AN EXPERIMENT ON SINTERING CHARACTERISTICS OF COARSE NANO-SCALE ALUMINA FOR MANUFACTURING STUDENTS

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1. Introduction

This paper describes an elementary experiment designed to elevate student understanding of the basic powder metallurgy process through hands-on, team-based lab activities on ceramic sintering. The experiment is done as a part of the course *MFGE 343 Metal Casting, Ceramics and Powder Metal Processes*, which is offered as either a 2.0 or 3.0 credit option at the junior level to manufacturing engineers. The objective of this course is to gain a general working knowledge of the theory and practice of metal casting, powder metallurgy (PM) and ceramic forming. The objective is realized through a combination of traditional lectures, problem solving using engineering theory, and selected hands-on activities to reinforce a basic understanding of the processes. The principal PM lab activity is a study on the densification behavior of sintered ceramics, that is performed on a one- or two-week rotation cycle in a cooperative manner by student teams. Data are shared between teams, independently analyzed by each team, and presented in a written report that must also interpret the data in light of the theoretical knowledge. The activity is scheduled in the second half of the semester so that the theoretical development of topics could be synchronized with the lab.

This paper describes 1) the learning objectives of the experiment, 2) the basic experimental methodology, 3) summary and analysis of student-generated data from the last seven years, 4) an assessment of the lab's educational value as perceived by the students, and 5) work in progress to add further educational `value' to the experiment.

2. Learning Objectives

The primary objective is to learn, through hands-on activities, the influence of sintering variables on the densification of ceramics. The lab enables the students to explore the effects of sintering temperature, sintering time, and compaction pressure on the density, porosity, and linear shrinkage of a technologically ascendant nano-ceramic. It requires the students to utilize MgO-doped alumina powders finer than those for which densification data are available in popular textbooks [1,2]. For example, the effect of sintering temperature (1200 – 1600 C) on the densification of relatively coarse MgO-doped Al_2O_3 (mean size: 1,300 nm and 800 nm) has been presented in [1,2]. By utilizing finer nanoscale MgO-doped Al_2O_3 (nominal size: 380 nm) for densification over the same temperature (1200-1600 C) and time (0.5 h to 4.0 h) as presented in the standard books, the students actually supplement the textbook information with their own. The activity supports a learning objective of the ceramics unit of MFGE 343, which requires that the student should `…….*be able to generate and analyze densification data on powder compaction and sintering….*'

In order to establish meaningful activities centered on experiential learning of the theoretical material, a series of closely-related lab activities were developed over the last seven years[1]. Each activity was designed to present the students with a specific learning objective, and included: 1) the effect of compaction load on density and porosity in single-action compaction, 2) the spatial variation of density and porosity within a part prepared using double-action compaction, and 3) the effect of sintering atmosphere on densification (using Fe and Cu metal powders).

3. The Experiment

High-purity alumina (doped with 0.05% MgO) was chosen for the student project because it is the best studied ceramic. The alumina powders specified as RC-HPF DBM were provided by Reynolds Metals Company (Bauxite, AR). The average particle size (from sedimentation analysis) was 380 nm, and the specific surface area (from the BET method) was 8.19 $m^2.g^{-1}$; these data were supplied by the manufacturer. The powder size analysis from sedimentation test shows that ~60% powders are finer than about 400 nm.

The equipment used by the students for this lab included: manual powder press (Carver, Inc.), punch and dies, sintering furnace (CM Rapid Temp), electronic balance, calipers, and ceramic carrier boats. Zinc stearate was chosen as the die lubricant[2].

A lab handout describing the experiment was given to students. The students were instructed in the use of the equipment through a demonstration. The number of pressed samples varied depending upon the class (and team) size in a given semester. Typically six to fifteen samples were pressed by each team either at a fixed load (20,000 lb) to obtain a consistent starting material or at several different loads (10,000 lb, 15,000 lb, 20,000 lb and 25,000 lb) to study the effect of load on densification. Sintering of Al_2O_3 was done in a programmable tube furnace under normal (air) atmosphere in the temperature range 1200 to 1600 C for different times (0.5, 1, 2 and 4 h). Each team had to compare the density, porosity and dimensional shrinkage of each sample before and after sintering. The sintered density, porosity, and percent linear shrinkage were calculated from weight and volume measurements. The percent bulk porosity[3] was estimated from: % porosity = $(d_{theor} – d_{exp})x100/d_{theor}$, where d_{theor} is the theoretical density of fully-densified alumina (d_{theor} = 3,970 $kg.m^{-3}$), and d_{exp} is the measured bulk density.

