ORGANIC BINDER BURNOUT IN ALUMINA PROCESSING

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Abstract. Incomplete binder removal may introduce severe defects during ceramic processing. This work presents a new method to eliminate polyethylene glycol used as a binder in pre-sintering steps of alumina parts. The effectiveness of the proposed method was evaluated by density and pore size measurements, as well as thermogravimetry (TG), differential thermal analysis (DTA), volumetric physical adsorption analyzer (BET), and Fourier transformed infrared spectroscopy (FTIR). The results show that the new method, although relatively slow in comparison with traditional procedures, yields smaller pore sizes and better mechanical properties of the final products.

Introduction

Binders are processing additives used for producing ceramic parts from powders. They consist of polymeric molecules or colloidal particles, which are adsorbed in order to promote a bridge between the ceramic particles. Their main purpose is to increase the ceramic green body strength for ease handling [1].

The polyethylene glycol (PEG) formula is $H\text{-}(CH_2 - CH_2 - O)_n\text{-}OH$ where “n” represents the number of existent groups of ethylene oxides, is largely used as binder in the ceramic industry. PEG is susceptible to oxidation due to attack from free radicals, since high deformations at chain folders in its lamellar structure reduce the activation energy for hydrogen removal. The PEG thermal degradation produces compounds of low molecular weight, diminishing both its melting point and the heat of fusion [2].

The thermolysis of addictives, not removed during drying, is an important step prior to densification at sintering. The binder incomplete withdrawal as well as an uncontrolled thermolysis may introduce a new defect population into the ceramic green body. Such defects may reduce both the quality and the performance of the ceramic final piece. The binder burnout depends on the binder material composition, the released gas nature, as well as its flux in the environment and in ceramic pores [1].

Experimental Procedures

The investigated materials were: alumina from Treibacher Scheifmittel (which is similar to alumina APC-2011 SG from Alcoa), HP niobia from Mining and Metallurgy Brazilian Company (CBMM), and the 200 molecular weight polyethylene glycol (PEG) 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 resulting powder mixture was then dried in an oven. The dried powder mixture was deagglomerated and then sieved. Finally, the powder mixture was uniaxially pressed at 80 MPa before being sintered at 1400 ^{o}C for 3 hours.

PEG thermal analyses were carried out on a Shimadzu DTA-50 equipment. The samples were placed in a platinum crucible under nitrogen atmosphere with 30 mL/minute flow rate, heating rate of 20^{o}C/minute, over a temperature range from 25 to 1000^{o}C.

Thermogravimetry (TG) tests were performed on the milled powder mixture using 5 mg sample inside a platinum crucible. A synthetic air atmosphere with 30 mL/minute flow rate, 20^{o}C/minute heating rate, and temperature ranging from 25 to 1000^{o}C were applied. The TG equipment used was a Shimadzu TGA-50.

The samples also underwent infrared spectroscopy tests using a model Spectrum 100 Perkin Elmer Spectrometer, in the region between 4000 – 650 cm^{-1}, applying attenuated total reflectance (ATR). The transmission spectra were obtained with 4 cm^{-1} resolution, 6 scans by test, and then processed in a Perkin Elmer data management, Spectrum Express model.

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^{o}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 x10^{-3} g under constant temperature, in a Gehaka scale BK 300 model.

Results and Discussions

Polyethylene glycol Investigation: The first step of this work was to carry out DTA and TGA analysis on as-received PEG in order to verify the binder behavior under heat treatment. These results are shown in Fig. 1 and Fig. 2, respectively.

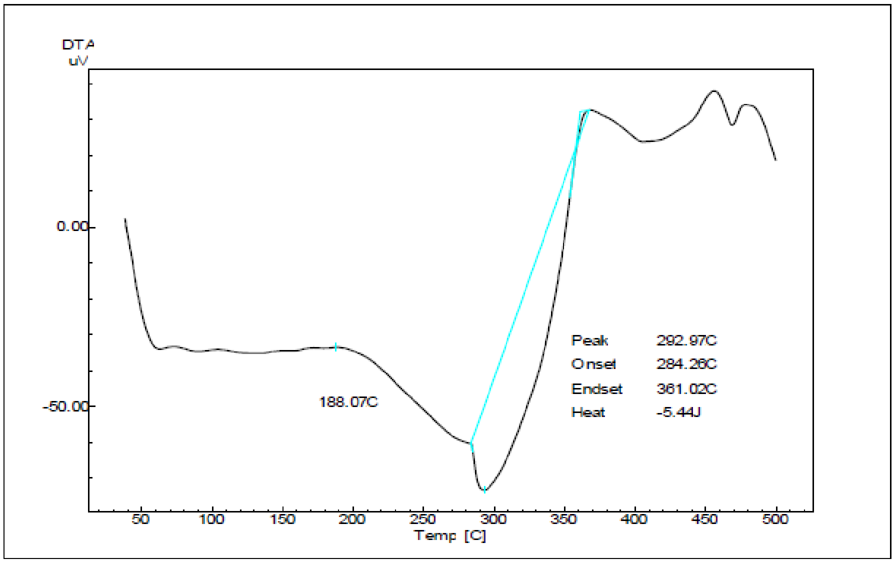

Fig. 1: DTA of PEG.

