

CERAMIC COMPOSITES SiOC/Al₂O₃/TiC OBTAINED BY ACTIVE FILLER CONTROLLED PYROLYSIS

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Abstract. Ceramic matrix composites materials (CMC's) based on SiOC/Al₂O₃/TiC were obtained through polymeric precursors method. Mixtures of a polysiloxane resin with alumina-powders as inert filler and Ti-powder and Al-powder as reactive filler were molded and pyrolysed at 1000 - 1400 °C in inert atmosphere for 60 minutes. The ceramic samples obtained were characterized respect to microstructure by scanning electron microscopy (SEM), the presence of crystalline phases by X-ray diffraction (XRD) and the mechanical strength by four-points bending testing. The analyses reveals porous ceramic matrix composite materials with glass matrix of SiOC and crystalline alumina embedded by TiC particles. Superior mechanical and physical properties were observed in infiltrated samples after pyrolysis with the polysiloxane, with Al and with a special commercial glass for infiltration of dental porcelain. Density, porosity and mechanical strength values ranged 2.34 – 2.62 g/cm³, 15 – 33% and 30 – 42 MPa, respectively.

Keywords: CMC's, pyrolysis, polysiloxane, reactive filler, infiltration.

1. INTRODUCTION

In recent decades several advanced materials were developed to meet specific needs through their superior properties. Additionally, this development has required energy efficiency coupled with the satisfaction of environmental requirements, both in the processing and final product. Compliance with these technical requirements associated with the commercial feasibility constitutes the "poor man's technology", ie to achieve maximum quality with minimum resources.

These needs have stimulated research to develop new technologies and processing routes compatible with advanced materials commercially usable. The polymer pyrolysis combined with the furnace atmosphere or inert / reactive loads, converting the polymer into a ceramic material endowed with particular properties, is a technology that fits this category (Chantrell and Popper, 1965; Yajima *et al.* (1976); Greil, 1995).

Conventionally, dense advanced ceramic materials are obtained by processing at high temperatures, high pressures and long lead times on special equipment, requiring large energy resources and resulting high cost final product (Acchar *et al.* (2008)).

The ceramic processing via the polymeric precursor processing method gives complex geometries ceramic matrix composite materials, with phases and properties designed so faster, at lower temperatures and using simple equipment and technologies of polymer processing (Greil, 1995). The growing number of published papers related to the production of ceramic matrix composite materials (CMCs) by polymer pyrolysis is indicative of the technological importance of this route processing (Radovanovic *et al.* (1999); Dernovsek *et al.* (2000), Wang *et al.* (2009); Tavakoli, 2010). However, the polymeric precursor route has major disadvantages the high residual porosity and volumetric shrinkage of ceramic bodies, reducing the mechanical strength and dimensional and geometric stabilities.

In this work, ceramic matrix composite materials based on SiOC/Al₂O₃/TiC have been developed aimed at meeting energy / environment requirements by the polymeric precursors method.

Mixtures of a polysiloxane resin with alumina-powders and Ti-powder and Al-powder filler were molded and pyrolysed, adopting simpler equipment and at lower temperatures than those adopted in conventional ceramic composite material processing.

The obtained ceramic composite material provides mechanical strength and thermal stability provided by the alumina matrix reinforced by particles of refractory titanium carbide. There are possible applications in the automotive industry, aeronautics or electronics. In the automotive industry, for example, materials with these characteristics allow us to obtain lighter internal combustion and more resistant to heat engines, ensuring greater energy efficiency and reduce emissions, complying with environmental requirements. In the airline industry, coating of turbine blades and heat resistant to wear. And, in the electronic industry, heat-resistant components are potential applications.

The research in this paper seeks to - circumvent the disadvantages of this relatively new processing technique – by investigating the processing parameters that influence the final properties of the ceramic composite materials, such as pyrolysis temperature, Al content in the starting composition as densifier, and the presence of infiltrating agents.

