milling Al_2O_3 with isopropyl alcohol for 4 hours in an attrition mill with a central rod, a jar and alumina balls. The milled material was dried, de-aggregated in an agate mortar with pestle and then sieved (100 Mesh). The standard specimen without any polymer additions, denominated A0, was axially compacted and then isostatically pressed at 200 MPa and sintered in nitrogen atmosphere at 1650 °C in a (Astro) furnace with graphite heating elements. To the other specimens, Pt catalyst dilute in isopropyl alcohol was added to the polymer and this mixture in turn to Al_2O_3 . The material was homogenized in a mechanical mixer (Turbula, model T2C), dried at 50 °C for 30 min and then compacted axially in a hot press at 200 °C for 2 hours. The specimens were then pyrolyzed in a tube furnace in nitrogen atmosphere at 900 °C for 1 hour. The sintering of these specimens was done in a furnace (Astro) with graphite heating elements for 1 hour under nitrogen. This heat treatment was carried out in a graphite closed crucible. The heating rate was 5 °C/min up to 400 °C and 20 °C/min from 400 °C to the sintering temperature.

The apparent density of the sintered specimens was obtained with a He picnometer (Micromeretics, model 1330). X-ray diffraction analysis (Rigaku, model Multiflex), with CuK_α was used to determine the crystalline phases in the sintered specimens. The specimens were examined in a scanning electron microscope, SEM (Philips XL30). The specimens were also examined in a transmission electron microscope (Jeol, 200C) to identify the phases from the electron diffraction patterns and by chemical analysis using EDS (EDAX). Standard specimen preparation procedures were used [21]. Identification of the crystalline phases and the crystallographic orientations was done using the DIFPAT program [22]. The Vickers hardness measurements were done in a Buehler VMT-7 machine. On each specimen, 10 indentations were made with adequate distance between indentations, as suggested by Ponton and Rawlings [23]. To determine the type of crack emanating from the Vickers indentations, the specimens were polished with 6 μm diamond paste for 2 min. The equation [24] used to determine fracture toughness with radial cracks was

$$K_{Ic} = 0,0154 (E / H_v)^{1/2} (P/c^{3/2}) \quad (\text{A})$$

Where K_{Ic} is fracture toughness ($\text{MPa}\cdot\text{m}^{1/2}$), E the elastic modulus (GPa), H_v the Vickers hardness (MPa), P the applied load (N) and c the crack length (μm). The specimens were identified. A0 was the specimen without polymer additions and AXM represented alumina specimens with additives ($X = 1, 5$ or 10 wt%) of polymer PMS.

Results and Discussion

Al_2O_3 with PMS Addition

Alumina with 1%, 5% and 10% of PMS polymer precursor were used.

The X-ray spectra of the specimens A1M, A5M and A10M revealed at least two phases, alumina and $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$, (JCPDS 76-598), Fig. 1. The nitrogen reacted with the polymer decomposition products and these were retained.

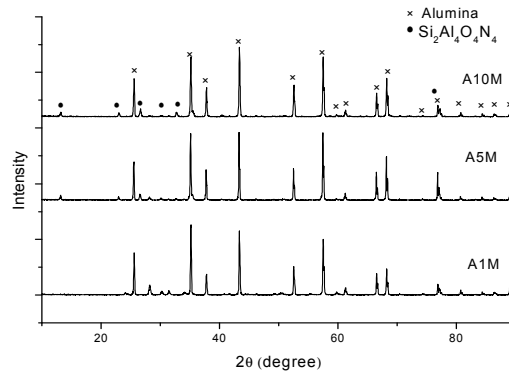


Fig. 1. X-Ray diffraction patterns of specimens A1M, A5M and A10M after pyrolysis and sintering.

Fig. 2 shows the dilatometry curve of specimen A10M. In the linear shrinkage curve, an inflection point starting at approximately 1300 °C can be seen, indicating significant shrinkage, due to formation of a liquid. Beyond this temperature, the sintering mechanism changed with possible formation of new phases. The total shrinkage was about 11% and in the plateau for 1 hour at 1650 °C there was slight shrinkage.

