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Utilization of NbC nanoparticles obtained by reactive milling in production of alumina niobium carbide nanocomposites

Vania Trombini[1,a], Ana Helena de Almeida Bressiani[1,b], Eliria. M. J. Agnolon Pallone[2, c], Roberto Tomasi[3,d],

[1] Instituto de Pesquisas Energéticas e Nucleares, São Paulo, SP, 05508-000, Brazil
[2] USP, Faculdade de Zootecnia e Engenharia de Alimentos, Pirassununga,SP, 13635-900, Brazil
[3] Universidade Federal de São Carlos - DEMa São Carlos, SP, 13565-905, Brazil
[a]vthernandes@ipen.br, [b]abressia@ipen.br, [c]eliria@usp.br, [d]tomasi@power.ufscar.br

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Abstract: The increased interest in nanostructured materials is due to improvements in the mechanical properties presented for these materials. Significant increases in properties such as hardness, wear resistance and in some cases, strength and toughness of nanostructured ceramics have been reported, compared to conventional ceramics. High-energy milling can lead to self-sustaining reactions in a variety of systems. In this study, reactive high-energy milling was used to synthesis niobium carbide (NbC) nanoparticles. The reaction products were de-agglomerated and mixed with commercial ultra-fine alumina powder to produce alumina matrix nanocomposites with 5vol% of nanometric NbC. Alumina/NbC nanocomposite produced using powder obtained by reactive present good microstructural characteristic, high densities, good hardness and higher toughness. What makes this material an interesting alternative for production of ceramic cutting tools.

Introduction

Several techniques to improve ceramics toughness have been proposed by many researchers and the addition of second-phase particles in a ceramic matrix is widely studied. Nanocomposites constructed by dispersion of low percent of second-phase nano-sized particles within the matrix grains and on the grain boundaries present significantly improved strength with moderate enhancement in fracture toughness [1-5]. Due the improvement in mechanical properties this class of materials can be an interesting alternative for the production of cutting tools in order to increase cutting speed and productivity [6].

One possible route for the production of nanometric powder is Aluminothermite reactions that can be activated in a mixture of reactive powders by high-energy reactive milling [7-14]. Alumina/NbC reaction is highly exothermic, and takes place abruptly after a certain milling time (the ignition time, t_{ig}) and, once started; it proceeds in a self-sustained way, denominated self-propagating high-temperature synthesis - SHS process. For abrupt reactive milling, also called SHS type reactive milling (SHS-RM), ignition occurs when reaction rate and heat release rate are high enough for the reaction self-sustaining [14]. And several factors are important in order to achieve reaction during milling. Like type of milling equipment, size and material of the vial, milling media, the mill charge ratio, i.e. the milling balls to materials mass ratio and the milling atmosphere. Either the reactions may take place gradually as milling proceeds or abruptly, i.e., the integral reaction occurs promptly after an activation milling time. It was experimentally proved that, locally and during the short time of reaction, the products might reach high temperature causing fusion of reaction products leading to the formation of strong agglomerates or aggregates of reaction products. [10-14]. In this work, mixtures of Al_2O_3-NbC powders were synthesized by SHS-RM. The ceramic processing of the synthesized powders, included deagglomeration, inclusions dispersion and pressureless sintering, were evaluated regarding the final nanocomposite characteristics.

Experimental Procedure

To synthesis alumina-niobium carbide powders, a mixture of the reactants Al, Nb_2O_5 and C (carbon black), 0.8 mols of alumina was milled in high energy ball mill. The reaction, with alumina as diluents, is given by:

$$Nb_2O_5 + 3.3\ Al + 2C + 0.8Al_2O_3 \rightarrow 2\ NbC + 2.5\ Al_2O_3$$

Reactive milling was performed in a SPEX 8000 shaker/mill apparatus with hardened steel vial and balls (10mm in diameter) and charge:ratio of 4:1. The occurrence of the SHS-RM reactions was monitored by an external infrared detector positioned in the surface of the vial. In order to deaggregate and reduce particle size of the reaction products, was performed an additional SPEX milling during 1 hour after reaction. Following the high-energy milling, the powder obtained was dispersed in a planetary mill, for 1 hour in alcohol suspension with 0.2% of PABA (4-aminobenzoic acid) added as deflocculant. After drying at room temperature under airflow, the powders were characterized by determination of particle size distribution and XRD crystallite size (Scherrer method) [15-16].