Thus a polysiloxane was mixed with inert filler powder (Al_2O_3) and reactive (Ti, Al) filler, conformed to the warm and pyrolysed in inert atmosphere. The obtained ceramic composite materials were characterized with respect to bulk density, porosity and mechanical strength by four-points bending testing. Tests including X-ray diffraction to identify crystalline phases and analysis of the fracture surface by scanning electron microscopy.

2. MATERIALS AND METHODS

The polysiloxane was obtained from the mixture for 1 hour on a magnetic stirrer in presence of catalyst between the oligomers D4Vi and D1107 Dow Corning. The inert filler of α - Al_2O_3 APC 2011 SG, $1.5 \text{ m}^2 / \text{g}$, Alcoa, was mixed with the reactive load of Ti metal with purity of 99.7% and 100 mesh from Aldrich Chem, and the powder metal Al reactive load, Alcoa, for 1 hour under manual agitation. The inert filler and reactive filler were used as powders. The mixture of powders was added to the polymer blend and homogenized manually for 1 hour with the aid of a spatula. The mass obtained was deposited in a matrix of stainless steel AISI 304 and resigned under uniaxial press-fitted with heating plates at 80°C for 1 hour in order crosslinking polymer and sufficient mechanical strength to handle the green body.

The pressed green bodies were pyrolyzed at 1000°C , 1050°C , 1100°C , 1200°C and 1400°C in resistive furnace alumina tube MAITEC FTE-1600 / H, in argon atmosphere under a flow of $100 \text{ ml} / \text{min}$ for 1 hour, with heating rates of $3^\circ \text{C} / \text{min}$ and cooling to $5^\circ \text{C} / \text{min}$.

Some pyrolysed samples were infiltrated with the polysiloxane, with Al and with a commercial glass-specific infiltration of dental porcelains (lanthanum glass-ceramic system). Preparing for polymer infiltration was performed by immersing the sample in the polysiloxane in liquid, the vessel under vacuum. The preparation of the samples infiltrated with Al and the glass was performed by depositing a layer of infiltrating mixture with distilled water on one side of the longitudinal rectangular sample ($50 \text{ mm} \times 5 \text{ mm} \times 5 \text{ mm}$).

After preparation, samples were taken at the same pyrolysis oven under vacuum at a heating rate of $5^\circ \text{C} / \text{min}$ to 1000°C for 30 minutes, and cooling rate of $5^\circ \text{C} / \text{min}$.

The composition of the starting mix is shown in Tab. 1 and pyrolysis is shown in Fig. 1.

Table 1 – Composition of starting materials

Material	Weight %	% Total
Polymers		19.00
D ₄ Vi	10.10	
D1107	8.90	
Filler		81.00
Ti	25.00	
Al	25.00	
α - Al_2O_3	31.00	

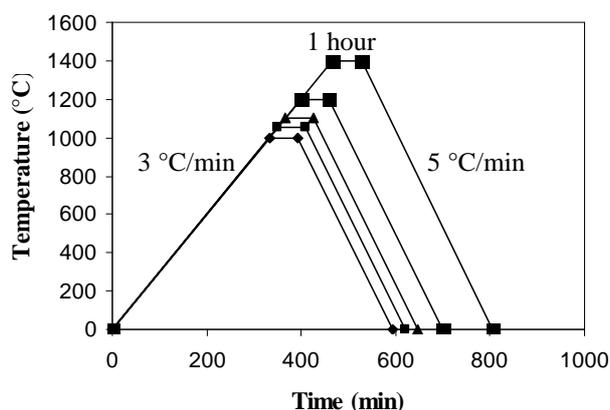


Figure 1. Schematic of the processing of ceramic composites $\text{Al}_2\text{O}_3/\text{TiC}$ pyrolysis at various temperatures.

The samples were investigated for the bulk density and porosity by Archimedes' principle, according to ASTM C 373/72. The samples were evaluated for resistance to bending machine bending test model four points Zwick / Roel Z2.5 according to ASTM C1161-94, with speed of loading of $0.5 \text{ mm} / \text{min}$. The fracture morphology of samples subjected to mechanical tests were analyzed by scanning electron microscopy (SEM) Philips XL30 in equipment – ESEM. The ceramic composite materials were subjected to elemental and compositional analysis by X-ray diffraction

and energy dispersive spectrometry (EDS) on Shimadzu XRD 6000 using Cu radiation / λ and angle of the beam of x-rays (2θ) ranging from 10° to 90° .