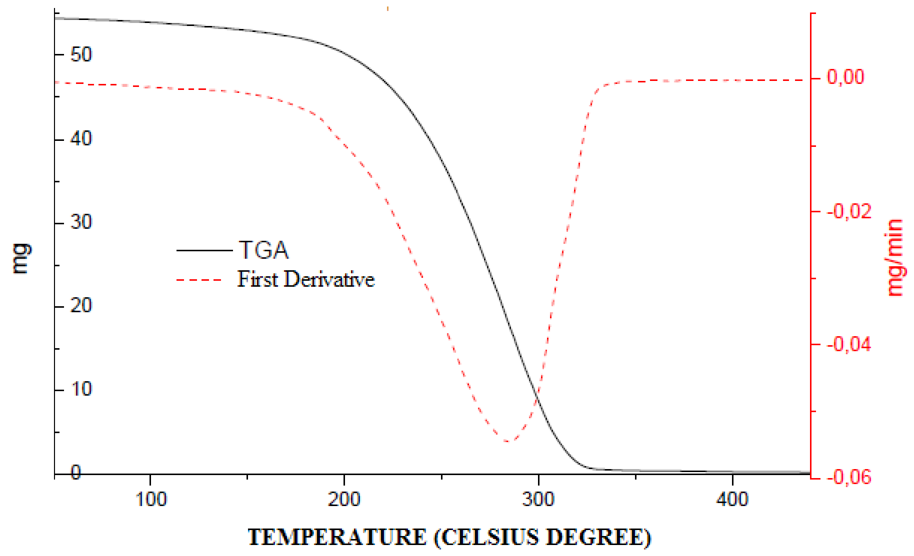

Fig. 2: TGA do PEG

The DTA results showed in Figure 1 revealed a peak at 292.97^{o}C indicating that PEG is evaporating at this temperature. The endothermic behavior observed corresponds to the binder evaporation. This temperature is coherent with that predicted in the literature. The TGA test on PEG exhibited a curve shape similar to those obtained by other researchers, revealing binder mass loss occurring in a single step. It was also observed that the beginning of the mass loss occurred at 235.54^{o}C, and the end of this phenomenon took place at 329.52^{o}C. In addition, the mass loss first derivative with respect to temperature, revealed that 283.78^{o}C corresponded to the highest mass loss rate temperature, point at which 99.33% of total mass loss is observed [1, 2, 3].

Investigation of polyethylene glycol added to ceramic powder: Considering that inter and intra molecular interactions strongly influence the polymer thermal decomposition beginning temperature, the next step was to perform TGA test on binder added to powder. Figure 3 shows the results. It could be observed that the binder mass loss took place along more than one step, and modifications occurred both in the beginning temperature and in the first derivative. The amount of mass loss was 1.26% of the total mass, which is in accordance to the amount of binder previously added to the powder [4].

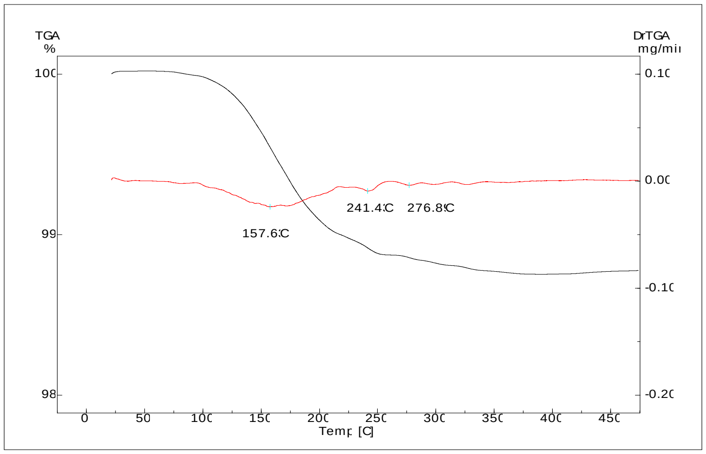

Fig.3: TGA of binder added to powder.

Comparing the TGA results from Figures 2 and 3, a reduction in the beginning temperature of the binder mass loss can be observed, as shown in the Table 1. In addition, the TGA curve shape was changed, indicating that the binder mass loss occurred along more than one stage.

