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Measurement of agglomerate strength distributions in agglomerated powders

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Iowa State University, 1987
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Measurement of agglomerate strength distributions in agglomerated powders

by

Muhsin Ciftcioglu

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

Approved:

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In Charge of Major Work

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For the Graduate College

Iowa State University
Ames, Iowa

1987
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GENERAL INTRODUCTION

Ceramics are playing an increasingly important role in today's high technology industries, and most technical forecasts predict that their ultimate impact upon modern technology is just beginning to be realized. They are hard and chemically resistant, and are able to maintain these properties at high temperatures. As structural materials, they are generally lighter than their metallic counterparts. They also may have a wide range of electrical properties, electro-mechanical properties and electrooptic properties. This makes them useful as insulators, semiconductors, superconductors, sensors, and transducers. It also accounts for the fact that the electronics industry is the major consumer of ceramics products today.

The use of ceramics as structural materials, especially in hostile environments and at high temperatures, also will increase in the near future. Increasing the efficiency of energy conversion processes can help to relieve the strain on our dwindling energy resources. New high-performance ceramic materials can help; their use can permit these processes to be operated at the higher temperatures necessary to achieve substantially greater thermodynamic efficiencies. The major impediment to their widespread use lies not in our inability to fulfill the necessary design requirements, or to overcome their inherent brittleness, but in our inability to prepare them in commercial quantities with reproducible properties. Thus, a major research effort is concentrated on improving reproducibility, so that the great potential of ceramics can become a reality. Currently the cost of reject material may constitute a
major, and in some cases, the major operating cost of a high-performance ceramic manufacturing facility.

The production of nearly pore-free ceramic materials with uniform microstructures is essential in high-performance applications. The general ceramic fabrication scheme involves preparing the powder, forming the green compact, and sintering it to final form. The powder preparation steps, which may involve chemical precipitation, drying and calcination, are considered to be crucial operations in the production of high quality ceramics. Strangely enough, this was not always thought to be the case. Only in relatively recent years has the importance of the powder preparation steps come to be realized. This recognition of the importance and the interrelation of all the processing steps in making a ceramic material has caused the words "Ceramic processing" to be coined to describe, collectively, all of these operations. One of the major fundamental questions yet to be answered, as put forth in a recent report on Ceramic Processing (1) is, "What are the interparticle forces and mechanisms that cause particle agglomeration during processing ?". Answers to such questions fall into the domain of the colloid chemist. Related questions are "What is the effect of agglomerates in ceramic processing ?", "How can agglomeration be best controlled ?", and "How can agglomerates be characterized in a quantitative fashion ?".

The presence of relatively strong agglomerates, which do not break down upon compaction, can give rise to a nonuniform pore size distribution in the green compact. The coarse pores remain as pockets of porosity after sintering and thus the sintered ceramic has a nonuniform density. Uniform particle packing is necessary to achieve fully dense materials. Controlling the degree of agglomeration and the strength of
the agglomerates permits much greater control of the properties of the sintered product.

This work was carried out in order to find a means of measuring, in a quantitative fashion, the strength distributions of agglomerated particles in ceramic powders. The increasing number of papers which have appeared in the literature in recent years describing the adverse effects of agglomerates in ceramic powders have been necessarily qualitative because there has been no way of quantifying agglomerate strength.

**Powder processing**

Powder processing is the name given to the preparation and conditioning of powders in a number of different fields such as ceramics, catalysis, electronics, powder metallurgy, etc. Ceramic powders can be prepared in many different ways. Mechanical comminution, or the reduction of bulk materials into finer particles by grinding, is the oldest method of powder preparation. It is inexpensive, but not very suitable for ceramic powder preparation. Dusting may create a health hazard, the comminuted particles are angular and rarely equiaxed, and the operation inherently produces a broad particle size distribution.

Chemical techniques for powder preparation can yield fine, homogeneous material with closely controlled purity, homogeneity and particle properties (2). Chemical methods can be classified into two major categories: vapor-phase techniques and solution techniques.

Most vapor-phase methods can yield fine, unagglomerated or weakly agglomerated powders, and are receiving attention currently as a means of preparing nonoxide structural ceramics such as silicon carbide and silicon nitride.
The simplest of the solution techniques involves removal of the solvent from an aqueous or organic-based solution containing dissolved salts (precursors) of the desired materials. Techniques such as codecomposition, emulsion drying, spray drying, citrate processing and freeze drying are examples of this kind of processing. There are a number of excellent reviews on these and other chemical techniques for ceramic powder preparation (2-6).

Precipitation from solution, removal of the solvent by filtration and decomposition of the solids to the desired product is the oldest and most common chemical method for ceramic powder preparation. Important variables such as pH, direction of solution mixing, stirring rate, reactant concentrations, temperature, and method of washing, filtering, and drying the precipitates, can change the powder characteristics drastically.

It is now believed that an ideally sinterable powder should have fine, equiaxed, unagglomerated, submicron size particles with a narrow size distribution. Homogeneous precipitation from solution by controlled generation of the precipitant, in situ, can yield very small, monosize particles which are spherical in most cases (7-10). The use of these powders, if they can be closely packed together, can yield uniform green microstructures and high density green compacts which will sinter to high densities.

The nature of agglomerates and their effects on powder behavior

Contemporary ceramic manufacturing operations involve fine powders in the 0.1-10 μm range. Such fine powders always contain agglomerates. It is routine to control powder characteristics such as surface area and
particle size distributions, and it is important to keep these properties within desired limits. However, it is now well recognized that, more important than these, the nature of any agglomerates present may often play an even more important role in determining the behavior of ceramic powders (11,12). Agglomeration in ceramic powders can be both beneficial and deleterious, depending on the process and the type of agglomerate. A fine, fluffy powder may be intentionally agglomerated by a process such as spray drying to create free-flowing granules which enhance packing, but which are easily crushed when the powder is pressed.

A number of physical characteristics of the agglomerates are important. In an agglomerated powder, the microstructure, strength, size and size distribution of both the agglomerates and the particles from which they are formed, and the nature of the bonds between the particles in the agglomerate dictate the powder's ability to yield desirable ceramics (13,11). All of these may affect the processing cycle, but the most important characteristic is the nature of the adhesive bonds, which determine the strength of agglomerates. Van der Waals forces, adsorbed moisture, or binders used in granulation may result in weak agglomerates. The most common and deleterious type of strong agglomerates are those with solid bridges formed during calcination or initial stage sintering. Phase transformations during calcination can also produce strong agglomerates.

The nature of agglomerated particles in a powder determines its compaction behavior. The production of high density, high quality ceramics depends on the ability to form a high density compact with a uniform pore size distribution (14). This is often difficult to do with agglomerated powders, which may pack nonuniformly. Agglomerate
deformation and fracture, filling of coarse pores, and 'knitting' of agglomerates are essential to achieve compacts of the high quality required for the manufacture of technical ceramics.

The packing density of loose powders is very low for fine powders, a phenomenon due primarily to the presence of weak agglomerates. Granulation may be used to increase the low bulk densities of these powders. Dry or semi-dry pressing of ceramic powders in a die is one of the most widely used forming operations in ceramic industry, and granulation facilitates flow of the powder into the die.

Strong agglomerates, which resist compaction, in powder compacts are widely known to retard sintering (15). Rhodes (16) studied the sintering characteristics of yttria-stabilized zirconia and found that the existence of agglomerates inhibited the sintering kinetics. Herring (17) predicted that using fine powders could enhance sintering kinetics, and formulated laws which are known as Herring scaling laws. The rate of densification is inversely proportional to some power of particle size. Although there is still confusion over whether the agglomerate size or the crystallite size is the most important to consider in sintering, crystallite size seem to be the important factor when the Herring scaling laws are considered (18). Milling can reduce the size of agglomerates, or may even break them up into their primary constituents. In both cases the decreased particle size enhances densification.

An agglomerate free compact must be produced in order to derive full benefit of the Herring scaling laws. Rhodes (16) has shown that agglomerates control the final sintered densities which could be achieved for very fine yttria-stabilized zirconia. He presented micrographs showing that during sintering the dense agglomerates pulled away from the
surrounding matrix, leaving a lenticular crack where the agglomerate became partly detached from the matrix. This adverse effect increased with increasing agglomerate size. A fine, agglomerate-free centrifuge-casted powder compact sintered to theoretical densities about 300°C below the normal sintering temperatures.

Pores that are much larger than the average particle size can not be removed during sintering because there is no driving force for elimination of such oversize porosity. This nonuniformity in the green body results in inhomogeneous sintering, leaving both dense and porous regions in the sintered body. Sintering studies on alumina and zirconia compacts have shown that specimens initially of high density, but containing pores much larger than the average particle size, sinter to less than 95% of theoretical density.

Pressed compacts with a broad range of pore sizes, inhomogeneously distributed, also are difficult to sinter to high densities, whereas compacts with a uniform distribution of pores smaller than the average particle size exhibit optimum sintering behavior (15,19). Powders containing agglomerates which are strong enough to resist the usual compaction pressures usually form compacts with a broad range of pore sizes. During sintering of these compacts the denser areas reach a limiting density and pockets of porosity remain (13). Rapid grain growth is inevitable in the dense regions because there is no porosity to control grain growth in these areas.

The attainment of uniform, fine grain size and high sintered densities, both of which are necessary to reach high mechanical strength in the product, depends strongly on the starting green density, and this is adversely affected by the presence of agglomerates. Vasilos and
Rhodes (20) pressed different yttria-stabilized zirconia compacts from powders with different agglomerate sizes and found that, in their sintered specimens, the nonuniform pore structures were spaced at intervals very close to the agglomerate sizes. When the agglomerates were removed by sedimentation from a suspension of the powder, so that only the basic crystallites remained, the resulting powder sintered to 99.5% of the theoretical density, with an average grain size of only 0.2 μm at a temperature of only 1100°C, which is 400°C below the normal sintering temperature. Similar results were obtained for yttria-stabilized zirconia (21-23); sintered specimens prepared from deagglomerated powder had fine, uniform grain sizes with significantly higher flexural strength.

Burke et al. (24) studied the role of particle size distribution in the sintering of UO₂, concentrating on the analysis of the entire particle size distribution curve, rather than on a single number (mean value etc.) to characterize the powder. The powders were examined after gently dispersing them, and then after treating them ultrasonically. Cumulative mass particle size distribution curves were differentiated and the peaks fitted to normal distributions. They observed that ultrasonic treatment essentially reduced the coarse fraction into fine and medium size fractions. The sintered density increased with increasing fraction of fine particles; the ultrasonic energy promoted deagglomeration in this study.

In an earlier application of ultrasonic energy to the investigation of agglomerated particles, Johnson et al. (25) used an ultrasonic probe to determine the fraction of strong agglomerates present in a series of commercial alumina powders. They found that the fraction of strong
agglomerates affected the flow properties of the powder, its pressed density, and its fired density. They also speculated that the strong agglomerates may have been the cause of low density defects in otherwise dense alumina electronic substrates. They used wet sieving, and called the fraction of powders resistant to dispersion on coarse sieves the fraction of "hard (strong)" agglomerates.

Roosen and Hausner (26), working with calcia-stabilized zirconia, found that agglomerates interfered with the formation of a homogeneous microstructure. They claimed that freeze drying, which they used in their study, prevented the formation of strong agglomerates and led to a homogeneous pore structure in the powder compacts. Another study, by Tremper et al. (27) on alumina powders, concluded that it is necessary to mill the powders to break the agglomerates, and that the median agglomerate size after milling should be less than 2 μm.

Sintering kinetics also are affected by the presence of agglomerates. Dynys and Halloran (28) found that strong agglomerates in alumina powders decreased the shrinkage rates in isothermal initial stage sintering by as much as a factor of 10. Similar observations were made for intermediate and final stage sintering.

