

CHARACTERIZATION OF CERAMIC COMPOSITES DERIVED FROM POLYSILOXANE/Nb/Al/Al₂O₃ BY AFCOP PROCESS

WILSON ACCHAR

Programa de Pós-Graduação em Engenharia Mecânica, UFRN, CEP: 59072-970, Natal-RN, Brazil

e-mail: acchar@dfte.ufrn.br (corresponding author)

YGOR A. FONSÊCA

Programa de Pós-Graduação em Engenharia Mecânica, UFRN, CEP: 59072-970, Natal-RN, Brazil,

MARCUS DINIZ

Programa de Doutorado em Engenharia e Ciência dos Materiais, UFRN, CEP:59072-970, Natal-RN, Brazil

Abstract: *Ceramic matrix composites were prepared by the active-filler-controlled polymer pyrolysis process (AFCOP) using a polysiloxane network filled with metallic niobium and aluminum, as active filler and alumina as inert filler. The mixture was blended; uniaxially warm pressed and pyrolyzed in flowing argon at 1400 °C during one hour. Thermogravimetry was used to follow the weight changes during the pyrolysis process. X-ray diffraction was carried out in order to identify the presence of crystalline phases, such as Al₂O₃, Al₃Nb, Nb₃Si, Nb₅Si₃, NbSi₂, NbC and Nb₂C. The specimens were also characterized by infrared spectroscopy, flexural strength and differential thermal analyze (DTA). The influence of a polymer infiltration on the flexural strength of the sintered bodies was also investigated. The results have indicated a good potential for this system to obtain a multiphase material in the Al-Nb system at 1400 °C. This work shows also that the strength of the composite material could be increased by a polysiloxane impregnation and pyrolysis cycle.*

Keywords: *composite materials, niobium, polymeric precursor, polysiloxane*

1. Introduction

In the last years a considerable development in a ceramic composite ceramic material processing has been observed, with the introduction of a variety of sintering methods, many of them based in high pressure and temperature of processing (Acchar et al.(2000), Acchar, Vieira et al. (2000), Acchar, Schwarze et al.(2003), Acchar, Greil et al. (2001). However, these methods usually involve high costs. Ceramic preparation via active-filler-controlled polymer pyrolysis (AFCOP) is a new and very promising technique for processing of advanced ceramics in complex shapes (Greil (1999), Schiavon et al.(2002), Kroll (2005), Herzog et al. (2005), Song et al.(In press), Colombo et al.(2000), Gozzi et a.(2001) and Greil (1994) . The main advantages of such polymer-derived ceramics are the applicability of polymer-processing methods, the low sintering temperatures when compared to conventional powder sintering processes and the possibility to synthesizing new compounds. Composites derived from Nb/Al₂O₃-filled polymer have been studied (Dernovsek et al.(2000), Acchar and Wolff (2001) and Acchar and Wolff (In Press)). The presence of niobium carbide on an alumina matrix led to a material with good hardness and wear resistance. However, the metallic niobium can also oxidize leading to niobium oxycarbide (NbO_xC_y), as well niobium oxides (NbO, NbO_x, etc), which degrades the mechanical properties of the sintered composite material.

The presence of metallic aluminum in the mixture used in this work has the objective to prevent the niobium oxidation and to generate an in situ alumina ceramic phase. The purpose of this work is to investigate the formation of reaction bonded niobium carbide ceramics derived from polysilsesquioxane-Nb-Al-Al₂O₃ mixtures. The influence of a polymer impregnation process on the strength of the sintered samples was also studied.

