Effect of Milling Medium on Alumina Additivated with Niobia

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Abstract. Niobia has been successfully used as sintering additive to alumina in order to lower its sintering temperature. This effect can also be obtained by reducing the ceramic particle size. This work investigated the effect of two milling media on the microstructure and properties of sintered alumina with 4wt% niobia. The as-received powders were submitted to ball and planetary milling and then sintered at 1450^{o}C. The planetary milling medium was more efficient in reducing particle size when compared to ball milling. However, planetary milling caused significant contamination in the niobia powder, from the alumina balls used as milling agents. It forced composition balance in order to keep the original proposed formulation. The planetary milled sintered samples showed better densification and lower grain size in comparison with ball milled ones. It could be concluded that the milling medium choice directly affected both microstructure and properties of the sintered alumina with 4wt% of niobia.
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Introduction

Milling processes are largely used in ceramic processing [1]. They aim to reduce the ceramic average particle size, get rid of impurities, lower the particle porosities, modifying particle size distributions and, disperse and alter particles shape. Some processes also provide both dispersion and effective homogenization. Upon milling, many particles are simultaneously and repetitively submitted to tensions in the milling zone. For each applied tension several cracks may occur in a given particle. The particle fracture involves pre-existing cracks propagation as well as crack initiation. The σ stress required to fracture is given by Griffith [2] relation defined as:

$$\sigma = \sqrt{\frac{2E\gamma}{L}} \qquad (1)$$

E is the elastic modulus, γ is the fracture surface energy, and L is the crack length. For brittle materials, γ falls between 10^{-2} and 10^{-1} J/m^2.

When a particle is repetitively fractured, each small fragment tends to be stronger. The larger existing cracks in the original particle propagate first leaving microcracks in the new particles. The probability of failure upon minimum fracture stress is reduced. As the fragmentation proceeds, the

fracture stress may increase up to some possible plastic deformation. In this case, the particle can no longer be milled, and the milling limit is achieved [3].

Materials and Methods

The samples processing was based on a mixture of a high purity alumina powder with 4 wt% of niobia powder together with 1.3 wt% of polyethylene glycol (PEG) as binder in water. Eventually the mixture was dried in an oven and then sieved after deagglomeration. The prepared powder mixture was uniaxially pressed at 60 MPa. The obtained green bodies were sintered at 1450^{o}C during 3 hours, after binder burnout.

Millings were carried out in a Marconi ball mill model MA 500, with alumina balls as milling agents each one with 30 mm diameter, for 12 hours, and a planetary mill PM 100, for finer powders, during 30, 60, and 120 minutes at speed of 500 rpm. Particle size analyzes of the ceramic powder were done both in the as-received powders and in the comminuted one. The equipment used in this procedure was a CILAS 1064 particle analyzer. A software yielded a particle size distribution curve represented by 100 classes throughout a size analyze range of 0.04 up to 500 μm.

X-ray diffraction (XRD) of the sintered ceramics were performed in a PANALYTICAL X-Ray diffractometer, model X'Pert, with Bragg-Bretano parafocal geometry. The source used was copper ($\lambda_{Cu\ K\alpha}$ = 1.549060 Angstrons, 40 kV, 40 mA). The 2θ scanning angle followed 0.0492^{o} step within an angular interval from 9.9870^{o} to 89.9997^{o} in the equatorial pattern. The diffraction patterns analyzes were performed by using X'Pert HighScore Plus from PANalytical and TOPAS from Bruker AXS programs to quantify the present phases, to determine lattice parameters, and to detect possible phase transformations during the sintering process.

The fractured sintered ceramic samples were sputter-coated with gold, in order to assess the electronic images from their surfaces by scanning electron microscopy. This procedure was also used to measure samples grain sizes.

The methodology employed to determine sintered samples hardness values was based on ASTM C 1327-03 standard. Indentations were made by using 1 kgf (9.8 N) load. The equipment used was a BUEHLER microhardness tester for 15 seconds upon the applied load.

