J Mater Sci (2008) 43:597–601
DOI 10.1007/s10853-007-1539-4

5TH BRAZILIAN MRS MEETING

The effect of polysiloxane on the properties of Al_2O_3-NbC composite material produced by pyrolysis process

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Received: 19 October 2006 / Accepted: 19 January 2007 / Published online: 5 May 2007

Abstract Recently, studies have been developed in order to obtain Al_2O_3-NbC composite materials. The reinforced materials have shown good potential to be used as cutting tool materials at high-speed cutting and high temperature as a substitute to WC-Co material. The main disadvantage to produce these alumina-reinforced materials is the necessity to use pressure assisted sintering or high sintering temperatures to produce dense bodies. Manufacturing of composite ceramic materials derived from polymer reactive filler has been intensively investigated. Polymer pyrolysis is a relatively new and very promising method for obtaining ceramic material in complex shapes and lower sintering temperatures. This work investigated a ceramic composite matrix based in SiC_xO_y and Al_2O_3 and reinforced with NbC obtained by means of the active fillers pyrolysis process. The results obtained in this work demonstrate that using a mixture of polysiloxanes produces a composite material with better properties when compared to others polymer materials.

Introduction

Active-filler-controlled polymer pyrolysis (AFCOP) is a very good and promising method for the manufacturing of ceramic materials in complex shapes [1–8]. The advantages of such polymer-derived ceramics are the applicability of polymer-processing techniques and the homogeneity of the precursors on a molecular level [9]. The use of polymer and reactive fillers to produce ceramic composite materials also has the advantage of decreasing the sintering temperature; when compared to other processing methods that involve high costs as well [10, 11]. Composites derived from Nb/Al_2O_3-filled polymer have already been studied [12–14]. The works indicate that is possible to obtain a ceramic matrix reinforced with niobium carbide by using the AFCOP process. During pyrolysis the polymer decomposes and the solid and gaseous decomposition products react with the active fillers to form new carbides phases. The in situ formation of NbC led to a material with high hardness and wear resistance. However, the main disadvantage of this method is the low-density values of the pyrolyzed materials, as well as the presence of niobium oxidation products, which weaken the resulting composites [14, 15]. The strategy used in this work is 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 inert filler. The polymetilsiloxane has the advantage of being more thermally stable during the heating process, causing to improve the reaction time between the carbon and niobium (reactive filler). The presence of aluminum has the objective of avoiding the formation of the niobium oxides. The results presented in this work 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 NbC crystalline phases, during the pyrolysis of filled-polysiloxane.

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In the present work the formation of reaction bonded niobium carbide ceramics derived from polysiloxanes-Nb-Al-Al_2O_3 mixtures was investigated and the ceramic products were characterized. The main objective of this work is to produce a ceramic composite matrix reinforced with niobium carbides, without the presence of niobium oxides.

Experimental procedure

The starting powders consisted of a commercially available functional siloxane cyclic oligomer, (D_4Vi) and poly(methylsiloxane) (PMHS) (Dow Corning) with high purity level, metallic niobium with 99 wt.% purity (Chemical Engineering College of Lorena, Brazil), metallic aluminum and α-Al_2O_3 (Alcoa,Brazil). Specimens were prepared containing a fixed concentration of 60 wt.% polymer and 40 wt.% of Al_2O_3/Nb/Al filler, in wt/wt ratio of 25/20/36, respectively. Samples with dimensions of 50 × 5 × 5 mm^3 were uniaxially warm pressed at 80 °C in a steel mold under a load of 20 MPa during 30 min. Pyrolysis of the materials was carried out at 1200 °C and 1400 °C for 3 h, using a Maytec FTE-1600/H tube furnace. The composite materials obtained were characterized by infrared spectrum (IR), thermogravimetry (TGA), X-ray diffraction (XRD), flexural measurements, scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). Thermogravimetry analysis (TGA) was performed under flowing argon (Shimadzu 60 H), with a heating rate of 10 °C/min. X-ray diffraction patterns were carried out in a diffractometer (Shimadzu, model XD3A) using Cu Kα radiation ($\lambda = 0.15418$ nm) as an incident beam. The mechanical strength of the composite material (average of five specimens for each value) was measured with a universal testing machine (Zwick-Roell, 2.5 kN) in a four-point bending tests using spans of 10 and 20 mm, at a constant cross-head speed of 0.4 mm/min. Apparent density and porosity were determined by using the Archimedes water displacement method. 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. The morphology and the microstructural aspects of the fracture surface were observed by SEM in a Philips XL30-ESEM microscope, operating with an accelerating voltage of 25 kV. The instrument was also equipped with an energy-dispersive X-ray spectroscopy (EDS).