Also, it was noticed that there was a detectable modification in the binder thermal degradation mechanism when it was added to powder when compared to the binder alone, since the first derivative curves from Figures 2 and 3 were different in shapes. The lower values of onset, endset, and first derivative temperatures of PEG added to powder revealed that the polymeric chain underwent alteration when mixed to the comminuted powder, by means of the mechanical breaking of the chemical bonds. This promoted a size reduction in the macromolecules chains leading to an increase of mobility as well as more efficient heat transport, favoring the thermal degradation [4].

Table 1: TGA Temperatures of PEG and PEG Added to Powder

Mass Loss Temperatures	PEG	PEG Added to Powder
Beginning [^{o}C]	235.54	125.74
End [^{o}C]	311.99	213.49
First Derivative [^{o}C]	283.78	157.63 / 241.43 / 276.89
Final [^{o}C]	329.52	372.64

The increase in the degradation final temperature of the powder may be explained by the alumina hydration. The alumina dehydration occurs at temperatures above 320^{o}C [1].

Based on the assessment of the obtained results a new route for binder elimination was proposed, as shown in Figure 4. In this new route the temperature is varied from 25^{o}C up to 375^{o}C at 0.5^{o}C/min rate with a dwell time at 158^{o}C.

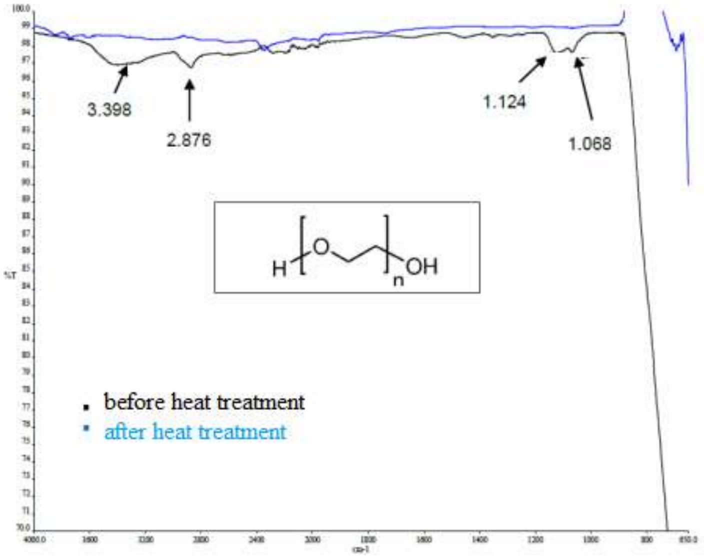

Fig.4: FTIR of powder with and without binder.

In order to confirm if the new route proposed was able to promote the binder removal it was performed an infrared spectroscopy analysis of powder before and after the heat treatment, as shown in Figure 5. Before binder burnout, 4 bands were localized at 3398, 2876, 1124, 1068 cm^{-1} corresponding to OH, C-H, C-O-C, and C-O groups, respectively, indicating the presence of polyethylene glycol. After heat treatment such bands were absents, indicating that the binder burnout had been successfully, eliminating organic components from the green bodies [5, 6, 7].

Comparison between burnout routes

The PEG elimination from green bodies was traditionally carried out by heating the samples from 25°C to 500°C, maintaining 1°C/min heating rate and a dwell time of 1 hour at the final temperature, in order to guarantee binder elimination as shown in Figure 6. The green body should survive, upon thermolysis, without forming cracks or expanded pores when the proper burnout route is chosen. Based on this facts, analyses of pore sizes, cracks detection, and density measurements were performed for the traditional and new binder burnout routes. Cracks were not encountered in the sintered samples processed with the two investigated routes. On the other hand, as shown in Table 2, the new route exhibited smaller pores and slightly higher densities than those observed for the traditional route. Green bodies containing smaller pores usually show better densification under sintering as compared with samples of larger pores [8].

Table 2: Densities and Pore Sizes from the Investigated Binder Burnout Routes

Employed Binder Burnout Route	Average Density [g/cm^3]	Average Pore Size [Angstrom]
Traditional	3.53 ± 0.02	71.69
New	3.56 ± 0.01	41.14

Conclusions

The obtained results demonstrated that:

1. It is not necessary to keep the dwell time of 1 hour at 500°C, as practiced in the traditional binder burnout route, since the binder elimination from powder, as well as alumina dehydration take place at temperatures below 373°C. Higher temperatures will favor enlargement of stable pores.
2. The lower heating rate of 0.5°C/min used in the new route collaborated for reducing the pore size as compared with the higher heating rate of 1.0°C/min practiced in the traditional route, with no statistically significant density alteration.
3. The new route proved to be more efficient than the traditional one, in spite of the longer time. The smaller pores obtained improve the ceramic mechanical strength since this property is related to defects size.

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