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Ceramic composites derived from polysiloxane/Al/Nb by AFCOP process

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Abstract. In this work, ceramic matrix composites (CMC) were prepared by AFCOP process, using a polysiloxane network filled with metallic niobium and aluminum powders as active fillers. The liquid polysiloxane precursor was loaded with a suitable polymer/filler ratio in relation to stoichiometric Nb : C and Al : O molar ratios. Changing Al for α-Al_2O_3, which acted as an inert filler, non-stoichiometric conditions were obtained. The mixtures were blended, uniaxially warm pressed, and pyrolysed in flowing argon at 800, 1000 and 1200 ºC. Thermogravimetry was used to follow the weight changes during the pyrolysis process. X-ray diffraction was used to identify the formation of new crystalline phases, such as Al_2O_3, NbC, Nb_2C and Al_3Nb in the composites. Sintered specimens were also characterized by SEM and EDS. The results indicated good potential for this system to obtain multiphasic composite material in the Al-Nb system at lower temperatures.

Introduction

Polymer pyrolysis is a relatively new and very promising technique for the processing of advanced ceramics in complex shapes [1]. The main advantages of such polymer-derived ceramics are the applicability of polymer-processing techniques; the homogeneity of the precursors on a molecular level; the low processing temperatures, when compared to conventional powder sintering methods; and the possibility of synthesizing new compounds [2].

Ceramic preparation via active-filler-controlled polymer pyrolysis (AFCOP) has been studied, in a broad range of multicomponent systems [3], as a promising technique for the preparation of monolithic ceramics. In this approach, ceramic or metallic powders are introduced into a preceramic polymer, which acts as a preceramic binder during the processing of the green body, and as a ceramic matrix source at higher temperatures [4]. Employing reactive filler particles, the reactions of these particles, with the decomposition products of the polymeric phase or the reactive gas atmosphere, promote volume expansion. Consequently, near-net shaped crack-free composites can be achieved, due to the compensation of polymer shrinkage by the appropriate filler expansion [3].

Composites derived from Nb/Al_2O_3-filled polysiloxane have already been studied [5], by using a poly(methylsiloxane) filled with 40 vol.% of a mixture of metallic niobium (reactive filler) and alumina (inert filler), which was pyrolysed in an inert atmosphere up to 1450 ºC. The *in situ* formation of NbC led to a material with high hardness and wear resistance. However, the metallic niobium can also be oxidized leading to niobium oxycarbide, NbO_xC_y, as well as niobium oxide, which weaken the resulting composites.

The results presented in this article are a first step towards understanding the role of metallic aluminum in the prevention of Nb oxidation and also in the generation of an *in situ* ceramic phase of Al_2O_3, with concomitant formation of SiC and NbC crystalline phases, during the pyrolysis of filled-polysiloxane.

The above strategy was used to obtain ceramic matrix composites (CMC), using a polysiloxane network filled with metallic niobium and aluminum powders as active fillers, and also Al_2O_3 powder as an inert filler. $Al/Nb/Al_2O_3$-filled polysiloxane, in different compositions, were prepared with suitable polymer/filler ratios, in relation to stoichiometric Nb : C and Al : O molar ratios. Changing Al for α-Al_2O_3 powder, non-stoichiometric conditions were obtained. The compacts were prepared by mixing the powders with liquid siloxanes, bearing Si-H and Si-vinyl groups, forming the siloxane network *in situ*, by means of the hydrosilylation reaction. The siloxane network is able to produce at 1000 ºC, a silicon oxycarbide glass with a high amount of carbidic groups as well as a free carbon phase [4, 6]. The pyrolysis of the resulting filled systems were carried out at 800, 1000 and 1200 ºC, in an argon atmosphere, giving rise to novel ceramic matrix composites. These composites were characterized by thermogravimetry (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The relationships between composition and microstructure of the resulting composites were discussed.

Experimental procedure

Starting Materials: Commercially available functional siloxane cyclic oligomer, 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (D_4Vi) and poly(methylsiloxane) (PMHS), 30 cst, were supplied by Dow Corning; platinum divinylcomplex, 2-3% in vinyl terminated poly(dimethylsiloxane) was purchased from Hüls. Metallic Nb with mean particle size of 22 µm and purity of 99 wt%, was supplied by the Chemical Engineering College of Lorena (Brazil). Metallic Al, with mean particle size of 22 µm, and α-Al_2O_3, with particle size of 2 µm, were purchased from Alcoa. All materials were used as received.