Results and discussion

Figure 1 compares the TGA analysis of two different polymer precursors. The first one, used in this work, is the polysiloxane and the second one, which was investigated in earlier work, is the poly(methylsilsesquioxane-PSS) [15]. The PSS show a multi-step weight loss behavior during the heating process that can be attributed to the volatile loss of the H_2O, absorbed in the material, through Si–OH and Al–OH condensation, and also by the volatile organic loss (CH_4). The polysiloxane used in this work shows a more stable thermal behavior and a lower weight loss, when compared to PSS. This type of polymer material reduces the escape of siloxanes volatiles, increasing the ceramic yield and promoting a better reaction between the polymer and the active filler (Nb). The high thermal stability observed may be associated to the high cross-linking degree of the polymer, making the polysiloxane a good polymer material to be used in the active filler pyrolysis process. The infrared spectrum of the composite material pyrolyzed at 1200 °C is illustrated in the Fig. 2. A wide absorption band can be observed, with a maximum in ≈ 1090 cm^{-1}. This band is associated to the Si–O–Si sites of the silicon oxycarbide amorphous matrix [4, 16]. The presence of alumina introduced as a raw material (inert filler) and produced by the reaction between aluminum (active filler) and oxygen from the polymer causes the presence of a absorption band at 600 cm^{-1}, which is a peak characteristic for Al–O–Al. The material also exhibits a band at 460 cm^{-1}, which can be attributed to the presence of NbC. Similar results were also reported in others works [15, 17].

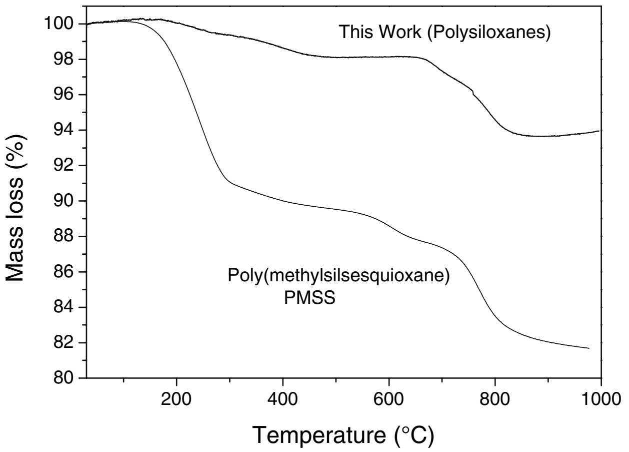

Fig. 1 Thermogravimetric behavior of polysiloxane (this work) and poly(methylsesquioxane) [15]

Figure 3 shows the XRD pattern of the composite material pyrolysed at 1,200 and 1,400 °C. The X-ray diffraction analysis identified the presence of Nb_3Si, Al_3Nb, Al_2O_3, as well as the formation of NbC and a small peak of aluminum. The silicide formation observed is in agreement with the results founded in other polymer pyrolysis systems, with the presence of active filler [5, 14, 17]. No evidence of niobium oxides was observed. This fact

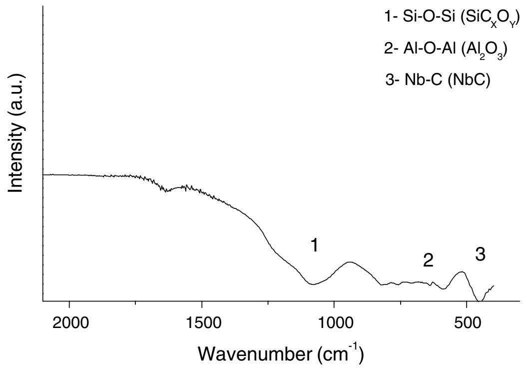

Fig. 2 FTIR spectra of the sintered material

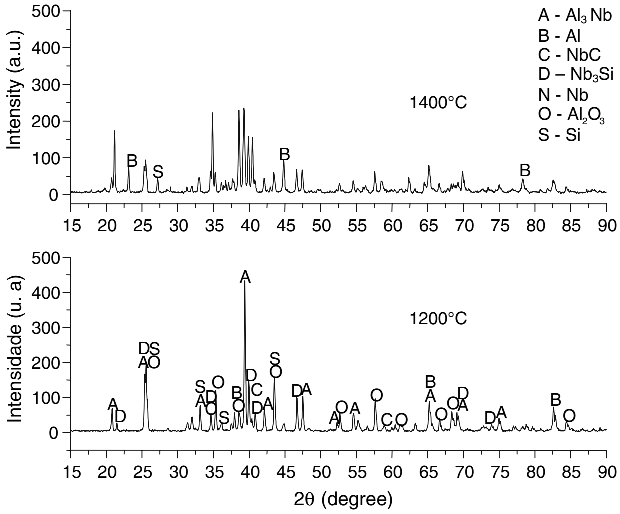

Fig. 3 X-ray diffraction pattern of the sintered material

suggests that the addition of aluminum has effectively avoided the oxidation of niobium. X-ray diffraction analyses indicate that aluminum and niobium react with other elements according to:

$$\mathrm{Al} + \mathrm{Nb} + \mathrm{SiO_xC_y}\ (\mathrm{polymer}) \Rightarrow \mathrm{Al_2O_3} + \mathrm{Al_3Nb} + \mathrm{NbC} + \mathrm{Nb_3Si} + \mathrm{SiO_{x-m}C_{y-n}} \quad (1)$$

