Materials Science Forum Vols. 727-728 (2012) pp 740-745
Online available since 2012/Aug/24 at www.scientific.net
© (2012) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/MSF.727-728.740

Evaluation of compaction behaviour of spray-dried alumina by Hg porosimetry and SEM.

A. A. Santos, I. C. Cosentino, L. A. Genova

CCTM - Instituto de Pesquisas Energéticas e Nucleares – IPEN/CNEN

Av. Prof. Lineu Prestes 2242, São Paulo - SP - Brasil 05508-000

lgenova@ipen.br

Keywords: compaction, spray-drying, alumina, mercury porosimetry

Compaction is a widely used fabrication process for ceramics due to its low cost and high productivity. The majority of defects are formed at this stage and, consequently, the evaluation of the process parameters is extremely important. Alumina spray-dried powders were pressed varying pressure, temperature and humidity conditions. Scanning electron microscopy (SEM) analysis was performed to observe the micro-structural evolution of the fractured surfaces in different compaction conditions. The Hg porosimetry analysis showed the decrease of intra and intergranular porosities until complete elimination of the intergranular porosity, as the pressure increased. The glass transition temperature of the binder (T_g) affects the microstructure of green bodies significantly: powders pressed at higher temperatures than T_g presented more intergranular porosity elimination at the same compaction pressure, through plastic deformation and fracturing of granules. Hg porosimetry analysis was suitable for measurement of the pressure in which total elimination of intergranular porosity occurs, join point (P_{join}): this result was confirmed by SEM.

I- Introduction

The powder compaction process is the most widely used forming technique for shaping ceramic products, since traditional ceramic as floors until advanced ceramics for technical applications. This process is characterized by high productivity but it has a serious problem, namely the density gradient originated during the die cavity filling and the subsequent compaction operation[1]. Therefore, the process requires a high control of all parameters involved in order to guarantee to obtain samples with high homogeneity of the green density, which ensures a sintered body of high quality and low population of microstructural defects. Thus, it is extremely important to understand the variable that controls the compaction mechanisms and interfere in the homogeneity of the green density along the compacted body.

The characteristics of granules obtained by spray-drying largely determine the characteristics of the compacted body[2-4]. The morphology and distribution size of granules affects its flowability and the die fill density (loose density). Furthermore, the mechanical strength of the granules, their response to the applied pressure, largely due to added organic additives (binder, plasticizer and lubricant), determines the compact density and homogeneity.[5-8]

The glass transition temperature of the binder (T_g) affects the microstructure of green bodies significantly. If the granules are compressed at a temperature below the binder T_g, their polymeric chains are rigid and act as a barrier to deformation and crushing of granules, reducing the green density and leading to defects: this is due to the maintenance of the granule relics or rest of the initial granule structure and the inter-granular porosity. In addition, under these forming conditions, there is a reduction in the transmission of the applied pressure and, thus, a tendency to form a heterogeneous density distribution[9,10].

On the other hand, if the compaction occurs at temperatures above T_g, the chains of binder are flexible, thus facilitating the sliding of the particles comprising the granules, resulting in higher densification of the particles, lower defect population and greater green density homogenization.

The forming process of granular materials can be shared in three distinct stages: the first is controlled by rearrangement and packing of granules; in the second stage, the granules deform or fracture to fill interstitial voids in the packing structure; finally, in the third stage, further plastic deformation occurs by reduction of intragranular porosity. The transition between the first and second stages is associated with the onset of the plastic yield of the granules (an apparent yield stress P_y), while the transition between the second and third stages (named joint point, P_{join}) is associated with the junction of granular surfaces and the substantial elimination of interstitial voids[11].

The forming behavior depends on the characteristics of the granules and properties of the binder, specially its T_g. Therefore, the ideal for compaction process is that the binder may present T_g below the processing temperature (room temperature). It is known that the T_g of PVA, the most commonly used binder for ceramic materials, is affected by the presence of plasticizers, such as polyethylene glycol (PEG) and the adsorbed moisture. In this article, the effect of moisture on the compaction behavior of a spray-dried alumina was evaluated, and then it was related to T_g behavior of the PVA-PEG additive. Granules with different humidity conditions were formed under different pressure and temperature conditions. The compact density and porosity were determined by Hg porosimetry and the fracture surfaces were observed by SEM.