Preparation of Ceramic Bodies: In this study, homogenous neat mixture of D_4Vi and PMHS was submitted to platinum-catalyzed hydrosilylation reaction, in the presence of 1 wt% Pt-catalyst. The preceramic network was built by the reaction between $Si\text{-}CH{=}CH_2$, from D_4Vi cyclic oligomer, and Si-H, from the PMHS linear polysiloxane chain. In order to obtain green compacts, different proportions of the micron-particle-size Nb, Al and α-Al_2O_3 powders (shown in Table 1) were intimately blended with the liquid polysiloxane precursor mixture, before the cure. The mixture was then uniaxially pressed (~80 MPa) in a steel mould, and the stabilization of the green parts was achieved by thermal crosslinking reaction at 70 ºC, during a period of 2 hours. Pyrolysis of the monolithic materials was carried out from 25 to 800 ºC at 2 ºC/min, followed by the pyrolysis up to 1000 and 1200 ºC, at 2 ºC/min, using Edgcon 5P and Thermolyne F59340-CM tube Furnaces, respectively. Both furnaces are equipped with an internal alumina tube. The pyrolyses were carried out under argon flow (~100 mL/min) and holding time of 1 h at the maximum temperature.

Table I. Composition of the green compacts prepared with the mixture of the preceramic polymer and Al, Nb and Al_2O_3 powders.

Sample	Weight (%)			
	Polysiloxane	Al	Nb	α-Al_2O_3
COMP 1	18.7	63.0	18.3	-
COMP 2	18.5	42.7	19.4	19.4
COMP 3	18.5	23.2	19.4	38.9

Measurement Techniques: Thermogravimetry (TGA) was performed on a thermobalance (2950 TA instruments), under flowing argon (100 mL/min), with a heating rate of 10 ºC/min up to 980 ºC. For the ceramic composites, the thermo-oxidation study was performed with milled samples, which were analyzed in synthetic air flow at 10ºC/min. X-ray diffraction (XRD) patterns were collected with a diffractometer (Shimadzu, model XD3A) using Cu Kα radiation (λ=0.15418 nm) as an incident beam. Morphological characterization was performed by scanning electron microscopy (SEM) in JEOL – JSM 6360LV and JSM T-300 microscopes, operating with an accelerating voltage of 25 and 20 kV, respectively. The energy-dispersive X-ray spectroscopy (EDS) was carried out in a Noran Be-detector instrument as an accessory of JSM T-300. Al, Si and Nb mapping were recorded in the Kα lines at 1.49, 1.74 and 2.16 eV, respectively.

Results and Discussion

Thermogravimetry

Figure 1 shows the curves of weight loss as a function of the temperature for the preceramic polymer precursor and the three green compacts. In the preceramic polymer curve, two-steps of weight loss can be observed from ~520 to ~670 ºC and from ~670 to ~900 ºC. The first event was associated to organic evolution, such as CH_4 and siloxane volatile segments, and the second was related to the mineralization step, giving rise to a silicon oxycarbide (SiC_xO_y) product [7]. These events led to a high ceramic yield, 84.2 %, at 1000 ºC, due to the high crosslinking degree of the preceramic polymer, making this polysiloxane an appropriate precursor in CMC technology. The green compacts prepared using this polymer showed higher ceramic yields, following the COMP1 > COMP2 ≅ COMP3 order. As Al has a low melting point of ~660 ºC, near this temperature it becomes highly active, with a typical reactive filler behavior. As a consequence, changes in the TGA curve profile were observed, when compared to the polymer itself. Al reacted with the decomposition products of the polymer near its melting point, and this reaction was more active for the richer Al composition (COMP1). After ~850 ºC, an increase in the residue weight was observed, due to the reactions involving Nb active filler in addition to those of Al.

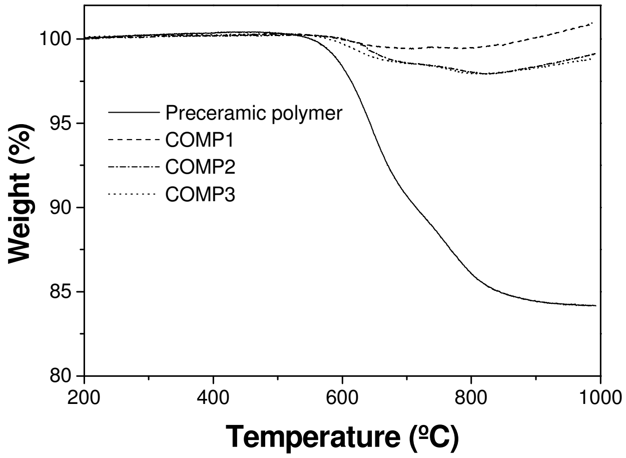

Fig. 1: TGA curves for preceramic polymer and green compacts of COMP1, COMP2 and COMP3.