The presence of niobium oxidation products was reported in a previous Nb-polymer system, that did not use aluminum as active filler [14]. A thermodynamic analysis of the expected phases was performed in earlier works [13, 14]. By analyzing the X-ray patterns, the increase of the NbC peaks with the increase of the temperature was observed, as well as the decrease in the Al_3Nb peaks. A peak of small intensity, corresponding to aluminum, was also observed, which indicates that the aluminum content used in this work as active filler was excessive. Table 1 summarizes the porosity, density and strength values obtained in this work. The results indicate that the composite materials display high porosity values, around 30%, similar to the reported works [11, 13]. The temperature increase has practically slight influence on the porosity values, a feature which is not in agreement with others works [13, 14, 17]. The density values presented in Table 1 show a reverse dependence of the sintering temperature. The density decrease caused by increasing the temperature can be attributed to the aluminum effect. The presence of aluminum excess, in the composite material, identified in the X-ray diffraction (Fig. 3) may cause an improved on density of the specimens at 1200 °C. Aluminum comes into the porous ceramic material at this temperature, filling pores and increasing the density of the samples. The increase of the density values by using aluminum in this temperature range was also reported to other materials, such as B_4C + (Al,Si)[18] and Al_2O_3 + Al–Mg alloys [19]. The works have indicated a weight gain and an increase of the density of the samples through the infiltration of aluminum into the porous ceramic preforms. The formation of a positive capillary pressure among a molten metal and a solid ceramic is the governing principle of the pressureless infiltration [19].

Table 1 Porosity, density and strength values obtained in this work

	Porosity (%)	Density (g/cm^3)	Flexural strength (MPa)
Sintered at 1200 °C	32	2.22	45 ± 5
Sintered at 1400 °C	30	2.20	55 ± 6

At 1400 °C the material manifests a divergent behavior, showing a decrease of the density values. The viscosity of the aluminum melting at this temperature is too low, causing the migration of the aluminum through the sample. Aluminum contamination was detected in the samples support, indicating an aluminum loss and as a consequence a density decrease of the materials at this temperature, as observed in Table 1. The strength values of the composite materials are also reported in Table 1. The composite materials show a constant strength level, remaining practically unchanged, regardless of the sintering temperature. During the increase of the temperature from 1200 °C to 1400 °C the decrease of the density and porosity concurrently takes place, responsible for the constant mechanical behavior. In this case, the increase of the sintering temperature does not cause any improvement in the mechanical properties of the samples. The flexural strength value obtained in this work at 1200 °C (≈45 MPa) is comparable to the observed in poly(siloxane) derived NbC composite ceramics [13]. At 1400 °C the strength value obtained in this work (≈55 MPa) is significantly lower as compared to the published work (≈85 MPa) [13]. The results presented