Both strong and weak agglomerates can cause inhomogeneous shrinkage around isolated regions, and thus create local microstresses (29). Reeve (30), working with BeO, was the first to observe and photograph examples of nonuniform shrinkage due to agglomerates. Kellett and Lange (31) also observed and photographed this phenomenon in alumina-zirconia composite powders. They found that cold-pressed and sintered material was only about half as strong as hot pressed powder even though it sintered to greater than 98% of theoretical density. Large (50-500 μm), irregular,
low-density areas were found on cut surfaces of the samples, the result of poorly sintered agglomerates. However, these areas were not the fracture origins. Instead, the strength limiting flaws were large, crack-like internal surfaces caused by differential sintering of agglomerates. By preparing special samples containing agglomerates of known density, they discovered that agglomerates whose density was less than that of the surrounding matrix would densify more rapidly, separating from the matrix as they shrunk, and leaving an internal crack in sintered samples of otherwise high density. These cracks could be minimized or eliminated by hot isostatic pressing and the strength limiting flaws in the materials then became the low density regions left by the poorly sintered agglomerates.

Lange and Metcalf (32) also found that if the agglomerates were denser than the surrounding matrix, the more rapidly densifying matrix would exert a compressive force on the agglomerates and, often, radial cracks would appear in the matrix around the agglomerates. In addition, they found that high density agglomerates could move within the compact during sintering, a result caused by the slightly nonisotropic distribution of the compressive forces exerted on the agglomerate by the more rapidly densifying matrix surrounding it. Their studies showed that agglomerates are not only detrimental from the standpoint of sintering behavior, but are also detrimental in attempts to achieve a strong structural ceramic.

In summary, the overwhelming evidence of these studies on the behavior of agglomerated powders shows conclusively that better control of agglomerate structure, or even finding a method of completely eliminating agglomerates, can be the key to improving the properties of
sintered ceramic materials.

**Powder compaction**

Die compaction is one of the methods by which ceramic powders are pressed into a wide range of shapes (33-35). The mechanism of powder compaction is considered to be a two stage process. The first stage involves sliding of particles past one another to fill those holes which are of the same order of magnitude as the particles themselves. The second stage involves filling of smaller voids by fragmentation and crushing of the original particles. A four stage compaction mechanism for porous, agglomerated (granulated) powders involves filling of pores between granules, fragmentation of granules, filling of pores between primary crystallites and fragmentation of primary crystallites (34).

Compaction studies can be carried out either manually or automatically. In the manual technique, powders are pressed under a variety of pressures and the density calculated from the dimensions and mass of the resulting pellets. One sample is needed for each pressure in order to obtain an accurate and representative curve of a continuous pressing operation. This technique is sensitive to operator errors. The same data can be obtained automatically by using an Instron machine to obtain a continuous recording of the stress vs strain curve under constant strain rate as the powder is pressed. This method produces the pressure-density (compaction) curve directly; only one sample is required and operator errors are reduced.

Recent studies (13,14,19,23,36-40) suggest that powder compaction data can give qualitative estimates of the strength of agglomerates and granules, but are of limited value in providing quantitative information
about agglomerate strength.

Duckworth (41), in 1953, suggested that the strength-porosity relation in ceramics could be described by an equation of the form:

$$\sigma = \sigma_0 \exp(-BP)$$

where $\sigma$ = strength of porous body

$\sigma_0$ = strength of nonporous body of the same material

$P$ = porosity expressed as a fraction of total volume

$B$ = an empirical constant.

Niesz et al. (19), in an attempt to put the use and interpretation of compaction curves on a more fundamental basis, assumed that Duckworth's semi-logarithmic relationship between mechanical strength and porosity was analogous to the semi-logarithmic relationship between pressure and density obtained in compaction. Since compaction pressure can be thought of as the isostatic compressive strength of a powder at the compacted density, the compaction pressure-density data should be similar to strength-porosity data.

Usually, compaction curves have two linear portions. In the low pressure region, compaction is believed to be due to particle rearrangement, which is controlled by particle-particle friction. The breakpoint between the two linear portions is due to the onset of granule or agglomerate break-up. Compaction in the high pressure region beyond the breakpoint then occurs by rearrangement of smaller particles formed from crushing of the agglomerates.

On the basis of these observations, Niesz (19) concluded that
compaction pressure data can show the presence or absence of agglomerates. The pressure at the breakpoint was used as an estimate of the minimum value of the agglomerate or granule strength (42). If the compaction curves for granulated (agglomerated) and bulky (unagglomerated) powders are plotted on the same graph, they intersect at a pressure which is called the "joining pressure". At this point the coarse intergranular pores are eliminated. Depending on the constitution of the powder, the breakpoint pressure can be low (<1 MPa) for powders granulated with organic binders, or high (>5 MPa) for powders containing strong agglomerates (42).

Using compaction data obtained for stabilized zirconia, Pampuch and Haberko (43) tried to relate observed breakpoint pressures to the strength of intraparticle crystallite-crystallite bonds through the Rumpf equation. For an agglomerated yttria stabilized zirconia powder, they obtained a value of 1.76 GPa for the strength of the crystallite-crystallite bonds. This value was found to be close to 1% of the Young's Modulus, E. A general "rule of thumb" in the evaluation of the strength of ceramics is that the theoretical strength of ceramic bonds is about 10-20% of the Young's Modulus and the actual achievable strengths are around 1% of theoretical strength values. Their estimated value falls between the above two approximations. However, this is a rough estimate and may not be valid for other powder compaction data.

Compaction data produced continuously with a mechanical testing device can be used to characterize the powder compaction process and can give reproducible results. However, such curves cannot be utilized to show the presence or absence of small quantities of agglomerates in ungranulated powders, because there may not be an interconnected
pressure-transmitting network (42). Although these curves may be useful for granulated powders, the breakpoint pressure depends strongly on how the pellets are prepared for testing. For agglomerates, which may have a wide strength distribution, a clear breakpoint in the pressure-density compaction curve may be difficult to discern.

**Agglomeration**

Agglomeration occurs naturally in a powder because of adhesion forces which act between fine particles. Gravity forces acting on particles larger than a centimeter in size are much larger than the natural adhesion forces between particles; but gravity forces decrease rapidly, by the third power of particle diameter, while adhesion forces decrease by the first or second power of diameter.

The principal bonding mechanisms in agglomerates and in all forms of size enlargement processes are (44,45):

1. Attraction forces between solid particles
   a) Molecular Forces: Van-der-Waals forces, Chemical binding forces (valence forces)
   b) Electrostatic Forces.
   c) Magnetic Forces.

2. Interfacial forces and capillary pressure at freely movable liquid surfaces.
   a) Liquid bridges.
   b) Capillary forces at the surface of agglomerates filled with liquid.

3. Adhesion and cohesion forces in binders not freely movable.
   a) Viscous binders.
b) Adsorption layers (below 30-50 Å thickness)

4. Interlocking bonds in fibers, flat-shaped and bulk particles.

5. Solid bridges.
   a) Chemical reaction.
   b) Partial melting.
   c) Hardening binders.
   d) Crystallization of dissolved substances.
   e) Sintering.

Van-der-Waals forces, electrostatic forces, and liquid bridges are the most thoroughly studied bonding mechanisms. The strength of bonds formed between particles increase approximately from bonding mechanisms 1 to 5. Electrostatic forces are about an order of magnitude lower than Van-der-Waals forces. Liquid bridge forces are several times greater than Van-der-Waals forces.

Sintering is a research field of its own. The bonds formed between particles forming the agglomerates due to sintering are formed in the initial stages of sintering. The strength of bonds formed between particles is a function of particle size, surface tension, temperature and the amount of additional compressive forces on the particles. Usually the calculation of the sinter neck radius is difficult because of the complexity of the transport mechanisms that occur in sintering processes.

Most of the work done on the theoretical and experimental estimation of the strength of agglomerates, and the determination of the contributions of different bonding mechanisms, are done on spherical or cylindrical pellets made from powders of known properties. The various powder or pellet characteristics (e.g., pellet size, mean particle size
of the powder, amount of binder used in granulation, drying temperature of the granules, saturation ratio in liquid bridges, void fraction etc.) are correlated with the experimentally found pellet or granule strengths. Ideal conditions (spherical shape, monosize particles, uniform binder distribution etc.) are assumed in the theoretical derivations of the tensile strength of the granules; such ideal conditions are not usually encountered in real systems.

Rumpf (46) derived one of the best known equations for the determination of the strength of granules and agglomerates; the equation bears his name. He assumed that the granule is formed from monosize spherical particles. The basic assumptions made in this derivation were the existence of a very high number of bonds in the stressed region, a uniform distribution of bonds across the stressed section, and a uniform spacial distribution of both spherical particles and interparticle bonds in the granule. He further assumed that the effective bonding forces can be replaced by a constant mean force. Using the geometry and uniform distribution of spherical particles in the stressed cross-section of the granule, he estimated the number of bonds and multiplied the result by the mean bonding force.

The Rumpf equation may be stated as:

\[ \sigma = \left( \frac{9}{8} \right) \left( \frac{(1-\varepsilon)/\pi d^2}{kH} \right) \]

where \( \sigma \) is the tensile strength of the granule, \( H \) is the force required to break each bond, \( \varepsilon \) is the void volume fraction, \( d \) is the particle diameter and \( k \) is the coordination number (average number of particles touching each particle). For the determination of the coordination number the simplest relation is:
Inserting this relation into the tensile strength equation gives the usual form of Rumpf equation:

$$\sigma = 1.1 \left( \frac{(1-\varepsilon)}{\varepsilon} \right) H/d^2$$

The theoretical strength of a material can be defined as the tensile stress required to break atomic bonds and pull the structure apart. The theoretical strength of ceramic bodies under tensile loading can be estimated by using the equation (47):

$$\sigma_{th} = \left( \frac{E\gamma}{a_0} \right)^{0.5}$$

where $E$ is the elastic modulus, $\sigma_{th}$ is the theoretical strength, $a_0$ is the interatomic spacing, and $\gamma$ is the fracture surface energy. The Young's Modulus for yttria, the material most used in the present work, decreases with porosity and temperature (48-50). For theoretically dense yttria, the Young’s Modulus is 1715 kbars (2.55x10^7 psi) at room temperature. The fracture energy is grain size dependent (51) and is approximately 4632 ergs/cm^2 for yttria with a grain size of 5 µm. Taking $a_0=10.6$ Å, the theoretical strength of yttria will be:

$$\sigma_{th} = 3.97 \times 10^6 \text{ psi} \ (2.7 \times 10^5 \text{ atm.})$$

However, the theoretical strength of a ceramic material is never actually achieved because of the presence of flaws which concentrate stresses and lead to fracture at load levels much lower than the theoretical value.
The actual fracture strengths of most ceramics are only about one percent of the theoretical value. Theoretical strengths of ceramic materials vary from 0.1–0.2 E (47). The compressive strength is usually much higher than the tensile strength, and increases as the grain size decreases.

Treatment in ultrasonic fields

The technique developed in this work for measuring agglomerate strength is based upon fracture of the agglomerates in an ultrasonic sound field. Sound waves, whether sonic or ultrasonic, are fluctuations in the ambient pressure in the medium through which they are transmitted. The total instantaneous pressure of a plane progressive sound wave is largely a function of the amplitude of the pressure fluctuations and frequency of the sound wave. Two types of transducers—magnetostrictive and piezoelectric—are used to convert electrical energy into high power ultrasonic energy.

When rapid fluctuations occur in a medium, cavitation may take place. It is the sudden expansion and subsequent collapse of existing tiny gas bubbles in a liquid under the action of a passing sound wave. High amplitude shock waves produced by the collapse of these spherical cavities have been experimentally observed (52). Very high temperatures and pressures can be obtained very close to the collapsing bubble. One of the basic problems of research on acoustic cavitation is the determination of these pressure and velocity fields around and inside of the collapsing bubble (53).

