

# Ceramics Composites Derived From Polysiloxane / Al<sub>2</sub>O<sub>3</sub> / Ti

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**Abstract.** In this work alumina based composites ceramics with a polymeric precursor (polysiloxane) and metallic Ti with two different size particle distribution, Ti without milling (ATM) and 5h milling (ATM5), were characterized. PMS thermogravimetric curve indicates that the weight loss percentage was about 20%. The densities achieved were 3,50g/cm<sup>3</sup> and 3,70g/cm<sup>3</sup> for samples prepared with Ti as received and 5h milling, respectively. During decomposition of the polymer during pyrolysis and sintering, the particles of the matrix may react with carbon and Si from the polymer precursor, metallic Ti and gas atmosphere, nitrogen, to form different phases. The ATM samples presented Al<sub>2</sub>O<sub>3</sub> and TiCN. The specimens prepared with 5h milling Ti (ATM5) is constituted by mullite besides Al<sub>2</sub>O<sub>3</sub> and TiCN. The ATM5 samples have smaller densities than ATM but there is no significant difference in the hardness values.

## Introduction

Polymer-derived ceramics have attracted considerable attention for the last three decades and this field has drawn growing research interest [1,2,3]. Manufacture of bulk ceramic composites from materials in the system Si-Me-C-N-O (Me = Ti, Cr, V, Mo, Si, B, CrS<sub>2</sub>, etc.) from preceramic organosilicon polymers such as polycarbosilanes, polysilazanes or polysiloxanes has been possible by incorporating reactive filler particles into the liquid or solid polymer precursor [4]. Polysiloxanes have received attention as polymeric precursor of Si based ceramics because this class of polymers provides an easy and cheap route to the formation of such materials [5,6]. Composition and molecular structure of the polymeric precursor, the curing process, the pyrolysis and the atmosphere have been pointed out as variables that can determine the nature of ceramic products [1, 3].

Many ceramic materials can be produced from polymers such as SiC, Si<sub>3</sub>N<sub>4</sub>, SiOC, BN, B<sub>4</sub>C, AlN, TiC, TiN, etc. Several of these materials have potential applications such as structural materials, fibers, coating, catalyst supports, anodes in lithium ion rechargeable batteries, etc [7,8,9].

The aim of this work is to characterize alumina based composites ceramics with a polymeric precursor (polysiloxane) and metallic Ti with two different size particle distribution.

## Experimental Procedure

Commercial poly(methylsiloxane), PMS (MK, Wacker-Chemie), Ti (Brats, Brasil) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (A16-SG, Alcoa) were used as starting materials. The powder mixtures consisted of Al<sub>2</sub>O<sub>3</sub> spray dried, Ti, without milling (ATM specimens) and ball milled for 5h (ATM5 samples) and PMS. The pure Al<sub>2</sub>O<sub>3</sub> used as reference was denominated A1. 80 wt% Al<sub>2</sub>O<sub>3</sub>, 10 wt% Ti and 10 wt% PMS powders were mixed with a solvent (isopropilic alcohol), forming a viscous slurry, that was homogenized and deposited in a recipient for mechanic stirring at 50 °C, to attain the polymer cure. After dried, the mixture was sieved (150 $\mu$ m) to achieve a fine powder. The processing procedures include hot pressing (200 °C and 40MPa). Pyrolysis

(900 °C/ 1 h, N<sub>2</sub>) with a low heating rate (3 °C /min) and sintering (1550 °C/1 h, N<sub>2</sub>), also with a low heating rate until 400 °C/min and 20 °C/min from 400 °C until the sintering temperature.

The polymer was analyzed by thermogravimetry until 1300°C (Shimadzu, TGA 50H) with a heating rate of 10 °C/min in flowing nitrogen. The sintered materials were characterized by evaluation of apparent density measurements by the Archimedes method, X-ray diffraction analysis using monochromated CuK $\alpha$  radiation (Rigaku). The microstructure of the pyrolysed and sintered materials were examined by scanning electron microscope (SEM) (Philips, XL-30) equipped with energy dispersive spectroscopy (EDS). The hardness was evaluated by Vickers indentation (Buehler 5112).