II- Experimental Procedure

The spray-dried powder used in this study is a 92% alumina-based composition with 1wt% PVA-2wt% PEG organic additive. The spray-dried granule presents a spherical and donut-like shape (figure 1) and log normal grain size distribution with a median diameter of 150 µm. Pore size distribution was measured by mercury intrusion porosimetry in a Micromeritics Autopore III porosimeter. Figure 2 shows the bimodal pore size distribution of the used powder indicating inter and intragranular pores.

Before compaction, the spray dried alumina was distributed in small quantities (3 g) and conditioned for, at least, 36 h in a closed ambient with a controlled and constant relative humidity (rh), by using a silica gel for dry ambient (10% rh) and a saturated aqueous solution of NH_4NO_3 (for 64% rh) and KCl (for 85% rh). Thus, it was ensured that the granules were, subsequently, compacted with three different humidity conditions. After that, in order to evaluate the effect of temperature in the compaction process, samples of the granules with controlled humidity were poured into a 12 mm diameter cylindrical die, assembling the punches, with the ensemble maintained by, at least, 2 hr in three different temperature-controlled environments, until the set reached thermal equilibrium: 5 °C in a refrigerator at 25 °C in a laboratory room and 45 ºC in a furnace.

Samples were compacted using a universal testing machine Instron 4400 R at a rate of 0.5 mm/min, with a load recorded automatically until the maximum pressure, 400 MPa. The compaction curves obtained for different temperatures and humidity conditions allowed P_y and P_{join} to be estimated. With these values as a reference, bodies were pressed at intermediate pressures: the porosity was determined by mercury porosimetry and the fractured surface was observed by scanning electron microscopy.

III- Results and Discussion

Figure 1 shows the granules of the spray-dried based-alumina composition with the typical donut-like shape granules. Figure 2 allows to observe the pore size distribution of grains, with well defined inter and intragranular pores.

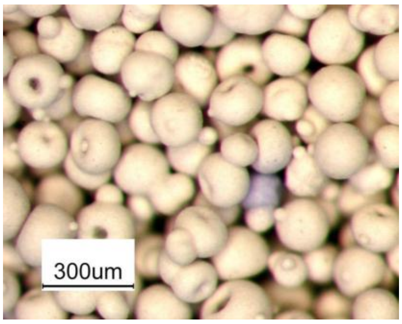


Figure 1 - Spray-dried alumina-based composition with the typical donut-like shape granules

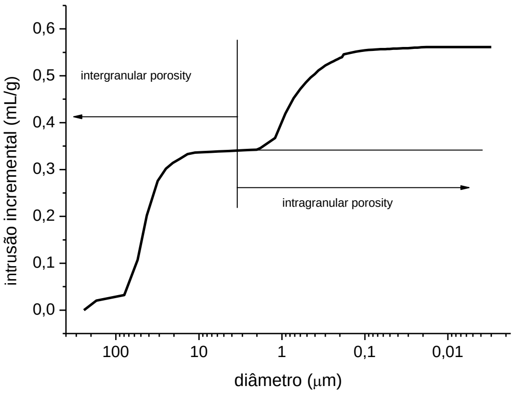


Figure 2 - Pore size distribution of grains with well defined inter and intragranular porosity.

Figure 3 shows the apparent density as a function of the applied pressure for bodies processed at different conditions of humidity and temperature. The compaction curves show quite clearly that the samples pressed at 40 °C and higher humidity acquire greater density than those pressed at 5 °C and lower humidity. Moreover, the pressure required for the granules begin to deform and/or fracture (P_y) is smaller at 45 °C than at 5 ^{o}C, suggesting that the compaction temperature was above T_g of the binder. In figure 4, it is possible to observe the same behavior.