The forces created by cavitation are widely used for cell disruption, depolymerization, and dispersion of solids in liquids or of two
immiscible liquids. In contrast to the wide variety of applications of ultrasonic irradiation of materials, there are only a few studies on the mechanism of the process involved. Acoustic liquid-liquid emulsification has been studied widely, and the disintegration of one phase into another is attributed to the action of impact forces from shock waves resulting from the collapse of cavitation bubbles (54). For a given intensity of the cavitation shock wave, the droplets will reach a critical stable diameter, after which further acoustic irradiation at the same intensity will produce no further change in size or size distribution.

In a recent review of ultrasonic degradation of polymers in solution (55), it was concluded that there appears to be a limiting chain length formed by ultrasonic irradiation, which means that chemical effects are not responsible for disintegration. Instead, mechanical stresses on the polymer molecule are thought to be the primary cause of the bond breakage. Polymer molecules are distorted and stretched as they enter the area of high velocity gradients and the ultimate rupture is caused from stress induced by the shock waves.

Doulah (56-58) studied the disintegration of biological cells, yeast cells, and polymers in solution. He also proposed a mechanism for the disintegration which includes the effects of shock waves. The collapsing bubbles in cavitating ultrasonic fields were viewed as power transformers by which acoustic energy is converted to concentrated hydrodynamic energy, in the form of shock waves, at the end of the collapse period. These waves were thought to produce eddies in the flow field. The larger eddies break up into smaller ones until they reach a size which can be damped by the viscosity of the medium. In this form of turbulent flow, the force needed to break the polymers and cells is created by
fluctuating velocities of the eddies. Those with scales larger than the polymer molecule will carry the molecule from place to place, while eddies smaller than the molecule will impart motions of varying intensities. As a result of these impacts, a dynamic force is set-up across the length of the macromolecule and when this force exceeds the bond strength, the molecule will disintegrate.

All of the possible mechanisms of the disintegration processes in cavitating ultrasonic fields are based on the effects of violent shock waves. If the suspended particles are in close proximity to the collapsing bubbles, estimated values of the shock wave amplitudes are sufficient to break up most solids, cells and polymers. It is most probable, however, that the particles are at some distance to the cavitation bubble centers. This fact can account for the existence of a limiting chain length in all depolymerization studies, and for a stable droplet size in emulsification studies.

Particles that are at a certain distance from the cavitation bubble centers have sufficient strength to resist shock wave intensities after a certain period of ultrasonic irradiation. Shock waves resulting from nearly spherical collapse of cavitation bubbles, although not considered to be the only cause of damage to surfaces, are believed to be the only cause of disintegration of suspended particles in a liquid. A nearly spherical collapse in solution away from solid surfaces is a sufficiently accurate collapse behavior for cavitation bubbles in such solutions.
Research objectives

There is sufficient evidence that the state of agglomeration and the nature of the agglomerates in a powder is a major factor in obtaining pore-free, dense ceramics. The purpose of this work was to develop a technique for determining the strengths of powder agglomerates quantitatively, and to explore the relationships of these measurements to the properties of both the powders and the final sintered ceramics. A better understanding of the relation between the powder preparation technique and the strength of the resulting agglomerates should certainly be of substantial value in choosing the proper powder preparation route; such a relationship does not exist now.

Ultrasonic energy was used to break the agglomerates in suspension. A constant frequency ultrasonic probe with variable amplitude was used to obtain different ultrasonic energy output levels. The effective intensity of shock waves created by cavitation in the suspending liquid was found by breaking hollow glass microspheres of known strength at various ultrasonic intensity levels. In this way, the breaking strength of the sound field was related to the energy output.

Powder agglomerates of yttria and yttria stabilized zirconia were made by different preparation techniques. Monosize powders of yttria also were prepared and packed to form model agglomerates of known porosity. These agglomerates were treated with the calibrated ultrasonic probe and, through in situ particle size determinations, data were obtained from which agglomerate strength distributions could be calculated. The agglomerated powders that were prepared were characterized by using compaction tests, surface area measurements,
mercury porosimetry, scanning electron microscopy, and particle size analysis to obtain a better understanding of the relation of powder agglomerate strength and other powder properties to sinterability and sintered microstructure.

Explanation of dissertation format

The dissertation contains four sections, each of which is written in a form suitable for publication in a technical journal. Each section contains a list of references cited in that section. References cited in the general introduction are found at the end of the dissertation.
SECTION I. DETERMINATION OF THE STRENGTH OF GLASS BUBBLES
BY MERCURY POROSIMETRY
ABSTRACT

The strengths of commercial glass bubbles were determined by a new method using a scanning mercury porosimeter. The method was found to be very simple and reproducible. Strength distributions for these bubbles were deduced from data for volume intruded vs pressure. Bubble densities and average aspect ratios were also calculated from experimental data. The average strength values were significantly lower than reported nominal values.
INTRODUCTION

Glass bubbles are used in a number of applications where they are introduced into a matrix material. The strength of glass bubbles, along with their density, is an important property for the syntactic foams in which they are used. The glass bubbles must be strong enough to survive a series of mixing and forming operations. Furthermore, the isostatic and uniaxial compressive strengths of syntactic foams are directly related to the strength of the glass bubbles they contain (1).

Glass bubbles are produced from solutions, powders, or metal alkoxides (2,3). Powders or droplets of solution to which a blowing agent such as urea has been added are dropped into a furnace where gases evolve. The pressure of the encapsulated gases and the viscous relaxation of the glass shell govern the expansion rate of the bubbles (3).

The strength of glass bubbles can be determined by several compression techniques. ASTM Standard Method of Test D3102 (4) describes an isostatic compression technique. In this test, the volume of glass bubbles collapsed during the application of pressure is determined as a function of pressure. This method is currently in use by several laboratories. 3M Co., one of the largest manufacturers of glass bubbles, reports strength as the pressure at which a 10% reduction in volume occurs. The test consists of placing a specific quantity of glass bubbles in a rubber balloon containing glycerin, and then placing the sealed balloon into an oil pressure chamber. The pressure and the corresponding volume change occurring in the sample are recorded on an X-Y recorder. A pressure versus collapsed volume curve is thus obtained. This test requires a special experimental set-up which includes two
pressure sensors (13.8 MPa and 138 MPa capacity), an isostatic pressure chamber, a high-pressure pump, and a recorder. This system requires calibration for each run. Details of the experimental set-up and procedure are given in ASTM D3102. Recently, ASTM D3102 was withdrawn as a standard method of test. According to the responsible subcommittee, the premise for the withdrawal was the lack of user response, most due to special design and cost of the experimental set-up, coupled with the tediousness of the procedure. (It is hoped that the method proposed here will alleviate these problems and allow the accumulation of a large number of measurements by independent researchers to assess the reproducibility and reliability of the method.)

A different approach has been used for determination of the strength of relatively large glass bubbles by Milewski and Marsters (5) at Los Alamos National Laboratory. Two different techniques have been described; namely, mechanical pull testing and internal pressurization burst tensile testing. In the former method, a bubble is firmly bonded to a jig on two opposite sides and is pulled apart. The load at failure is recorded and tensile strength is determined from the load and dimensions of the bubble. The latter method is performed by creating a pressure differential between the outside and inside of the bubble to cause it to fail in tension. Both tests developed at Los Alamos are useful for relatively large-sized and more or less perfect bubbles. Since testing is done on one bubble at a time, a significant number of tests must be made to obtain statistically meaningful results. These two techniques, like the former ASTM method, require special experimental set-ups, and are costly and tedious.

Mercury porosimetry is a widely used technique for pore analysis (6).
The technique determines the volume of mercury forced into pores as a function of pressure, which is then related to pore size by the well-known Washburn equation. The mercury porosimeter used in this study was a scanning porosimeter (Quantachrome Corp., Syosset, N.Y.) which is capable of applying pressures up to 415 MPa; however, any other porosimeter with a reasonable pressure range (for example ambient to 200 MPa) could be used. From the pressure-volume data, one can deduce the distribution of the isostatic compression strength of the glass bubbles. The method also allows determination of bubble bulk density, provided that the mass of the sample cell is measured before and after the test is conducted.
EXPERIMENTAL

Glass bubbles

The glass bubbles used in this study consisted of a soda-lime borosilicate glass (3M Co., St. Paul, MN) with almost perfect spherical shapes but with considerable variation in diameter and wall thickness. The coding of bubble type (according to 3M's scheme) and several physical properties are given in Table 1. In the coding, the letters correspond to a proprietary classification and processing code; the first set of numbers reflects nominal bulk density (i.e., 15 corresponds to 0.15 g/cm³), and the second set of numbers refers to nominal strength according to ASTM D3102 (in psi units). Percent floated is also given in the table. Apparently, types A and D are classified by water flotation and consist of 99% floated bubbles, while types B and C are not classified by flotation, and thus contain a higher percentage of bubbles which do not float. The density ranges reported indicate that types A and D have less variation than types B and C.

Procedure

Bubble strength was determined using a scanning mercury porosimeter. The sample cell was calibrated before each run; however, day-to-day calibrations were so reproducible that a calibration for each test would not have been necessary. Approximately 0.1 g (0.3 cm³) of sample was placed in a sample cell and weighed. The cell was then filled with mercury and weighed again. The whole assembly was placed in the pressure chamber, evacuated, and the experiment initialized. From this point on the progress of the experiment was microprocessor controlled. Pressure was increased by a preset value, and, after equilibration, the pressure
<table>
<thead>
<tr>
<th>Bubble Type</th>
<th>Bubble density (g/cm$^3$)</th>
<th>Test Pressure for compressive strength (MPa)</th>
<th>Floaters (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C15/250</td>
<td>0.15</td>
<td>1.72</td>
<td>90</td>
</tr>
<tr>
<td>A16/500</td>
<td>0.16</td>
<td>3.45</td>
<td>99</td>
</tr>
<tr>
<td>B28/750</td>
<td>0.28</td>
<td>5.20</td>
<td>90</td>
</tr>
<tr>
<td>A20/1000</td>
<td>0.20</td>
<td>6.90</td>
<td>99</td>
</tr>
<tr>
<td>B37/2000</td>
<td>0.37</td>
<td>13.80</td>
<td>90</td>
</tr>
<tr>
<td>A32/2500</td>
<td>0.32</td>
<td>17.24</td>
<td>99</td>
</tr>
<tr>
<td>B38/4000</td>
<td>0.38</td>
<td>27.60</td>
<td>90</td>
</tr>
<tr>
<td>D32/4500</td>
<td>0.32</td>
<td>31.03</td>
<td>99</td>
</tr>
</tbody>
</table>
and the volume were stored in memory. These steps were repeated until the peak pressure was reached. At the peak pressure, the process was reversed, and the same steps were repeated until the pressure had been returned to ambient. Pressure-volume data can be automatically plotted in various forms with this apparatus. In this particular study, plots of percent volume collapsed versus pressure and of dV/dP vs pressure were drawn. The sample cell was weighed at the end of the experiment for the determination of bubble density.
RESULTS AND DISCUSSION

Percent volume collapsed as a function of applied pressure for the samples tested is plotted in Figure 1. Several features are worth mentioning in these plots. Type B samples generally show an initial jump in collapsed volume at very low pressures (B28/750, B37/2000, B38/4000). This volume is about 10% and corresponds to the collapse of very weak or defective bubbles. Five to ten percent of the bubbles do not collapse even at 120 MPa except for the two weakest cases. This may be due to the presence either of solid glass spheres or broken glass or both. Reproducibility of the test is excellent, as indicated by duplicate runs on sample D32/4500 (Figure 1c).

The strength distributions of bubbles obtained by plotting dV/dP vs P are given on Figure 2. Again, in these plots, defective bubbles are clearly shown by an initial jump in the distribution curves. The somewhat stepwise changes in the distribution curves are believed to be due to the incremental data acquisition process and may be eliminated by recording the data in smaller intervals.