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[1] *These activities dealt with different aspects of the press-and-sinter process. Additionally, the theoretical discussion introduced the students to other PM processes as well, such as metal injection molding (MIM). Each semester the students also toured an industrial MIM manufacturing facility, and saw metal injection molding, debinding and sintering, and listened to the guest lectures by the practitioners.*

[2] *Early trials utilized polyvinyl alcohol (PVA) as a binder for alumina powders for better handleability of green compacts; subsequent runs, however, eliminated binder usage due to the time needed for blending.*

[3] *The actual measurements made by the students yielded only the bulk density and porosity in green and fired states; however, the theoretical development in lectures and assigned problems enabled the students to learn the procedure to estimate the open and closed porosity, apparent and true density, etc. from gravimetric measurements.*

4. Summary and Analysis of Student-Generated Data

4.1 Densification of sintered alumina: Figure 1(a) shows the average density of MgO-doped Al_2O_3 as a function of sintering temperature for four different sintering times. The data are based on measurements on three-hundred and thirty alumina specimens sintered over a span of seven years. The data replicate the well-known `S' shaped densification curve for ceramics [1,2]. The densification is accompanied by a decrease in the total porosity content with increasing temperature (Fig. 1(b)), exhibiting a trend opposite to that of the density, with near-zero porosity (full-densification) being attained for 380 nm size powders at ~1450 C. The effect of sintering time on densification, Fig. 2, shows that densification is rapid at higher temperatures (1450 C) than at lower (1350 C) temperatures, which is a consequence of the thermally-activated mass transport mechanisms of sintering. On a logarithmic scale, these data exhibit a linear trend that is consistent with a power-law relationship of the form $d = k.t^m$, where d and t are the density and time, respectively, and m and k are empirical constants. The theoretical instruction on the effect of sintering time required the students to understand and apply (through exercise problems), an empirical densification rate equation to the literature data.

Further analysis of the data of Fig. 1 would be useful for students majoring in Materials science and engineering. For example, the role of thermal activation during sintering can be revealed more clearly in an Arrhenius plot of the experimental data as natural logarithm of the density versus inverse temperature (Fig. 3). Two distinct linear regimes, each consistent with a formal Arrhenius-type relationship (i.e., $d = d_0.\exp[-Q/RT]$, with d and d_0 being the density at a temperature T and at room temperature, respectively) can be identified in Fig. 3 over different temperature ranges. A somewhat abrupt transition (slope change) occurs between these regimes at a critical temperature (~1400 C or 6.0×10^{-4} K^{-1}). Such slope transitions in a thermally activated process indicate a change in the activation energy, and consequently, a transition in the dominant mechanisms driving the process. A sintering mechanism with a low activation energy seems to operate above the critical temperature of 1400 C, and a mechanism with a high activation energy appears to operate below 1400 C. The detailed mechanisms of sintering were, however, not presented in the theoretical discussion for manufacturing students[4], but the importance of thermal activation and diffusional mass transport was emphasized through solved problems and exercises.

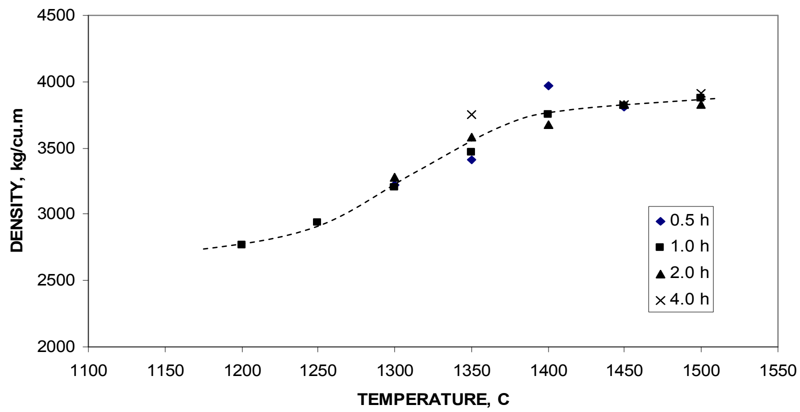
4.2 Additional Activities to Support the Learning Objectives

