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Surface Characterization of Alumina Reinforced with Niobium Carbide Obtained by Polymer Precursor

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Active filler controlled pyrolysis of polymers (AFCOP) is a recent method for obtaining near-net shaped ceramic bodies. Alumina based composites have been developed for use as cutting tools, so knowledge of the surface composition is extremely important because it is directly related to the hardness and wear resistance Samples containing a fixed concentration of 60 wt. (%) of polysiloxane and a mixture of metallic niobium and alumina powder were homogenized, uniaxially warm pressed at 80 °C and subsequently pyrolyzed in flowing argon at 1200, 1400 and 1500 °C. Analysis of the surface composition was carried out by X ray photoelectron spectroscopy, infrared spectroscopy, X ray diffraction and scanning electron microscopy. The results have indicated that the formation of the phases on the surface depends strongly on the niobium/carbon ratio in the raw materials.

Keywords: *alumina, niobium carbide, X ray photoelectron spectroscopy*

1. Introduction

Alumina-based composite materials have been intensively developed in order to find new technological alternatives to cemented carbides[1-3]. Update, WC-Co material is still the most used material for cutting tool applications[4]. The addition of hard refractory particles such as TiC, WC, NbC or mixed carbides causes a pinning effect, reducing the grain growth of alumina, which improves the mechanical performance of this composite materials[5-7]. Recently, manufacturing of alumina reinforced with carbides through the active filler controlled reaction pyrolysis of polymers has been widely investigated[8-10]. This process has the advantage to make possible to obtain samples with complex forms and sintered at lower temperatures, as compared to conventional methods. The tribological performance of these materials depends strongly on their superficial hardness, which is directly related to the presence of carbides on the surface. Superficial analysis using X ray photoelectron spectroscopy allows this to be studied efficiently in order to determine the surface composition; which influences directly the hardness and wear resistance of alumina reinforced with carbides. The photoelectrons excited and analyzed during the XPS experiments have an average escape depth of 20 Å, so the data from the interior are not included. X ray diffraction, infrared spectrum and scanning microscopy were also used to investigate the formation of niobium carbide[10,11].

The purpose of this work was to investigate the formation of niobium carbide on the surface of the composite material. The material was obtained from a mixture of a reactive polymer (polysiloxane), metallic niobium (active filler) and alumina (inert filler).

2. Experimental Procedure

Niobium powder (Department of Chemical Engineering of Lorena University-Brazil), α-alumina (CT 2000 SG, Alcoa) with a mean particle sizes of 22 μm and 1.0 μm, respectively, and a polymer (solid polysiloxane) were used. Two commercial polysiloxanes (Wacker-Chemie, GmbH, Germany) containing approximately 13.2 wt. (%) and 48 wt. (%) carbon were used as pre-ceramic precursor. Samples containing 60 wt. (%) of polysiloxane and a mixture of metallic niobium (reactive filler) and alumina powder (inert filler) were uniaxially warm pressed at 180 °C under a pressure of 5 MPa and sintered at 1200, 1400 and 1500 °C for 4 hours. The polymer/filler ratio was set at 60 wt. (%) polymer and 40 wt. (%) filler (niobium and alumina). The surface composition of the samples was characterized by X ray diffraction, infrared spectrum (IR) and X ray photoelectron spectroscopy (XPS). Crystalline phases were examined by X ray analysis using monochromate CuK_{α}-radiation. XPS analyses were performed on a commercial system (PHI,type ESCA 5600). The photoelectron was excited by monochromatized ALKα-radiation and the electron energy determined by a hemispherical analyzer with a pass energy of 46.95 eV and collected by a multichannel detector. The ratio of niobium to carbon atoms at the surface (R) was calculated considering the peak area divided by the sensivity factor (F_s) corresponding element through the following equation:

$$R\ (Nb/C) = (A_{Nb}/F_s) / (A_C/F_s) \quad (1)$$

where A_{Nb} and A_C are the peak area of niobium and carbon, respectively.

Microstructure of the pyrolyzed material was analyzed by scanning electron microscopy (Stereoscan MK, Cambridge Instr., Cambridge, GB). The Fourier transform infrared (FTIR) spectra transmission technique with KBr discs was applied, using a Bomem B100 spectrometer operating from 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1}.