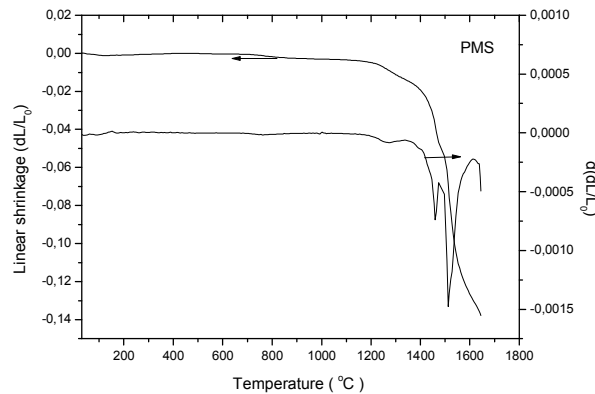


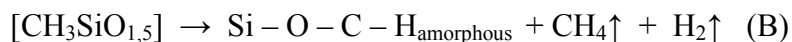
Fig. 2. Linear shrinkage of specimen A10M as function of temperature.

The apparent density (ρ) of the sintered specimens as determined by He picnometry and expressed as % T.D. (% theoretical density) as well as the mass losses of the PMS containing alumina specimens are shown in Table 1. The apparent density of the PMS containing specimens decreased gradually with increase in the quantity of polymer. These results suggest the formation of other phases with densities even lower than that of alumina, that is, SiAlON. The standard specimen and the Al_2O_3 specimen with 1% PMS showed the lowest mass losses.

Table 1- Apparent densities, %T.D. and mass loss of Al_2O_3 -PMS samples.

Sample	ρ_{apparent} (g/cm^3)	T.D. %	ΔM (%)
A0	$3,96 \pm 0,03$	99,5	1,2
A1M	$3,88 \pm 0,07$	97,5	1,2
A5M	$3,78 \pm 0,03$	95,0	2,9
A10M	$3,72 \pm 0,04$	94,0	4,7

Thermogravimetric analysis of PMS polymer in nitrogen revealed high rate of mass loss in the range 120-320 °C, due probably to loss of water and ethanol, as reticulation products [21,25]. Beyond about 500 °C, PMS started to decompose according to reaction (B) [21].



According to literature [15,25,26] the mass loss in a nitrogen atmosphere is related to loss of hydrogen and methane (CH_4) resulting in degradation of the polymer, loss of bonding and

consequent mineralization of the material. The mass loss was marked between about 600 °C and 1200 °C, however with a high output (79%) of the ceramic phase.

The crystalline structures of various grains were determined and typical micrographs of these are shown in Fig. 3.

The electron diffraction pattern and the results of indexing the region indicated by the arrows in both the bright and dark field (a, b, c) are shown in Fig. 3. The indexed phases were Al_2O_3 with a hexagonal structure and lattice parameter $a=b=0.476$ nm and $c=1.299$ nm and $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$, with hexagonal structure and lattice parameters $a=b=7.692$ nm and $c=2.99$ nm. The results are in agreement with the X-ray diffraction data (Fig. 1).