4.2.1 Powder Densification: Single-Action Compaction

Whereas all the alumina samples used for sintering were pressed via single-action compaction at a fixed (20,000 lb) load, several student teams were asked to press samples at different loads (10,000 lb, 15,000 lb, 20,000 lb, and 25,000 lb). The idea was to generate the well-known

[4] *A discussion of the role of transport processes at grain boundaries, surfaces and interfaces, and in the vapor- and bulk phases would be more useful for materials science and engineering students. Fundamental similarities of different thermally-activated processes were, however, highlighted in some manufacturing process courses (e.g., in the course MFGE 383 Coating and Finishing, the students learn that the rate of coating deposition in CVD follows an Arrhenius type behavior, and that a transition in the deposition rate at a critical temperature occurs due to the dominant mass transport mechanism changing from diffusion-control to interface-control. This course is taken by juniors usually in the spring semester following the MFGE 343 class in the fall semester).*

densification curve for green bodies. The mean green density and standard deviation for MgO-doped alumina (380 nm) from student work is plotted in Fig. 4 as a function of the compaction load. In spite of the considerable scatter in the data, there is a discernible trend, consistent with the theory, whereby the initial rise in the density subsides above a critical load (~20,000 lb in the present case), and a saturation density is eventually reached. In lectures, textbook data on densification of other ceramics were shared with the students to emphasize that this indeed was a general behavior for powdered materials. The scatter in the data is caused due mainly to the difficulty in handling the fragile green test samples, a rather crude method to estimate the density, and the variability in the extent of care exercised by students in handling and measuring.



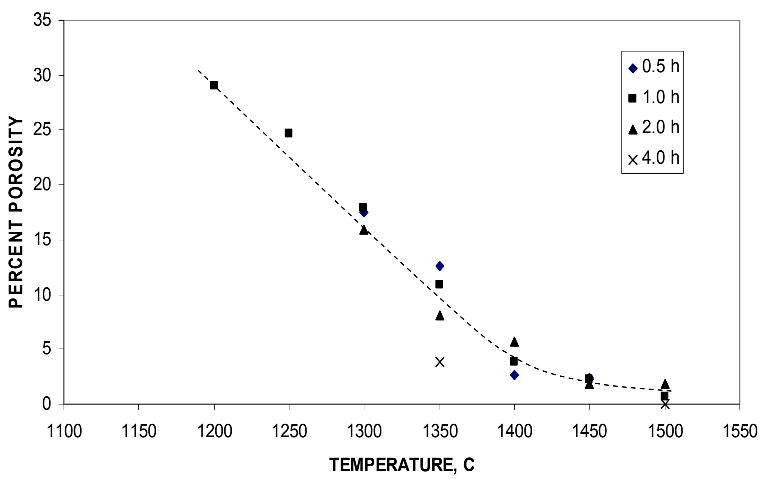


Fig. 1 (a) Average density, and (b) porosity of sintered Al_2O_3 as a function of temperature and time. Data are from student work on 330 separate samples from last seven years.

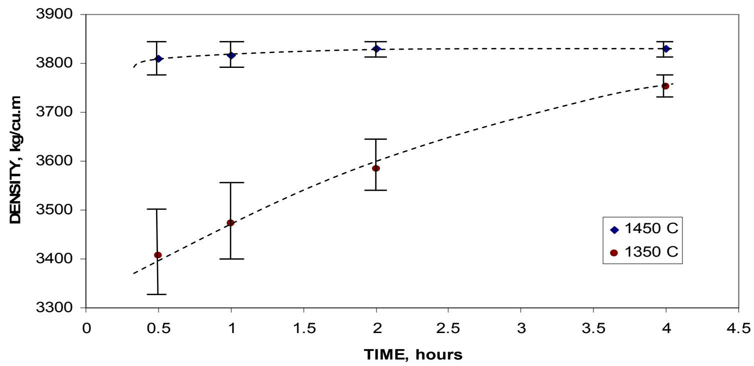


Fig. 2 The effect of sintering time on densification of Al_2O_3 at two different temperatures from student work.