2. Experimental Procedure

The raw materials consisted of two commercially available functional siloxane cyclic oligomer (Dow Corning), niobium (Brazil), aluminum (Brazil) and alumina powder (Alcoa) with average particle size of 16 μm , 22 μm and 2.0 μm respectively. Aluminum acetylacetonate was added as a curing catalyst (0.1 wt. %). In order to obtain green compacts, 30 wt.% Nb, 5 wt.% Al and 46.5 wt.% Al₂O₃ powders were intimately blended with the liquid polysiloxane precursor (18.5 wt.%). The mixture was then uniaxially pressed (40 MPa) in a steel mould and stabilization of the green parts was achieved by thermal crosslinking reaction at 80 °C during a period of two hours. The pyrolysis of the composites was carried out in a tube furnace in argon flux of 100mL/min, at a heating rate of 10°C/min, from T_{amb} to 800°C, followed by a cooling to T_{amb}. After this step the samples were pyrolysed in argon flux of 100mL/min in a tube furnace, (Thermolyne FS59340-CM59300) at 1400 °C. The heating schedule was: from T_{amb} at 800°C, at heating rate of 300°C/min, followed by a second heating rate of 10°C/min, from 800°C to the final pyrolysis temperature, followed by an isotherm of 60 min. After this the samples were cooled to T_{amb} at a rate of 10°C/min. The CMCs obtained were characterized by infrared spectrum (IR), thermal analyses (TGA and DTA), X-ray diffraction (XRD) and flexural strength. The infrared patterns were obtained in a Bomem B100 or Perkin Elmer spectrometer which operates from 4000 and 400 cm⁻¹, with a resolution of 4 cm⁻¹, utilizing the conventional transmission technique with KBr plates. TGA and DTA analysis were performed at a heating rate of 10 °C/min in argon flux, in the temperature range from 30 to 1000 °C and 30 to 1500 °C, respectively. The identification of crystalline phases was carried out by X-ray diffraction in an X-ray spectrometer Shimadzu XD6000, using CuK α radiation (1,5418Å). A four-point bending test was used to measure the room temperature bending strength. A minimum of five samples was used to determine the average value of bending strength. This work has also investigated the influence of a polysiloxane impregnation and pyrolysis cycle on flexural strength of the composite material. The manufacturing of the polymer-infiltration-pyrolysis includes three stages: 1- Ceramic matrix composites (CMC) is infiltrated with polymer precursor in vacuum, 2- The precursor is cured into a solid and 3-CMC is pyrolyzed again at 1400 °C during one hour in argon. In this work the CMC was submitted on only one cycle.

3. Results and Discussion

The thermogravimetric analysis of the preceramic polymer has shown a weight loss event from 600- 900 °C, which can be attributed to the evolution of volatiles organic, such as CH₄ and the mineralization process (Fig. 1). The mineralization stage occurred from ~700 to ~900 °C. In this stage, the sample becomes rich in organic and hydrogen radicals. The entrapped free radicals can react with Nb and Al giving rise to silicides and carbides derivatives. As aluminum has a low melting point, at 660.4 °C, it becomes highly active from this temperature, changing significantly the TGA curve profile when compared to the polymer itself. It may be concluded that niobium and aluminum acts as active filler during the pyrolysis, reacting with the decomposition products of the polymer. The presence of Nb₂C, NbC and Al₂O₃ phases are the evidence of this behavior.

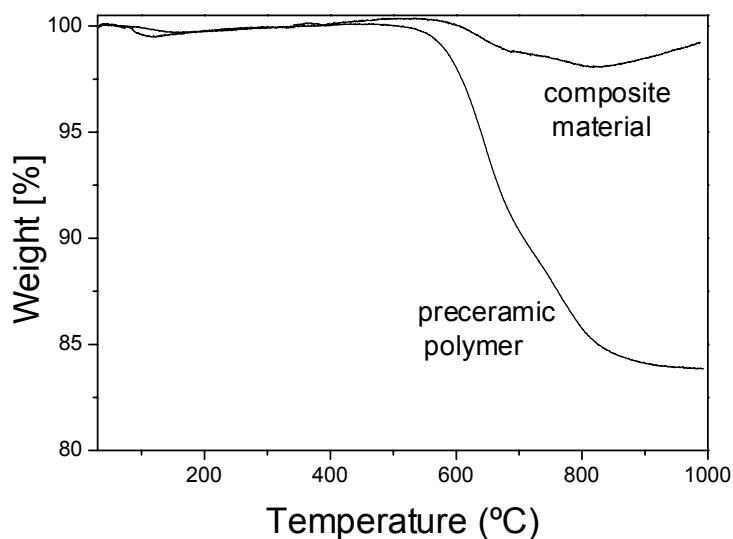


Figure 1. TGA curves for the composite material and the preceramic polymer.