For nanocomposite production the powder obtained by reactive milling was mixtured to high pure alumina (Sumitomo, AKP-53) in order to obtain alumina nanocomposite with 5vol% of inclusions. These powders were mixed in alcohol suspension with 0.2 wt% of PABA and 0.5 wt% of oleic acid in a conventional ball mill. After drying the mixtures at room temperature under flowing air, cylindrical specimens were formed by uniaxial pressing at 60 MPa and isostatic pressing at 200 MPa. The sintering was performed in a furnace with tungsten heating element at 1550°C for 1h with heating rate of 10°C/min, under high vacuum. Densities of sintered samples were measured by Archimedes method. SEM was used to observe the microstructure of the sintered samples. A Buehler apparatus was used to carry out the microhardness and toughness measurements (ASTM C 1327-99 [17]).

Results and Discussion

Fig. 1 shows XRD pattern for powder obtained by reactive milling and can be observed only the presence of expected reaction products. XRD patterns shows that reaction activated by reactive milling is a self-sustained reaction and can be considered complete.

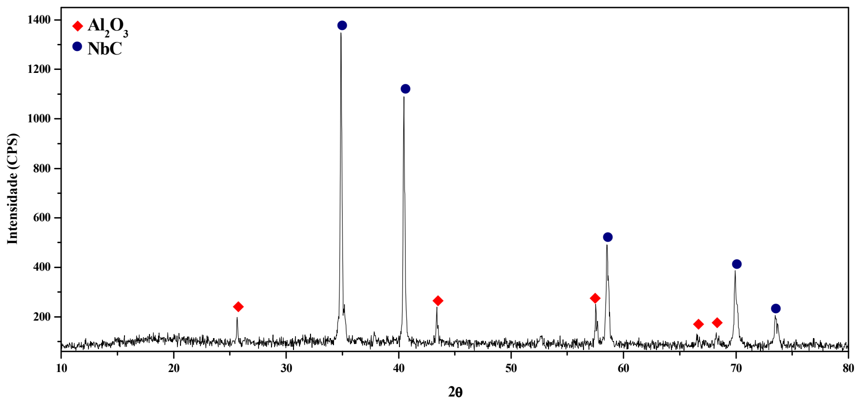

Figure 1. XRD pattern for alumina/NbC powder obtained by reactive milling.

Characterization results of alumina/NbC powder after deagglomeration are presented below. Table 1 present crystallite size measured by XRD, specific surface area and particles size calculated using SSA of this powder. Difference between crystallite size and particles size can be attributed to the presence of dense clusters of crystallite formed by alumina and NbC, which are not measured by BET test.

Table 1. Crystallite size measured by XRD, specific surface area and particles size calculated using SSA of alumina/NbC powder obtained by SHS-RM.

Crystallite Size [nm]	Specific Surface Area [m^2/g]	Mean Particles size [nm]
26.5	14.65	75.7

Table 2 present apparent density of alumina samples containing 0, 5vol % of NbC inclusions pressureless sintered, it is possible observe that sub-micrometric alumina present density of 98.4%DT when sintered at 1400°C and for the nanocomposite, due the presence of NbC particle in alumina matrix, was necessary an increase in sintering temperature of 150°C for obtaining density near to pure alumina. In Table 2 can be observed that higher sintering temperature did not promote significant improvement in apparent density of NbC nanocomposite. For the other side observing Fig. 2 (a) and (b) that present micrographs for the nanocomposite sintered at 1550 and 1600°C, is possible note that the increase in sintering temperature cause undesirable grains grow. Comparing Fig. 2 (a) and (b) and Fig. 3 can be observed that for sample sintered at 1550°C the presence of NbC particle promote more homogeneous microstructures to be obtained compared with alumina without inclusions Fig. 3. And for sample sintered at 1600°C the effect of NbC particles in grain grows control was not so efficient

Table 2. Sintering temperature, holding time and apparent density (given in percentage of theorical density (%TD)), of pressureless sintered alumina samples containing 0 and 5 vol % of NbC.