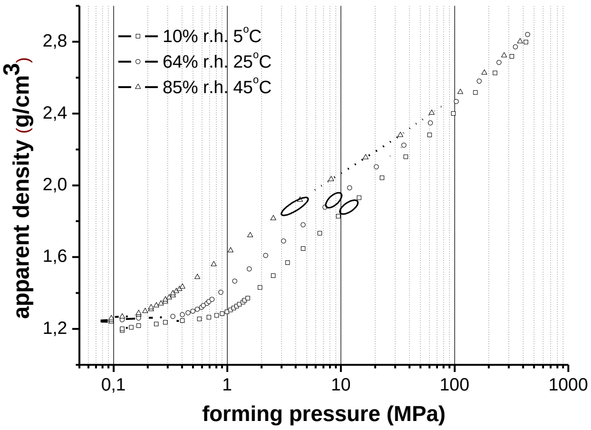


Figure 3 – Compaction curves of the granules pressed at different conditions of humidity and temperature. Intervals detached in the graph correspond to the forming pressure ranges in which intergranular porosity elimination occurs, as detected by mercury porosimetry analysis.

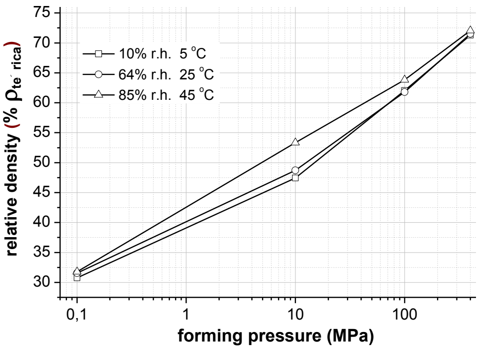
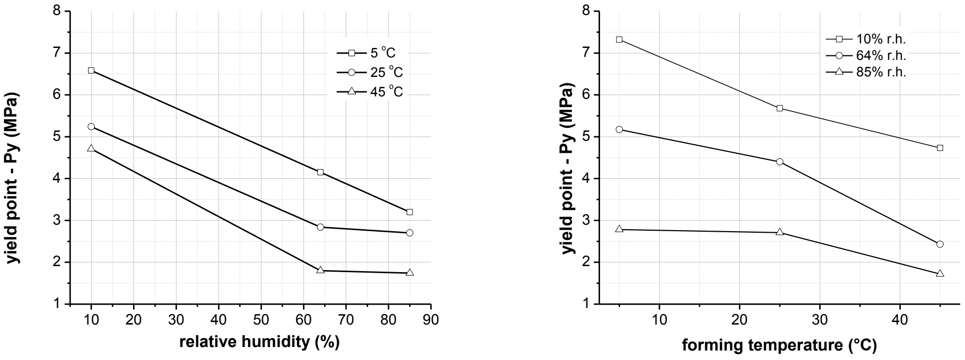


Figure 4 – Effect of the compaction pressure in the green density at different conditions of humidity and temperature.

Figure 5 shows yield point versus relative humidity (a) and forming temperature (b). These curves allow us to evaluate how these parameters interfere with the mechanical strength of the granules. For all employed conditions in these tests, higher temperatures or relative humidity, lower P_y and, thus, lower mechanical strength of the granules are related to the variation of binder T_g value.



(a) (b)

Figure 5 – Effect of the compaction humidity and temperature on the yield point.