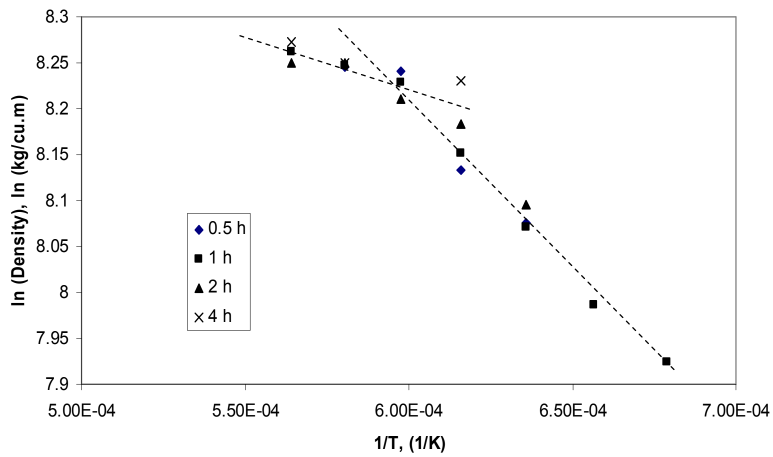


Fig. 3 An Arrhenius plot of the data of Fig. 1(a) showing linear densification regimes, and possible transition between these regimes.

In order to understand the effect of compaction load on the green strength for part handleability, students utilized a simple rattle test. The test measures the green strength (from weight loss measurements) of pressed parts after rattling the latter for a definite time in a desktop tumbler designed to be rotated in a gyratory motion. Measurements indicated that higher compaction loads generally yielded stronger green coupons as would be intuitively expected.

4.2.2 Powder Densification: Double-Action Compaction

The effect of compaction on density distribution was evaluated in Fe powders pressed in double-action mode in an open-ended cylindrical die using two movable punches. The pressed bars were carefully sectioned into thin slices on a low-speed saw, and each slice was identified as to the location it came from in the original bar. The bulk density (as % of theoretical density) of each disc was measured and plotted as a function of the distance from the punch (Fig. 5). The

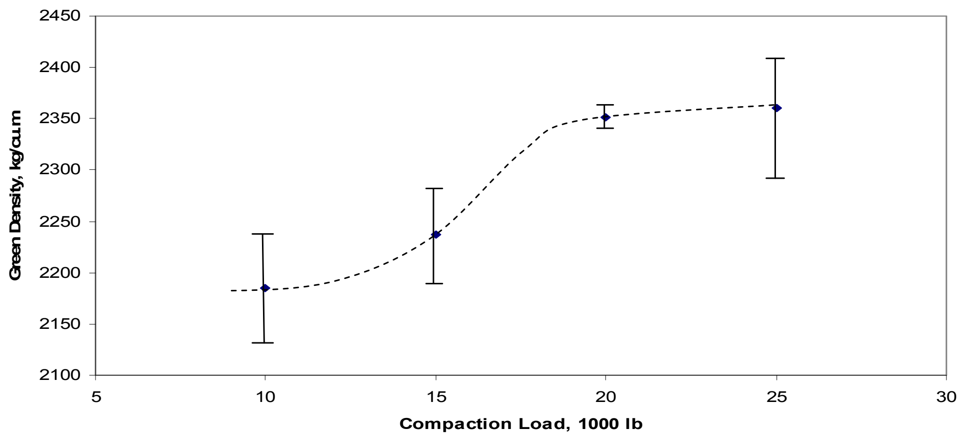


Fig. 4 Green density versus compaction load for MgO-doped Al_2O_3 from student work.