The specific surface area and the pore sizes were assessed from 0.3 g of ceramic powder (alumina and niobia) as well as the powder mixture to be sintered. The referred powders were previously degassed with nitrogen at 250^{o}C for 4 hours. The measurements were performed in a Micrometrics Automatic Physical Adsorption Analyzer, model ASAP 2000.

Results and Discussions

The particle size results obtained from ball and planetary milling of alumina are shown in Table 1, where it could be seen that the size reduction was much more significant and efficient in the planetary mill in comparison with ball mill. Smaller particles sizes increase the ceramic reactivity during sintering leading to better densification, as observed. On the other hand niobia powder underwent contamination in the planetary mill, when compared to ball milling. The contaminant element was alumina, employed as milling agents. The severe niobia contamination took place because niobia is softer than alumina. As a result, it was necessary to adjust the mixture composition, when incorporating planetary milled niobia, to maintain the alumina composition in the proportion of 4 wt% of niobia. Table 2 shows the contamination degree observed in the niobia powder submitted to 1.5 hours planetary milling, after chemical analysis by X Ray Fluorescence (XRF). The high efficiency of reducing particle size observed

in the planetary mill was set for a milling time of 2 hours, since longer times would certainly produce colloidal particle sizes. Colloidal particles would be a barrier for the composition homogenization since they have a spontaneous agglomeration tendency.

Table 1: Results for ball and planetary milling for alumina powder

Particle Diameter	Ball Mill	Planetary Mill		
	[12h]	[0.5 h]	[1 h]	[2 h]
At 10% of Size Distribution [μm]	1.28	1.28	0.47	0.08
At 50% of Size Distribution [μm]	3.20	2.88	0.81	0.44
At 90% of Size Distribution [μm]	6.15	5.32	1.34	1.86
Average Size [μm]	3.50	3.11	0.87	0.75

Table 2: XRF results from niobia powder after 1.5 h planetary milling

Compound	Concentration [%]
Lost On Ignition (LOI)	0.36
Al_2O_3	62.226
SiO_2	1.653
ZrO_2	0.125
Nb_2O_5	35.596

Table 3 presents characteristics properties of sintered samples at 1450^{o}C for 3 hours, for processing both in ball and in planetary milling. As expected, ceramic processed by planetary milling yielded denser samples than those from ball milling. The sintering driving force is a function of the average particle size since it affects the amount of surface area [4]. The smaller the average particle size, the larger is the sintering driving force. Table 1 pointed out the existence of a significant size particle difference for the two used mills. This size difference was reflected in the value of surface area which was about four times greater for the powder processed in the planetary, when compared to the ball mill. Other properties of sintered samples were influenced by the milling medium. For instance, the microstructural property of grain size was governed by the powder average particle size, as exhibited in Table 3. This is an expected result since that when the starting powder has low average particle size, then diffusion distances become shorter and diffusion is facilitated benefiting pore elimination and improving densification. In addition, smaller particles lead to smaller grains at ceramics sintering, and it was observed in this work. Hardness was other property dependent on the particle size. The microhardness mechanical property for sintered samples was significantly larger for those processed in the planetary mill when compared with samples from ball mill processing. Such behavior may be

explained by both better density and lower grain size occurring in the samples whose powders were prepared in planetary mill instead of ball mill. According to Hall-Petch equation [5], the material strength is inversely proportional to grain size. If the material is stronger, then its microhardness should also increase since the material penetration resistance becomes higher [6]. These effects were observed for the two milling media employed in this work, revealing outstanding behavior for the samples submitted to planetary milling processing in comparison with those from ball milling. Figures 1 and 2 show the microstructure from the sintered samples for ball and planetary milling respectively.