Sample	Alumina	Alumina/5vol%NbC	
T[°C]/Time	1400/1h	1550/30min	1600/30min
[%TD]	98.4	97.2	97.6

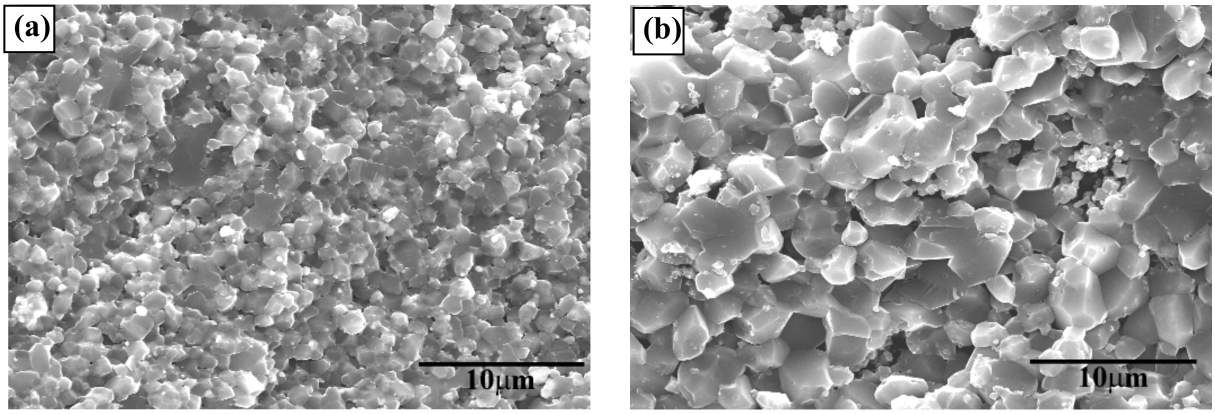

Figure 2. Micrographs of alumina samples containing 5%vol of niobium carbide inclusions pressureless sintered at (a) 1550 °C e (b) 1600°C.

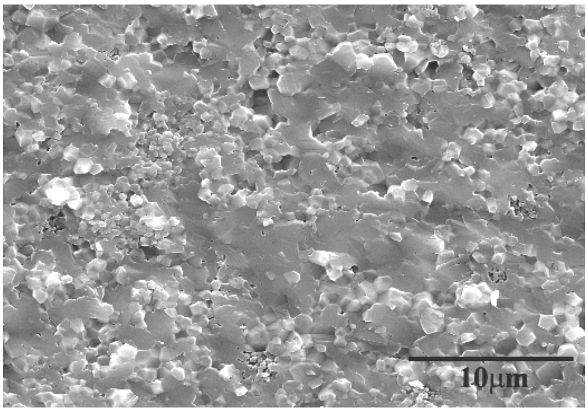

Figure 3. Micrographs of alumina samples pressureless sintered 1400°C.

In Table 3 are presented microhardness and toughness results for alumina samples containing 0 and 5% vol of niobium carbide inclusions. Compared with pure alumina, NbC nanocomposite present smaller micro hardness, these reduction possibly occurred due the smaller density presented by nanocomposite. By the other side NbC nanocomposite present an improvement of about 30% in toughness. The effect of NbC particles can be seen in detail in Fig. 4, in the interior of the alumina grain, these "slots" can consume energy of a propagate crack, and can be responsible for the increase in the nanocomposite toughness.

Table 3. Microhardness, Toughness and apparent density of alumina samples containing 0 and 5vol% of niobium carbide inclusions pressureless sintered at 1550 °C and pure alumina pressureless sintered at 1400 °C.