theoretical discussion and exercise problems in the class required the students to calculate the pressure distribution in both single- and double-action compaction. Figure 5 also shows the calculated pressure distribution (normalized with respect to a constant punch pressure) in double-action compaction, which qualitatively mimics the experimental density variation. The minimum pressure and minimum density occur at the mid-plane or neutral axis. This was done to illustrate the physical effects of attenuation of transmitted pressure with distance within the compact due to die-wall friction. Interestingly, whereas most students seemed to comprehend the standard mathematical derivation for pressure distribution (which requires knowledge of elementary calculus and mechanics), many students had difficulty grasping the meaning of the neutral axis

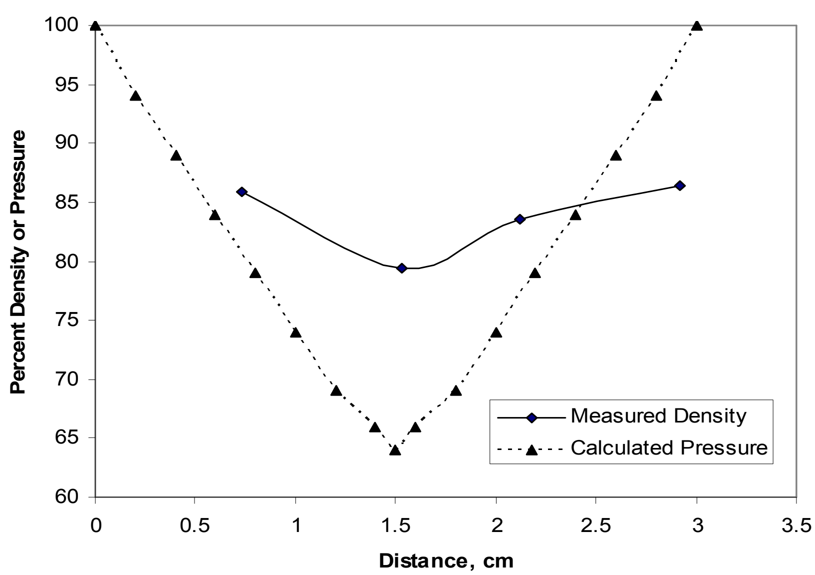
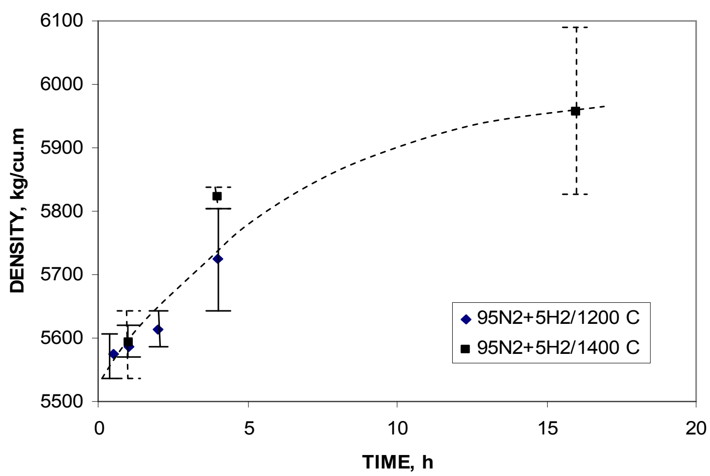


Fig. 5 Density variation and theoretical pressure distribution in double-action compaction in a Fe bar (friction coefficient=0.3, radial-to-axial pressure ratio=0.5, die diameter=2 cm).

as the plane at which the pressure gradient in the compact became zero (initially, many students understood this to mean that the pressure itself would be zero at the neutral axis). Another conceptual difficulty encountered by a majority of the students was related to the effect of die diameter on the level of compaction at a given depth. At first, most students intuitively felt that at a fixed depth, more compaction would be achieved in a small diameter die than in a large diameter die, until the contrary was shown to be true through an analysis of pressure distribution.

