

Alumina-NbC composites fabricated by spark plasma sintering

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ABSTRACT

The incorporation of niobium carbide in alumina-based composites has been shown to improve the properties of composite material. The main disadvantage to get a dense composite material is the necessary high sintering temperature. The spark plasma sintering (SPS) process uses a high heating and cooling speed and lower sintering temperature, making this sintering process a suitable method to produce an alumina-NbC composite material at lower temperatures. The sintering behavior of alumina-NbC composites fabricated by spark plasma sintering (SPS) was investigated at 1350, 1400, and 1450 °C. X-ray diffraction patterns of sintered bodies revealed only the presence of alumina and NbC crystalline phases. No oxidation products or new crystalline phases were presented after the sintering process. SPS process has produced dense alumina-NbC samples comparable to other alumina-hard particle systems. Microstructural observation revealed inhibition of alumina grain growth in regions near NbC particles. Fracture surfaces showed a mixture of intergranular and transgranular fracture mode.

Keywords: Alumina. Niobium carbide. Spark plasma sintering.

RESUMO

A incorporação de carbeto de nióbio em compósitos à base de alumina mostrou melhoras nas propriedades do material compósito. A principal desvantagem para obter um material compósito denso é a necessidade de altas temperaturas de sinterização. O processo de sinterização por Spark plasma (SPS) utiliza uma alta velocidade de aquecimento, resfriamento e temperaturas de sinterização mais baixas, tornando esse processo de sinterização um método adequado para produzir alumina com NbC em temperaturas mais inferiores. O comportamento de sinterização de compósitos de alumina-NbC fabricados por sinterização por Spark plasma (SPS) foi investigado em 1350, 1400 e 1450 °C. O padrão de difração de raios X dos corpos sinterizados revelou apenas a presença de fases cristalina de alumina e NbC. Nenhuma oxidação ou nova fase cristalina estavam presentes após o processo de sinterização. O processo SPS produziu amostras densas de alumina-NbC, assim como em outros sistemas de partículas duras de alumina. A observação da microestrutura revelou uma inibição do crescimento de grãos de alumina em regiões próximas às partículas de NbC. As superfícies de fratura mostram uma mistura do modo de fratura intergranular e transgranular.

Palavras-chave: Alumina. Carbeto de nióbio. Sinterização. Spark plasma.

1 Introduction

Alumina is the most widely used ceramic material in structural applications (GITZEN, 1970; DORRE; HUBNER, 1984). Several synthesis routes such as hot-pressing, sintering pressureless, microwave, and reactive milling have been investigated to produce alumina-based composite materials with better properties (PALLONE *et al.*, 2003; GUSTAFSSON *et al.*, 2008; CASTRO; BENTHEM, 2013; BENAVENTE *et al.*, 2014).

Niobium carbide (NbC) particles exhibit a high melting point, high hardness, low chemical reactivity and have been widely used as reinforcements in ceramic materials. Several authors report the good potential of niobium carbide as a grain inhibitor and reinforcing element in alumina and zirconia matrix. The results published in the literature show that dense alumina and zirconia composite materials with good mechanical properties can be obtained by hot-pressed (ACCHAR *et al.*, 2001; ACCHAR; SEGADAES, 2009; ACCHAR; SILVA; CAIRO, 2010; TROMBINI *et al.*, 2012; ACCHAR *et al.*, 2019). The incorporation of NbC improves the hardness, flexural strength, and wear behavior of monolithic ceramic material. The main disadvantage of these materials is the elevated sintering temperatures to achieve dense samples.

Spark plasma sintering (SPS) is a relatively new method that takes only a few minutes to complete a sintering process compared to conventional sintering (MUNIR; ANSELMINI-TAMBURINI; OHYANAGI, 2006; LIU *et al.*, 2013). The fast heating rates used in the process allow rapid densification with minimal grain growth. Simultaneous application of rapid heating and pressure application leads to high densification at lower sintering temperatures compared to conventional sintering methods, especially with hot-pressing sintering. The main disadvantages of SPS are the limited sample size, shape complexity, and the cost of equipment. Studies described in the literature demonstrated the spark plasma sintering might produce dense samples of composite materials at lower temperatures with good mechanical properties and homogeneous microstructure (NAYAK *et al.*, 2013; HUSSAINOVA *et al.*, 2014; CHEN *et al.*, 2016; XIA *et al.*, 2016; SAEIDABADI; SALAHI; EBADZADEH, 2019; ZHAO *et al.*, 2019).

