Alumina Bar Synthesis Methods Compared Through Weibull Moduli: A Study in Slip Casting vs. Die Pressing Techniques

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Abstract

Strengths of alumina-based ceramics was investigated through calculated Weibull Moduli and SEM imaged fracture surfaces. Two methods of ceramic manufacturing were explored; die pressing and slip casting. The resulting test bars were subjected to three-point bend testing, and Weibull moduli were calculated from the obtained data. Literature suggests slip cast bars have higher fracture stresses than die pressed bars, but the experiments run found the inverse to be true. An overall higher Weibull modulus of 4.52 was found for die pressed bars while the modulus of 2.67 was found for slip cast bars. This disagreement is likely due to the complex process of slip casting leading to imperfections in bar creation. SEM imaging of fractured surfaces yielded no substantial differences in microstructure. Visual analysis of fractured bars did show that slip cast bars had smoother fracture surfaces.

Introduction

Ceramic materials are attractive design components for industrial applications that require high temperature stability, strength, and light weight parts.[1, 2] Industries like aerospace and nuclear energy[1] are continually working toward how to best utilize ceramics in their designs, with a focus on introducing ceramics into increasingly large structural components.[3] Aluminum oxide, Al_2O_3 (alumina), is a versatile and abundant compound used in ceramic processing; it is naturally occurring in the mineral corundum, and can be harvested in a high yield from the mineral bauxite through the Bayer process which allows for a lower cost of the material.[4] Aside from the low cost, alumina has an inertness, high modulus of elasticity,[5] and hardness that suits the needs it fills in manufacturing and is used to make porcelain, alumina laboratory ware, crucibles, high temperature cements, wear resistant parts, medical components,[4] and dental ceramics.[5]

Particle size is one of the main contributing attributes to a successfully produced ceramic. Low porosity and a fine grain size yield a higher strength ceramic.[4] Before sintering a green body, a method of powder processing should be chosen that maximizes particle packing and uniformity to minimize post-sintered shrinking.[4] For high density packing, a broad range of particle sizes are required.[4] Ball milling is a powder processing method that yields that broad range of particle sizes by placing the powder in a rotating container with a grinding media for a specified amount of time so that the ceramic particles are successfully broken down into smaller pieces.[4] Milling increases green density, the density of the powder compact, and densification behavior of ceramic parts.[4] Ball milling can be done through a wet process or a dry process. Wet ball milling yields a more homogeneous particle size than dry milling and requires more time to dry the powder,[4] for the purposes of this experiment a dry process was used.

Additives to ceramics can make steps in the manufacturing go smoother and augment final physical properties of ceramics. Binders add strength to the green bodies, so the ceramic can keep shape before sintering, and can come in the form of organic and inorganic.[4] Organic binders decompose to gases during densification while inorganic binders make up part of the finished ceramic.[4] Binders and lubricants are chosen based on what shape-forming process the ceramic is undergoing, die pressing or slip casting, since each have different attributes that aid in these processes.

Die pressing is a shape-forming process that, through compression, forms the ceramic through utilizing binders and lubricants. Uniaxial pressing employs a force that is applied in one direction and the powder ceramic mixture is compressed in the shape of the die desired.[4] The binder allows for the ceramic to remain in the shape of that die until sintering.[4] Die pressing can create an inhomogeneous stress distribution throughout the compressed ceramic when the powder compacts[6]; binders and lubricants can reduce wall and particle friction which lessens the density variations in green compacts.[7] Polyvinyl alcohol (PVA) was used in this experiment as a binder, which is considered a softer granule binder and can lead to sticking in the die components in die-pressing, reducing production rates.[4]

Slip casting is a method of ceramic shape-forming using a porous cast and water suspended ceramic particles. A successful slip cast depends on the rheological properties of the slip which is controlled by deflocculants[8] and favors using smaller ceramic particle sizes for the best results.[4] Materials made by slip cast tend to have a reduced porosity, fewer defects, and higher toughness than die pressed samples.[5] Porosity is a useful quality for ceramics because it contributes to the lighter weight of the product, but the more porosity induced the less strength the product will have. Alumina particularly has less compression strength, once sintered, the more porosity it has.[9]