Strengths at 10% volume reduction reported by the manufacturer and obtained in this study are presented in Table 2 for comparison. Strength values at 50% volume reduction (median) and those at the maximum (mode) of the distribution curves are also presented in Table 2. Inspection of the table shows that values reported by the manufacturer are consistently higher than the values obtained in this study. Nominal reported values are about 4 to 7 fold higher in the unfloated samples and 1.5 to 3 fold higher in the floated ones than in this study. Values at the maximum are also lower than reported values except for the A16/500 and B38/4000. Our strength values at 50% volume reduction are comparable to those reported
Figure 1a. Percent volume collapsed vs pressure for C15/250, A16/500 and B28/750 type glass bubbles

Figure 1b. Percent volume collapsed vs pressure for A20/1000, B37/2000, A32/2500 and B38/4000 type glass bubbles
Figure 1c. Percent volume collapsed for D32/4500 type glass bubbles

Figure 2a. Strength distribution of D32/4500 type glass bubbles
Figure 2b. Strength distributions of C15/250, A16/500 and B28/750 type glass bubbles

Figure 2c. Strength distributions of A20/1000, B37/2000, A32/2500 and B38/4000 type glass bubbles
Table 2: Strength values determined for glass bubbles by mercury porosimetry

<table>
<thead>
<tr>
<th>Bubble Type</th>
<th>Nominal Value (MPa)</th>
<th>P_{a10} (MPa)</th>
<th>P_{b50} (MPa)</th>
<th>P_{cmax} (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C15/250</td>
<td>1.72</td>
<td>0.47</td>
<td>1.30</td>
<td>0.86</td>
</tr>
<tr>
<td>A16/500</td>
<td>3.45</td>
<td>2.32</td>
<td>5.68</td>
<td>4.14</td>
</tr>
<tr>
<td>B28/750</td>
<td>5.20</td>
<td>1.00</td>
<td>5.66</td>
<td>2.76</td>
</tr>
<tr>
<td>A20/1000</td>
<td>6.90</td>
<td>2.35</td>
<td>6.69</td>
<td>4.48</td>
</tr>
<tr>
<td>B37/2000</td>
<td>13.80</td>
<td>3.52</td>
<td>16.92</td>
<td>12.07</td>
</tr>
<tr>
<td>A32/2500</td>
<td>17.24</td>
<td>8.29</td>
<td>20.15</td>
<td>10.34</td>
</tr>
<tr>
<td>B38/4000</td>
<td>27.60</td>
<td>3.93</td>
<td>34.33</td>
<td>30.34</td>
</tr>
<tr>
<td>D32/4500</td>
<td>31.03</td>
<td>12.12</td>
<td>34.60</td>
<td>22.07</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Pressure at 10\% volume reduction.

\textsuperscript{b}Pressure at 50\% volume reduction.

\textsuperscript{c}Pressure at the maximum of dV/dP versus P plot.
by the manufacturer at 10% volume reduction. These discrepancies can not
be explained by the testing procedure, but may be due to sampling and
handling procedures. Samples were taken randomly, and no precaution was
taken against aging and scratching of bubbles in our study.

The stress (σ) on a thin-walled (a>20) glass bubble under uniform
isostatic compression was given by (7,8):

\[ \sigma = \frac{P \cdot a}{4} \]  \hspace{1cm} (1)

where a is the aspect ratio (defined as ratio of diameter to wall
thickness) and P is the pressure applied. At failure this stress
Corresponds to the strength of the glass microsphere. According to
buckling theory, at the critical pressure the sphere wall buckles and the
spherical symmetry is perturbed, causing failure. This critical buckling
pressure is defined as (8):

\[ P = \frac{8E}{a^2 [3(1-v^2)]^{1/2}} \]  \hspace{1cm} (2)

Combining Eqs.(1) and (2) yields a theoretical strength for a perfect
bubble as:

\[ \sigma = \frac{2E}{a [3(1-v^2)]^{1/2}} \]  \hspace{1cm} (3)

where v is the Poisson's ratio and E is Young's modulus. The average
aspect ratio is calculated from experimentally determined intruded volume
\( V_B \) and known glass volume \( V_G \) as:

\[ a = \frac{2}{1 - [(V_B/V_B)/(V_B/V_G + 1)]^{1/3}} \]  \hspace{1cm} (4)
Taking $0.21$ for $v$, $2.55 \text{ g/cm}^3$ for the glass density, and $6.9 \times 10^4 \text{ MPa}$ for $E$, average aspect ratios (Eq.(4)) and theoretical critical buckling pressures (Eq.(2)) of bubbles were calculated, and are reported in Table 3. The measured pressures at 50% volume reduction are also shown in Table 3. The theoretical critical buckling pressure is about 20 times higher than the experimentally determined collapse pressure for the low-strength bubbles and 4 times higher in the high-strength bubbles. The theoretical strength values represent the strength of perfect spheres. Since the failure occurs at the weakest point (or the largest aspect ratio portion of the bubble), the degree of deviation from theoretical strength is a measure of perfection of the glass bubbles. In addition to nonuniformity of the aspect ratio, scratches and aging will lower the observed strengths. Table 3 shows that, as the aspect ratio decreases, the difference between theoretical and measured strength decreases as well, indicating that the bubbles become more uniform.

Average bubble densities calculated in this study were compared to those reported by the manufacturer (see Table 4). Although our values were lower than reported values (except for A20/1000 and A16/500), the deviation was <16% for samples of higher strength bubbles and <7% for lower strength samples.
Table 3: Average aspect ratios and theoretical strengths of glass bubbles

<table>
<thead>
<tr>
<th>Bubble Type</th>
<th>Average Aspect Ratio, a Eq.(4)</th>
<th>Critical Buckling pressure Eq.(2), MPa</th>
<th>Critical stress at failure Eq.(3), MPa</th>
<th>Pressure at 50% volume Reduction, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>C15/250</td>
<td>105</td>
<td>29.6</td>
<td>776</td>
<td>1.30</td>
</tr>
<tr>
<td>A16/500</td>
<td>88</td>
<td>42.0</td>
<td>925</td>
<td>5.68</td>
</tr>
<tr>
<td>B28/750</td>
<td>55</td>
<td>109.0</td>
<td>1492</td>
<td>5.66</td>
</tr>
<tr>
<td>A20/1000</td>
<td>73</td>
<td>61.5</td>
<td>1119</td>
<td>6.79</td>
</tr>
<tr>
<td>B37/2000</td>
<td>47</td>
<td>149.0</td>
<td>1742</td>
<td>16.90</td>
</tr>
<tr>
<td>A32/2500</td>
<td>53</td>
<td>114.0</td>
<td>1527</td>
<td>20.20</td>
</tr>
<tr>
<td>B38/4000</td>
<td>42</td>
<td>186.0</td>
<td>1945</td>
<td>34.30</td>
</tr>
<tr>
<td>D32/4500a</td>
<td>48</td>
<td>142.0</td>
<td>1703</td>
<td>34.70</td>
</tr>
<tr>
<td>D32/4500b</td>
<td>48</td>
<td>143.0</td>
<td>1708</td>
<td>34.60</td>
</tr>
</tbody>
</table>

*aFirst run.*

*bSecond run.*
Table 4: Comparison of nominal densities of glass bubbles with experimental values determined from mercury porosimetry

<table>
<thead>
<tr>
<th>Bubble Type</th>
<th>Density (g/cm³)</th>
<th>Nominal value</th>
<th>Range</th>
<th>Experimental density</th>
</tr>
</thead>
<tbody>
<tr>
<td>C15/250</td>
<td>0.15</td>
<td>0.12-0.18</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>A16/500</td>
<td>0.16</td>
<td>0.14-0.18</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>B28/750</td>
<td>0.28</td>
<td>0.25-0.31</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>A20/1000</td>
<td>0.20</td>
<td>0.18-0.22</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>B37/2000</td>
<td>0.37</td>
<td>0.34-0.40</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>A32/2500</td>
<td>0.32</td>
<td>0.30-0.34</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>B38/4000</td>
<td>0.38</td>
<td>0.35-0.41</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>D32/4500(1st run)</td>
<td>0.32</td>
<td>0.30-0.34</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>D32/4500(2nd run)</td>
<td>0.32</td>
<td>0.30-0.34</td>
<td>0.31</td>
<td></td>
</tr>
</tbody>
</table>
CONCLUSIONS

Mercury porosimetry is a reliable and commonly-employed technique for the determination of pore size distribution in solid materials. In this study we have adapted this technique to determine the strength distribution, density, and average aspect ratio of glass bubbles. The results have shown that commercially available and readily accessible instruments can be used to determine the strength and density of glass bubbles reliably and routinely. Data acquisition and retrieval by available microprocessor-controlled instruments make this technique very attractive for this application. The procedure and data analysis can be completed in several hours, providing information about the average strength, its distribution, apparent and true density, as well as information on degree of perfection of samples of hollow microspheres.
ACKNOWLEDGEMENT

This work was done with the financial support of Engineering Research Institute of Iowa State University. Special thanks are extended to Profs. D. M. Martin and M. F. Berard for their valuable contributions. Glass bubbles used in this study were kindly provided by 3M Co.; their contribution is appreciated.
REFERENCES


SECTION II. MEASUREMENT OF AGGLOMERATE STRENGTH DISTRIBUTIONS IN AGGLOMERATED POWDERS
Strength distributions of particle agglomerates in six different yttria powders were measured using a calibrated ultrasonic sound field. The density of sintered pellets was directly related to the agglomerate strength of each powder. No systematic relation to the sintered density was observed for bulk densities or pressure-density compaction data for the loose powders, or for pore size distributions or green densities for the pressed compacts. Although all of the powders were agglomerated, no breakpoints were found in the compaction curves.
INTRODUCTION

Most ceramic powders contain agglomerates. Agglomerates which do not break up during pressing retard compaction, create a nonuniform pore size distribution in the compact, and may produce internal cracks which may act as strength-limiting flaws in the sintered product. A reliable means of characterizing the strength of these agglomerates is useful in predicting powder behavior during compaction and sintering.

Pressure-density compaction curves may give qualitative information about the nature of any agglomerates present (1-5) but are of limited value in providing quantitative information about agglomerate strength. Niesz et al. (1) assumed that the semilogarithmic pressure-density relationship observed during the compaction of granulated powders was analogous to that which exists between mechanical strength and porosity and that the pressure at the breakpoint between linear portions of the curve was a measure of the strength of the granules. After testing agglomerated alumina powders, they concluded that compaction data also can show the presence of agglomerates in an ungranulated powder.

However, agglomerates may not always be detected from compaction data produced continuously with a mechanical testing device because there may not be an interconnected pressure-transmitting network. The agglomerates also may have a sufficiently wide distribution of strengths that they break over a broad range of pressures. In these cases a breakpoint may not be discernible in the pressure-density compaction curve. Dynys and Halloran (3) found no breakpoints in their compaction curves for fully agglomerated alumina powder or for specially prepared mixtures containing 6% to 92% agglomerates. Yet, during compaction of a mixture of 70% agglomerated and 30% unagglomerated powder the agglomerates broke in the
same fashion as they did in a fully agglomerated powder. The unagglomerated powder in the mixture had no "cushioning" effect, but it did retard compaction. At a given pressure, the green density was inversely proportional to the amount of agglomerated powder present.

Pressure-density compaction curves show only the change in total porosity during compaction. Mercury porosimetry, on the other hand, can be used to obtain the size distribution of the pores (more accurately, the capillary intrusion radius). One can thus differentiate between important properties of a green body such as low porosity consisting of large, broadly distributed pores and higher porosity consisting of small pores of narrow size distribution. The pore size distribution also may be bimodal, showing peaks representing pores within the agglomerates and pores among the agglomerates. Whittemore (6) has been instrumental in introducing mercury porosimetry into the study of ceramic powders.