Brazil holds the main niobium reserve, making the use of niobium carbide in alumina materials

very strategic (U. S. GEOLOGICAL SURVEY, 2018). Recent studies have demonstrated the possibility to get a dense Alumina-NbC material by spark plasma sintering (ALECRIM *et al.*, 2017; SALEM *et al.*, 2018). The results obtained are satisfactory, which shows the good potential of this method to get dense alumina-NbC bodies. However, more experiments have to be done to confirm the initial results.

The purpose of this study is to investigate the properties of an alumina-NbC composite material manufactured by spark plasma sintering.

2 Theoretical Reference

The great interest in nanostructured materials is due to gains that this characteristic can cause in the obtained products. Nanostructured materials are those materials that contain at least one of minimal measurements, less than 100 nm (QUINA, 2004). This results in changes in diffusion properties, great microstructural stability to the growth of grain, a decrease in the size of gaps, and superplasticity when compared with macroscopic surfaces (BROOK; MACKENZIE, 1993).

2.1 Alumina- Niobium carbide composite

The incorporation of hard refractory particles in alumina-based composites can inhibit the growth of matrix grains, contributing significantly to improving the mechanical properties of the composite (ACCHAR *et al.*, 2019).

Transition metal carbides are one of the most promising ceramic materials in the preparation of ceramic composites since established chemical bonds confer specific properties to these materials. Niobium carbide shows properties compared to other refractory carbides (WC, TiC, SiC) used to obtain hard metals. It has a high melting point, high hardness and toughness, and low chemical reactivity (ACCHAR; SEGADAES, 2009).

The advantage of using NbC as reinforcement for Al₂O₃ is that both materials have a similar coefficient of thermal expansion and reduce the residual stresses produced during the heating and cooling processes, which can lead to the formation of cracks in the brittle materials, causing a decrease in resistance values. Thus, Al₂O₃ and NbC are thermomechanically compatible (ALECRIM *et al.*, 2017).

2.2 Spark Plasma Sintering (SPS)

Spark plasma sintering (SPS), also known as current sintering (CS), field-assisted sintering technique (FAST), pulsed electric current sintering (PECS), electric current activated/assisted sintering (ECAS), and current activated pressure-assisted densification (CAPAD), combines electric current and uniaxial pressure to consolidate powders. The benefits of SPS, compared to conventional sintering, are high heating rates and short sintering times while maintaining a nanoscaled microstructure. These benefits are associated with the Joule heating and electric current/field effects on mass transport. In a typical experiment, the powder is loaded into graphite pressing tools.

For clarity, we distinguish between the cylindrical pistons, transmitting the mechanical force and supplying electric current to the sample (here called punch), and the surrounding hollow cylinder shaping the sample (here called matrix). This punch-matrix-sample assembly is placed inside the SPS apparatus, and a low voltage together with a mechanical load is applied to the assembly. The electrical resistance of the pressing tool and sample (powder) controls the path of the electric current. If the powder is electrically conductive, current flows partially through the sample and pressing tools. If the powder is electrically insulating, all current flows solely through the tools. In both cases, heat is produced in graphite tools by the Joule heating and transmitted to powder by heat conduction. Although in a conducting powder, the current passes through the sample, the dissipated energy (Joule heating) within the sample is low, and most of the heat is produced in the graphite tools. However, the electrical (and thermal) conductivity of the sample increases during SPS due to densification, which, in turn, changes the spatial and temporal electric and thermal field distribution (GORZYNSKI; ANSELMITAMBURINI; WINTERER, 2020).

3 Experimental Procedure

The starting powders consisted of alumina with a high purity level of 99.9% (Taimei Chemicals, Tokyo, Japan) and niobium carbide (Herman Starck, Germany) with an average particle size of 150 nm and 20 μm , respectively. Al_2O_3 on its own and with 30 wt.% NbC

was dry-mixed during four hours in a planetary ball mill containing alumina grinding media. The niobium carbide content used in this work was chosen due to the best mechanical results demonstrated in the literature (ACCHAR *et al.*, 2001, 2009, 2019).

Composites were prepared by spark plasma sintering (SPS Dr. Sinter 211 Lx, Japan) at 1350, 1400, and 1450 $^{\circ}\text{C}$ at a constant load of 40 MPa, and a heating rate of 65 $^{\circ}\text{C}/\text{min}$ for five minutes. After sintering, composites were allowed to cool naturally to room temperature. The apparent density of sintered bodies was determined using the Archimedes water displacement method, as specified by the European Standard EN 99.