4.2.3 Sintering of Metal Powders – Effect of Atmosphere

The importance of a non-oxidizing sintering atmosphere for metal powders was emphasized in the theoretical discussion during lectures. Test were also performed on the effect of atmosphere on the densification behaviors of Fe and Cu powders. Unlike the Al_2O_3 that was sintered under normal ambient atmosphere, Fe and Cu powders were sintered either in an atmosphere of $5H_2+95N_2$, or under a cover of $50\%H_2+50\%N_2$. The results on sintering (Fig. 6) show that near-



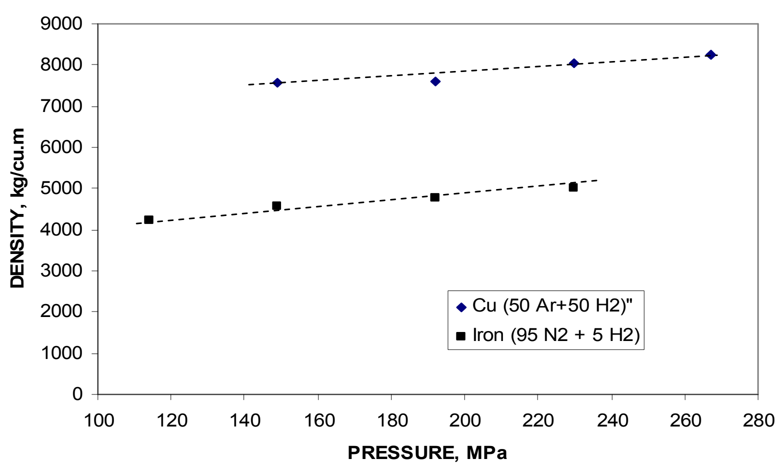


Fig. 6 (a) Density versus time for iron powders sintered at two temperatures, and (b) density versus pressure for iron and copper powders sintered under different atmospheres.

theoretical densities were achieved in Cu compacts at elevated temperatures under a protective atmosphere composed of equal fractions of H_2 (a reducing gas) and N_2 (an inert gas). For the iron compacts, complete densification could not be achieved in diluted forming gas ($5H_2$+$95N_2$), suggesting that a stronger reducing atmosphere (i.e., higher H_2 content) was necessary. Likewise, relatively better densification was achieved in pressed Fe coupons under a cover of forming gas ($5H_2$+$95N_2$) than in air atmosphere (as expected, in the latter case, there was virtually no densification due to extensive oxidation of the powders).

5. Student Assessment of the Project

Whereas a formal metric to assess the educational value of the experiment as perceived by the students was not employed in this study, student comments, documented in their project reports did provide some indication of both the usefulness and needed modifications in the activity. Student comments from their reports are reproduced below verbatim:

- *'The results look very realistic and conceivable'.*
- *'In conclusion, we would say that this was a good lab'.*
- *'This project backed up the information given in class. It was interesting to see where the information in class came from'.*
- *'This type of experiment can be used to further determine correct firing times and temperatures for other ceramic materials'.*
- *'Overall, the experiment proved very useful. It reinforced some ideas and principles that had been presented in class. It allowed for out of class research that normally would have been bypassed and real world experience with the reality of team of individuals following a timeline'.*
- *'In our estimation, PM is an effective way to control essential factors in parts, such as density and porosity, by simply manipulating a few variables like material used, pressure, temperature and time'.*

Several suggestions to improve the lab activity also emerged. These included:

- *'have one group member do all the compacting to achieve a more uniform density plot…each person in one group would press consistent densities, but there was variation between different group members' values'*
- *'Have one person press the parts on the same machine. Different people pressing and using different machines can give too much variation to the part'.*
- *'Time is a factor; get started early on the project as sintering takes a great deal of time'.*
- *'Plan enough time to complete the project ahead of time (pressing parts, sintering parts, and completing a report take a lot of time)'.*
- *'Use the same press for all trials'.*

Whereas the student concern about the variability of compaction between different teams is valid, it was felt necessary to have each group go through all the steps in order to benefit from a hands-on approach. Unlike an upper level course in which the reliability of the lab data can not be sacrificed at the expense of experiential learning (and different teams can be allowed to handle different aspects of a project), the course MFGE 343 provides the students a first exposure to ceramics and PM. This requires that all the students be able to gain appropriate lab experience. Some variability in the green density was caused due to the inferior handleability (low green strength) of pressed parts as compared to sintered parts (whose densities were higher and more consistent). In view of this, use of PVA as a binder might be reinstated in future lab projects on ceramic sintering. The recommendation concerning early start to the lab activity in the semester, while appropriate, is difficult to implement since the first quarter of the semester is devoted exclusively to foundry processes, and no introduction to ceramics is offered until the beginning of the second quarter. Given the time constraint to accomplish the stated course and lab objectives, the sintering lab was considered to be an adequate hands-on introduction for the manufacturing students. For each team, the entire project took approximately 12-15 hours to complete (excluding the time needed for sintering, which typically took 24 hours to complete each thermal cycle. Student presence during this time was, however, not required). Further educational value will be added to this experiment through data analysis and property characterization, as discussed below.