## Results and discussion

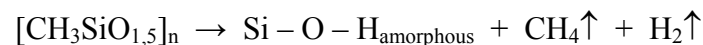
The bulk densities values of the hot pressed and sintered A1, ATM and ATM5 samples are compiled in Table 1.

Table 1- A1, ATM and ATM5 bulk densities.

Sample	Density [g/cm <sup>3</sup> ]
A1	3,75
ATM	3,50 ± 0,02
ATM 5	3,70 ± 0,03

The ATM and ATM 5 densities increased from 3,50 to 3,70 g/cm<sup>3</sup>, respectively, due the Ti milling but both are still smaller than A1 (pure Al<sub>2</sub>O<sub>3</sub>) density.

Fig. 1 shows the weight loss resulting from thermal degradation of the polysiloxane during heating. In the range of 150 and about 400 °C the weight loss is 10% and probably is due water and ethanol as reticulated products. Above 400 °C the polymethylsiloxane begins to decompose according to the following reaction:



Cleavage of Si-(CH<sub>3</sub>) and CH<sub>4</sub> prevails between 600 and 800 °C. The organic-inorganic conversion, with the formation of SiOC glass, occurs between 700 and 900 °C and starts the mineralization process of the material [10, 11, 12]. The total weight loss between room temperature and 1300 °C is 20%.

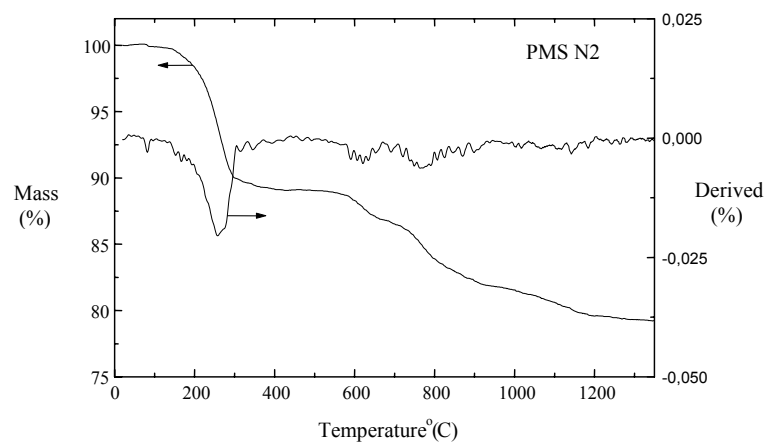


Figure 1- TG curve and the corresponding rate of weight change curve of PMS at a constant heating rate of 10 °C/ min in N<sub>2</sub> atmosphere.

Fig. 2 shows Ti powders without milling (a) and 5h milling (b) and is evident the difference between both. It is observed that agglomeration of ATM5 powders is higher than that of ATM.