Densification of the ceramic is the sintering process; particles bond together and a loss of porosity takes place.[4] Bonding occurs at the grain boundaries where material transport happens.[4] Sintering is thought to be motivated by surface tension since surface free energy decreases as the particles grow together.[10] The shrinkage of the ceramic during sintering is equal to the loss in porosity, sintering under a vacuum can reduce the amount of porosity in dental ceramics from 5.6% to 0.56%.[5] During alumina sintering specifically, if brought up to 1300°C, grain growth and further compaction occurs, the extent of the compaction and the crystallite size depend on the specifics of the sintering process.[11] Crystallites are in a random orientation at high temperature and residual stress will be induced in individual crystallites by the thermal anisotropic contraction during cooling since alumina is an anisotropic crystal.[11]

This experiment will be looking at the strength of die pressed alumina bars compared the strength of slip cast alumina bars through strength testing and Weibull statistics. While slip casting is generally regarded in industry to be superior to die pressing, the complexity of slip casting and its abundance of processing steps will introduce more room for user error, which could lead to a high variability in defect density in slip cast bars. By calculating the Weibull modulus for each set of bars produced, the consistency and repeatability of each ceramic synthesis process can be determined, with higher moduli indicating less variability between samples, and lower moduli implying a wide spread of defect density from one sample to the next.[12]

Materials and Methods

Slip cast bars

Using Solidworks, a CAD model of a bar was created. This model was printed with PLA using a 3D printer, and then placed in an Oomoo™ mold. After imprinting, the 3D printed bar was removed and placed in a different location in the mold ten times. A polymer mixture was made using TableTop Epoxy Resin mixed with TableTop Epoxy Hardener in a 1:1 ratio. This polymer mixture was placed into the Oomoo™ mold in the 10 molds made by the 3D bar. After 2 days, the polymer mixture hardened into 10 polymers that were removed. A plaster of Paris mixture was created using 5000 mL of powder and 2500 mL of water. The 10 polymers were inserted into the plaster of Paris mixture to create a plaster of Paris mold for the slurry used to create the slip-cast bars.

The slurry for the slip-cast bars was created by first dry ball-milling Al_2O_3 into a fine powder. Then 250 g of the Al_2O_3 powder was mixed with 107.5 mL water, 7.5 g of Darvan C as a deflocculant, and 12.5 g of polyvinyl alcohol (PVA) as a binder. Two slurry mixtures were created, and in one slurry an additional 10 mL of water was added to reduce viscosity. The slurry was placed into a vacuum chamber to remove bubbles before pouring, and finally, the slurry was poured into the plaster of Paris mold and left to dry for two days. The slurry became a ceramic slip-cast bar after drying that was then removed for sintering.

Die pressed bars

The slurry for the die press bars was created by first ball-milling Al_2O_3 into a fine powder. 40 mL of water was mixed with 40 g of PVA. 25 mL of that solution was placed into a breaker and filled to 200 mL using water. Then the solution was mixed with 250 g of the Al_2O_3 fine powder. The slurry was then ball-milled for 15 minutes. The slurry dried over five days back into powder form.

The powder was then placed into a die under an initial load of 2 tons. After maintaining a 2 ton load for around 30 seconds, the bar pressure was increased and maintained at 6 tons for another 30 seconds. 25 total bars were made using this process.

Sintering and characterization

All bars (slip cast and die pressed) were sintered together in a furnace. Temperature was ramped at 5 °C/min from room temperature to 500 °C. Bars were gettered at 500 °C for 3 hours to allow gasses to escape the bars as they were heated, preventing explosions and fractures in the bars. After the low temperature phase, the bars were then heated at 5 °C/min from 500 °C to 1500 °C and held at 1500 °C for 3 hours. Finally, the bars were brought back to room temperature at a cooling rate of 5 °C/ min.