3. RESULTS AND DISCUSSION

3.1. Pyrolysis temperature

The influence of pyrolysis temperature on the physical and mechanical properties of the obtained ceramic composite materials is condensed in Tab. 2.

Table 2 - Influence of pyrolysis temperature on the physical and mechanical properties of the obtained ceramic composite materials.

Temperature (°C)	Density (g/cm ³)	Porosity (%)	Mechanical strength by 4pts bending testing (MPa)
1000	2.33±0.30	33±3	37.3±1.9
1050	2.34±0.28	37±4	36.9±1.8
1100	2.38±0.23	38±3	30.5±1.5

It is noted in Tab. 2 that increasing the temperature enhances the densification, as expected in powder processing. However, the porosity is increased simultaneously, reflecting the drop in mechanical strength. This occurs due to entrapment of volatiles from the polymer decomposition during pyrolysis; pressurized, increases the average pore diameter, simultaneous to the consolidation of the ceramic body.

This phenomenon is more pronounced the higher processing temperature, as observed in this study, in which samples pyrolysed at 1200 °C and 1400 °C had their properties damaged, breaking up the handling.

3.2. Aluminum content

The Al content in the starting composition of the ceramic composite materials objectives densify them by filling the pores by capillary effect. His influence on the final properties of ceramic bodies is shown in Tab. 3.

Table 3 - Properties of pyrolyzed ceramic composite materials according to the Al content in the composition.

Al content (%)	Density (g/cm ³)	Porosity (%)	Mechanical strength by 4pts bending testing (MPa)
5	2.73±0.30	26±3	35.0±1.80
15	2.34±0.28	33±4	30.0±1.90
25	-	-	0

It was observed that pyrolyzed ceramic bodies with 25% by weight of aluminum had cracks deep and extensive. The formation of liquid phase due to the excess of aluminum, with different linear coefficient of thermal expansion in relation to the matrix, promotes thermal stresses that are not supported by the structure, causing cracks and impairing the mechanical strength, as also observed by (Diniz, 2007) and (Alexandrino *et al.* (2006)). The densification and the improvement of mechanical strength properties are increased the lower the Al content for ceramic composite SiOC/Al₂O₃/TiC materials. The effect of Al as an agent of mass diffusion and pore-filling is responsible for the increase in the densification and mechanical strength, even with minimal content that this study was limited to 5%.

It was also observed that the absence of Al in the starting composition caused blackening of the samples due to excess free C coming from the bond breaking of the polymer network during pyrolysis. The presence of Al in the pores provides resistance to leakage of C to the sample surface as the organic-inorganic conversion is consolidated, giving the lighter colored ceramic body.

3.3. Influence of infiltration

The infiltration of pyrolyzed ceramic composite materials promoted the densification of these ceramic composite materials, associated with reduced porosity and increased mechanical strength, as shown in Tab. 4.

Table 4 - Physical / mechanical properties of ceramic composite materials infiltrated with Al, glass and polymer.

Temperature (°C)	Condition of infiltration	Infiltrant	Time (min.)	Density (g/cm ³)	Porosity (%)	Mechanical strength by 4pts bending testing (MPa)
control				2.34±0.28	33±4	30.0±1.5
1000	vacuum	aluminum	30	2.60±0.30	25±2	36.0±2.0
1000	vacuum	glass	30	2.61±0.31	24±2	35.0±1.8
1000	vacuum	polymer	30	2.60±0.31	19±1	42.0±2.3

The three infiltrators gave equal density to the ceramic composite materials. Al and glass gave similar porosity, however, the polymer shows better properties due to the effective infiltration properties by immersion under vacuum and its conversion of organic- ceramics, closing the open porosity with a infiltrating material similar to the matrix, giving the composite isotropic characteristics, translating into superior properties.