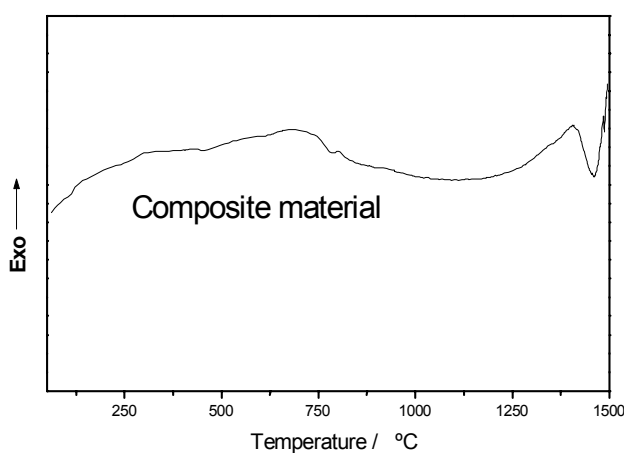


Figure 2 . DTA curve for the composite material.

DTA curve for the composite material is showed in Fig. 2. This thermal analyze shows a wide exothermal peak around 500 to 800 °C, that is associated to the reactions among the polymer degradation products and/or carbon phase with Nb and Al, forming new crystalline phase described in Fig. 4. In this stage also occurred the mineralization of the polymer, with the formation of the amorphous matrix of silicon oxycarbide (SiC_xO_y). The DTA curve shows also another exothermic peak at approximately 1430 °C, that can be attributed to the formation of mullite ($3 \text{ Al}_2\text{O}_3 \cdot 2 \text{ SiO}_2$).

The infrared spectra of the CMCs pyrolyzed at 1400°C show a large absorption band, with maximum in $\sim 1090\text{cm}^{-1}$ (Fig. 3). This band was associated to the Si-O-Si sites of the silicon oxycarbide amorphous matrix. The absorption band at $\sim 800\text{cm}^{-1}$ corresponds to Si-C sites from SiC_xO_y matrix. At $\sim 600 \text{ cm}^{-1}$ the samples with Al_2O_3 show a peak characteristic of Al-O-Al. The absorption at $\approx 460\text{cm}^{-1}$ is characteristic of NbC.

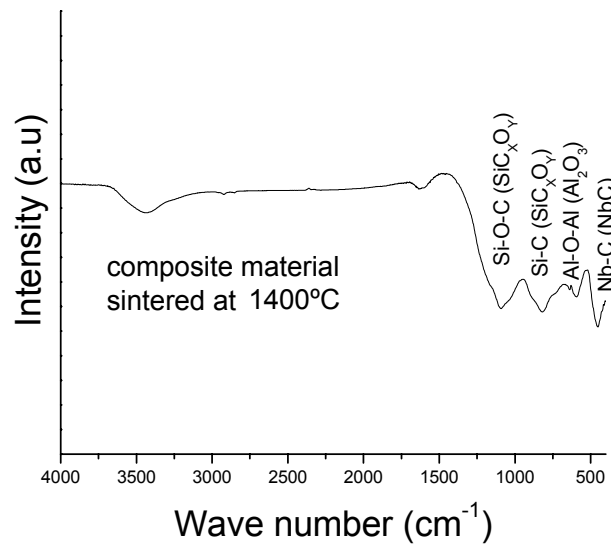


Figure 3. IR spectrum for the composite material sintered at 1400 °C.