6. Work in-Progress

6.1. *Mechanical Properties:* The theoretical discussion in class introduces the students to the effect of porosity in sintered parts on the flexural strength (modulus of rupture), hardness, and other mechanical and physical properties. It is, however, planned to have the students characterize the hardness and flexural strength of their sintered samples and *discover* the quantitative relationship between the porosity content and the mechanical properties through active learning. Preliminary data on flexural strength of two hundred and fifteen student-sintered Al_2O_3 coupons from last several years are presented in Fig. 7; the basic trend agrees with the theoretical result in that the flexural strength decreases with increasing porosity content (rather precipitously at low porosity contents). For many ceramics, the flexural strength exponentially decreases with the porosity content, following the equation: $\sigma = \sigma_0.\exp(-nP)$, where σ and σ_0 are the flexural strength of the porous and non-porous ceramic, respectively, n is an empirical constant and P is the porosity. The student will test the applicability of this equation to their data. Due to the use of non-standard test coupons[5], however, the test results of Fig. 7 are not accurate and might not be used in actual part design. However, such data have educational value.

6.2 *Particle Size Effects on Sintering*: The effect of particle size on densification can be understood by students by comparing their data on fine alumina with the textbook data on coarse alumina [1,2]. Currently, the particle size effects are discussed in lectures and exercise problems, and it would provide educational value for the students to discover these effects themselves. Coarse and fine alumina will be sintered to study the effect of powder size. As an example, text book data on coarse (1300 and 800 nm) powders are superimposed on student data (from Fig. 1) in Fig. 8, which shows that fine (380 nm) powders exhibit faster sintering kinetics than coarse powders, consistent with the fact that the larger surface area of fine powders provides a larger driving force for sintering (i.e., minimization of surface area). Near-theoretical density (3970 $kg.m^{-3}$) is achieved in nearly 4 hours. However, coarse powders need higher temperatures to attain full densification. This suggests the importance of using fine ceramic powders for rapid or

[5] *The three-point bend test was done on non-standard round coupons. The flexural strength was calculated from the relationship for rectangular bars that are used in standard MOR tests on ceramics:* $MOR = 3F.L/2b.h^2$, *where F is the breaking force, L is the gap between the supports (0.55" in our tests as opposed to 1"in the standard test), b is the width of the specimen, and h is the specimen thickness.*

low-temperature sintering of ceramics. Moreover, the densification (or shrinkage) data on different size powders could be displayed in an Arrhenius plot (similar to Fig. 3) to identify the transition temperatures and relative magnitudes of activation energies for various nano-scale powders.

