Comparative Study of Solid-Phase and Liquid-Phase Assisted Sintering of Nb_2O_5-Doped Alumina

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Abstract. This work investigated the sintering behavior of alumina doped with 4wt% niobia. Three sintering temperatures were investigated: 1400°C, 1450°C and 1500°C. The first temperature leads to solid-phase assisted sintering (SSS) while the other ones develop liquid-phase assisted sintering (LPS). The presence of liquid phase in the second case is due to an eutectic reaction occurring at 1440°C ± 20°C in the alumina-niobia system. The sintering behavior was assessed by measuring the final densities. The results indicated that the 1400°C solid-state sintering, comparatively, was better. This paper proposes that defects associated to the substitution of Al^{+3} by Nb^{+5} in the alumina cation sub-lattice, fostered diffusion and SSS. Sintering at 1500°C presented the lowest density, apparently due to niobate (liquid phase) loss, at this temperature as observed by XRD results.

Introduction

Sintering can occur in the presence or absence of a liquid phase. In the former case, it is called liquid phase sintering (LPS), and in the latter case one has solid state sintering (SSS) [1]. LPS requires that the investigated compositions and the sintering temperatures are chosen with some liquid to be formed during this heat treatment process. The microscopic driving force operating during sintering is the reduction of the excess energy associated to surfaces. The energy reduction can happen by the reduction of the total area by increasing the average particle size, and/or by substituting solid/vapor interfaces by solid/solid interfaces in the grain boundaries, leading to densification, with concomitant grain growth. Densification and grain growth are competitive mechanisms since both contribute to lower the system free energy. Therefore, if one desires to dense, then the grain growth should be inhibited. It can be accomplished by precipitating a second phase at grain boundaries pinning and preventing them from growth. Concomitantly, the densification mechanism will be effective without excessive grain growth. The Al_2O_3-Nb_2O_5 phase diagram [2], shown in Figure 1, reveals the presence of aluminum niobates as well as an eutectic reaction occurring at 1440°C. Therefore, at sintering temperatures of 1450°C and 1500°C it is expected to operate LPS on niobia doped alumina. On the other hand, for sintering temperature at 1400°C, SSS will be the sintering mechanism taking place for niobia doped alumina. Defects are generated upon doping, and they contribute to improve the diffusive processes during sintering. As a result, pore reductions as well as grain growth are promoted. Also, second phase precipitated along the grain boundaries serve to pin the boundaries, favoring densification rather than grain growth.

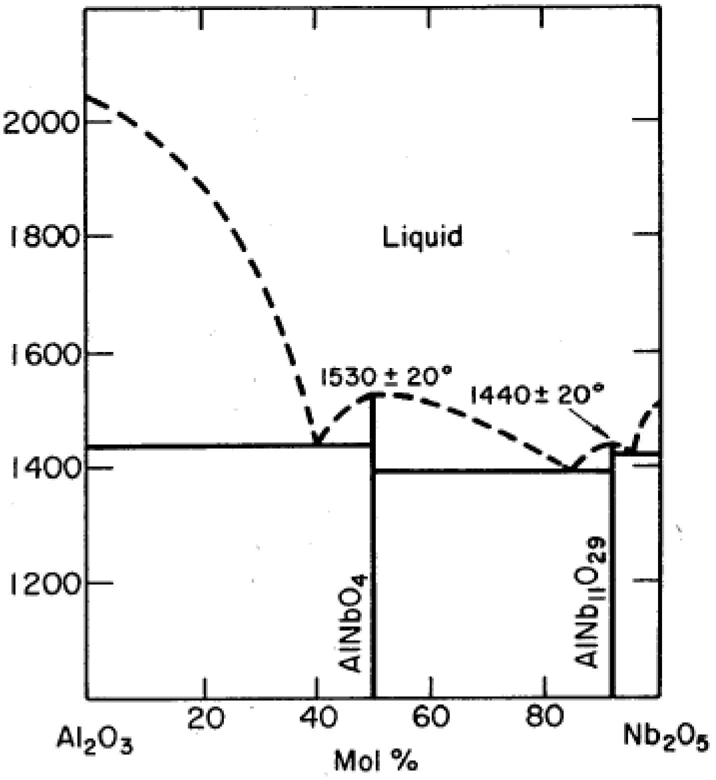

Figure 1: Phase diagram of Al_2O_3-Nb_2O_5 system [2].