Table 3: Influence of milling media on the powder and on the properties of sintered samples

Property	Ball Milling	Planetary Milling
Density [g/cm^3]	3.65 ± 0.01	3.83 ± 0.08
[%] of Theoretical Density	91.2	95.6
Average Grain Size [μm]	4.74	2.84
Vickers Microhardness [GPa]	12.98 ± 0.8	16.98 ± 0.8
Powder Surface Area [m^2/g]	3.88	15.28

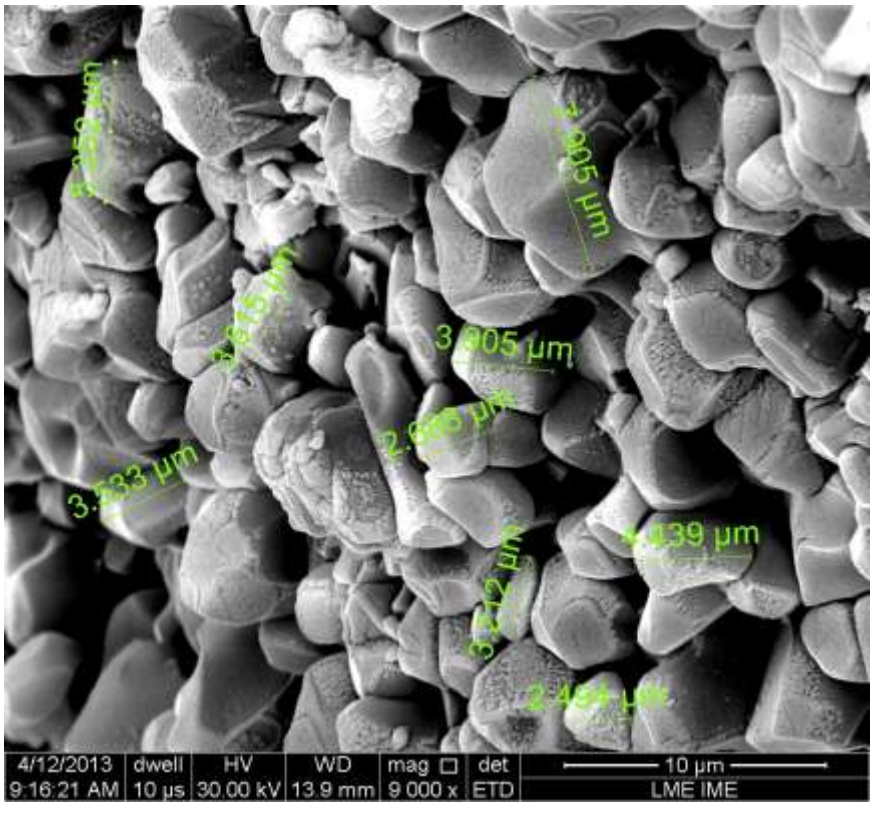

Fig.1: Microstructure of sample from ball milling processing sintered at 1450^{o}C.