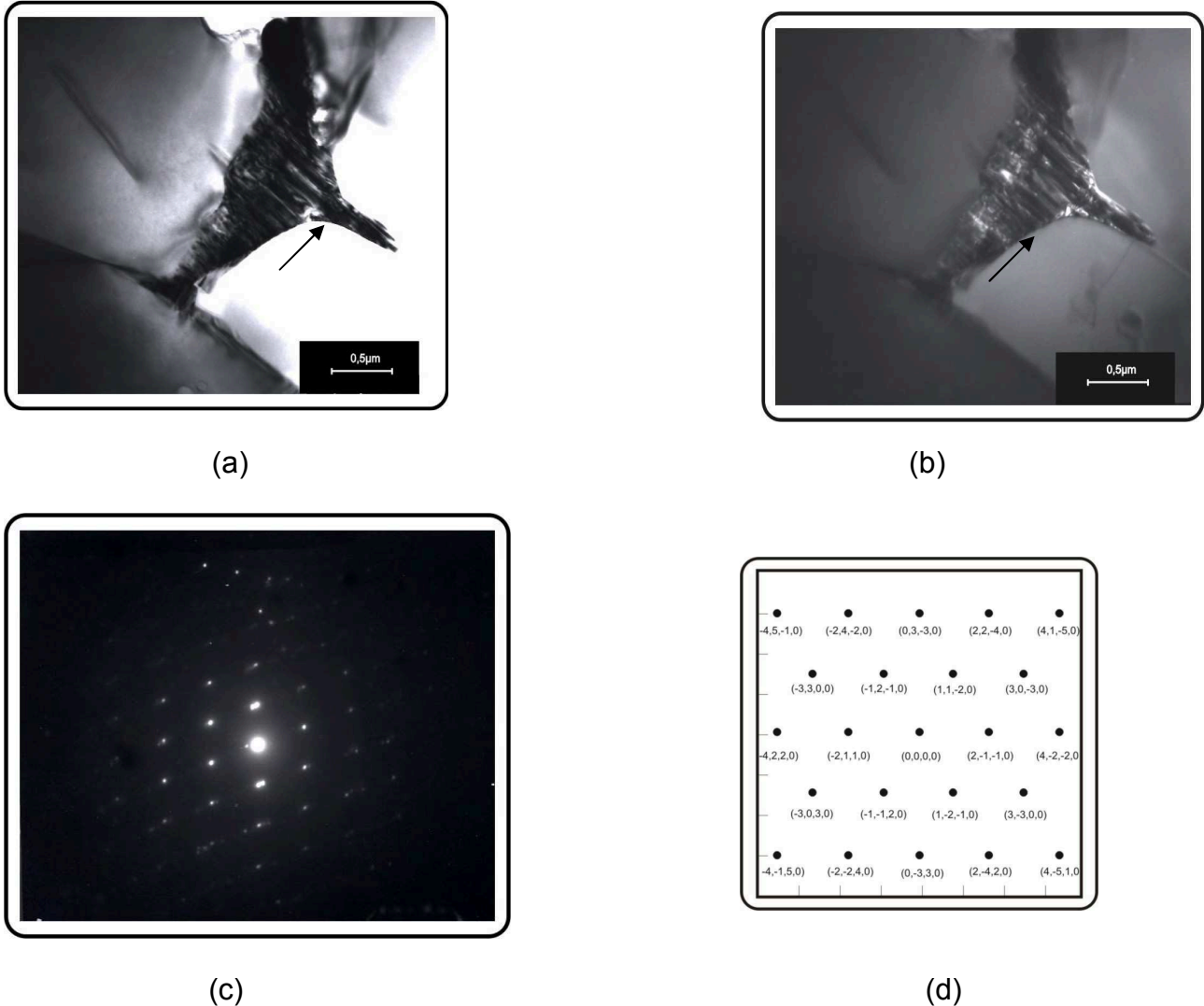


Fig. 3. TEM micrographs of specimen A10M (Al_2O_3 - $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$), (a)- Bright field, (b)- Dark field, (c)- Electron diffraction pattern and (d)- Pattern indexing of item (c).

Besides the electron diffraction pattern, the EDS technique was used with specimen A10M as shown in Fig. 4. The EDS spectrum (b) of the matrix phase (a) showed only the Al and O peaks. EDS analysis of a lighter region revealed besides Al and O, the presence of Si, from the secondary phase $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$, in agreement with the results obtained by electron diffraction analysis.