Experimental Procedures

The investigated materials were: alumina with 99.4 wt% purity from Treibacher Scheifmittel (which is similar to alumina APC-2011 SG from Alcoa), HP niobia with 99.5 wt% purity from Mining and Metallurgy Brazilian Company (CBMM), and a 200 molecular weight polyethylene glycol (PEG) binder from Vetec.

The samples fabrication process consisted in mixing alumina powder with 4 wt% niobia and 1.3 wt% of PEG in a ball mill. After that, the powder mixture was dried in an oven. The dried powder mixture was deagglomerated and then sieved. Then, the powder mixture was uniaxially pressed at 60 MPa before being sintered at 1400 °C in a JUNG furnace, and at 1450 °C and 1500 °C using a INTI higher temperature furnace. All sintering temperatures were held for 3 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 2θ 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 by 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 refinement was applied to the XRD results.

The fractured sintered ceramic samples were coated with a thin gold layer, by sputtering process, 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 ceramic pores average diameters were determined by means of an automatic analyzer of physical adsorption from Micrometrics (ASAP 2010 Model). The calculation involved 0,3 gram of sintered ceramic which was degassed with nitrogen in a temperature of 250°C for 2 hours.

The densities from sintered samples were measured by using the NBR 6220 standard from ABNT, which is based on Archimedes’ principle. The masses were obtained with precision of 1×10^{-3} g under constant temperature, in a Gehaka scale BK 300 model.

Results and Discussions

Table 1 shows the density results obtained for the alumina doped with 4wt% niobia after 3 hours at the investigated temperatures.

Table 1: Densities results as a function of the sintering temperatures

Sintering Temperature [^oC]	Measured Density [g / cm^3]	% of Theoretical Density
1400	3.53 ± 0.01	88.1
1450	3.65 ± 0.01	91.2
1500	3.49 ± 0.03	87.2

The densities results indicated that the best densification occurred at 1450°C sintering temperature, and the worst was that for the sintering temperature of 1500°C. According to the Alumina –Niobia phase diagram it is expected liquid phase formation at such temperatures. This liquid phase is associated with the niobate phase predicted in the phase diagram below the eutectic temperature. Therefore, it was expected to have a better densification behavior at 1500°C sintering temperature, for two reasons. The first is due to higher activation energy for diffusion in the highest temperature, and the second is the greater wetting capability by the niobate phase since the liquid phase viscosity decreases with the temperature increase. However it was not the case, and the explanation for this result may be due to the loss of niobate verified by XRD results. On the other hand, the sample densification obtained in the temperature of 1400°C was comparatively very good, if one considers the lower activation energy provided by the used low sintering temperature. In contrast with the other two results, solid state sintering was the sintering mechanism since at 1400°C liquid phase is not present as indicated by the phase diagram in Fig. 1. If the densification occurred at such low temperature, it could be attributed to an increased defect formation based on aluminum cation vacancies as well as oxygen anions vacancies, produced by Nb_2O_5 doping on Al_2O_3. By using the Kröger Vink [3] notation, it is possible to write the expected defect reaction produced by the introduction of niobia into alumina. This reaction is presented below:

$$3Nb_2O_5 \rightarrow 5Al_2O_3 \;=\; 6\,Nb^{\bullet\bullet}_{\mathbf{Al}} + 4\,V_{Al}^{'''} + 15\,O_O^{x} \qquad (1)$$

The Eq. 1 justifies the greater capability of niobia in creating vacancies in the alumina lattice, which comes from the valence difference between Nb^{+5} and Al^{+3}. In addition to defects creation, another reason for the densification behavior at 1400°C sintering temperature may be due to niobate solid phase precipitating in the alumina grain boundaries. It holds the grain boundary and the activation energy is carried to densify rather than grain growth at sintering. Fig. 2 shows approximately 5% of niobate at 1400°C.

Figures 2, 3, and 4, show XRD patterns with Rietveld refinement [4]. These results provided very important data regarding the amount of the niobate second phase in the investigated temperatures. They were useful to explain the sintering behavior observed at low, medium and high temperatures, as well as the sintering mechanisms taking place, LPS or SSS.