Phase development

The phase development of the Nb/Al/Al_2O_3-filled polysiloxane samples pyrolysed at 800, 1000 and 1200 ºC, was evaluated by XRD [8], as can be seen in Fig. 2. For **COMP 1** the Al_3Nb phase was the most intense in the diffractograms. However, the reactions among the fillers and preceramic polymer products were not complete at the temperatures studied. Metallic Al and Nb were also identified in the products. In addition, the presence of metallic Si and Al_2O_3 diffractions were observed, indicating the occurrence of oxi-reduction reactions between Al and the polysiloxane network. In this way, the presence of metallic Si could be correlated to the consumption of the oxygen from the polymer by the oxidation of Al. Indeed, energetically it appears more favorable to oxidize Al rather than Si [9]. For **COMP 2,** in addition to the peaks of the remaining metallic powders, there were diffractions of the Al_2O_3 added to the green body. However, the formation of Al_3Nb and $NbSi_2$ was also detected. With the decrease in the amount of Al, by replacement with inert Al_2O_3, there was enough Nb to react also with Si, forming $NbSi_2$. For **COMP 3,** which was prepared from a mixture with the lowest amount of metallic Al, $NbSi_2$, NbC and Nb_2C diffractions were observed, in addition to the formation of Al_3Nb. For all composites, just small differences were observed in the phase development as a function of the pyrolysis temperature. The diffractions of new crystalline phases were increased in intensity with the increase in temperature. No mullite formation was observed in the resulting COMP´s, because no silica sites remained in the obtained composites.