The phase development of the Nb/Al/Al₂O₃-filled polysiloxane samples pyrolyzed at 1400 °C is depicted in Fig. 4. The X-ray diffratograms showed the presence of Al₂O₃, Al₃Nb, Nb₃Si, NbSi₂, Nb₅Si₃, NbC and NbC₂ crystalline phases, what is in agreement with the thermal analyze and the infrared spectroscopy. The presence of niobium oxides phases was not detected in the X-ray diffraction analysis. The silicide formation observed in this work is common in the polymer pyrolysis with the presence of active filler (Dernovsek et al. (2000), Acchar and Wolff (2001) and Acchar and Wolff (In Press)). Figure 5 compares the flexural strength of the pyrolyzed and pyrolyzed and infiltrated specimens. The flexural strength of the infiltrated composite material was superior as compared to the pyrolyzed material. The flexural strength has increased from 159 to 190 MPa. It may be concluded that the polymer-infiltration pyrolysis process is a good method to improve the mechanical properties of the composite material. Further works are in progress in our laboratory in order to optimize such system and the infiltration method by increasing pyrolysis temperature and infiltration steps.

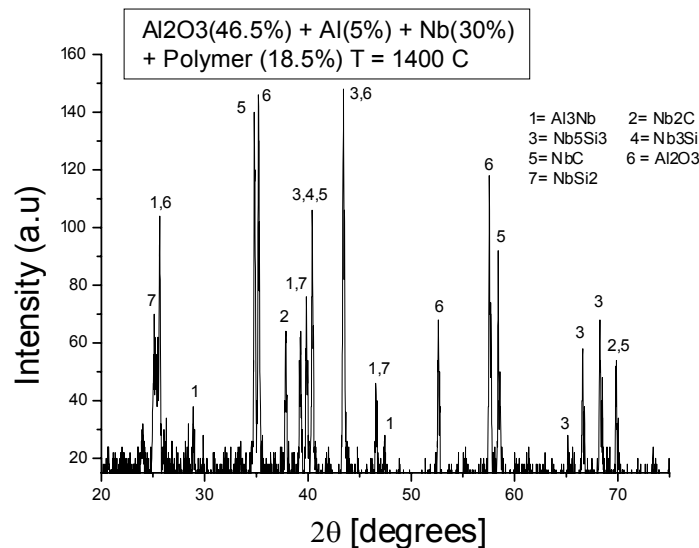


Figure 4. X-ray pattern of the composite material.

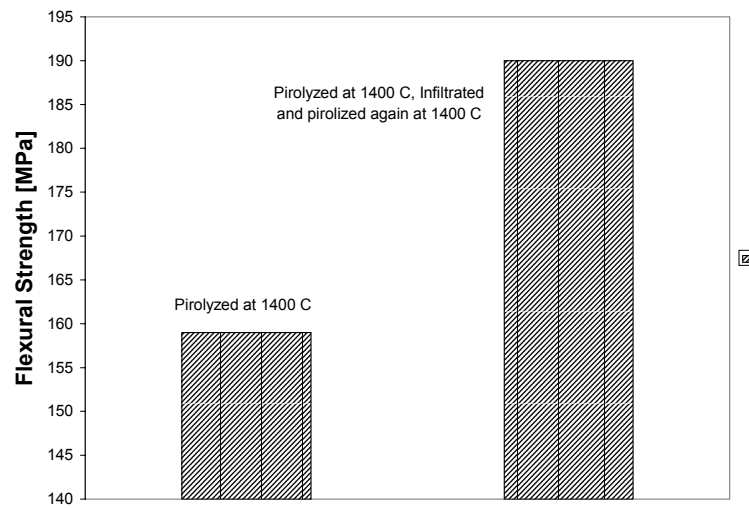


Figure 5. Flexural strength of the samples pyrolyzed and infiltrated.

4. Conclusions

In this work we have exploited the preparation of monolithic ceramic matrix composites by using the AFCOP process from a preceramic polymer as binder of Al/Nb/Al₂O₃ powders. The process allowed the obtainment of shaped samples. Al acted as reactive filler, preventing the oxidation of niobium and, it is also able to produce in situ Al₂O₃ by the reaction with the polymer decomposition products. The impregnation polymer process has showed to be a good method to improve the flexural strength of the composite material.

5. References

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