Sintering kinetics and microstructure development also are affected by the presence of strong agglomerates. Rhodes (7) found that the presence of agglomerates in yttria-stabilized zirconia powders limited the final stage sintered densities that could be attained. Dynys and Halloran (8) found that strong agglomerates in alumina powders decreased the shrinkage rates in isothermal initial stage sintering by as much as a factor of ten. Roosen and Hausner (9), working with calcia-stabilized zirconia, found that agglomerates interfered with densification and with the formation of a homogeneous microstructure.

Work reported initially by Reeve (10) on differential sintering of agglomerates and culminating in the recent experimental demonstration by Lange and Metcalf (11), that crack-like internal surfaces so generated can be strength-limiting flaws, shows that small numbers of unbroken
agglomerates are important even in ceramic compacts that sinter to very high density.

In the present work, the determination of agglomerate strength by measuring particle breakup at different energy input levels in an ultrasonic field is explored. Hollow glass microspheres of known strength distributions were used to find the effective breaking pressure of the shock waves created by collapsing cavitation bubbles at each intensity setting of an ultrasonic probe. After calibrating the probe in this fashion, the agglomerate strength distributions of six different yttria powders, each of which had been carefully characterized, were measured. The agglomerate strength of these powders was then related to their sintered densities.
EXPERIMENTAL

**Powder preparation and characterization**

The Y\(_2\)O\(_3\) powders were made by calcining hydrated yttrium hydroxycarbonate precursors, prepared in the laboratory using precipitation and dewatering techniques known from experience to produce materials containing agglomerates with widely varying characteristics. For powder A, the precursor was precipitated by adding an ammonia solution to an yttrium nitrate solution (direct strike). For powder B, the yttrium nitrate solution was added to the ammonia solution (reverse strike). The order of addition has a marked effect on the effective supersaturation level during precipitation and thus on the character of the precipitates formed (12). The slurries were suction filtered and the precipitates resuspended in dilute ammonia solution and filtered a second time. No additional dewatering techniques were used.

Powders C, D, E, and F were all prepared from reverse strike precursor precipitates. For powder C, the washed filter cake was further dewatered with consecutive washes of acetone, toluene, and acetone (13). After the final acetone wash, the cake was stirred in a hot mortar and pestle to evaporate the remaining acetone. Powder D was derived from a precipitate which had been aged in a controlled humidity chamber (Humid Flow Temperature and Humidity Chamber, Blue M Electric Co., Blue Island, IL) at 90°C and 95% r.h. for 5 days (14).

For powder E the precursor was freeze-dried (Using Model 75035 Bench Top Freeze Dryer, Labconco Corp., Kansas City, MO), and for powder F it was spray-dried (Using Model 190 Mini Spray Dryer, Brinkman/Buchi Instruments Co., Westbury, NY). After dewatering, all six yttrium
hydroxynitrate powders were oven dried overnight at 110°C, calcined at 1000°C for 2 hours to convert them to the oxide, and passed through a 200-mesh (74-μm) sieve to remove any larger particles that may have been present.

Particle size distributions were measured with a sedimentation-type particle size analyzer (Model 5000ET Sedigraph, Micromeritics Instrument Corp., Norcross, GA) which had a lower detection limit of 0.2 μm. Surface areas were found by the BET method (Using Model 2400D Sorptrackr, Micromeritics Instrument Corp., Norcross, GA), using nitrogen as the adsorbate. Samples of each of the powders were also examined using a scanning electron microscope (Model 100CX, Japan Electron Optics Labs, Tokyo, Japan). Pressure-density compaction curves were obtained on a testing machine (Model TT-CML, Instron Corp., Canton, MA) using a 9.5-mm-diameter tungsten carbide-lined die lubricated with stearic acid. It was operated at a constant low crosshead speed of 2.0 mm/min. and had a maximum full load of 70 MPa. To avoid any moisture differences resulting from changes in relative humidity, all of the compaction tests were made at the same time. Intrusion pore size distributions for the loose powders and their compacts (at 70 MPa) were obtained by mercury porosimetry (Using Scanning Porosimeter, Quantachrome Corp., Syosset, NY).

**Calibration of the ultrasonic medium**

The ultrasonic probe (Model TSD 500 Sonic Disruptor, Tekmar Co., Cincinnati, OH) produced sound waves of constant frequency (20 kHz) generated by the vibration of a piezoelectric transducer through a horn at the tip. The intensity of the cavitation in the liquid was
proportional to the energy output from the probe and could be varied by changing the amplitude of the vibrations. Water was used as the cavitation medium.

Eight different types of borosilicate glass microspheres, each type having a different breaking strength, were used to calibrate the probe. They were almost spherical in shape but varied considerably in size, from 20 to 130 μm with an average of ≈60 μm, and in wall thickness (15). The bulk densities ranged from 150 to 320 kg/m³.

Untreated samples of the microspheres were crushed in a mercury porosimeter at pressures to 414 MPa to obtain pressure-volume data from which frequency plots of their strength distributions were made. Then, for each intensity setting of the probe a 0.5 vol% water suspension of microspheres of the appropriate strength distribution—chosen so that about one-half of them would be broken—was irradiated for a sufficiently long time that no further breakage occurred. After irradiation, the microspheres were filtered out of the cavitation medium and crushed in the mercury porosimeter to obtain data from which a frequency plot of the strength distribution of the treated microspheres was made.

When the strength distributions of the glass microspheres before treatment and after treatment at a specific setting of the ultrasonic probe were compared, as shown in Figure 1, a distinct pressure was observed below which the two curves diverged, indicating that most of the microspheres of lesser strength had been broken during the ultrasonic treatment. This value was taken as the breaking pressure of the cavitation medium at that energy input level. The procedure was repeated for each intensity setting, and it was found that the breaking pressure of the cavitation medium could be varied from 1 to 76 MPa.
Figure 1. Strength distribution curves for hollow glass microspheres before and after exposure to a cavitating medium created by ultrasonic sound waves at a specific intensity level.
Treatment of powders in the ultrasonic medium

After the breaking pressures for the various settings of the ultrasonic probe had been determined, each of the yttria powders was tested by dispersing a sample in water and treating it at successively higher ultrasonic intensity levels. The concentration of the yttria suspensions was kept close to that of the microsphere suspension used to calibrate the ultrasonic probe (≈0.5% by volume). Particle size distributions of the suspended particles were measured periodically during irradiation, and treatment was continued at each intensity level for 30 minutes after stabilization. The ultrasonic irradiation ceased to have an effect on the particle size distribution after 1 to 2 hours, depending on the powder and the intensity level of the sound field. These size distribution data were used to calculate agglomerate strength distributions for the yttria powders.

Sintering studies

For sintering experiments, powder samples were dry pressed at 35 MPa in a 9.5-mm-diameter tungsten carbide-lined die lubricated with stearic acid. The resulting 5-10 mm thick pellets were then pressed isostatically at 70, 140, and 210 MPa. They were vacuum-sintered in yttria crucibles, using 20°C/min heating and cooling rates, and held for 2 hours at 1700°C, a typical sintering temperature for yttria. The sintered densities were measured using a water displacement method and compared with the theoretical density of 5031 kg/m³.
RESULTS

Powder characterization

The structure of the agglomerates in the yttria powders could be seen from scanning electron photomicrographs. They were clusters of smaller agglomerated particles which were called aggregates (Agglomerates and aggregates are poorly defined in ceramics literature; the words are sometimes used interchangeably, or to define weakly and strongly bonded agglomerated particles. Note that in the present work the word aggregate is used to define a tightly bonded subunit of an agglomerate). The aggregates, in turn, were composed of still smaller particles called crystallites. This type of structure is typical of the three-particle system found in powders obtained by aqueous precipitation (16-18). The crystallites were fully dense and were the particles nucleated from solution during precipitation of the precursor. They were generally in the 10 nm size range, as determined by TEM, and were amorphous or partially crystalline before calcination, depending on the conditions of precipitation. The crystallites coagulated in the precipitator to form the aggregates, which were small, tightly bonded assemblages which had a relatively low porosity, were rather equiaxed, and had a narrow size distribution. Van de Ven and Hunter (19) have reported that the aggregate size is determined by the maximum shear field in the precipitator.

Most of the agglomerates were formed in the precipitator by the coagulation of aggregates, although some of the larger ones were probably formed during the filtration, washing, and drying of the precursor precipitate. The agglomerates were more porous and less tightly bonded
than the aggregates and had a broader size distribution. This particle structure persisted through the calcination step, which served mainly to convert the yttrium hydroxynitrate to yttrium oxide and also to strengthen the bonding at the contact points among crystallites in the aggregates and among aggregates in the agglomerates. Only the agglomerates were broken during ultrasonic treatment. The bonding within the aggregates was too strong to be affected by the intensities used in the present work.

The particle size distributions shown in Figure 2 agreed well with observations from scanning electron microscope pictures. Before treatment, the agglomerates in powder C ranged from 2 to 30 μm. After treating the powder at an effective cavitation pressure of 76 MPa, the size distribution curve peaked at ≈0.35 μm, which is approximately the 0.25 μm aggregate size found from micrographs such as Figure 3a. The 1-5 μm aggregates of powder F (Figure 3b) were spherical, with a broad size range reflecting the distribution of drop sizes obtained from a spray nozzle. The aggregate size distribution in the SEM micrographs again agreed well with the curve in Figure 2b for the ultrasonically treated powder.

Figures 3c and 3d represent extremes of the type of agglomerate structure found for powders A, D, B, and E. The structure varied progressively from the light, fluffy particles of powder A to the dense, glassy, sharp-edged particles of powder E. The 0.1 μm aggregates in these four powders could be seen by SEM but are not evident in Figures 2c-2f because the lower limit for the particle size analysis was 0.2 μm. The amount of breakage to particle sizes <0.2 μm can be inferred, however, from the area under the curves for the treated and the untreated
Figure 2. Particle size distribution curves for six different yttria powders before and after exposure to an ultrasonic breaking pressure of 76 MPa: (A) powder C; (B) powder F; (C) powder A; (D) powder D; (E) powder B; (F) powder E
Figure 3. Scanning electron microscope photographs of agglomerated yttria powders: (A) powder C (bar=2 μm); (B) powder F (bar=5 μm); (C) powder A (bar=5 μm); (D) powder E (bar=5 μm)
powder. For example, powder A was almost completely broken into particles <0.2 μm whereas powder E was only slightly broken into such small particles. If the measurement limit of the particle size analyzer had been lower, one would have expected to see a large peak in the particle size distribution at ≈0.1 μm for the treated powder in Figure 2c.

**Powder compaction tests**

The results of the powder compaction tests are shown in Figure 4. The bulk densities of the various powders ranged from 15% to 37%, but there was no systematic relation between bulk density and sintered density. After compaction to 70 MPa, the pressed densities of all of the powders, except for powder C, fell within a narrow range from 35% to 42%, but again there was no systematic relation to the sintered density. Also, although all of the powders were agglomerated, there were no obvious breakpoints in the compaction curves.

**Pore size distributions**

Intrusion pore size distributions for the unpressed powders and for the pellets from the uniaxial compaction tests are shown in Figure 5. The bimodal nature of many of the curves indicates two different pore populations: the large pores among the agglomerates and the smaller pores within the agglomerates. Comparisons among the curves illustrate some of the advantages and also some of the difficulties in using them to predict sinterability.