3. Results and Discussion

Figures 1, 2 and 3 show the results obtained on the surface by XPS for the material containing 10 wt. (%), 20 wt. (%) and 40 wt. (%) Nb, respectively. We observe that the spectrum of the sample with 10 wt. (%) Nb shows peaks corresponding to aluminum and niobium, as well as those due to the presence of the carbon (C), which is introduced by the polymer. The presence of niobium is directly related to the niobium carbide on the surface. In contrast, the spectra in Figure 2 does not show any characteristic peaks of niobium, whose absence can be assigned by three causes. The first refers to the absence of the niobium carbide phase, the second formation of the oxides and sub-oxides of niobium (NbO, NbO_2, etc.), and the third to the diffusion of niobium towards the interior of the sample. Therefore this study shows a reduction in the niobium carbide peak

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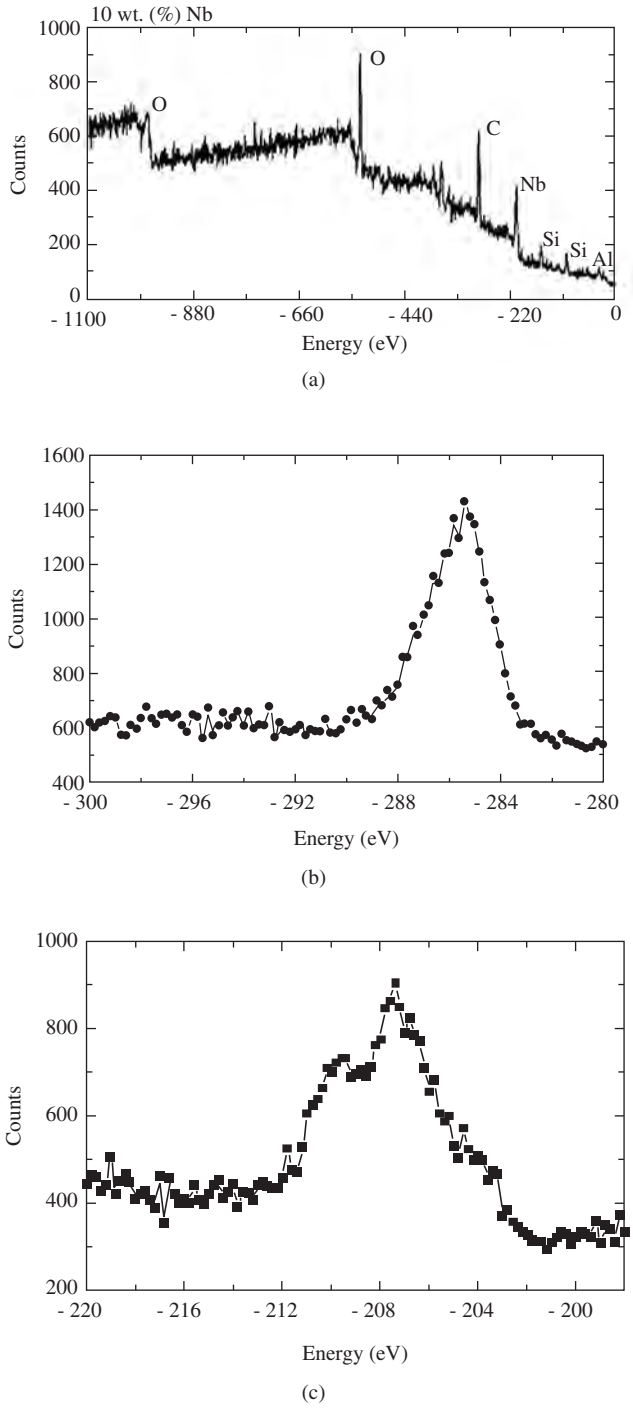

Figure 1. XPS analysis of the sample with 10 wt. (%) Nb, showing the spectrum of: a) general chemical specimens; b) carbon; and c) niobium.

