Processing and Properties of Niobia-Doped Alumina Sintered at 1400°C

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Keywords: Alumina, Solid-Phase, Sintering

Abstract. Niobia is used as a sintering additive in alumina processing because it lowers the sintering temperature. This work investigated the influence of sintering dwell time at 1400°C on the properties of 4 wt% niobia doped alumina. The sintered ceramics were characterized by scanning electron microscopy (SEM), and X rays diffraction (XRD) with Rietveld refinement. Measurements of density, average grain size, hardness, and elastic constants were also performed. The results show that both the microstructure and the mechanical properties were depend on the time at sintering temperature due to their influence on the defect sizes.

Introduction

Sintering is a thermally activated process, which is dependent on time and temperature [1,2]. This process follows three stages: initial, intermediary, and final. Densification takes place mainly during the intermediary stage, where thermal driving force coming from the sintering temperature regulates the magnitude of the needed diffusion processes toward pore elimination. In order to lower the sintering temperature, sintering additives are usually employed in order to reduce the activation energy barrier for diffusion at sintering temperature. Grain growth also occurs during sintering, concomitantly with densification. It takes place mainly in the sintering final stage. Both mechanisms are able to reduce the system total free energy. They do it by substituting more energetic interfaces for less energetic ones, as well as by reducing the total interfacial area between grains by increasing the average grain size. If one desires densification, then grain growth should be inhibited. Sometimes the additive forms a liquid phase, when the sintering temperature goes above the eutectic temperature of the system consisting of the ceramic and its additive. In such situation liquid phase assisted sintering is developed. When the sintering temperature holds below the eutectic temperature, then the additive precipitates in the ceramic grain boundaries, inhibiting their growth, favoring the densification. This work focuses on low temperature alumina sintering (1400°C), doped with 4 wt% Nb₂O₅ looking at the dwell time influence at sintering temperature on the sintered alumina properties. According to the alumina - niobia phase diagram, shown in Fig. 1, solid niobate is expected to be present as a second phase precipitated along the alumina grain boundaries. This second phase hinders alumina grain growth enhancing densification. In addition, when Nb₂O₅ dopes Al₂O₃ aluminum vacancies are created, as illustrated in the defect reaction shown in the Equation 1 using Kröger – Vink [3] notation. Increasing vacancies concentration facilitates the diffusive processes taking place at sintering temperature, assisting densification and resulting in a more efficient pores reduction.

$$3Nb_2O_5 \rightarrow 5Al_2O_3 = 6Nb_{Al}^{"} + 4V_{Al}^{"} + 15O_0^{x}$$
 (1)



Fig. 1: Alumina – Niobia Phase Diagram [4].

Experimental Procedures

The investigated ceramic composition was made of the following materials: alumina from Treibacher Scheifmittel (which is similar to alumina APC-2011 SG from Alcoa), HP niobia as additive, from Mining and Metallurgy Brazilian Company (CBMM), and polyethylene glycol (PEG) with 200 of molecular weight as binder, from Vetec.

The samples fabrication process consisted in the mixture of alumina powder with 4 wt% niobia and 1.3 wt% of PEG in a ball mill. The powder mixture was dried in an oven. The dried powder mixture was deagglomerated and then sieved. Finally, the powder mixture was uniaxially pressed at 60 MPa before being sintered at 1400 °C for 1, 2, 3, 5, 8, and 12 hours. X ray diffraction (XRD) analyses 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 20 scanning angle followed 0.0492° step within an angular interval from 9.9870° to 89.9997° in the equatorial spectra. The diffraction analyses were performed using X'Pert HighScore Plus from PANalytical and TOPAS from Bruker AXS programs, to quantify the present phases and to assess lattice parameters changes, as well as to exam if any alteration occurred during the process. Rietveld [5] refinement was applied to the XRD results. In order to obtain scanning electron microscope images from the fractured sintered ceramic surfaces, the samples were coated with a thin gold layer, by sputtering process. The images obtained were also used to measure samples average grain sizes.

The sintered samples were characterized by measuring density, average grain size, microhardness, and elastic constants. NBR 6620 standard from ABNT (Technical Standard Brazilian Association), based on Archimedes' method was used for density evaluation. Grain size was measured from fractured samples surfaces observed in a scanning electron microscopy (SEM). Microhardness was performed by Vickers indentation. The elastic constants (ν , λ , E, and G) were obtained from ultrasound tests where elastic wave velocities in the ceramic (longitudinal and transverse) were measured. A head block Krautkramer MB4S was used to obtain the elastic waves signals that were read in a ECHOGRAPH 1080 (Karl-Deutsch Model) ultrasound facility.