Powders B, D, and E all sintered to low densities. For powders B and D, the similarity of the particle size distributions, the compaction
Figure 4. Pressure-density compaction curves for six different yttria powders. Numbers in parentheses are sintered densities of pellets subsequently pressed at 70 MPa and vacuum-sintered at 1700°C for 2 hours.
Figure 5. Pore size distribution curves for loose yttria powders and pellets from the powder compaction tests: (A) powder C; (B) powder F; (C) powder A; (D) powder D; (E) powder B; (F) powder E
curves, and the pore size distributions show that they should exhibit similar sintering behavior. The bimodal pore size distributions in the compacts show that the agglomerates were not destroyed completely during pressing. Also, broad pore size distributions remain. These powders sintered to 77% and 79% theoretical density. Powder E, which sintered to only 71% theoretical density, contained small, dense agglomerates which were essentially unbroken during pressing. The steeper slope of the compaction curve in Figure 4 is probably a result of fracture of the sharp edges of the angular-shaped agglomerates. The pore size distribution was reasonably uniform because of the more narrow particle size distribution, but the pores were large. Thus, the information obtained from porosimetry measurements on pellets of powders B, D, and E was consistent with their sintered densities.

For powders C, F, and A, all of which sintered to >90% theoretical density, there was no such consistency. Their sinterability was, in each case, the result of a different combination of powder characteristics. The porosimetry curve for the pressed pellet of powder C most resembles those of powders B and D, which sintered poorly. However, the compaction curve in Figure 4 shows that powder C had a high bulk density and formed a tightly compacted, high density pellet. On the other hand powders A and F had low bulk densities and produced low density compacts. However, pressing destroyed the large, weak agglomerates in powder A and only very small interaggregate pores of uniform size remained, as shown by the single sharp peak at 0.02 \( \mu \text{m} \) in Figure 5c. Powder F had the lowest bulk density of any of the six powders and also had the largest aggregate size; but the SEM aggregate size of \( \approx 1.2 \mu \text{m} \) and the BET particle size of 0.03 \( \mu \text{m} \), calculated from the surface area, showed that the aggregates
were quite porous. Porosimetry showed that these aggregates were substantially, but probably not completely, crushed during compaction.

In general, the particle characterization data presented so far permit a qualitative assessment of the sinterability of the six yttria powders, but an actual ranking of them according to their subsequent sintered densities would be difficult.

**Agglomerate strength calculations**

Agglomerate strength curves for the yttria powders were calculated in a manner similar to the method used by Rumpf (20). Since the agglomerates break by rupture of the bonds at the contact points among the aggregates, the strength distribution is a function of the number of contact bonds broken in the cavitating medium at each intensity level.

The aggregates were assumed to be spherical, of the size determined from SEM photographs of the powder. The particle size distribution of the untreated powder was divided into ten size intervals, and the size at the midpoint of each interval was used in the calculations. To find the number of aggregates in each average size agglomerate, an agglomerate porosity of 0.4 was assumed (17). For calculating the number of contact bonds among the aggregates, an average coordination number of eight was used, as found from Rumpf's analysis of random packing of spheres. Since each contact point is common to two aggregates, the average number of contact bonds for aggregates not exposed to the surface of the agglomerate is four. A correction was made to account for the fewer contact bonds of surface aggregates, so the average number of contact bonds per aggregate was somewhat less than four. This number decreased with decreasing agglomerate size because the percentage of surface
aggregates increased.

One hundred aggregates, distributed in size according to the mass fraction of material in each size fraction, were used as a basis of calculation. The total number of bonds in the 100 aggregates was then the mass-weighted sum of the average number of bonds per aggregate in each size interval. The procedure was repeated to find the number of bonds remaining after ultrasonically irradiating the powder at successively higher intensity levels.

For each of the yttria powders, the percent of original interaggregate bonds broken as a function of the ultrasonic breaking pressure is given in Figure 6. The differences in the strengths of the agglomerates in the six powders are clearly evident. The large, porous agglomerates in powder A broke up easily, even at very low breaking pressures, whereas for the smaller but very dense agglomerates of powder E only ≈ 8% of the bonds were broken at the higher pressure (76 MPa). Most of the breakage took place at the lower pressures along fracture lines where the bonding was weakest. At pressures above ≈ 15 MPa, fewer agglomerates were broken, even at significantly higher breaking pressures.

Sintering tests

The results of the sintering experiments are shown in Table 1. The order in which the powders sintered, from highest to lowest density, did not change for pellets pressed isostatically at 70, 140, and 210 MPa. For those pressed at 70 MPa the relation of the sintered density to agglomerate strength, green density, powder surface area, and agglomerate
Figure 6. Agglomerate strength curves for six different yttria powders
Table 1: Green densities and sintered densities of isostatically pressed yttria powders

<table>
<thead>
<tr>
<th>Powder</th>
<th>70 MPa</th>
<th>140 MPa</th>
<th>210 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressed (%)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Sintered (%)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Pressed (%)&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>A</td>
<td>40.9</td>
<td>96.1</td>
<td>46.3</td>
</tr>
<tr>
<td>F</td>
<td>37.0</td>
<td>94.0</td>
<td>NA&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>C</td>
<td>53.8</td>
<td>90.9</td>
<td>NA&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>D</td>
<td>37.6</td>
<td>79.2</td>
<td>41.2</td>
</tr>
<tr>
<td>B</td>
<td>40.9</td>
<td>77.0</td>
<td>44.2</td>
</tr>
<tr>
<td>E</td>
<td>42.6</td>
<td>70.6</td>
<td>46.6</td>
</tr>
</tbody>
</table>

<sup>a</sup>Percent of theoretical density.

<sup>b</sup>NA = insufficient powder available.
strength is given in Table 2. No systematic relation was found except for the agglomerate strength measurements, where a direct correlation existed. This is shown further in Figure 7. Figure 8 shows optical micrographs of polished and etched specimens for each powder compact. The results are best discussed by grouping the six powders into three pairs - powders A and F, powders C and D, and powders B and E - an arrangement which occurs naturally in the agglomerate strength curves in Figure 6.

Both powders A and F, which had the weakest agglomerates by a considerable margin, sintered to the highest densities. Powder A had only 0.1 μm aggregates and was uniformly packed. Although it sintered well, the grain size was large. This powder would have yielded a better microstructure at a higher pressing pressure and a lower sintering temperature, but the determination of optimum sintering conditions was not the purpose of the present work. Powder F, which also sintered to a high density, produced a much smaller grain size.

Powders C and D sintered to intermediate densities. The agglomerate strength curves are similar, but powder D sintered to a much lower density. The large difference in the sintered densities of the two powders can be attributed to the difference in particle morphology. The spheroidal agglomerates in powder C produced a pellet with a high green density. However, the angular particles of powder D yielded a low density pellet with a broad pore size distribution. The optical micrograph of the sintered pellet still shows characteristics of the pore structure of the green compact.

Powders B and E sintered to the lowest densities and had the strongest agglomerates. The agglomerates were also dense and angular.
Table 2: Relation of measured properties to sintered density

<table>
<thead>
<tr>
<th>Powder</th>
<th>Sintered density (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Bonds broken at 76 MPa (%)</th>
<th>Green Density&lt;sup&gt;b&lt;/sup&gt; (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Surface Area&lt;sup&gt;c&lt;/sup&gt; (m&lt;sup&gt;2&lt;/sup&gt;/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>96.1</td>
<td>94.3</td>
<td>40.9</td>
<td>23.7</td>
</tr>
<tr>
<td>F</td>
<td>94.0</td>
<td>83.3</td>
<td>37.0</td>
<td>20.1</td>
</tr>
<tr>
<td>C</td>
<td>90.9</td>
<td>47.3</td>
<td>53.8</td>
<td>4.5</td>
</tr>
<tr>
<td>D</td>
<td>79.2</td>
<td>42.8</td>
<td>37.6</td>
<td>34.4</td>
</tr>
<tr>
<td>B</td>
<td>77.0</td>
<td>23.2</td>
<td>40.9</td>
<td>52.2</td>
</tr>
<tr>
<td>E</td>
<td>70.6</td>
<td>8.5</td>
<td>42.6</td>
<td>30.5</td>
</tr>
</tbody>
</table>

<sup>a</sup>Percent of theoretical density.

<sup>b</sup>Isostatically pressed at 70 MPa.

<sup>c</sup>Loose powder.
Figure 7. Sintered density of powder pellets vs interaggregate bonds broken during ultrasonic irradiation of loose powder at a breaking pressure of 76 MPa.
Figure 8. Optical micrographs of etched and polished yttria pellets pressed isostatically at 70 MPa and sintered at 1700°C: (A) powder A; (B) powder B; (C) powder C; (D) powder D; (E) powder E; (F) powder F (bars=50 μm)
Remnants of the pores in the green pellets can still be seen in the micrographs of the sintered pellets, although more of a grain structure has begun to develop in areas of the pellet made from powder B. In the micrograph of the sintered pellet of powder E, the pore structure of the green compact still predominates.
DISCUSSION

The use of mercury porosimetry to measure the strength distributions of the hollow glass microspheres used to calibrate the ultrasonic probe is probably a valid technique. The results were reproducible to within 5%-10% of the mean strength value for each setting of the ultrasonic probe. The question of whether the actual mechanism of breakage for the glass microspheres, which had no open porosity, and for the powder agglomerates, which were porous, must remain undecided until more is known about the behavior of the particles in relation to the local pressure waves in a cavitating medium. Nevertheless, the environment of the glass microspheres and the powder agglomerates was the same when they were subjected to the ultrasonic radiation. It would have been interesting to compare the ultrasonic breaking pressures with breakpoints in the powder compaction curves, but no such breakpoints were observed.

The question of fracture versus attrition as a mechanism of agglomerate breakup during irradiation was addressed by irradiating samples of powder C at different suspension densities, 2 and 12 wt%. The size distributions after irradiation were the same for both samples. Thus particle-particle collisions, if they occurred to any significant extent, did not produce any chipping or grinding action which freed individual aggregates. This result was also evident from examining the particle size distributions of the individual powders irradiated at increasingly high intensities and from the observation that the particle size distributions of all ultrasonically irradiated powders became constant after 1-2 hours and did not change after extended irradiation.

The curves in Figure 6 become rather flat at higher breaking pressures, producing a plateau from which a single value may be obtained
to characterize the strength of the strong agglomerates in each powder, as was done in Figure 7. It is tempting to speculate that a correlation could be found among such curves for a variety of different powders, at least for oxide ceramics. It is too early, however, to postulate such a relationship. Other powder characteristics also influence the results. For example, the small difference between the agglomerate strengths of powders C and D is inconsistent with the large differences between their sintered densities because of the effect of particle morphology. Also, the microstructure of powders A and F were greatly different even though their agglomerate strengths and sintered densities were similar. One would expect, therefore, that physical properties such as mechanical strength of the pellets would be different.

The use of Rumpf’s method for calculating the number of contact bonds in the agglomerates is approximate. Spherical aggregates were assumed. For some of the powders the actual shape of the aggregates were angular and very nonspherical. This could have produced errors in the bond calculations. A better test of the method could have been made if the aggregates had actually been spherical. Monodisperse, spherical particles of yttria in the 0.1 to 0.3 μm size range have been prepared and agglomerates of these particles are being studied. There are also errors involved in the use of the sedimentation-type particle size analyzer, because of both the nonspherical nature of the agglomerates and because of their varying porosity. The difficulty in making such corrections has been discussed by Dynys and Halloran (8). A reliable method of measuring agglomerate porosity would be especially helpful in obtaining more accurate size distributions.