3.4. Identification of phases

The XRD patterns of pyrolysis samples are shown in Fig. 2. Their analyses revealed the presence of Al₂O₃ phases originated from the raw material as inert filler and also the reaction of Al as the active filler with decomposed Si-O-Si sites of the polymer, forming Al-O-Al bonds; and the phase TiC, generated by the reaction of decomposed polymer C with Ti present in the raw material as active filler.

The presence of TiSi₂ phase is in agreement with published literature (Kaindl *et al.* (1999); Dernovsek *et al.* (2000)) where silicides are expected in ceramic composite materials produced via polymer pyrolysis with reactive filler. The phase AlTi₃ arises because of the reactivity of Ti with Al. This phase in ceramic composite materials based on SiC, is responsible for deterioration of mechanical properties due to reaction with the same ceramic phases at temperatures above 1000 ° C, as reported by (Paransky *et al.*, (1996)) and, by analogy, explains the fragility of the ceramic samples processed above 1000 ° C, in this work.

As was not identified the formation of titanium oxide, this suggests that Al acted effectively to prevent this stage, as suggested by (Acchar *et al.* (2008)).

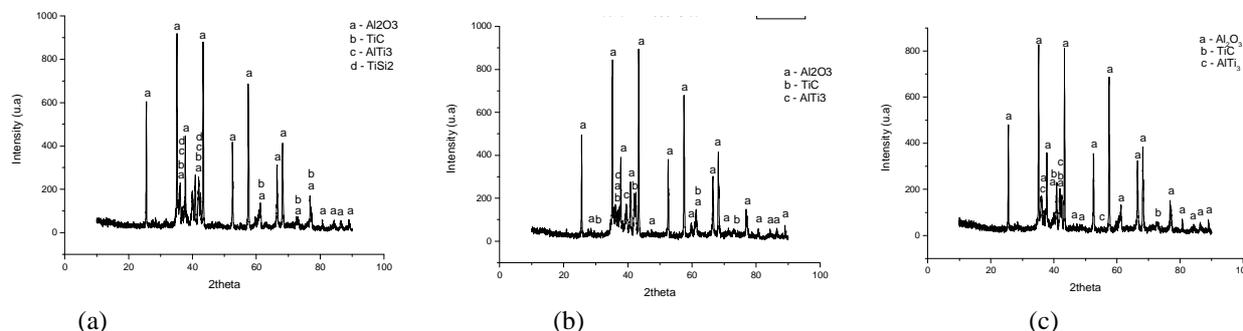


Figure 2. Standard X-ray diffraction of sintered samples (a) 1000 ° C (b) 1050 ° C and (c) 1100 ° C.

Based on the XRD patterns, Eq (1) represents the path of the reaction between the components subjected to pyrolysis:



3.5. Microstructure analysis

Microstructural analysis of the pyrolysed and infiltrated ceramic composite materials was performed using scanning electron microscopy (SEM) of their fracture surfaces.

3.5.1. Pyrolysis

Microscopy reveals a porous structure with TiC particles homogeneously dispersed in the matrix of SiOC / Al₂O₃, identified by X-ray diffraction, as Fig. 3.

This also occurred in pyrolysed samples at 1050 °C and 1100 °C, and the porosity inherent in the processing technique using polymeric precursors. However, the pore size appears larger as increasing the pyrolysis temperature and / or Al content in the starting composition.