Results and Discussions

Table 1 shows the properties of 4 wt% Nb_2O_5 doped Al_2O_3 sintered at 1400°C as a function of the sintering time.

Sintering Time	Density \pm SD	% of the	Average Grain	Vickers
[h]	$[g/cm^3]$	Theoretical	Size	Microhardness
		Density	[µm]	[GPa]
1	3.23 ± 0.042	80.7	NA	NA
2	3.44 ± 0.013	86.0	NA	NA
3	3.53 ± 0.004	88.1	3.73	11.34
5	3.61 ± 0.019	90.2	4.67	12.72
8	3.68 ± 0.004	91.9	5.64	14.23
12	3.76 ± 0.014	93.9	7.28	15.61

Table 1: Properties of 4 wt% niobia doped alumina sintered at 1400°C.

Obs: "NA" means not available due to excessive porosity in the samples.

The density evolution at 1400°C sintering temperature as a function of dwell time may be better visualized by looking at the Fig. 2. This figure shows that samples became denser when the dwell time at sintering temperature increased. This effect is expected if one considers that densification depends on diffusion which is a thermally activated phenomenon, therefore time and temperature dependent. When densification occurs, it contributes to reduce the system total free energy, since solid to solid less energetic interfaces replaces solid to vapor more energetic ones [1]. On the other hand another mechanism is competing to reduce the system Gibbs free energy, which is the grain growth [1]. Table 1 shows a tendency of grain growth with the increase in sintering dwell time, revealing that the precipitation of niobate second phase at alumina grain boundaries was not so effective to hinder the grain boundary, lowering density magnitude. Fig. 3 presents the diffraction pattern, with Rietveld [5] refinement, of the investigated ceramic sintered at 1400°C. It could be observed 4.92% of niobate as second phase precipitated in the alumina grain boundaries. Fig. 4 shows the scanning electron microscopy (SEM) of a fracture surface from the sample sintered for 8 hours showing white lines along alumina grain boundaries corresponding to the precipitated niobate. Table 1 also shows that the microhardness increased with increasing density, which may be explained by the reduction of pore fraction which promotes the strenghening of the ceramic as well as it hardness.



Fig. 2: Density evolution as a function of time at sintering.



Fig. 3: Diffraction pattern of sintered 4 wt% Nb₂O₅ doped Al₂O₃ at 1400°C.



Fig. 3 : Fracture surface SEM of sintered sample for 8 hours.

Table 2 presents the elastic constants for the investigated samples obtained by performing ultrasound measurements. From transverse and longitudinal elastic waves velocities, C_S and C_L , respectively, it was possible to determine υ , λ , E, and G, as predicted by Meyers [6].

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Sintering	CL	Cs	υ	λ	E	G
Time	[m/s]	[m/s]	(Poisson)	(Lamé)	(Longitudinal)	(Transversal)
[h]				[Gpa]	[Gpa]	[Gpa]
3	9,282±11	5,523±02	0.23	88.76±0.66	263.78±0.65	107.57±0.20
5	9,514±51	5,567±10	0.24	103.08±3.28	277.05±3.09	111.94±0.99
8	9,706±29	5,604±06	0.25	115.59±1.98	289.16±1.81	115.67±0.58
12	9,917±30	5,643±06	0.26	130.22±2.12	301.73±1.83	119.68±0.59

Table 2: Elastic wave velocities and elastic constants of 4 wt% Nb₂O₅ doped Al₂O₃ sintered samples

The obtained values showed that for longer dwell time both the elastic wave velocities and the elastic constants were higher due to higher densification observed for longer sintering time. Since elastic constants are directly proportional to the elastic wave velocities, then the results are in agreement with the literature. The results obtained in this work are in agreement with those obtained by Medvedovski [7] for alumina. The higher values of microhardness for longer sintering times at 1400°C, which resulted in denser alumina, are also coherent with the higher measured elastic constants values.

Conclusions

 The investigated sintering time of niobia doped alumina at 1400°C revealed that both densification and grain growth took place since both average grain size and density were higher for longer times.
The niobate second phase located at the alumina grain boundaries was able to cause alumina

2. The niobate second phase located at the alumina grain boundaries was able to cause alumina densification, but it was not able to sufficiently pin the grain boundaries to prevent grain growth.

3. Both elastic wave velocities and elastic constants of the studied ceramic increased with longer sintering times for denser samples.

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