Dilatometric analysis was carried out in a Netzsch 402 PC dilatometer in an argon atmosphere with a heating rate of 20 $^{\circ}\text{C}/\text{min}$. That is the maximum heating rate of equipment and was used to simulate the SPS condition.

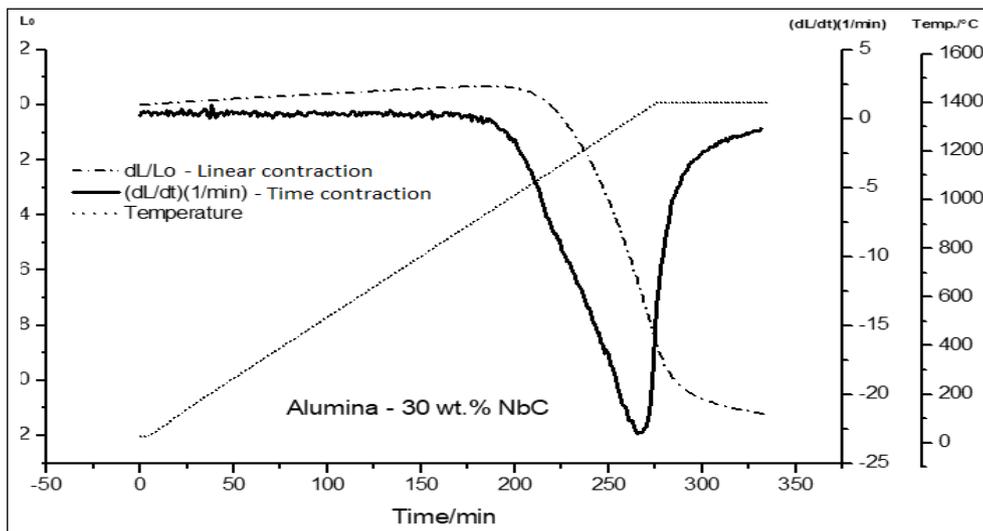
X-ray diffraction analyses with a scanning rate of 2 $^{\circ}$ min^{-1} (Shimadzu XRD-600) and scanning electronic microscopy (SEM) (Zeiss, Auriga) were carried out to identify crystalline phases and microstructural aspects of specimens, respectively.

The Fourier transformation infrared spectroscopy (FTIR) was applied using the Fourier-transform infrared spectroscopy (FTIR, Perkin-Elmer) with a resolution of four cm^{-1} .

4 Results and Discussion

Figure 1 shows the dilatometric result of alumina doped with niobium carbide. Composite material shows a uniform expansion up to ~ 1000 $^{\circ}\text{C}$, followed by a strong contraction. Two distinct regions described the dilatometer behavior of the material. The first one refers to the temperature range before starts, and the second region can be correlated to contraction of material that has a maximum contraction rate at approximately 1200 $^{\circ}\text{C}$. This behavior is similar to other studies published in the literature for alumina-NbC composite materials (ACCHAR *et al.*, 2009, 2019). dL/dL_0 means linear contraction or retraction, in percentage (%). (dL/dt) (1/min) means the derivative of dL/dL_0 . In this curve, we can see more details about thermal events of expansion and contraction.