The ordering of the sintered densities of the six yttria powders
according to their agglomerate strengths and the lack of any uniform correlation between sintered density and any of the other powder characterization parameters measured shows again the importance of powder agglomerates in ceramic processing, particularly the strength of the bonding among the aggregates. It seems reasonable that similar results could be obtained for other kinds of powders, and work in this area is continuing.
CONCLUSIONS

In the present work the use of a calibrated ultrasonic sound field to measure the strength of agglomerates in ceramic powders was explored. The sintered densities of six different agglomerated yttria powders could be correlated directly with the strength of the agglomerates in each powder. However, no such uniform correlation was found with the bulk densities or surface areas of the powders, or with the compaction curves, pressed densities, or intrusion pore size distributions of the pressed pellets. Although all of the powders were agglomerated, no breakpoints were found in the powder compaction curves.
ACKNOWLEDGEMENT

This work was conducted through the Ames Laboratory which is operated by Iowa State University for the U.S. Department of Energy under contract No. W-7405-Eng-82. This work was supported by the Director of Energy Research, Office of Basic Energy Sciences.
REFERENCES


SECTION III. EFFECT OF AGGLOMERATE STRENGTH ON SINTERED DENSITY FOR YTTRIA POWDERS CONTAINING AGGLOMERATES OF MONOSIZE SPHERES
ABSTRACT

The effect of agglomerate strength on sintered density was determined for several yttria powders made by intentionally agglomerating 0.1 μm, monodisperse yttrium hydroxycarbonate precursor spheres and calcining separate portions of the precursor at different temperatures to vary the strength of the intraagglomerate bonds. In this way, the effects of differences in particle morphology and other characteristics among the powders were minimized and the effect of agglomerate strength could be seen more clearly. The sintered density of the yttria powders decreased with increasing agglomerate strength, and even a small fraction of unbroken fragments of agglomerates in the pressed powder caused a substantial decrease in the sintered density.
INTRODUCTION

The production of nearly pore-free ceramic materials with uniform microstructures and high strength, uniform transparency, or homogeneous electrical properties is essential in high-performance applications. Most ceramic powders contain agglomerates, formed during powder preparation, which make it difficult to achieve these goals. Some ceramic powders, especially those with very fine primary particle sizes may even be intentionally agglomerated to enhance their flowability during die-filling and pressing. In either case, it is essential that the agglomerate structure be destroyed when the powder is pressed if the full potential of the fine primary particle size and the resulting uniform distribution of small pores is to be realized when the compact is sintered.

Strong agglomerates, which do not break down during pressing, produce compacts with nonuniform pore size distributions in which the coarser pores may remain in the sintered body. Because they also may cause differential sintering, which results in crack-like internal surfaces which can act as strength-limiting flaws (1), even very small fractions of strong agglomerates are believed to influence the sintering behavior of ceramic compacts.

In earlier work (2), a technique was described for measuring the strength distribution of particle agglomerates. Six different yttria powders containing various types of agglomerates, were studied. The sintered density of the powders was shown to be directly related to the strength distributions of the agglomerates, even though no consistent relation between sintered density and other measured parameters such as powder surface area, compact green density, or mercury porosimetry curves.
for the compacted powders was found. Particle shape factors also had a profound influence on the microstructure of the sintered yttria compacts.

In the present work, the effect of agglomerate strength on sintered density was studied for a series of yttria powders in which variations in other powder properties were minimized. These powders were prepared from a yttrium hydroxycarbonate precursor consisting of sub-micron sized monodisperse spheres which were agglomerated intentionally. Separate portions of the agglomerated powder were then calcined at different temperatures to convert the hydroxycarbonate to the oxide and to produce geometrically similar agglomerates whose strength varied with the calcination temperature.
EXPERIMENTAL

Powder preparation and characterization

The yttrium hydroxycarbonate precursor was prepared by homogeneous precipitation in aqueous solution. Such particles have been reported earlier (3) and the effect of precipitation conditions has been described elsewhere (4). In the present work, sufficient urea was dissolved in 0.02 M yttrium nitrate to produce an yttrium to urea mole ratio of 0.09 and the solution was heated to boiling for one hour. Under these reaction conditions, monodisperse spherical particles approximately 0.1 μm in diameter are formed. The precipitates were suction filtered, washed once with distilled water and once with acetone, then air dried and passed through a 200 mesh (74 μm) sieve to break up the precursor cake. The precursor particles, which were lightly agglomerated, passed through the sieve easily. Six batches of precursor powder prepared in this fashion were calcined in air for 2 h at 600, 800, 1050, 1100 and 1200°C, and labeled as powders A through F respectively.

The size of the individual yttria spheres was measured from SEM photomicrographs. Particle size distributions for the agglomerated powders were measured with a sedimentation type particle size analyzer (Model 5000ET, Sedigraph, Micromeritics Inst. Corp., Norcross, GA) which had a lower detection limit of 0.2 μm. Surface areas were found by the BET method (Using Model 2400D Sorptrackr, Micromeritics Inst. Corp., Norcross, GA), using nitrogen as the adsorbate. Pressure-density compaction curves were obtained on a testing machine (Model TT-CML, Instron Corp., Canton, MA) using a 9.5 mm diameter tungsten carbide-lined die lubricated with stearic acid. It was operated at a constant low crosshead speed of 2.0 mm/min. and had a maximum full load of 70 MPa.
All of the compaction tests were carried out at the same time in order to avoid any differences which might have occurred because of changes in relative humidity. Intrusion pore size distributions for the loose powders and for their uniaxially pressed compacts (at 70 MPa) were obtained by mercury porosimetry (Using Scanning Porosimeter, Quantachrome Corp., Syosset, NY).

The strength distributions of the agglomerates in each of the six yttria powders were measured by dispersing a sample of the powder in an aqueous medium (a dilute sodium pyrophosphate–water solution) and subjecting it to consecutively higher ultrasonic breaking pressures from 1 MPa to 76 MPa using a calibrated ultrasonic probe (Model TSD500 Sonic Disruptor, Tekmar Co., Cincinnati, OH) as has been described earlier (2). The effective breaking pressure of the cavitation-induced shock waves in the sound field at each intensity level of the ultrasonic probe had been determined by first breaking hollow glass microspheres with known strength distributions (5). Particle size distributions of the suspended powders were measured periodically during irradiation at each intensity level and treatment was continued in each case for 30 minutes beyond the time at which no further changes occurred. The constant size distribution data at each ultrasonic intensity level were used to calculate the agglomerate strength distribution for each powder.

**Sintering studies**

For the sintering experiments, 0.8 g powder samples were dry pressed to 35 MPa in a 9.5 mm. tungsten carbide-lined die lubricated with stearic acid, and then pressed isostatically to 70 or to 210 MPa. The pellets pressed to 70 MPa were placed in yttria crucibles and sintered in air at
1400°C for 2 h, using 20°C/min. heating and cooling rates. Those pressed to 210 MPa were sintered in vacuum under the same conditions. Sintered densities were measured using a water displacement method and compared with the theoretical density of 5031 kg/m³. Optical micrographs of polished and etched surfaces of the pellets were also taken.
RESULTS

Powder characterization

The precursor spheres, about 0.125 μm in diameter, had a very narrow size distribution, typically with a geometric standard deviation in the range 1.07 to 1.09 (4). After calcination the diameter decreased by about 25%, so that the diameter of the oxide spheres was approximately 0.1 μm. Before calcination, agglomerates of the powder could be broken down to individual spheres easily by treatment in an ultrasonic bath. After calcination the strengths of the intraagglomerate bonds in each of the resulting oxide powders were much stronger, increasing in strength with increasing calcination temperature. The SEM photomicrographs in Figure 1 show the intraagglomerate structure of several of the oxide powders. The small spheres can be seen easily, especially in Figure 1a. This powder was calcined at the lowest temperature (600°C). Figure 1b was taken at a lower magnification and shows an entire agglomerate of the same powder. These two pictures are typical of powders A, B, and C. The necks between the spheres were small and little visual change could be observed from photomicrographs of the three powders.

For powders D and E, the necks between the spheres were more substantial, as shown in Figures 1c and 1d. For powder F, calcined at the highest temperature (1200°C), considerable densification within the agglomerate occurred. This can be seen in Figures 1e and 1f.

Particle size distributions, measured with the sedimentation type particle size analyzer, for the agglomerates in the precursor powder and in powders A and F, are shown in Figure 2. The dotted lines for the precursor powder, and the broken lines for the calcined powders were
Figure 1. Scanning electron microscope photographs of agglomerated homogeneously precipitated yttria powders: (A) powder A (bar=0.5 μm); (B) powder A (bar=1 μm); (C) powder D (bar=0.5 μm); (D) powder E (bar=0.5 μm); (E) powder F (bar=0.5 μm); (F) powder F (bar=1.0 μm)
Figure 2. Particle size distribution curves for the homogeneously precipitated powder precursor and for calcined powders.
obtained using the solid densities of 3120 (measured by mercury porosimetry) for yttrium hydroxycarbonate and the commonly accepted value of 5031 kg/m$^3$ for yttrium oxide. From these curves, one can see that the size distribution curves for powder A and powder F are not greatly different and that the differences in the sizes of the agglomerates among the six powders were not important variables.

Other investigators also have used the density of the solid for such curves, even though the agglomerates are porous. Some, however, have recognized that the agglomerate porosity should be taken into account if accurate results are to be obtained (6,7). The solid lines in Figure 2, therefore, are agglomerate size distributions obtained using agglomerate densities of 2207 and 4020 kg/m$^3$, determined by mercury porosimetry, and assuming that the pores were filled with liquid during the particle size measurement. This correction produced a 42% increase in the mean ($d_{50}$) value of the mass size distribution for powder A (9.5 μm to 13.16 μm) but only a 12% increase (9.9 μm to 11.1 μm) for powder F. Still, the shape of the two curves for powders A and F, which represent the two extremes in agglomerate porosity for the six powders, and the corrected mean values of 13.16 μm and 11.1 μm show that the differences in the agglomerate size distributions were not important variables.

**Powder compaction tests**

The continuous uniaxial powder compaction curves, shown in Figure 3, for powders A, B, and C were almost coincident, with bulk densities around 25% and pressed densities, at 70 MPa, around 42%. However, for powders D, E, and F the bulk and pressed densities were substantially higher. The shape of all the compaction curves was the same. Also,
Figure 3. Pressure-density compaction curves for powders A through F. Numbers in parentheses are sintered densities of pellets subsequently pressed isostatically at 70 MPa and air-sintered at 1400°C for 2 h.
although all of the powders were agglomerated, there were no discernible breakpoints in the curves.

**Pore size distributions**

Intrusion capillary pore size distributions for the loose powders and for the pellets pressed uniaxially at 70 MPa in the mechanical testing machine are given in Figure 4. The peak at around 0.02 \( \mu m \), which is due to intraagglomerate porosity, decreases steadily for powder A through powder F. For powder F the porosity distribution in this size range is so diffuse that a peak can no longer be seen. These results, which are consistent with the SEM photomicrographs in Figure 1, reflect the increasing growth of necks among the spherical particles which make up the agglomerates.