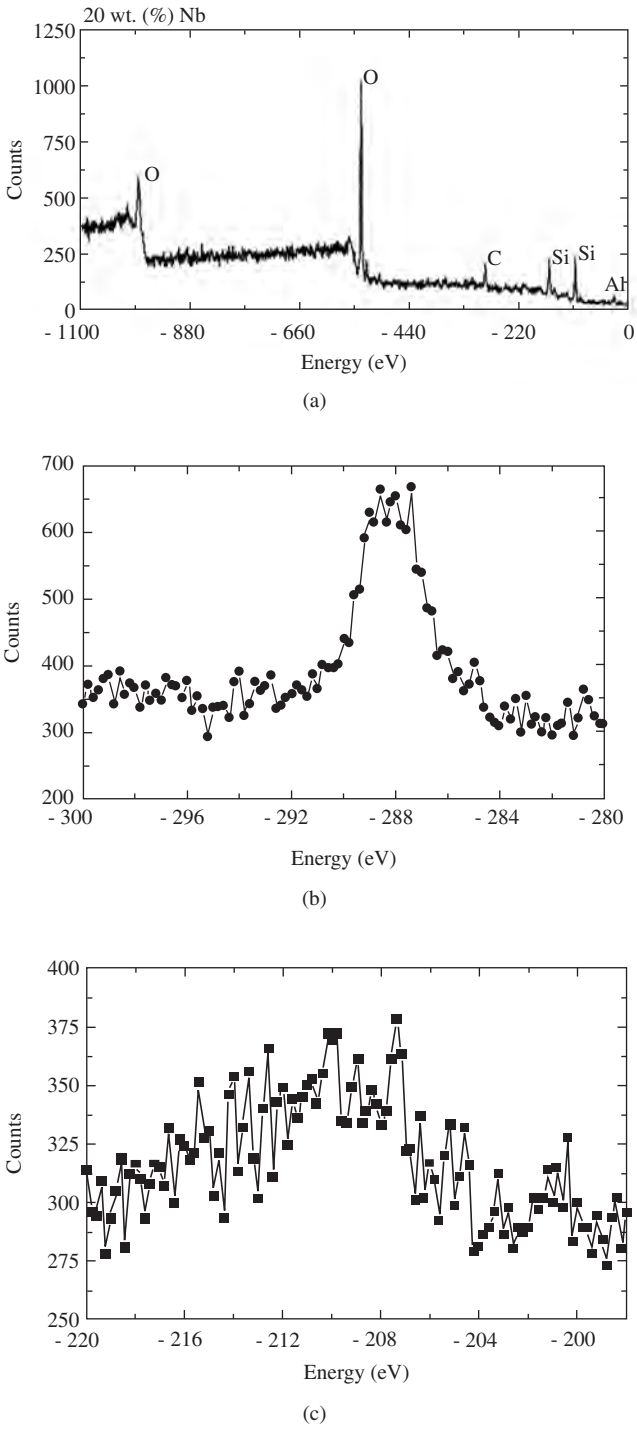

Figure 2. XPS analysis of the sample with 20 wt. (%) Nb, showing the spectrum of: a) general chemical specimens; b) carbon; and c) niobium.

and the appearance of peaks corresponding to the NbO and NbO_2 for niobium concentrations higher than 10 wt. (%). The ratio of niobium to carbon of the material containing 10 wt. (%) Nb was determined by Equation 1 and showed a numerical value of 0.1. This result indicates that the contribution of niobium in the surface of the material is higher than that of carbon. For this reason, it may be concluded that the carbon present on surface is bonded to the niobium and that the remaining niobium reacts with oxygen forming niobium oxides and sub-oxides. The use of a higher Nb content with the same polymer (13.2 wt. (%) C) will produce a great amount of free niobium available to react with the oxygen. XPS analysis with Nb content higher as 10 wt. (%) don't show the presence of the characteristic and well defined Nb peak, what is associated to the formation of oxides and sub-oxides of niobium on the surface.

Figure 4 shows X ray diffraction pattern for the sample with 40 wt. (%) of Nb sintered at 1200, 1400 and 1500 °C, prepared from

polymer which has a larger carbon concentration (48 wt. (%)) with the purpose to investigate the formation of oxide and sub-oxides of niobium. This analysis shows the presence of the niobium carbide phase, as well as two metallic phases Nb_3Si and Nb_5Si_3 and the complete absence of the oxide phases of niobium. This different behaviour can be explained by the presence of the higher carbon content in the polymer, sufficient to develop the reaction Nb + C ⇒ NbC, thus avoiding free niobium and consequently the niobium oxidation.