Figure 1 – Dilatometric curves for alumina and alumina- 30 wt.%NbC materials

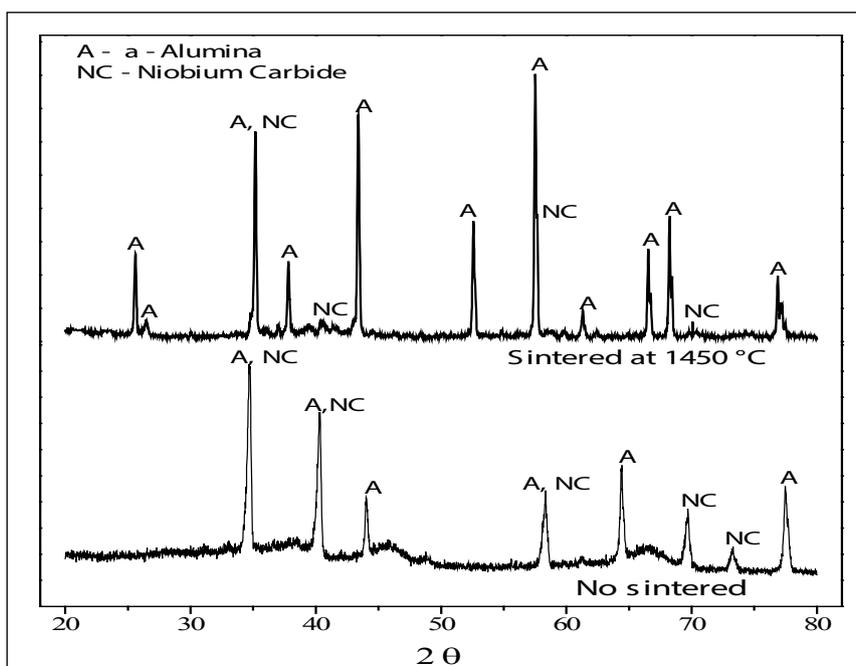


Source: Research data

Figure 2 shows a typical X-ray diffraction pattern of alumina-NbC material before and after the sintering process. Both materials show the same crystalline phases. The sintering process has caused no modification. X-ray diffraction analysis shows the presence of Al_2O_3 and niobium carbide. No presence of niobium oxides NbO, NbOx, or formation of a new crystalline phase were found. Analogous results have

been reported for alumina-niobium carbide composites (ACCHAR *et al.*, 2001, 2009). On the other hand, alumina-WC sintered by the SPS process has shown the formation of a new crystalline phase (W_2C) during the SPS process (HUANG *et al.*, 2010; CHEN *et al.*, 2015, 2016). The presence of this carbon-deficient phase is related to carbon interdiffusion from the graphite punches.

Figure 2 – X-ray diffraction pattern of alumina-doped with niobium carbide

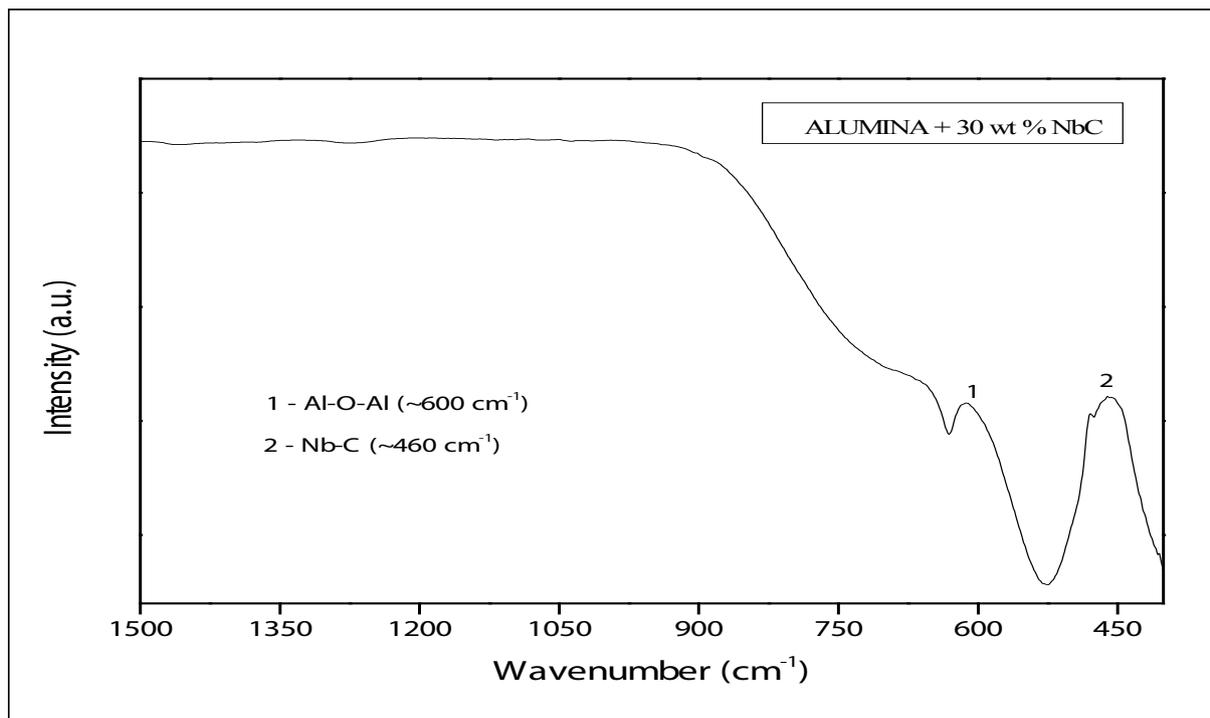


Source: Research data

The FTIR absorption spectra of Figure 3 in the region between 400 and 1500 cm^{-1} showed stretching vibration at approximately 460 cm^{-1} that is characteristic of a low-frequency IR band of large particle size of Nb-C group (SCHUBERT; LEWIS, 2012). The presence of Nb-O group was not found