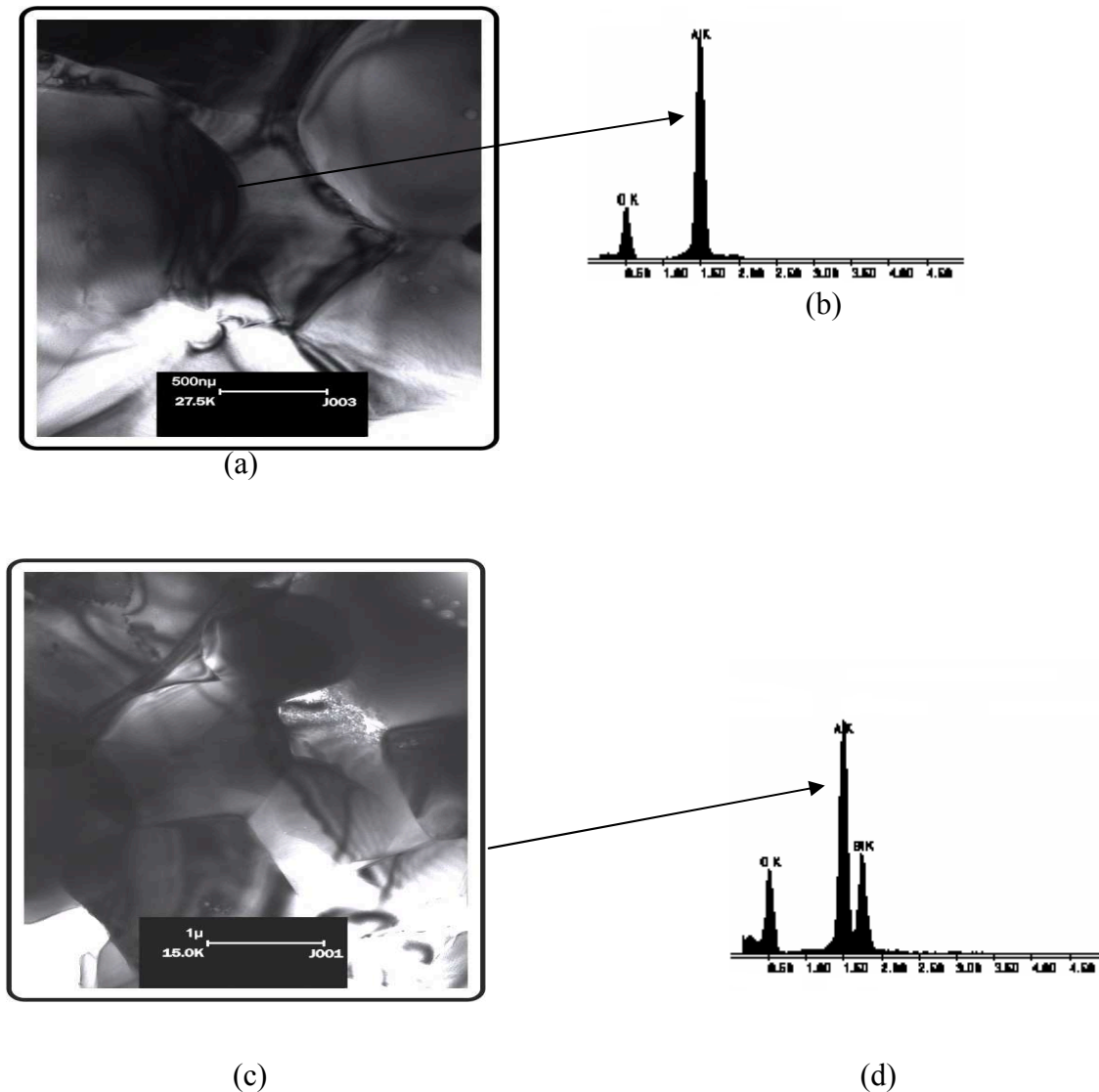


Fig. 4. Bright field TEM image (a) and (c); EDS spectra (b) and (d) of sample A10M ($\text{Al}_2\text{O}_3 - \text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$).

The Vickers hardness (H_v) values of the specimens A0, A1M, A5M and A10M varied from 14.9 GPa to 16.5 GPa as shown in Table 2. The materials prepared with polymer precursor additions showed higher hardness than the standard specimen. Generally, hardness depends mainly on porosity and grain size of the material. This property is also influenced by defects and micro-cracks under the indentation [27]. The hardness values of specimens were close to those reported in the literature for polymer precursors [28].