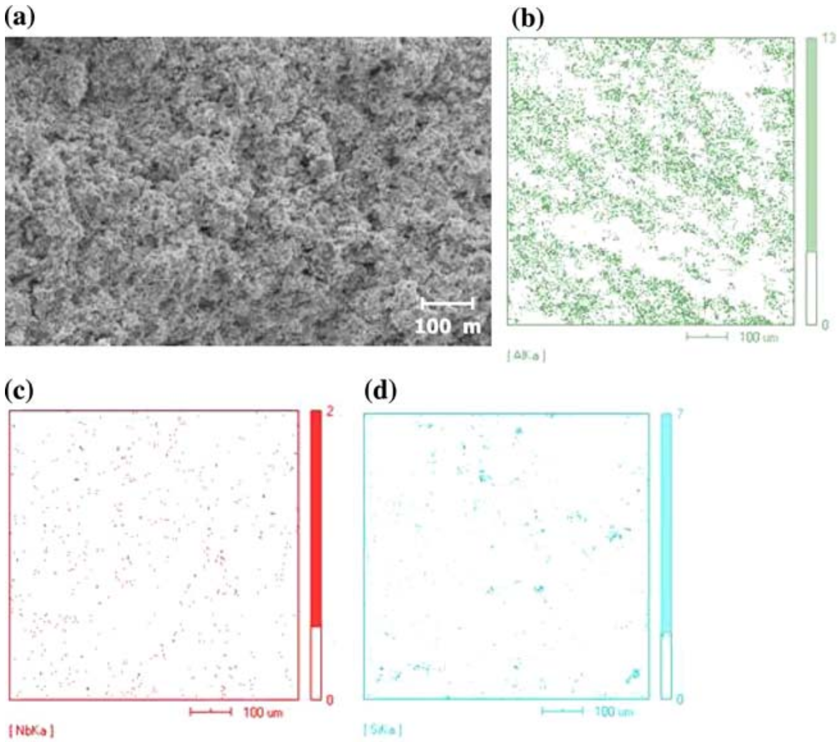

Fig. 4 Surface fracture (**a**) and element mapping of the material sintered at 1,200 °C (**b**-Al, **c**-Nb and **d**-Si)

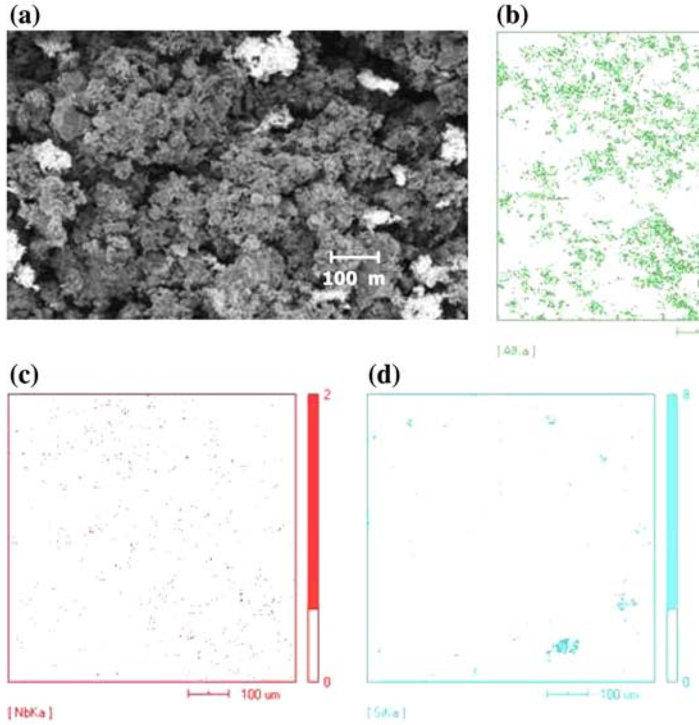

Fig. 5 Surface fracture (**a**) and element mapping of the material sintered at 1,400 °C (**b**-Al, **c**-Nb and **d**-Si)

above indicate that 1400 °C is not adequate to sintern a composite ceramic material with high aluminum content. The temperature or the aluminum content must be decreased.

A typical SEM image and element mapping for the composites sintered at 1200 °C and 1400 °C is illustrated in the Figs. 4 and 5, respectively. The composites showed a significant porosity level, which is in agreement with the results presented in Table 1. From the elemental mapping, as can be seen that the distribution of Al, Nb and Si and as a consequence the crystalline phases identified in Fig. 3 were homogeneously distributed in the material. At 1400 °C the elemental mapping indicates a decrease of the aluminum points in Fig. 5b, in agreement with the perspective of aluminum loss. The difference observed in the elemental distribution can also be related to the porosity level observed in the samples. The decrease of the aluminum in the elemental mapping at 1400°C is associated with an increase of the porosity level, as described in Table 1.

The results described in this work indicate that the incorporation of aluminum metallic caused principally three effects: (1) avoids the niobium oxidation (positive effect); (2) reduces the porosity of the samples at 1200 °C through the melting filling (helpful effect) and (3) increases the porosity level at 1400 °C, due the aluminum loss (negative effect). Further studies are still under way to investigate two main aspects: the positive effect of the aluminum content in the porosity level and its influence on the properties and microstructure of the composite material.

Conclusions

In this work, the characterization of a reaction bonded niobium ceramic matrix composites, by using the AFCOP process, from a preceramic polymer (polysiloxane) as binder of Al/Nb/Al_2O_3 powders, was investigated. The use of polysiloxane has evidenced a stable thermal behavior, when compared to PSS. X-ray diffraction analyses show that niobium reacts with silicon and aluminum, forming new crystalline phase as $NbSi_3$, Al_3Nb and NbC. The high porosity and density values observed are related basically to the polymer's gaseous decomposition and the aluminum loss. The addition of aluminum as an active filler has avoided the niobium oxidation and contributed to the porosity level of the specimens. The effect of the aluminum on the porosity has showed to be dependent of the pyrolysis temperature.

Acknowledgements The Authors of this work thank to CNPq for the financial support and the Material Engineering Department of Lorena Chemical Engineering University, for the niobium powder.

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