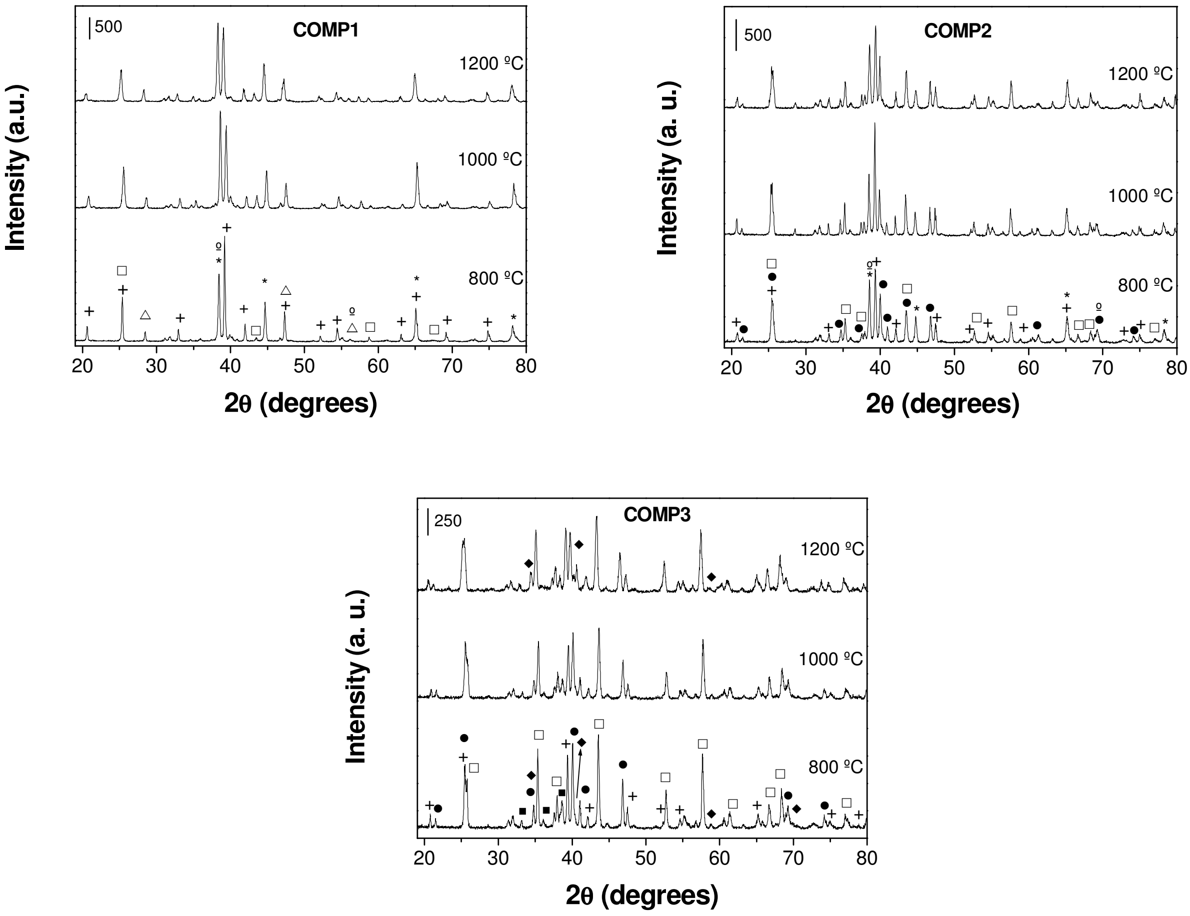

Fig. 2: XRD patterns of **COMP1 COMP2** and **COMP3** at different pyrolysis temperature. Marked peaks: + Al_3Nb; △ Si; * Al; ° Nb; □ Al_2O_3; ● $NbSi_2$; ◆ NbC; ■Nb_2C.

Phase morphology

The green compacts produced from the mixture of polysiloxane and the ceramic powders were visually crack free. The morphology of the ceramic composite samples was analyzed by SEM and EDS. Fig. 3 shows the SEM macrographs of COMP1 and COMP2 at different pyrolysis temperatures. The segregation of the metallic and ceramic phases was observed in all of the samples. The smooth and gray phases in Fig 4A are the metallic phases, which are richer in Al and Nb, as can be seen in Figs. 4B e C, respectively. In the EDS elemental mapping, these polished metallic surfaces are the harder parts of the composite, dispersed in a ceramic matrix. The Si-mapping, which is the element that has the lowest amount in the CMC´s, is dispersed in smaller domains in the sample, as can be seen in Fig. 4D.

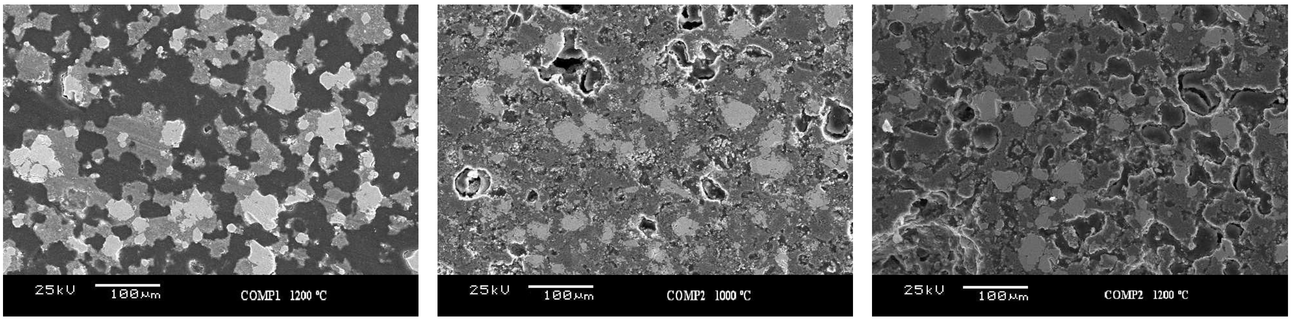

Fig. 3: SEM micrographs of polished fracture surfaces of COMP1 and COMP2 pyrolysed at 1000 and 1200 ºC.

COMP2 displayed a new morphology (Fig. 3), when compared to COMP1. The presence of alumina powder led to a more uniform dispersion of the ceramic and metallic phases. We also believe that more alumina could be formed *in situ* in this sample, due to the seeds that allow the alumina nucleation. For this sample large pores could also be observed. Such pores were formed in the ceramic skeleton, maintained by the alumina powder, which retained sample shrinkage. For the sample pyrolysed at 1200 ºC, more pores could be observed. However, at this temperature, a poor adhesion between the metallic and ceramic phases was observed. There was still an excess of metallic Al, as identified in the XRD patterns (Fig. 2), in this composition.