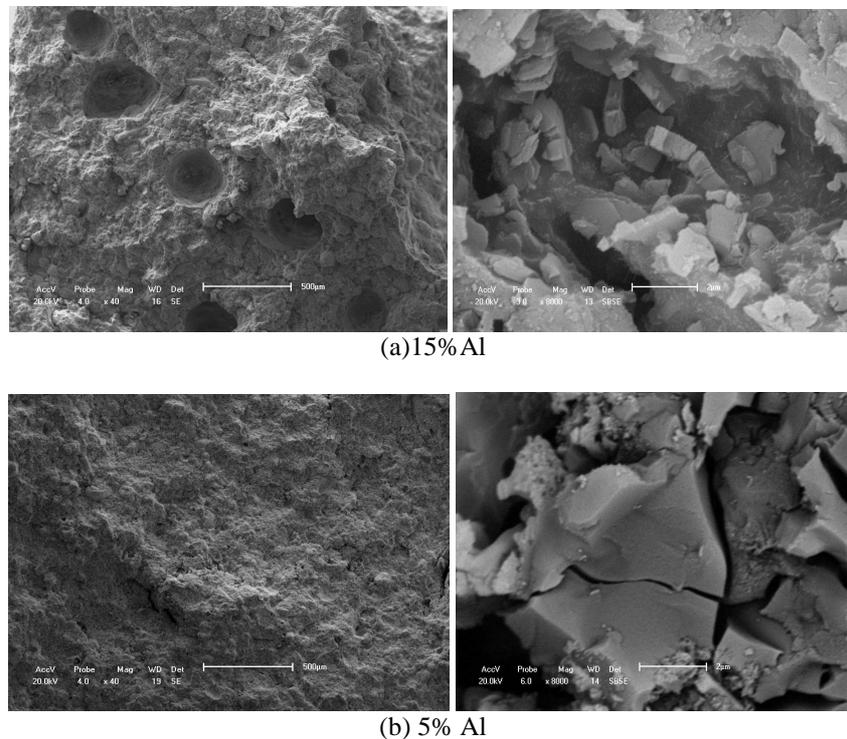


Figure 3. SEM image of Al₂O₃ / TiC pyrolysed ceramic composite material samples with various levels of aluminum.

It was observed that the samples processed at lower temperatures and with lower Al content are presented microstructurally more cohesive, explaining the properties shown in Tab. 2 and Tab. 3.

3.5.2. Infiltration

Microscopy reveals that the infiltrators became surface and sub-surface samples with the most dense and filled porosity, as Fig. 4. Figure 4 (a) shows that the Al melt effectively penetrated the pores below the surface deposition to 71.9 micrometres, densifying the samples and showing greater mechanical strength compared to a control sample, as shown in Tab. 4. In Figure 4 (b) it is observed that the filling of pores by glass penetration has reached 1 / 3 smaller than that obtained with Al (50 µm). The lower viscosity of aluminum makes it more effective in filling in pores by capillary effect aided by vacuum suction.

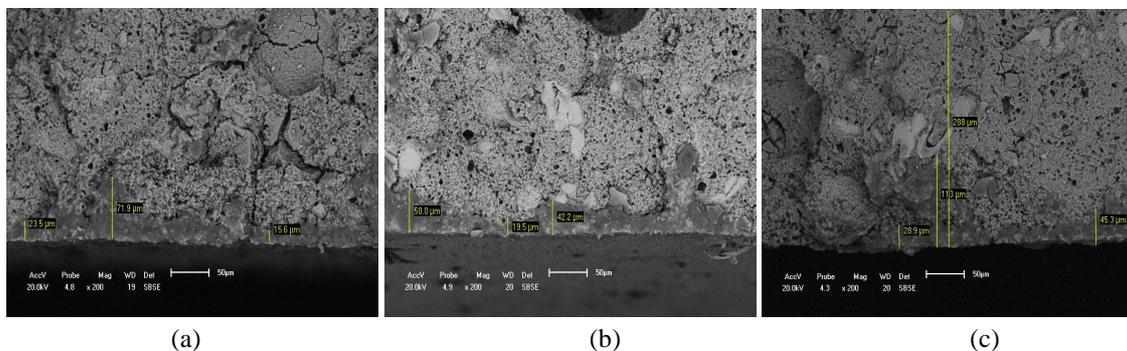


Figure 4. SEM image of fracture surface of ceramic composite materials infiltrated with (a) Al, (b) glass and (c) polysiloxane.

In Figure 4 (c) it is observed a dense infiltration layer near the edge, which is repeated for the four edges of the fracture surface of the ceramic body, because the samples were infiltrated with the polymer by immersion in liquid by vacuum 60 minutes before being introduced into the oven. This, coupled with the lower viscosity of polysiloxane favored so that it satisfied the porosity more effectively than Al and glass, allowing a penetration (113 µm) to the core

of the ceramic body, making it denser and with reduced porosity, when compared with Fig 4 (a) and Fig. 4 (b). The filling of pores by polysiloxane and its conversion into ceramic composite material has committed to a structure with superior properties compared to other infiltrators, explaining the observed results in Tab. 4.