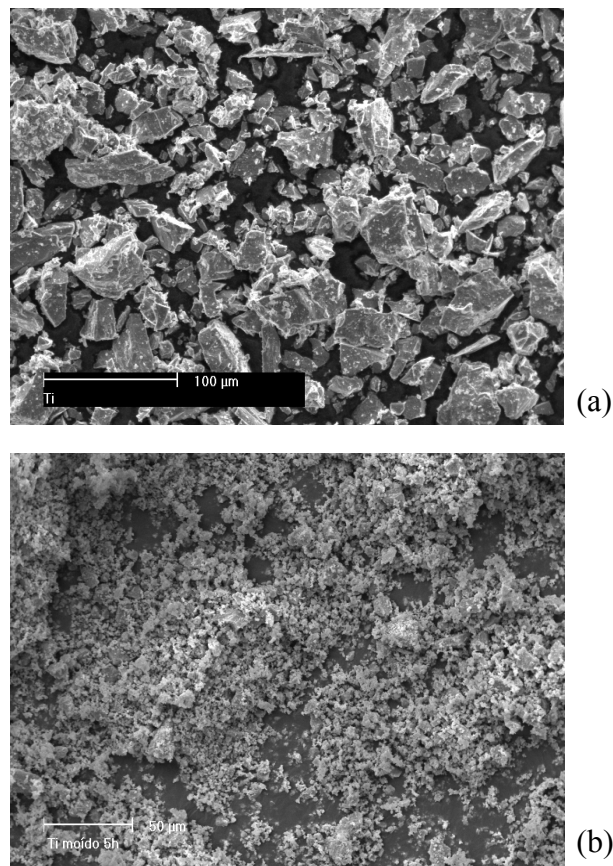
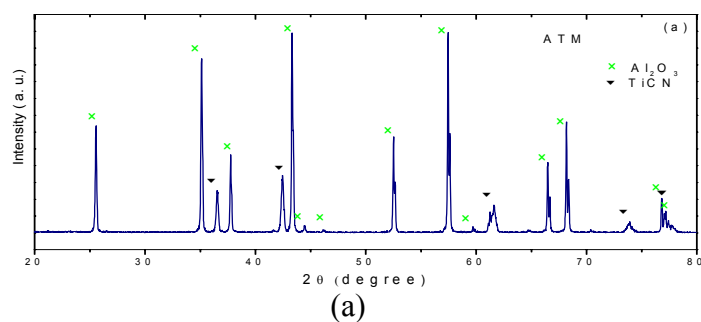


Figure 2- Ti powders without milling (a) and 5h milling (b).

During decomposition of the polymer pyrolysis and sintering, the particles matrix may react with carbon and Si from the polymer precursor, metallic Ti and gas atmosphere, nitrogen, to form different phases. The green body, which is initially a mixture of metal, polymer and ceramic, becomes gradually a multiphase ceramic compound during thermal treatment. The phases resulting from pyrolysis and sintering were identified from X-ray diffraction patterns, Fig. 3. The samples prepared without Ti milling (ATM) presented  $\text{Al}_2\text{O}_3$  and TiCN. The specimens prepared with Ti milled for 5h (ATM5) is constituted of mullite besides  $\text{Al}_2\text{O}_3$  and TiCN. TiCN is very attractive for cutting tools due to its low friction coefficient [13]. The mullitization process begins about 1200 °C and is caused by the formation of mullite directly from the reaction between transition  $\text{Al}_2\text{O}_3$  and the glassy silica phase [14].



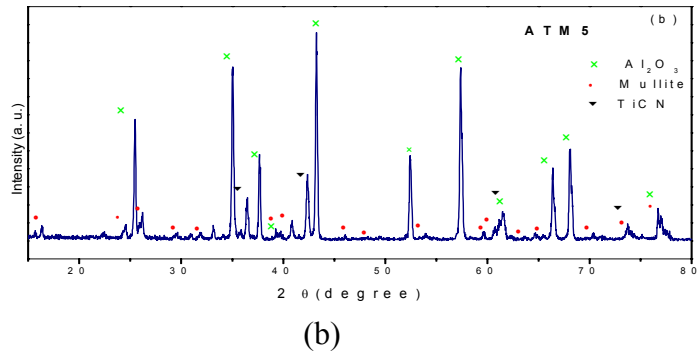


Figure 3- X-ray diffraction patterns of ATM (a) and ATM5 (b) samples.

Polished surfaces of pyrolysed and sintered samples observed by SEM can be seen in Fig. 4.