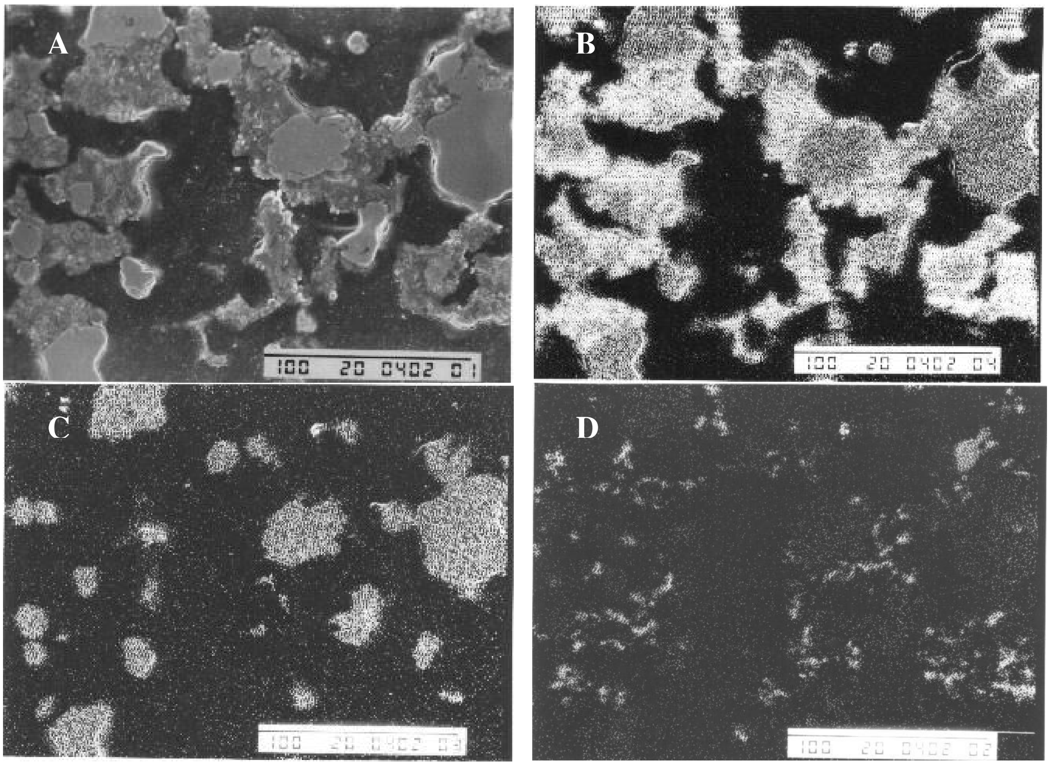

Fig. 4: SEM micrograph (A) and EDS mapping of Al (B), Nb (C) and Si (D) of polished fracture surfaces of COMP1 pyrolysed at 1200 ºC.

Oxidative thermal analysis

TGA curves in air flow of milled composite samples pyrolysed at 1000 ^{o}C, were registered to verify their stability against oxidation. TGA curves were registered in airflow of milled composite samples, pyrolysed at 1000 ºC. The TGA curves are displayed in Fig. 5. The composites displayed a weight loss of 1 to 3 %, in the range of 100 to 630 ºC, in the following order: COMP3 >

COMP2 > COMP1. For the richest Al sample (COMP1), the highest weight gain was observed after 600 ºC, due to the oxidation of the remaining Al. Such behavior was followed by the COMP2 and COMP3 samples. This oxidation behavior was increased in part due to the finely milled shape of the samples.

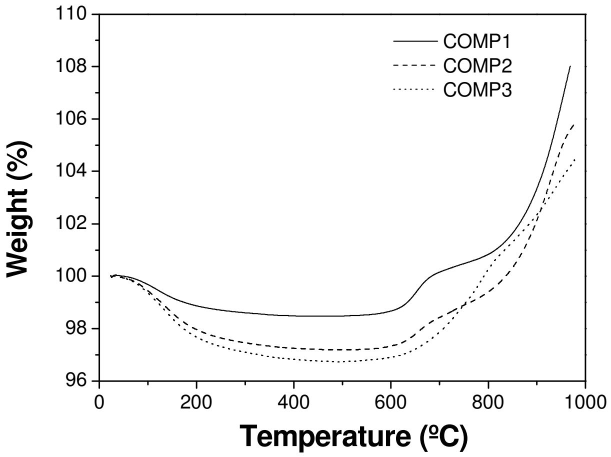

Fig. 5: TGA curves for of milled COMP1, COMP2 and COMP3 samples pyrolysed at 1000 ºC.

Conclusions

In this work, the preparation of monolithic ceramic matrix composites, by using the AFCOP process, from a preceramic polymer as binder of $Al/Nb/Al_2O_3$ powders, was investigated. Al and Nb acted as reactive fillers. Al acted as an inhibitor of Nb oxidation, producing *in situ* Al_2O_3, due to the reaction with the precursor polymer. Such reactions led also to the formation of metallic Si. For samples with higher amounts of Al (COMP1 and COMP2), the preferable product was Al_3Nb. At lower amounts of Al (COMP3), in addition to the Al_3Nb phase, NbC and Nb_2C crystalline phases were also obtained. The low oxidation resistance of the prepared CMC was due to the excess of non-reacted aluminum. Further work is in progress in this laboratory to optimize such systems by increasing the pyrolysis temperature as well as decreasing the Al content in the green compacts.

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