Groups combined all bars and 20 slip-cast bars and 20 die press bars were chosen for stress testing. Bars were characterized using a 3-point bend test on an Instron 5969 Dual Column Tabletop Testing System. Weibull moduli were calculated using this data and the width and thickness dimensions of each bar.[12] One slip-cast bar data set and one die-press bar data set had errors and were not used in calculations. Images of fracture surfaces of bars were taken using a Hitachi TM3030Plus Tabletop Microscope (SEM) with SE and BSE Detectors.

Results

Weibull Modulus

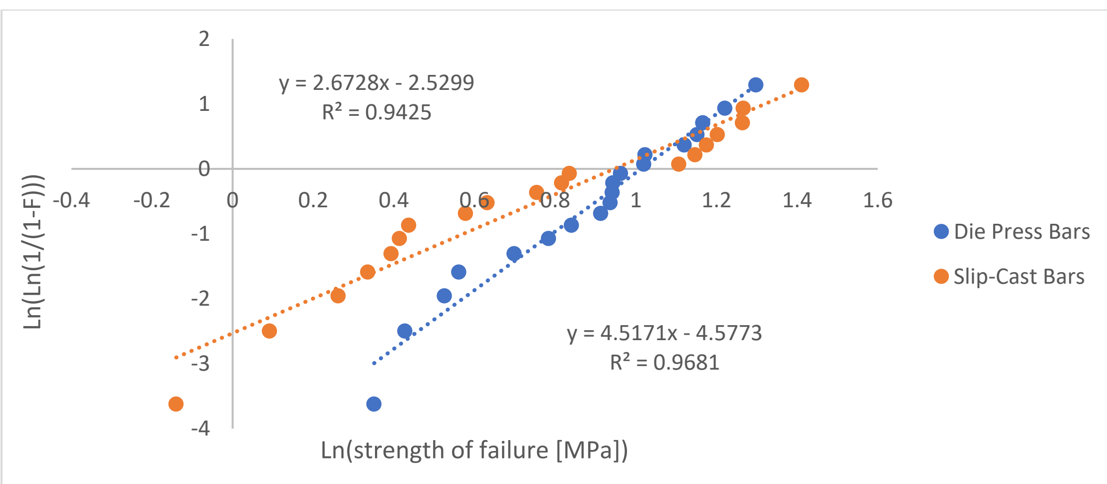

Figure 1: Graph of Weibull Modulus for Die Press bars (blue) and Slip cast Bars (orange). The equation for slip cast bars is located in the upper left corner of the graph. The equation for the die press bars is located at the bottom right corner of the graph. Note the gap in failure stress for slip cast bars between 0.8 and 1.1 on the x axis. Alternatively, the die pressed bars show a clustering around 1 on the x axis.

Figure 1 documents the failure strengths of each bar and the Weibull modulus for each manufacturing technique. By reading the slopes of each dataset, the Weibull modulus for die pressed bars and slip cast bars was found to be 4.52 and 2.67, respectively.

SEM Images

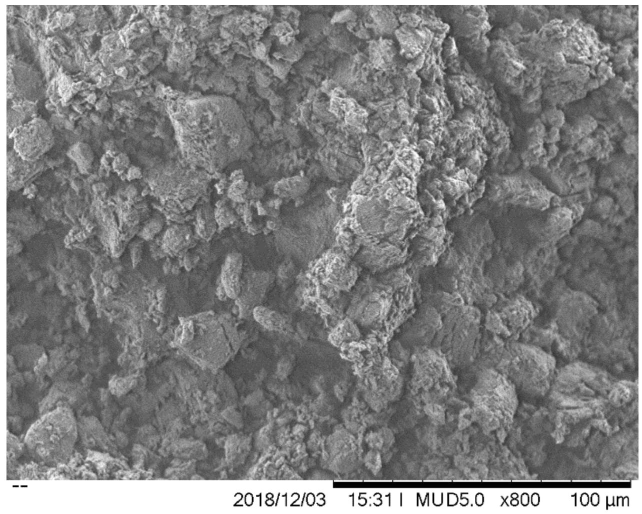

Figure 2: Die pressed bar fracture surface at 800x magnification. Images generally had large variation in height in the plane normal to the image. This was especially obvious with simple visual inspection of fracture surfaces.