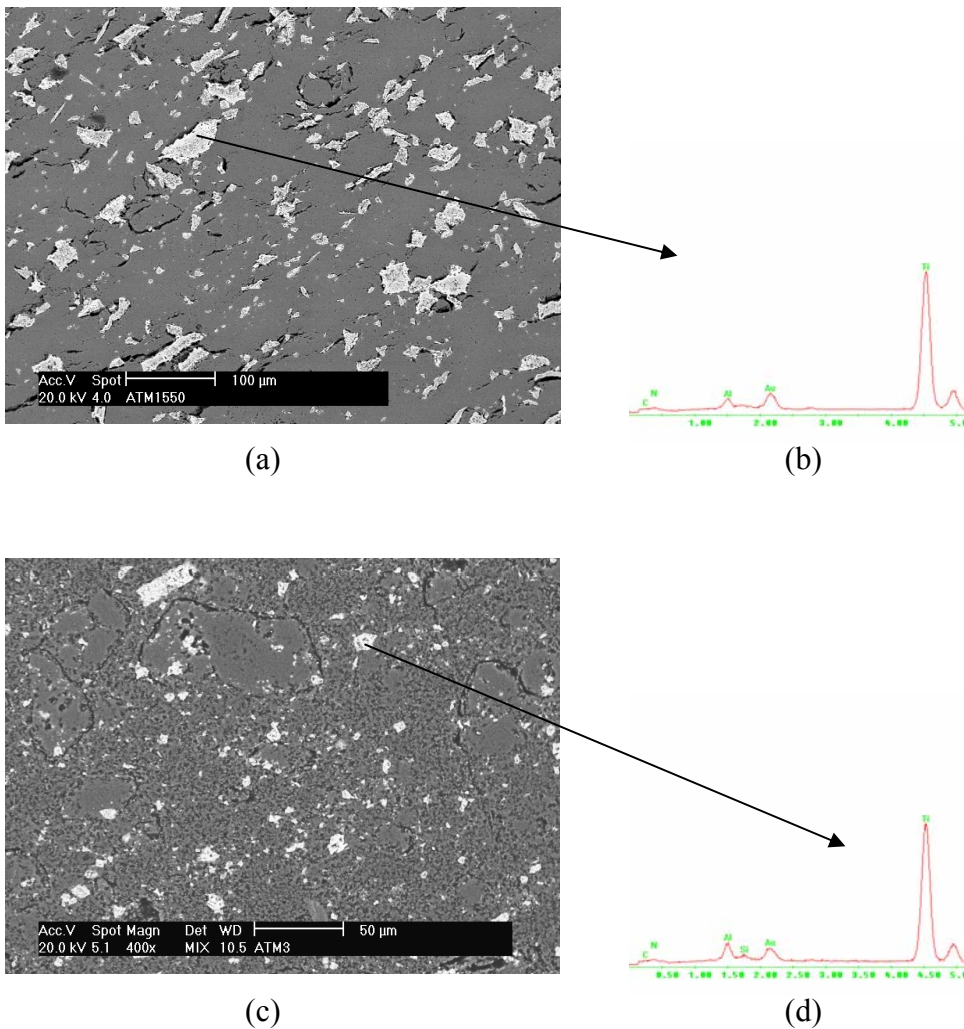


Figure 4- SEM micrographs and EDS of ATM and ATM5 samples.

ATM specimens present texture due to the Ti big particles size, Fig. 4 (a). By the other hand ATM5 samples don't have preferential orientation and present several densified regions, Fig. 4 (c). Comparing ATM and ATM5 samples, the former has smaller pore quantities than the ATM. Elemental analysis with energy dispersive spectroscopy (EDS) during SEM

observations was used to distinguish the phases. The bright phases are TiCN in ATM and ATM5 samples, Fig. 4 (b) and (d).

The hardness of the resulting multiphase compound was determined by Vickers indentation, Table 2.

Table 2- A1, ATM and ATM5 Vickers hardness.

Sample	Vickers hardness
	[GPa]
A1	16,2 ± 0,8
ATM	10,3 ± 0,5
ATM 5	9,3 ± 0,5

There is no significant difference in the ATM and ATM5 hardness values but were relatively low and smaller than that of A1 sample.

### Conclusions

The material had relatively low densities and hardness compared to pure alumina. The ball milled Ti provided a more dense and uniform microstructure. The major phases formed upon sintering were Al<sub>2</sub>O<sub>3</sub> and TiCN (ATM specimens) and Al<sub>2</sub>O<sub>3</sub>, TiCN and mullite (ATM5 samples). The preparation of ceramic composites using small amounts of precursor polymers shows a suitable process for alumina-based ceramics with high potential for the fabrication of complex shape pieces, using a simple forming route.

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