Sample	Microhardness [Gpa]	Toughness[Mpa.m$^{1/2}$]	Density [%DT]
Alumina/ 5vol % NbC	17.7 ± 1.5	4.6 ± 0.2	97.2
Alumina	20.0 ± 0.5	3.2± 0.2	98.4

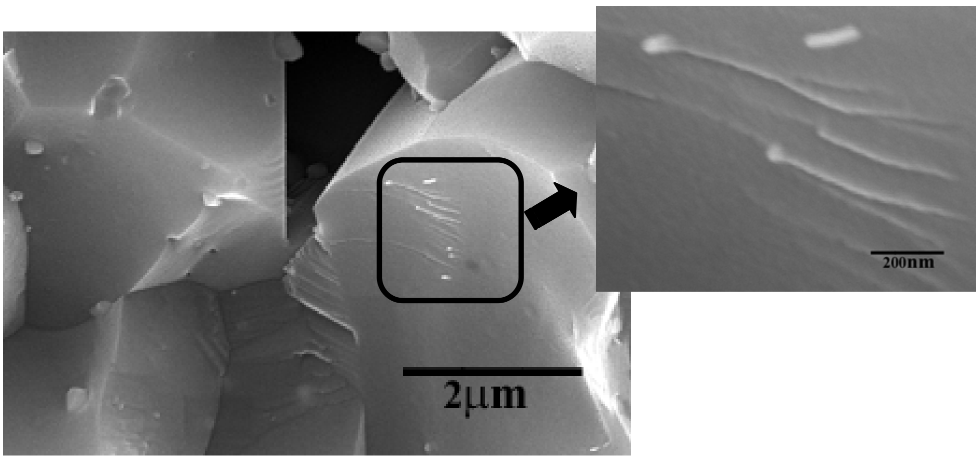

Figure 4. Micrographs of alumina samples containing 5vol % of niobium carbide inclusions pressureless sintered at 1550°C.

Results presented for this material were enough to production of ceramic cutting tools, Fig. 5 present photography of ceramic cutting tools of alumina containing 5% vol of niobium carbide inclusions pressureless sintered at 1550 ^{o}C.

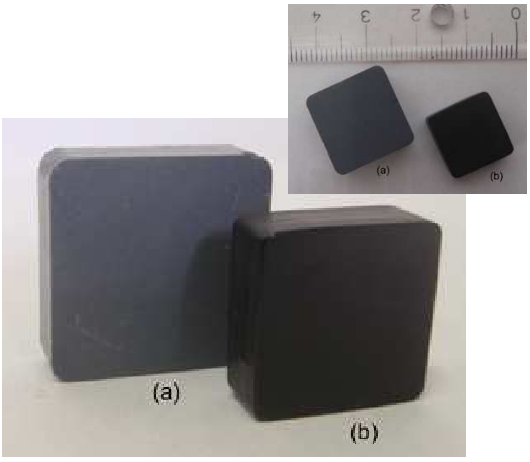

Figure 5. Photography of ceramic cutting tools (SNG M 120412TN-020D) of alumina containing 5% vol of niobium carbide inclusions (a) before sintering and (b) pressureless sintered at 1550 ^{o}C.

Conclusions

Reaction Nb_2O_5+ 3.3 Al + 2C + 0.8Al_2O_3 $\rightarrow$2 NbC+ 2.5 Al_2O_3 is of the self-sustained type (SHS) and allied to additional planetary ball milling for complete dispersion of reactive products is an excellent method to produce powder mixtures with nanometric crystallite size.

Sintering results indicated that the addition of even a small amount of nanometric NbC inclusions to an alumina matrix decreased the sinterability of alumina being necessary an increase in sintering temperature.

The presence of NbC particles promote better homogeneity in alumina nanocomposite microstructure compared to pure alumina.

High densities and high values of hardness and toughness presented by alumina/NbC nanocomposite make this material an interesting alternative for production of ceramic cutting tools.

Acknowledgements

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