The fracture toughness (K_{Ic}) values for Al_2O_3 -PMS varied from $3.72 \text{ MPa}\cdot\text{m}^{1/2}$ to $4.47 \text{ MPa}\cdot\text{m}^{1/2}$ (Table 2). It can be concluded that the fracture toughness increased with small additions of the polymer, where as with additions of 10% polymer, there was no change.

Table 2- Vickers hardness and fracture toughness of A0, A1M, A5M and A10M samples.

Sample	H_v (GPa)	K_{Ic} ($\text{MPa}\cdot\text{m}^{1/2}$)
A0	$14,9 \pm 0,6$	$3,72 \pm 0,18$
A1M	$15,6 \pm 0,6$	$4,47 \pm 0,18$
A5M	$16,3 \pm 0,7$	$4,11 \pm 0,17$
A10M	$16,5 \pm 0,7$	$3,72 \pm 0,13$

Conclusions

PMS additions to alumina resulted in the phase $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$ formed.

This investigation revealed that the addition of PMS to alumina reduced the density of the sintered material.

The sintering studies in nitrogen atmosphere (1650 °C/1h) revealed that the highest densities were obtained for specimens with 1wt% PMS.

The materials prepared with ceramic polymer precursors had higher hardness than the standard specimen.

Small quantities of PMS increased the fracture toughness.

The preparation of ceramic composites using small additions of ceramic polymer precursors has been shown to be viable for alumina based materials. It is a simple forming route with a large potential for obtaining pieces with complex shapes.

References

- [1]- E. Bernardo, G. Parciannello, P. Colombo, J.H., Adair, A.T. Barnes, J.R. Hellmann, B.H. Jones, J. Kruse, J.J. Swab, SiAlON ceramics from preceramic polymers and nano-sized fillers: Application in ceramic joining, *J. Eur. Ceram. Soc.* 32 (2012) 1329-1335.
- [2]- P. Greil, Active-filler-controlled pyrolysis of preceramic polymers, *J. Am. Ceram. Soc.* 78 (1995) 835-848.
- [3]- H. Schmidt, P. Buhler, P. Greil, Pyrolytic conversion of poly(methylsiloxane) to silicon (oxy)carbide. In: Proceedings of Conference of ECRS, Riccione, Italy, 1995.
- [4]- O. Dernovsek, J.C. Bressiani, A.H.A. Bressiani, W. Acchar, P. Greil, Reaction bonded niobium carbide ceramics from polymer-filler mixtures, *J. Mater. Sci.* 35 (2000) 2201-2207.
- [5]- A. Kloneczynski, G. Schneider, R. Riedel, R. Theissmann, Influence of boron on the microstructure of polymer derived SiCO ceramics, *Adv. Eng. Mater.* (2004) 64-68.
- [6]- R. Rice, Ceramics from polymer pyrolysis, opportunities and needs- A material perspective, *Am. Ceram. Soc. Bull.* 62 (1983) 889-892.
- [7]- J.S. Lee, T. Yano, Fabrication of short-fiber-reinforced SiC composites by polycarbosilane infiltration, *J. Eur. Ceram. Soc.* 24 (2004) 25-31.
- [8]- P. Colombo, T.E. Paulson, C.G. Pantano, Synthesis of silicon carbide thin films with polycarbosilane (PCS), *J. Am. Ceram. Soc.* 80 (1997) 2333-2400.
- [9]- J. Zeschky, T. Höfner, C. Arnold, R. Weißmann, D. Hourlier, M. Scheffler, P. Greil, Polysilsesquioxane derived ceramic foams with gradient porosity, *Acta Mater.* 53, (2005) 927-937.
- [10]- R. Riedel, L. Toma, C. Fasel, G. Miehe, Polymer-derived mullite-SiC based nanocomposites, *J. Eur. Ceram. Soc.* 29 (2009) 3079-3090.
- [11]- W.M. Qiao, S.Y. Lim, S.H. Yoon, I. Mochida, L.C. Ling, J.H. Yang, Synthesis of crystalline SiC nanofiber through the pyrolysis of polycarbomethylsilane coated platelet carbon nanofiber, *App. Surf. Sci.* 253 (2007) 4467-4471.
- [12]- O. Goerke, E. Feike, T. Heine, A. Trampert, H. Schubert, Ceramic coatings processed by spraying of siloxane precursors (polymer-spraying), *J. Eur. Ceram. Soc.* 24 (2004) 2141-2147.
- [13]- M.A. Schiavon, K.J. Cuiffi, I.V.P. Yoshida, Poly(borosilazanes) as precursors of Si-B-C-N glasses: synthesis and high temperature properties, *J. Non-Cryst. Solids* 353 (2007) 2280-2288.
- [14]- T. Erny, D. Suttor, P. Greil, Properties of novel polymer derived ceramic composites, in: Proceedings of the 4th Europ. Ceram. Soc. Conf., Italy, 1995.