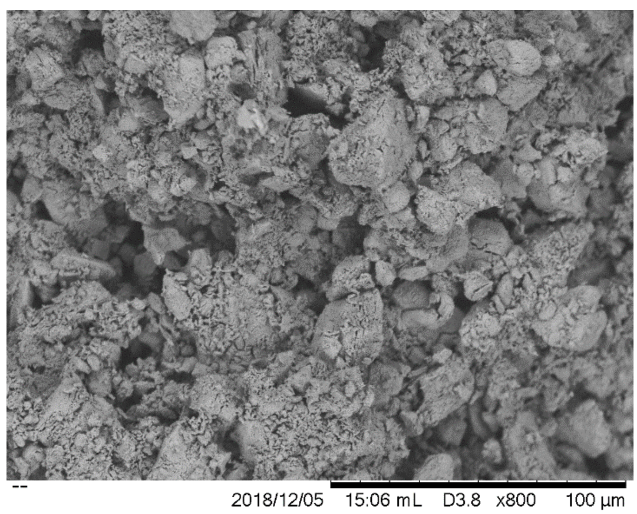

Figure 3: Slip cast bar fracture surface at 800x magnification.

Figure 2 shows an image of a die press bar fracture surface at 800x magnification. Figure 3 shows an image of a slip-cast bar fracture surface at 800x magnification. Both images were taken using secondary electron imaging.

Discussion

Fracture strength

Slip cast bars showed an average failure stress of 2.29 MPa, while die pressed bars failed slightly higher, around 2.51 MPa. In addition to being stronger than slip cast bars, the die pressed bars had a Weibull modulus of 4.52, which is almost 70% higher than the slip cast Weibull modulus of 2.67. In short, the die pressed bars had higher strength and more reliability in their manufacturing than slip cast bars. Both bars showed substantially more variability in their behavior than other literature on alumina bars, which documented Weibull moduli closer to 17.4.[13] The strength and consistency of die pressed bars likely is a direct result of its simplistic procedure. Slurries for slip casting had to be mixed, vacuumed, and poured into a porous plaster of Paris mold with its own defects. Alternatively, die pressed bars were merely compressed and then directly sintered. Each step of slip casting stands as an opportunity to introduce bubbles and pores into a final sintered bar, and ceramics only need a single substantial defect to become their site for fracturing.

While slip cast bars had more variability than die pressed bars, the *average* fracture stresses for each set of samples were within 10% of each other. This suggests that slip cast bars performed substantially worse, but also at times better than the aggregate die pressed bars. In fact, slip cast bar performance could be categorized into two groups, with “poor” samples holding egregious defects or bubbles within the samples, and “fair” samples being generally free of extreme defects.

Considering the slip casting process, large defects tend to appear more readily than in die pressing, with a single large bubble introduced during pouring leading to easy and catastrophic failure in a stress test. Alternatively, if pouring a slip into its mold was carried out successfully, with no bubbles being introduced to the bar, the slip cast bar can be expected to perform quite well. This reasoning can be reflected in the data from Figure 1, with an apparent gap in yield stress values for slip cast bars between 0.8 and 1.1 on the x axis. It is reasonable to postulate that the far right cluster of slip cast bars are all relatively free of defects, and all bars below x = 0.8 have some large defect introduced through the slip casting process.

Alternatively, the die pressing process, with simple uniaxial pressure being used to create each bar shape, does not allow for large pores or defects to appear as readily as slip casting. Beyond large holes that can appear in each bar, the opportunities for defects to appear are less substantial, which could explain the higher Weibull modulus measured for die pressed bars. In fact, instead of fracture stresses dividing into two different clusters, the yield stresses for die pressed bars show a grouping around x = 1, where seven of the nineteen bars all cracked (Figure 1).