(980-990 cm^{-1}), indicating any formation of Nb-oxidation products as shown in x-ray diffraction analysis (Figure 2). The absence of oxidation products in FTIR absorption spectra for alumina-NbC composite materials was also reported in other works (ACCHAR; WOLFF, 2005; SALEM *et al.*, 2018).

Figure 3 – FTIR absorption spectra of the alumina with 30 wt%. NbC sintered at 1450 °C by SPS process



Source: Research data

Table 1 compares density values obtained in this work with other studies of alumina doped WC and SiC materials produced by the SPS method. Alumina-NbC fabricated by hot-pressed was also included for comparison purposes. It is clear to see that density

values increase for higher sintering temperatures for all composites materials, as expected. At 1550-1600 °C, alumina-SiC and WC composite materials reach almost full density.

Table 1 – Comparison of relative density values found in the literature for alumina doped with carbide particles and sintered by the SPS process

Material	Relative density [%]	Sintering parameters
Alumina + 30 wt.% NbC [This work]	85 - 93	SPS 1300- 1450 °C (40MPa)
Alumina +5 vol%NbC (ALECRIM <i>et al.</i> ,2017)	99	SPS 1440 – 1600 °C (80 MPa)
ZrO ₂ + 5 vol% (Al ₂ O ₃ -NbC) (SALEM <i>et al.</i> ,2018)	98,5 - 98,7	SPS 1300 – 1400°C (80MPa)
Alumina + 17 vol% SiC (BORRELL <i>et al.</i> , 2012)	99	SPS 1400 – 1550°C (80 MPa)
Alumina + 30 wt.% NbC (ACCHAR <i>et al.</i> , 2019)	94	HP 1500 °C (40 MPa)
Alumina + 17vol%ZrO ₂ + 28vol% NbC (SCHMITT-RADLOFF; KERN; GADOW, 2018)	98 - 99,5	SPS 1400- 1600 °C (40 MPa)
Alumina + TiC (KUMAR <i>et al.</i> , 2016)	93 - 99	SPS 1100 – 1500 °C (60MPa)
Alumina + WC (CHEN <i>et al.</i> , 2016)	87 - 90	SPS 1350 °C (50 MPa)
Alumina + WC (CHEN <i>et al.</i> , 2015)	93	SPS 1400 °C (50 MPa)
Alumina + WC (HUANG <i>et al.</i> , 2010)	Full density	SPS 1250 – 1650 °C (60 MPa)

Source: Research data

The density values obtained in this work are practically similar to alumina with WC or SiC composite materials obtained by the SPS, showing that it is possible to get a dense alumina-NbC composite material by using the SPS process compared under the same sintering conditions. The results described in Table 1 show the final relative density of composite material depends strongly on heating rate, the particle size of alumina as well as applied load. The benefit of high heating rates applicable in the SPS compared to the conventional hot-pressing process was before demonstrated in some papers (DEMUYNCK *et al.*, 2012; SCHMITT-RADLOFF; KERN; GADOW, 2018;). These studies also showed the applied load and starting

particle size influence the densification of the composite material.

The better densification process observed in the SPS process can be associated with the densification mechanism. Results obtained by other authors have concluded densification mechanism that occurs during the SPS combines surface diffusion and grain boundary diffusion. The faster neck formation during the increase of surface diffusion greatly improves the densification mechanism in composite materials (HUANG *et al.*, 2010; CHEN *et al.*, 2015). Results indicated grain boundary is the main diffusion mechanism at lower heating rates. The presence of an electric field and a resulting increase of electrical conductivity of samples at high temperatures and heating rates may originate from the presence of a surface diffusion mechanism that contributes to the densification process. The effect of pressure on sintering was also investigated (SCHMITT-RADLOFF; KERN; GADOW, 2018). The increase of pressure may produce a higher packing density of particles and breakdown of agglomerates as well as an increase of driving force of sintering, increasing densification of composite material.