- [15]- J. Cordelair, P. Greil, Electrical conductivity measurements as a microprobe for structure transitions in polysiloxane derived Si-O-C ceramics, *J. Eur. Ceram. Soc.* 20 (2000) 1947-1957.
- [16]- C. Liu, J. Zhang, J. Sun, X. Zhang, Y. Hu, Addition of Al-Ti-C master alloys and diopside to improve the performance of alumina matrix ceramic materials, *Ceram. Int.* 33 (2007) 1149-1154.
- [17]- W.D. Kingery, Structure and properties of MgO and Al₂O₃ ceramics, *Advances in Ceramics*, 10, The American Ceramic Society, USA, 1984.
- [18]- H. Björklund, Grain Morphology and Intergranular Structure of Si₃N₄ and Al₂O₃ Based Ceramics, PhD Thesis, Chalmers University of Technology, 1996.
- [19]- L.D. Hart, Alumina chemicals; science and technology handbook, In: Production, processes, properties, and applications for calcined and high-purity aluminas, T.J. Carbone, The American Ceramic Society, Inc., USA, 1990.
- [20]- L.M. Epure, S. Dimitrievska, Y. Merhi, The effect of varying Al₂O₃ percentage in hydroxyapatite/ Al₂O₃ composite materials: Morphological, chemical and cytotoxic evaluation, *J. Biom. Mat. Res.* 82A (2007) 1009-1023.
- [21]- A.L.E. Godoy, Estudo da influência da adição de polímeros precursores cerâmicos na sinterização de SiC e Al₂O₃, Tese, 2006, Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, São Paulo.
- [22]- DIFPAT – Programm developed by G. Carpenter e L. Benkis, Metallurgical Laboratory, CANMET, Ottawa, Canadá, 1990.
- [23]- C.B. Ponton, R.D. Rawlings, Vickers indentation fracture toughness test, Part I: Review of literature and formulation of standardized indentation toughness equations, *Mater. Sci. Tech.* 5 (1989) 865-871.
- [24]- G.R. Anstis, P. Chantikul, B.R. Lawn, D.B. Marshall, A critical evaluation of indentation techniques for measuring fracture toughness: I- Direct crack measurements. *J. Am. Ceram. Soc.* 64, (1981) 533-538.
- [25]- R.M. Rocha, Obtenção e caracterização de cerâmicas no sistema Si-Al-O-N-C empregando pirólise de misturas de polissiloxano e cargas, Tese, 2004, Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, São Paulo.
- [26]- J. Cordelair, P. Greil, Electrical characterization of polymethylsiloxane/MoSi₂ – derived composite ceramics, *J. Am. Ceram. Soc.* 84 (2001) 2256-2259.
- [27]- I.J. McColm, *Ceramics hardness*, edited by Plenum Press, USA, p.160, 1990.
- [28]- M.; Sternitzke, B. Derby, R.J. Brook, Alumina/silicon carbide nanocomposites by hybrid polymer/powder processing: microstructures and mechanical properties, *J. Am. Ceram. Soc.* 81 (1998) 41-48.