Fracture surface

SEM images of die pressed and slip cast fracture surfaces failed to reveal any substantial differences between the microstructures of each manufacturing method (Figures 2,3). Visual inspection consistently showed more roughness and uneven breaks with die pressed samples. This is likely due to the forced packing of alumina particles under high stresses. Alumina, having an anisotropic unit cell, will react to stress and heat differently in different directions, and this could also have led to clustering and non-random packing of particles before sintering.[11] When stress tested, the die pressed bars likely fractured along the lines of these clusters of similarly oriented particles. This is an inherent problem with die pressing that is not found in slip casting, which allows for random packing of powder particles.

Sintering and deformation

A majority of the slip cast and die pressed bars were severely deformed into an arch shape during sintering. Figure 4 shows a characteristic bend that most bars had during testing. This curvature already disqualifies the standard assumptions made when calculating 3 point bend tests, but data were gathered and reported on anyway.[14] It is also significant to note the direction that each bar deformed. Die pressed bars are expected to have some bowing that was detected due to the uneven pressure distribution inherent in uniaxial die pressing.[15] Different densities of grain packing will lead to different amounts of shrinkage during sintering, which led to irregular bar shapes. Alternatively, the slip cast bars seemed to deform such that the largest amount of shrinking happened toward the heating coils of the sintering furnace. The bars on the left of the furnace would arch toward the left heat source, and the bars on the right would arch to the right heat source. The slip cast bar in the center of the furnace had remarkably little deformation, and the degree of deformation increased with bars as they neared either edge of the furnace. This effect was anomalous, and could potentially be explained by the temperature gradient in the furnace. It is possible that sample faces exposed more directly to heat sources experienced more effective sintering, and in turn, shrinkage. If this were the case, the problem could potentially be fixed by using convection heating mechanisms, or by rotating the bars 90 degrees in the oven so that only their smallest faces are directly facing the heat sources.

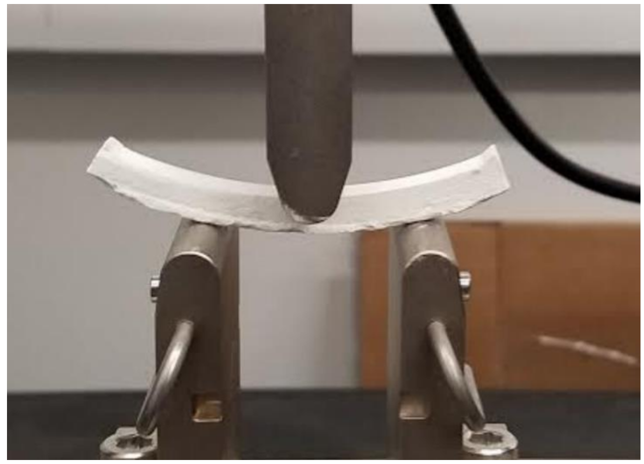

Figure 4: 3 point bend test of a slip cast bar. Bars from both slip casting and die pressing tended to have substantial bowing, as can be seen in the image.

Conclusion

The experiments run in this lab were performed to produce ceramic test bars using two methods, slip casting and die pressing. These two methods were compared with each other in an attempt to conclude which process produced higher quality bars in terms of Weibull's modulus and fracture surface analysis. Initial conditions based on research literature were used to produce standard quality bars for both die pressing and slip casting. Data collection from three-point bend tests performed on both die pressed and slip cast bars was compared against each other to find differences in bar strength and fracture surfaces.

The resulting data analysis showed an overall greater average strength in the die pressed bars. The die pressed bars required more force to break and had a calculated Weibull modulus nearly 70% greater than that found from the slip cast bars. Based on these results, the recommended process for manufacturing load-bearing alumina ceramic bars would be die pressing.

This result does not coincide with results seen in literature. The difference in experimental results is most likely a byproduct of an unrefined process in the creation of the slip cast bars. As mentioned above, the many steps required to produce a complete slip cast bar create more opportunities for error. Future experiments should focus more on proper mold creation, slip pouring, minimizing thermal gradients in sintering furnaces.

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