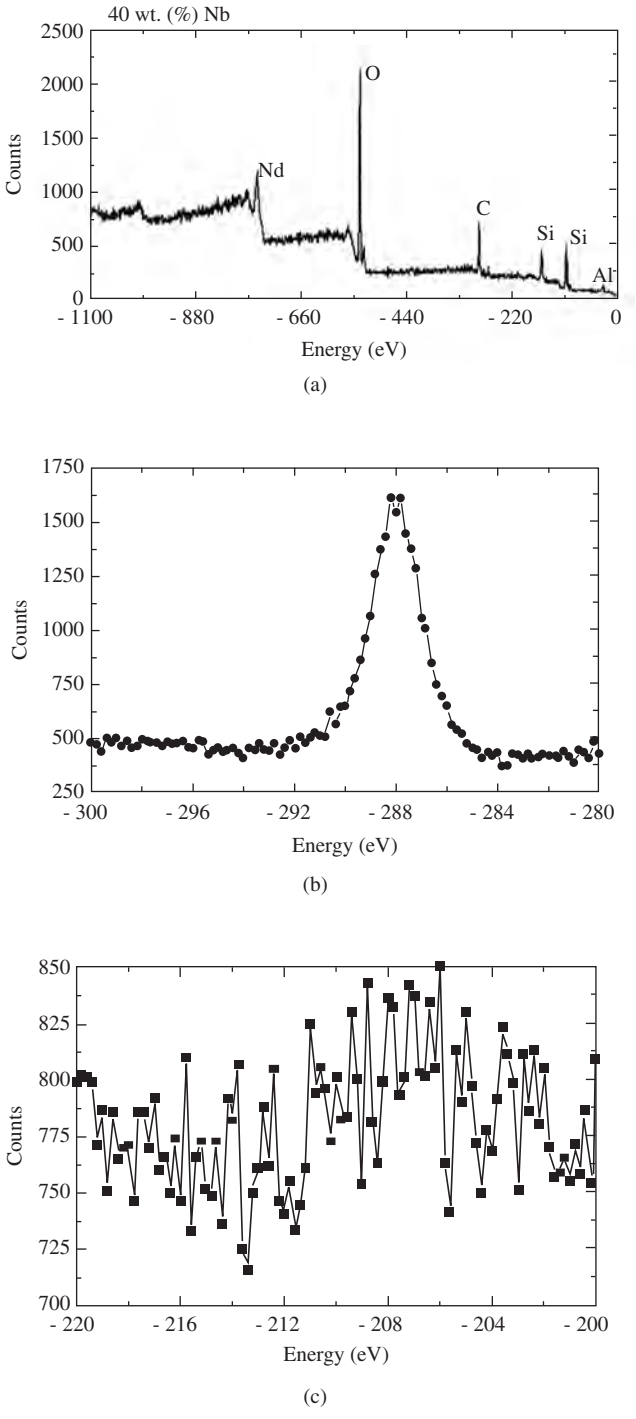

Figure 3. XPS analysis of the sample with 40 wt. (%) Nb, showing the spectrum of: a) general chemical specimens; b) carbon; and c) niobium.

The behaviour observed in this work is in agreement with the results reported in the literature[11]. This work shows that the use of a polymer with low carbon content leads to the formation of niobium oxides.

Figure 5 shows the FTIR spectra of the composite material prepared with the polymer with higher carbon content and 40 wt. (%) NbC pyrolyzed at 1400 °C. The material showed a band at approximately 1090 cm^{-1} associated with the Si-O-Si sites of the silicon oxycarbide amorphous matrix. The presence of alumina (15 wt. (%) Nb + 25 wt. (%) Alumina) caused this band to decrease considerably. The composite materials also exhibited two bands, one at ≅ 800 cm^{-1}, corresponding to Si-C sites in the SiC_xO_y matrix, and a small band at 460 cm^{-1}, which is characteristic of niobium carbide. For the sample containing Al_2O_3, a band characteristic of Al-O-Al could also be observed at ≈ 600 cm^{-1}.

No Nb-O bands were found, what is an evidence of the no formation of niobium oxides in an ambient with high concentration of carbon.

Figure 6 shows a typical SEM image of the microstructure of the composite material with 10 wt. (%) Nb pyrolyzed at 1200 °C, revealing bright filler particles embedded in the dark matrix of the SiOC-derived polymer. As can be seen, NbC formed on the surface of large particles. A similar morphology is observed in the literature[9].

By comparing the hardness of the material analysed in the present work with most traditional cutting tool materials (Table 1), we notice that the material Al_2O_3-NbC, which is prepared with a larger carbon content (48 wt. (%)), presents a hardness superior than that of the

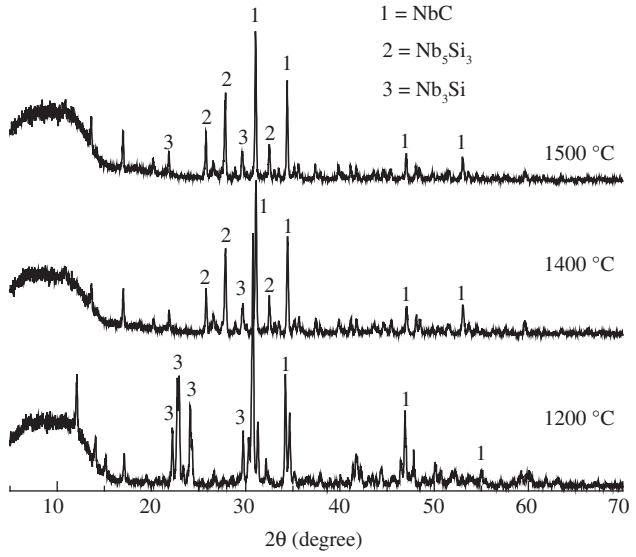

Figure 4. X ray diffraction pattern of the composite material with 40 wt. (%) Nb.