4. CONCLUSIONS

SiOC/Al₂O₃/TiC based ceramic composite materials can be obtained at lower temperatures than in conventional processing, using equipment and raw materials economically feasible. Processing temperatures and concentrations of Al above 1000 ° C and 5% by weight, respectively, tend to degrade the physical and mechanical properties of ceramic composite materials, being the parameters that most influenced the final properties, as well as the infiltration process after pyrolysis. The infiltration with a preceramic polymer (polysiloxane), preceded by the immersion of the sample under vacuum for 1 hour, is the most effective technique of infiltration aimed superior properties. The mechanical properties obtained does not allow application of the ceramic bodies as structural elements, but if the thermal stability, dimensional and/or geometric properties is the most important variable in selecting material for answering specific need, this is one of the most effective methods of production.

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6. REFERENCES

- Acchar W, Diniz M., Fonseca Y. A. A., Sousa C. R. C. and Lima E. S., 2008. "The Effect of Polysiloxane on the Properties of Al₂O₃-NbC Composite Material Produced by Pyrolysis Process", *J Mater Sci*, 43:597–601.
- Alexandrino, E. M., Silva, V. P. and Yoshida, I. V. P., 2006, "Obtenção de CMCs por Pirólise de Compósitos Precursores Poliméricos de Fibras Curtas de Sílica/Silicona", Sociedade Brasileira de Química (SBQ). 29a Reunião Anual da Sociedade Brasileira de Química, pôster, águas de Lindóia, Brazil.
- Chantrell, P. G. and Popper, P., 1965. "Inorganic Polymers for Ceramics", in *Special Ceramics*, Ed. P. Popper, Academic Press, New York, p 67.
- Dernovsek O., Bressiani J.C., Bressiani A.H., Acchar W. and Greil P., 2000, "Reaction Bonded Niobium Carbide Ceramics from Polymer-filler Mixtures", *Journal of Materials Science*, 35 2201-2207.
- Diniz, M.A., 2007. "Sinterização de Matrizes Cerâmicas à Base de Alumina Reforçadas por Carbetos a Partir de Precursores Poliméricos", PhD, Thesis, Universidade Federal do Rio Grande do Norte, Natal, Brazil.
- Greil, P., 1995. "Active-Filler-Controlled Pyrolysis of Preceramic Polymers", in *J. Am. Ceram. Soc.*, 78 (4), 835-848.
- Kaindl, A., Lehner W., Greil, P. and Kim, D.J., 1999, "Polymer-Filler Derived Mo₂C Ceramics", *Materials Science and Engineering* A260, 101-107.
- Paransky E., Gutmanas E. Y., Gotman I. and Koczak M., 1996. *Metallurgical And Materials Transactions* 2130 vol 27^a.
- Radovanovic, E., Gozzi, M. F., Gonçalves, M. C. and Yoshida, I. V. P., 1999, "Silicon Oxycarbide Glasses from Silicone Networks", *Journal of Non-Crystalline Solids*, 248 37-48.
- Tavakoli, A. H., Gerstel, P., Golczewski, J. A. and Bill, J., 2010, "Quantitative X-ray Diffraction Analysis and Modeling of the Crystallization Process in Amorphous Si-B-C-N Polymer-Derived Ceramics", *Journal of the American Ceramic Society*, Early View, Date: 2 January 2010.
- Wang, Y., Jiang, T., Zhang, L. and An, L., 2009, "Optical Absorption in Polymer-Derived Amorphous Silicon Oxycarbonitrides", *Journal of the American Ceramic Society*, Early View, Date: 19 September 2009.
- Yajima, S.; Havashi, J., Omori, M. and Okamura, K., 1976. "Development of Tensile Strength Silicon Carbide Fiber Using Organosilicon Polymer Precursor", *Nature*, V.261, pp.261-283.

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