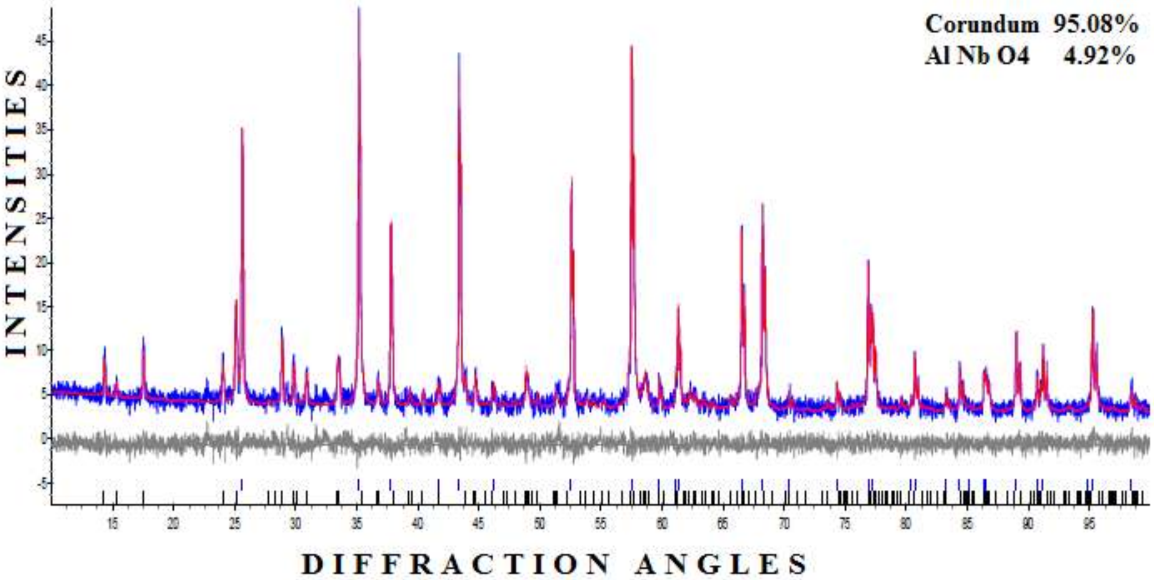

Fig.2: XRD with Rietveld refinement of sample sintered at 1400°C.

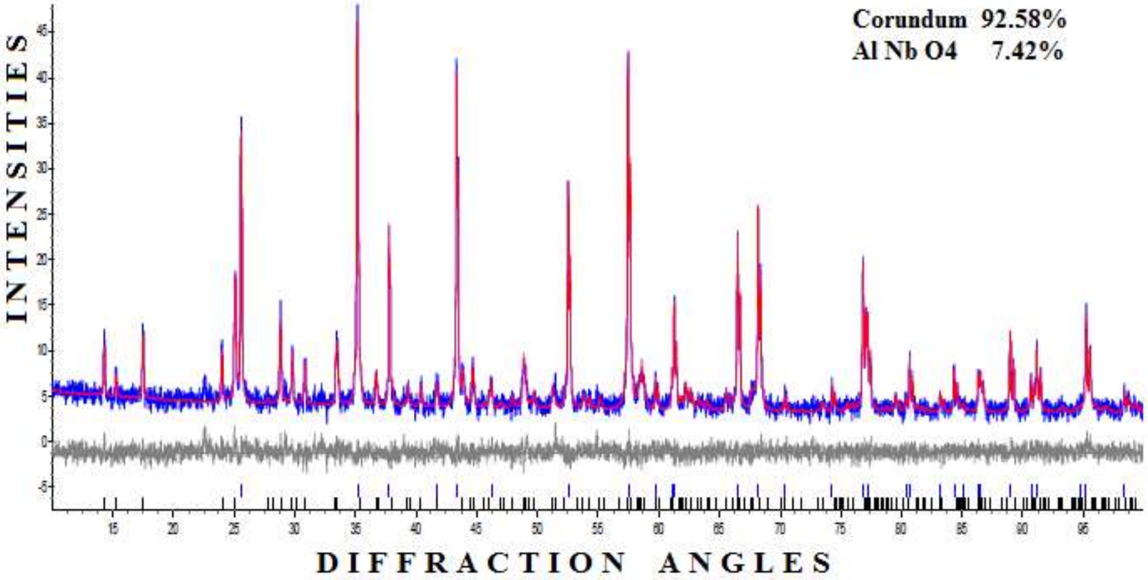

Fig. 3: XRD with Rietveld refinement of sample sintered at 1450°C.