Figure 6 shows the porosimetry curves for pellets obtained with different temperatures and humidity conditions. The curves show bimodal porous distribution, related to inter and intragranular porosity. For all different conditions, as the forming pressure increases, the intergranular porosity decreases until its complete elimination; the pressure in which it occurs is called P_{join}. This point (P_{join}) was found between 10 and 15 MPa for 10 % r.h and 5 ^oC (the most critical among the forming conditions analyzed), between 7.5 and 10 MPa, for 64 %r.h and 25 ^oC, and between 3 and 5 MPa, for 85 % rh and 45 ^oC (the most suitable of the three forming conditions) . Similarly to what occurred with the yield point, this reduction of the P_{join} is due to the decrease in the granule mechanical strength with the change in the binder T_g. When a powder is pressed at a higher temperature than T_g, the binder is easily deformed and high green densities can be achieved at moderate stresses. As the T_g of the binder is increased, it becomes stiffer, requiring higher compaction stresses to achieve a given density. Figure 6, also, shows the microstructures of the fracture surfaces in different temperatures and humidity conditions. As expected, in the most suitable of the three forming conditions, a greater deformation occurred. Compared to the literature, the conjunction of granular surfaces and the substantial elimination of intergranular porosity occurred at lower pressures.

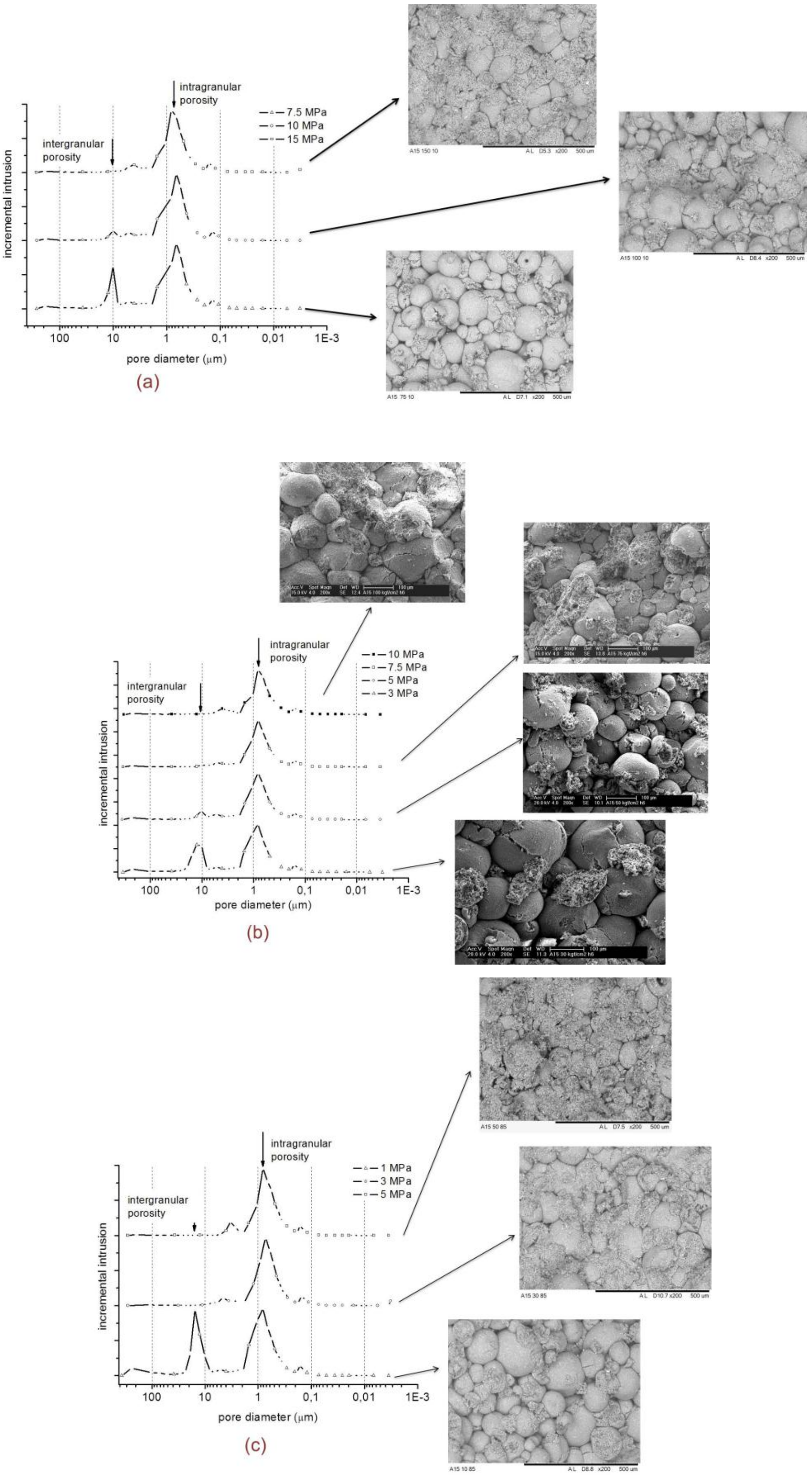


Figure 6 – Effect of the compaction pressure on porosity and SEM micrographs of spray-dried alumina powders, compacted in different conditions: (a) 10% rh and 5 °C, (b) 64% rh and 25 °C, (c) 85% rh and 45 °C.

IV – Conclusion

As the processing temperature and humidity increases, the binder glass transition temperature (T_g) and the granule mechanical strength decrease, resulting in:

- Increased green density,
- Decreased yield point (P_y),
- Decreased P_{join}, pressure in which the intergranular porosity elimination occurs, showed by mercury porosimetry.

We can confirm that the resistance of the granules depends strongly on the binder glass transition temperature.