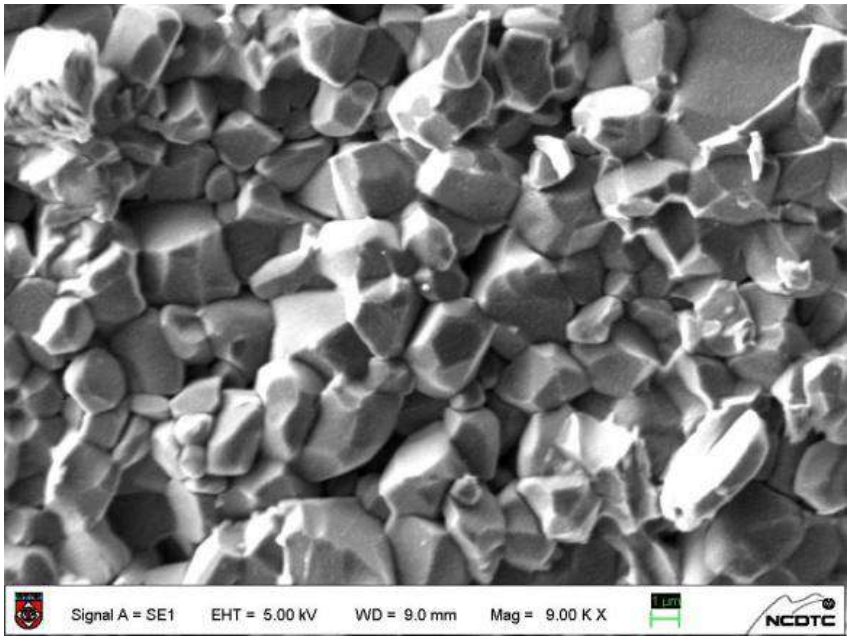

Fig. 2: Microstructure of sample from planetary milling processing sintered at 1450^{o}C.

The grain microstructures revealed not only the grain size difference regarding the milling media employed in this ceramic processing, but also it could be seen in both figures a clear presence of the aluminum niobate, along the grain boundaries. It is highlighted by the white lines surrounding the alumina grains. As a result, the niobate phase was able to wet the alumina grains enhancing the liquid phase sintering mechanisms. Fig. 3 shows a XRD pattern of a sintered sample with Rietveld [7] refinement showing the presence of $AlNbO_4$.

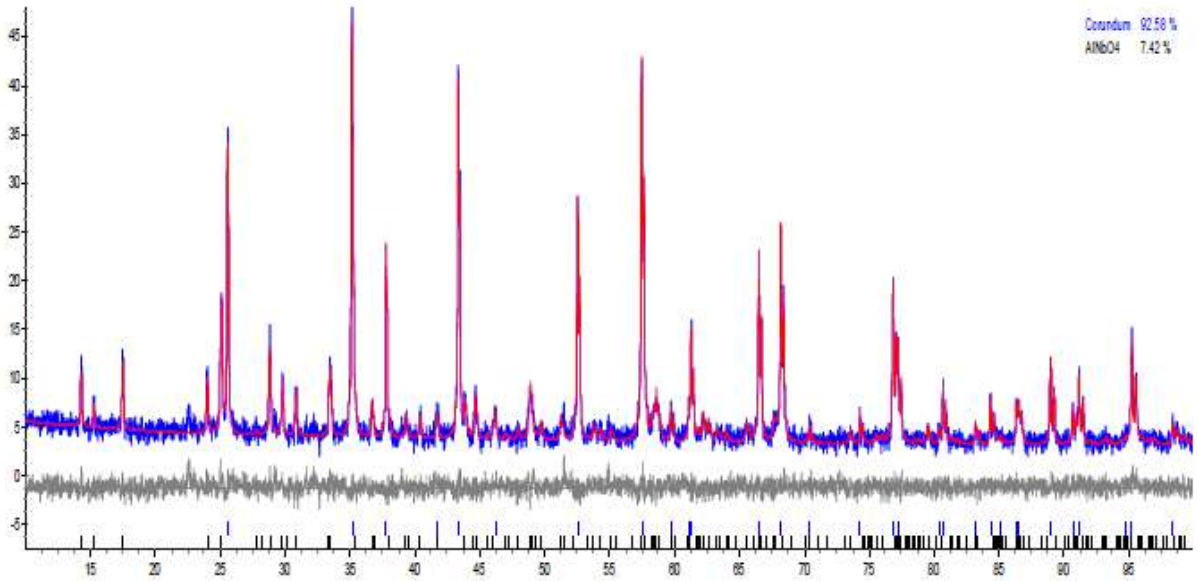

Fig. 3: XRD with Rietveld refinement of a 1450^{o}C sintered sample.

Conclusions

1. The planetary milling showed much better performance regarding particle size reduction when compared with ball milling.

2. The more energetic planetary milling introduced severe contamination in the niobia powder from the alumina balls milling agents. The mixture of alumina with niobia had to be adjusted to keep 4 wt% of niobia concentration in the studied composition.

3. The samples obtained from planetary milling processing showed better densification, higher specific surface area, greater microhardness, and smaller average grain size, in comparison with those from ball milling processing.

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