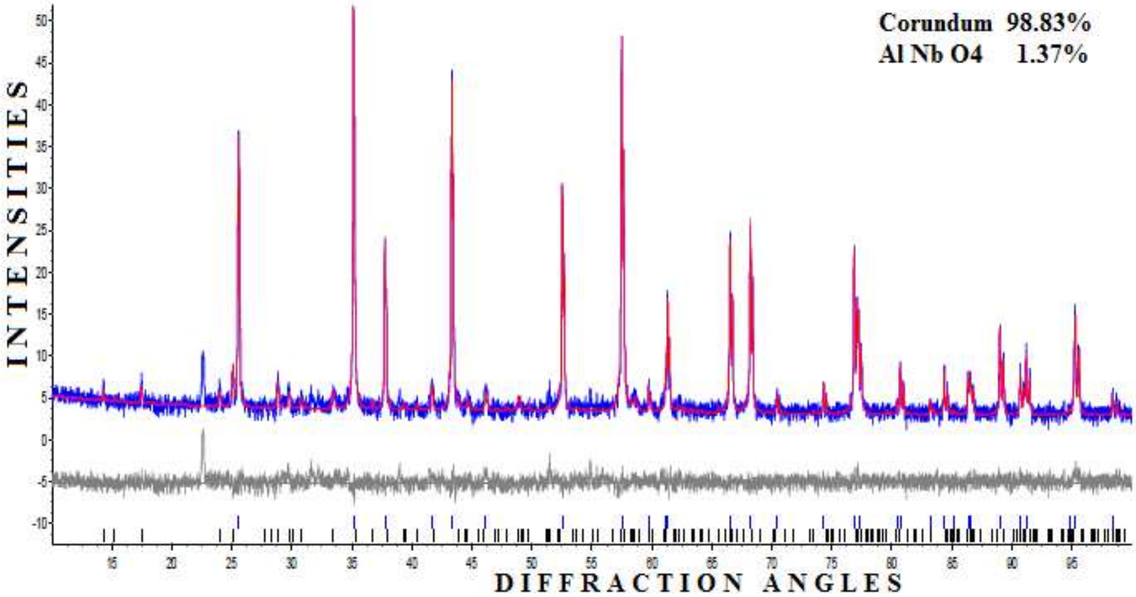

Fig. 4: XRD with Rietveld refinement of sample sintered at 1500^{o}C.

By comparing the amount of niobates in the XRD patterns, one realizes that at 1500^{o}C sintering the sample was depleted of the presence of niobate (only 1.37%), meaning that there was not enough liquid phase to promote densification. On the other hand, at 1450^{o}C, the sintering was accomplished with densification because there was enough amount of niobate (7.42%) wetting the alumina grains leading to a more efficient LPS process. Figure 5 shows a scanning electronic micrography of sample sintered at 1450^{o}C, where the fine white lines surrounding grain boundaries constituted the niobate phase wetting the alumina grains.

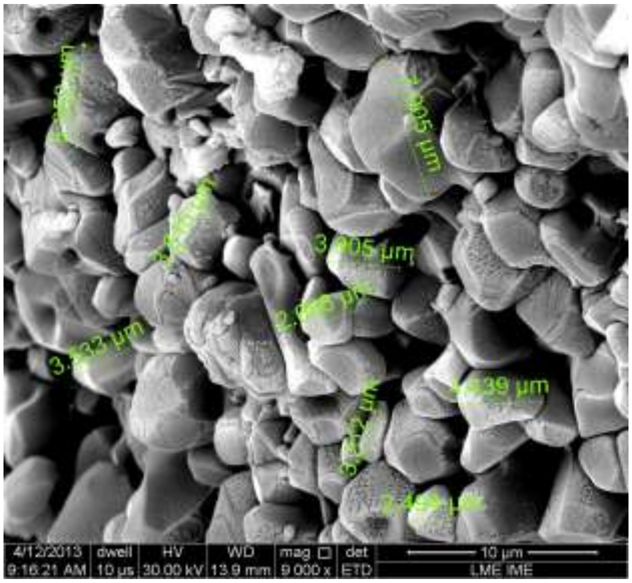

Fig. 5: Scanning electron microscopy of fracture surface from sample sintered at 1450^{o}C.

Conclusions

1. Niobia doping into alumina is able to activate LPS and SSS depending on the sintering temperature above or below the eutectic point predicted in the alumina- niobia phase diagram.
2. Comparatively, the densification behavior at 1400°C sintering temperature was good, since LPS was not activated and SSS took place. It could be a consequence of an increase in the defects concentration from doping with niobia, as well as the presence of niobate solid phase pinning the alumina grain boundaries.
3. The best density result was found for 1450°C sintering temperature, where there was enough niobate liquid phase wetting the alumina grain boundaries and LPS actuated in an efficient fashion.
4. The high 1500°C sintering temperature promoted niobate phase loss, and there was not enough niobate liquid phase able to promoting a good LPS at this temperature.

References

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