V – References

[1] Reed, J.S. Pressing. In: Reed. J.S. Principles of Ceramics Processing – Second Edition. Willey Inter-Science, 1995. p. 418-440.

[2] Takahashi, H.; Shinohara, N; Uematsu, K., Influence of spray-dry slurry flocculation on the structure of sintered silicon nitride. J. Ceram. Soc. Japan 1996, 104, 59-62.

[3] Bertrand, G.; Filiatre, C.; mahjoub, H.; Foissy, A.; Coddet, C.; Influence of slurry characteristics on the morphology of spray-dried alumina powders. J. Eur.Ceram. Soc., 2003, 23, 263-271

[4] Hotta, T.; Nakahira, K.; Naito, M.; Shinohara, N; Okumiya, M.; Uematsu, K. Origin of the strength change of silicon nitride ceramics with the alteration of spray drying conditions. J. Eur. Ceram. Soc. 2001, 21, 603-610.

[5] Zainuddin, M. I.; tanaka, S.; Uematsu, K.; Effect of segregation of a polyacrylic acid (PAA) binde ron the Green strength of dry-pressed alumina compacts. J. Am. Ceram. Soc., 2008, 91, 3896-3902

[6] Uppalapati, M.; Green, D. J.; Effect of external lubrificant on mechanical properties of dry-pressed green bodies., J. Am. Ceram. Soc., 2005, 88, 1397-1402

[7] Baklouti, S.; Coupelle, P.; Chartier, T.; Baumard, J.F.; Compaction behavior of alumina powders spray-dried with organic binders., J. Phys. III, 1996, 6, 1283-1291

[8] Balasubramanian, S.; Shanefielf, D. J.; Niesz, D. E.; Effect of externally applied plasticizer on compaction behavior of spray-dried powders.; J. Am. Ceram. Soc., 2002, 85, 749-754

[9] Brewer, J. A.; Moore, R. H.; Reed, J. S.; Effect of relative humidity on the compaction of barium titanate and manganese zinc ferrite agglomerates containing polyvinyl alcohol.; Am. Ceram. Soc. Bull., 1981, 60, 212-220

[10] DiMilia, R. A.; Reed, J. S.; Dependence of compaction on the glass transition temperature on the binder phase., Am. Ceram. Soc. Bull., 1983, 62, 484-488

[11] Mort, P.; Analysis and application of powder compaction diagrams.; Handbook of Conveying and Handing of particulate solids., Levy, A and Kalman, H. Ed.; Elsevier Science B.V., 2001

Advanced Powder Technology VIII
10.4028/www.scientific.net/MSF.727-728

Evaluation of Compaction Behaviour of Spray-Dried Alumina by Hg Porosimetry and SEM
10.4028/www.scientific.net/MSF.727-728.740