The density values obtained for alumina-NbC composite materials fabricated by hot-pressed and the SPS process are comparable, despite different sintering temperatures used in both procedures. The slight difference in density values can be attributed to the higher sintering temperature used in the hot-pressed technique.

Studies are still under way to verify the effect of niobium carbide content and heating rate on density values and microstructure and its dependence on mechanical properties.

The SEM micrograph was used to observe morphological features of the microstructure of composite material (Figure 4). The material showed a homogeneous microstructure, and there is no presence of pronounced grain growth of the alumina grains (Figures 4a and 4b). The composite material consisted of a matrix of fine alumina grains with large niobium carbide particles. Figure 4c shows the presence of a heterogeneous microstructure throughout the sample. The alumina grains close to NbC particles (region 1) seem to have a grain growth restriction compared to alumina grains outside the influence of NbC grains (region 2). Similar behavior of grain growth restriction due to the presence of NbC particles has also been observed in other studies (ACCHAR *et al.*, 2009, 2019). Figure 4d shows the fracture aspects of alumina grains in composite material.

Figure 4 – The SEM micrograph of alumina-NbC sintered at 1450 °C

Figure 4a

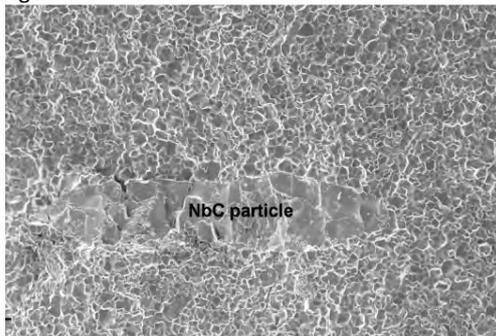


Figure 4b

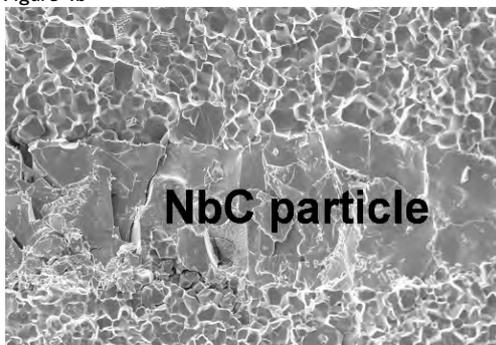


Figure 4c

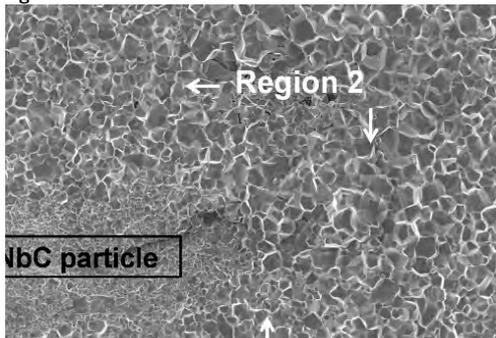
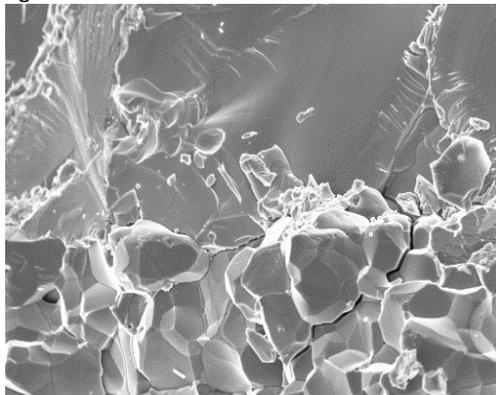


Figure 4d



Source: Elaborated by the author

The fracture mode consisted mainly of an intergranular fracture accompanied by a partial transgranular fracture, showing isolated pores.

5 Conclusions

It has been shown in this study that the SPS is a very efficient method to produce dense alumina-NbC samples. The crystalline phases presented after the sintering process are alumina and NbC. No oxidation products are identified. The composite material showed a slight restriction on the growth of alumina grains in regions proximate to NbC particles. The final relative density obtained is comparable to other alumina-hard composite materials produced by the SPS.

We believe the results reported in this work show the great potential use of the SPS process to get a dense alumina-NbC composite material at lower sintering temperatures.

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