Table 1. Comparison of the hardness values among the material obtained in this work with the traditional cutting tool material.

Material	Hardness (GPa)
Al_2O_3-WC[12]	17-18
WC-Co[4]	17-20
Al_2O_3 - 30 wt. (%) NbC[A]	17
Al_2O_3 - 30 wt. (%) NbC[B]	19
Al_2O_3-TiC[13,14]	19-20

[A]This work, polymer (13. 2 wt. (%) C);
[B]This work, polymer (48 wt. (%) C).

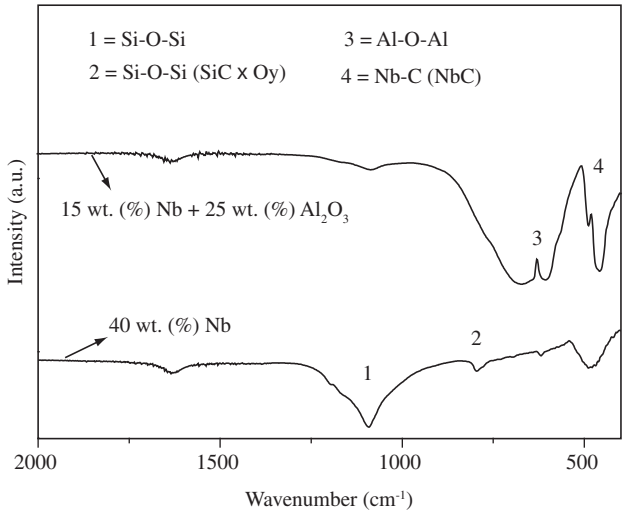

Figure 5. FTIR spectra of the composite material with 40 wt. (%) Nb and 15 wt. (%) Nb + 25 wt. (%) alumina sintered at 1400 °C.

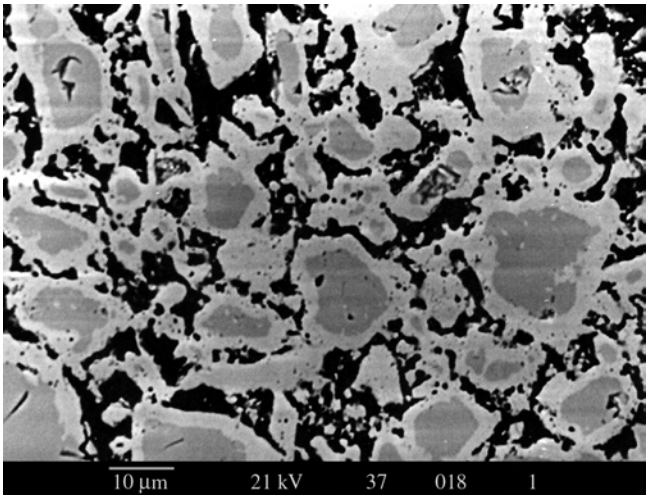

Figure 6. Micrograph of the composite with 40 wt. (%) Nb pyrolyzed at 1400 °C.

pure alumina, as well as that of material (Al_2O_3-NbC) with smaller carbon content (13.2 wt. (%) C), what is in agreement to the results observed for the XPS analysis. The hardness values are associated with the major NbC content present on the surface of the material. Otherwise the material with 48 wt. (%) of carbon has hardness similar and comparable to that of alumina-TiC and WC-Co materials.

Further studies are still under way to investigate the dependence of the carbon and niobium content on the tribological properties of alumina-NbC obtained by active fillers pyrolysis process.

4. Conclusions

The results from the surface characterization of alumina-NbC obtained by polymer precursor revealed that:

- It is possible to obtain niobium carbides on the surface of the composite material by using the filler controlled pyrolysis process;
- The presence of niobium carbide and niobium oxides on the surface is associated with the carbon content of the polymer;
- The use of a polymer with higher carbon content produces a composite material with hardness values comparable to the other cutting tool materials; and
- XPS analysis show to be a good method to investigate the presence of niobium carbide on the surface.

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