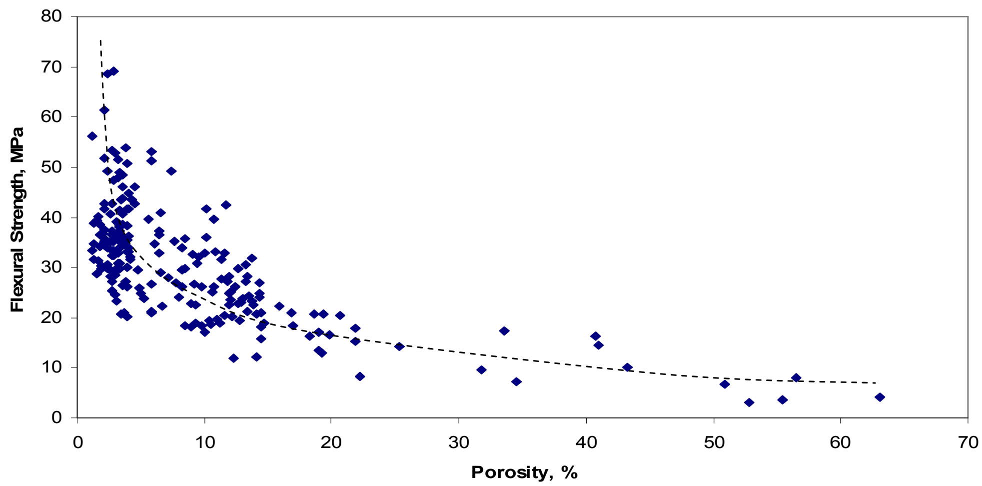


Fig. 7 Flexural strength versus porosity in MgO-doped alumina from student samples.

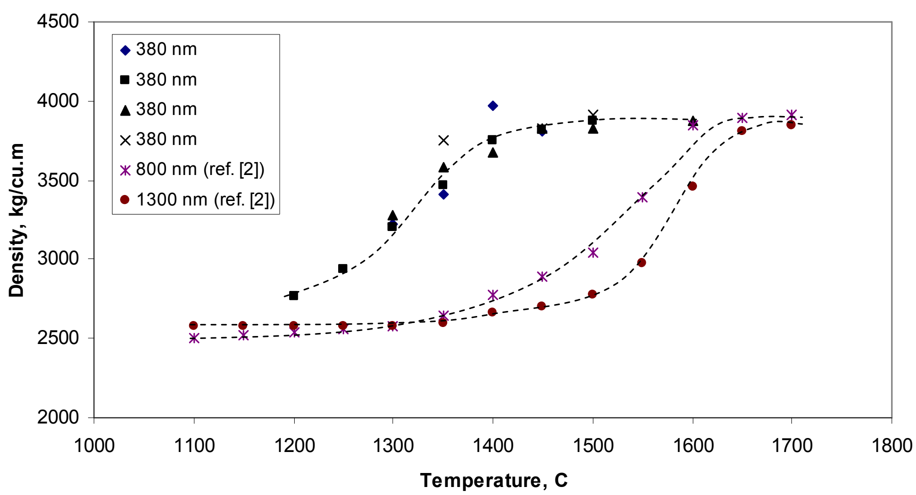


Fig. 8 Comparison of densification kinetics of coarse and fine MgO-doped alumina powders. Data for 1300 and 800 nm powders are from ref. [2].

Overall, the sintering project described in the paper allows active and cooperative approaches to be incorporated in teaching powder metallurgy principles. Preliminary student comments confirm the project's usefulness in learning the new material. Recent studies [3] show that active learning approaches in introductory materials science courses lead to increased knowledge and comprehension. Furthermore, retention and depth of learning improve through active participation in group work, and the opportunity to work in teams improves the communication and social skills. Additionally, the experiment exposes the students to advanced materials such as nanoceramics, in line with the current efforts in academia to incorporate novel and emerging materials and technology in engineering curricula [4,5].

7. Summary

An elementary experiment on the densification of fine alumina ceramics by powder compaction and sintering was described. The learning objectives, principal lab activities, an analysis of student-generated data from the last seven years, and student assessment of the lab, were presented. Overall, the student evaluations were positive, generally confirming the educational value of the activity. Some methodological concerns in the execution of the lab also emerged from student assessment. Work in progress to add further educational `value' to the lab activity was discussed.

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References

1. W.D. Kingery, H.K. Bowen and D.R. Uhlmann, Introduction to Ceramics, 2nd ed., John Wiley & Sons, Inc., New York, 1976.
2. J.S. Reed, Principles of Ceramic Processing, John Wiley & Sons, New York, 1988.
3. C. Demetry and J.E. Groccia, `A comparative assessment of students' experiences in two instructional formats of an introductory materials science course', *J. Engineering Educ.*, 86(3), 1997, 203.
4. N. Yu and P.K. Liaw, 'Ceramic-matrix composites: An integrated interdisciplinary curriculum', *J. Engineering Educ.*, 87(5), 1998, 539.
5. `All things great and small' (nanotechnology major at University of Toronto), *ASEE Prism*, Nov. 2002.

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