The pore size distributions for the loose powders all have an interagglomerate porosity peak at 2-3 \( \mu m \). Upon pressing, this peak disappeared completely for powder A, leaving a uniform, fine, pore size distribution. Starting with powder B, a second small peak appears at around 0.1 \( \mu m \). This represents the compressed remnants of interagglomerate pores, and shows that agglomerate breakdown was not complete. The pore size and the pore volume associated with this second peak in the compressed powders increases steadily; the agglomerates are increasing in strength and larger fragments remain after pressing. For powder E, the interagglomerate and the intraagglomerate pore volumes are nearly equal, and for powder F almost all of the pore volume is associated with the pores between unbroken dense agglomerates. The distribution of the interagglomerate and intraagglomerate porosity of the six powders is summarized in Table I.
Figure 4. Intrusion pore size distribution curves for loose yttria powders and for pellets from the powder compaction tests: (A) powder A; (B) powder B; (C) powder C; (D) powder D; (E) powder E; (F) powder F
Table I: Distribution of interagglomerate and intraagglomerate porosity for loose and for pressed powders with increasingly strong agglomerates

<table>
<thead>
<tr>
<th>Powder</th>
<th>Intruded Volume (cm³)</th>
<th>Interagglomerate Porosity (%)</th>
<th>Intraagglomerate Porosity (%)</th>
<th>Intruded Volume (cm³)</th>
<th>Interagglomerate Porosity (%)</th>
<th>Intraagglomerate Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(600)</td>
<td>0.693</td>
<td>65.4</td>
<td>34.6</td>
<td>0.242</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>B(800)</td>
<td>0.643</td>
<td>65.8</td>
<td>34.2</td>
<td>0.269</td>
<td>25.7</td>
<td>74.3</td>
</tr>
<tr>
<td>C(1000)</td>
<td>0.676</td>
<td>73.7</td>
<td>26.3</td>
<td>0.257</td>
<td>31.1</td>
<td>68.9</td>
</tr>
<tr>
<td>D(1050)</td>
<td>0.582</td>
<td>75.9</td>
<td>24.1</td>
<td>0.211</td>
<td>36.0</td>
<td>64.0</td>
</tr>
<tr>
<td>E(1100)</td>
<td>0.489</td>
<td>80.0</td>
<td>20.0</td>
<td>0.200</td>
<td>55.0</td>
<td>45.0</td>
</tr>
<tr>
<td>F(1200)</td>
<td>0.417</td>
<td>88.0</td>
<td>12.0</td>
<td>0.165</td>
<td>75.8</td>
<td>24.2</td>
</tr>
</tbody>
</table>

*Numbers in parentheses are temperatures, °C, at which the precursor powders were calcined.*
**Agglomerate strength calculations**

Size distribution curves for powders A and F before ultrasonic treatment, and after ultrasonic treatment at breaking pressures of 1 MPa and 76 MPa (Figure 5) show that the agglomerates in powder A are more easily broken than those in powder F. Data from such curves were used to calculate the agglomerate strength distributions of the powders. In the previous work (2), the particles in the powder agglomerates were not spherical but were assumed to be so for the calculations. In the present work, however, the particles making up the agglomerates were actually spherical and were the same for all of the powders. Since the agglomerates break by rupture of the bonds at the contact points of the spheres, the strength distribution is a function of the number of contact bonds broken in the cavitating medium at each intensity level. For each of the six powders, the percent of original contact bonds among the spheres broken as a function of the ultrasonic breaking pressure is given in Figure 6. The differences in the strengths of the agglomerates in the powders are clearly evident. At the maximum breaking pressure of 76 MPa, 90% of the bonds within the agglomerates were broken in powder A while only 25% were broken for powder F.

**Sintering tests**

The results of the sintering experiments are shown in Table II. The order in which the powders sintered, from highest to lowest density, did not change for pellets pressed isostatically at 70 MPa and sintered in air or pressed at 210 MPa and sintered in vacuum, as shown in Figure 7 where there is a direct correlation between sintered densities and
Figure 5. Particle size distribution curves for powders before treatment and after treatment, and after exposure to ultrasonic breaking pressures of 1 MPa and 76 MPa.
Figure 6. Agglomerate strength curves for six different yttria powders
Table II: Green and sintered densities of isostatically pressed yttria powders

<table>
<thead>
<tr>
<th>Powder</th>
<th>Compaction Pressure: 70 MPa</th>
<th>210 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressed (%)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Air Sintered (%)&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>A</td>
<td>40.0</td>
<td>93.8</td>
</tr>
<tr>
<td>B</td>
<td>39.0</td>
<td>85.0</td>
</tr>
<tr>
<td>C</td>
<td>40.7</td>
<td>83.3</td>
</tr>
<tr>
<td>D</td>
<td>43.0</td>
<td>79.6</td>
</tr>
<tr>
<td>E</td>
<td>47.8</td>
<td>74.0</td>
</tr>
<tr>
<td>F</td>
<td>51.6</td>
<td>60.6</td>
</tr>
</tbody>
</table>

<sup>a</sup>Percent of theoretical density.
Table III: Relation of measured properties to sintered density

<table>
<thead>
<tr>
<th>Powder</th>
<th>Bonds broken</th>
<th>Sintered Density at 76 MPa (%)</th>
<th>Green Density (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Surface Area (m&lt;sup&gt;2&lt;/sup&gt;/g)&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>93.8</td>
<td>90</td>
<td>40.0</td>
<td>26.1</td>
</tr>
<tr>
<td>B</td>
<td>85.0</td>
<td>81</td>
<td>39.0</td>
<td>20.6</td>
</tr>
<tr>
<td>C</td>
<td>83.3</td>
<td>70</td>
<td>40.7</td>
<td>19.2</td>
</tr>
<tr>
<td>D</td>
<td>79.6</td>
<td>57</td>
<td>43.0</td>
<td>12.4</td>
</tr>
<tr>
<td>E</td>
<td>74.0</td>
<td>51</td>
<td>47.8</td>
<td>7.8</td>
</tr>
<tr>
<td>F</td>
<td>60.6</td>
<td>26</td>
<td>51.6</td>
<td>2.5</td>
</tr>
</tbody>
</table>

<sup>a</sup>Isostatically pressed at 70 MPa.

<sup>b</sup>Percent of theoretical density.

<sup>c</sup>Loose powder.
agglomerate strength. The sintered density (Table III) varied inversely with the BET surface area of the loose powder, increasing as the powder surface area decreased. As shown in Table II, the sintered density also varied inversely with the green density of the pressed compact, except for the first three powders, whose green densities were essentially equal. The sintered densities of the compacts for both air and vacuum sintering vs the percentage of original bonds broken at 76 MPa ultrasonic breaking pressure plots are shown in Figure 7. The curves, which have almost linear portions, show the nature of the direct correlation between agglomerate strength and sinterability of the powders.

Optical micrographs of polished and etched pellets for each powder pressed at 70 MPa and sintered for 2 h at 1400°C are shown in Figure 8. The grains are 1-5 μm in size, about an order of magnitude larger than the original spheres. Grain growth occurred due to random packing of the spheres in the agglomerates and to the relatively high sintering temperature employed. Barringer et al. (8) found that dense, ordered packings of monosize spherical particles retard grain growth and sinter to high densities at low temperatures. Similar results have been observed at 1100°C for ordered, and even partially ordered, packings of the yttria spheres used in the present work. Thus, although the usual sintering temperature for commercial yttria powders is 1700-1800°C, 1400°C is still a relatively high temperature for the type of powders reported here. The pores are mostly outside the grains. As the strength of the agglomerates in the powders increases, the structure of the sintered pellet becomes more and more similar to the structure of the green compact. The dense regions, whose sizes are on the order of the
original agglomerates, are surrounded by a porosity network that becomes increasingly interconnected.
Figure 7. Sintered density of powder pellets vs interagglomerate bonds broken during ultrasonic irradiation of loose powder at a breaking pressure of 76 MPa.
Figure 8. Optical micrographs of etched and polished yttria pellets pressed isostatically at 70 MPa and sintered at 1400°C in air: (A) powder A; (B) powder B; (C) powder C; (D) powder D; (E) powder E; (F) powder F. Bars= 50 μm
DISCUSSION

The major differences in the six powders studied was in the strength of the necks among the particles within the agglomerates. All of the powders had the same monosize spherical primary particles, and the size distributions of the agglomerates were very nearly the same. The effects of changes in particle morphology were thus essentially eliminated. This was confirmed by the smooth variation of sintered density with powder surface area in Table III. This correlation is often not seen when powders with different particle morphologies are compared. The most easily discernible effect of agglomerate strength alone, however, can be seen in the results for powders A, B, and C. The compaction curves were almost identical for these three powders and their green densities were the same, within reasonable experimental error. Still, the sintered density decreased substantially from powder A to powder C as the strength of the agglomerates increased.

An even more critical view of the importance of agglomerate strength, or perhaps more accurately, the presence or absence of an agglomerate structure in the pressed compact can be seen in the results for only powders A and B. For powder A, the agglomerate structure was completely broken down when the powder was pressed, as shown in the mercury porosimetry data in Figure 4, whereas evidence of unbroken fragments of agglomerates can be seen for powder B. For the loose powders the total intruded volume (Table I), and also its distribution between interagglomerate and intraagglomerate pores was equal for both powders. For the pressed pellets, the total intruded volume also was nearly equal, but its distribution between interagglomerate and intraagglomerate porosity was significantly different, reflecting a residual agglomerate
structure in the pellets pressed from powder B. This difference was confirmed in the agglomerate strength versus sintered density data in Figure 7.
CONCLUSIONS

Yttria powder agglomerates formed from monosize spherical aggregates were prepared from a common precursor powder by calcining at various temperatures. The agglomerates in the six powders, which had about the same size, shape and morphology, were characterized. Agglomerate strength distributions of the powders were obtained by a technique which involves the use of ultrasonic energy. A direct correlation between agglomerate strength and sintered densities of the powders was found.
ACKNOWLEDGEMENT

This work was conducted through the Ames Laboratory which is operated by Iowa State University for the U.S. Department of Energy under contract No. W-7405-Eng-82. This work was supported by the Director of Energy Research, Office of Basic Energy Sciences.
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SECTION IV. MEASUREMENT OF AGGLOMERATE STRENGTH DISTRIBUTIONS IN AGGLOMERATED YTTRIA STABILIZED ZIRCONIA POWDERS
ABSTRACT

Sintered densities of pellets of several different yttria-stabilized zirconia powders were found to correlate directly with the measured strength of the agglomerates in the loose powders. No systematic correlation was observed between sintered density of the compact and surface area or tap density of the powder, or between sintered density and green density of the compact. The phenomena of differential sintering was studied by mixing two powders having weak and strong agglomerates. Large voids and cracks surrounding the strong agglomerates were observed in the sintered microstructures.
INTRODUCTION

Most ceramic powders contain agglomerates, which form during powder preparation. Vasilos and Rhodes (1) were the first to provide clear experimental evidence that agglomerates interfere with the densification process. The difference in pore sizes between the agglomerates and the surrounding powder matrix in a yttria stabilized zirconia compact caused differential sintering and the subsequent formation of internal crack-like pores in the sintered body. They were able to sinter a centrifuge cast compact, from which the agglomerates had been removed by sedimentation, to near theoretical density at 1100°C — several hundred degrees lower than the normal sintering temperature. Lange et al. (2,3) showed that the crack-like internal surfaces caused by differential sintering of agglomerates can be fracture-initiating flaws.

The preparation of powders which are completely unagglomerated, or powders in which the agglomerates are weak enough to break down completely when the powder is pressed, has become an important aspect of ceramic processing. In earlier work by the authors on agglomerated yttria powders, the strength distributions of the agglomerates formed from irregularly shaped particles were determined by a technique which involved the use of a calibrated ultrasonic field. The sintered densities of the pressed powders were shown to be directly related to the strength of the agglomerates. There were no consistent correlations between sintered densities and other measured properties of the powders or the pellets (4). Later, the effect of particle morphology was eliminated by using powders consisting of agglomerates of monosize spherical particles (5). With these powders it was possible to show a clear effect of agglomerate strength on sintered density when all other
properties of the powders and the pressed compacts were essentially the same. Here the effect of agglomerate strength on sintered density is extended to a variety of yttria-stabilized zirconia powders.

There are basically two routes for the preparation of stabilized zirconia powders. Coprecipitation from a water solution of the mixed chlorides is the one which is most often used commercially. In this technique, described by Haberko (6), a final ethanol dewatering step is used to produce weak agglomerates which break up easily when the calcined powder is pressed (7,8). Substitution of the alcohol, which has a lower surface tension than water, minimizes the effect of surface tension forces at the contact points of the intraagglomerate particles during drying of the precipitate. It also reduces solid bridge formation at the contact points because the precipitate is less soluble in the alcohol.

The second route (9) involves the use of metal alkoxides. A mixed alcoholic solution of a zirconium and a yttrium alkoxide is either thermally decomposed in a vapor-phase reaction (10) or hydrolyzed by adding an appropriate amount of water (11-13). Both methods can yield very fine powders which are highly sinterable. Monodisperse yttria-stabilized zirconia powders with submicrometer size, spherical particles also have been prepared by controlled hydrolysis of alcoholic solutions of the mixed alkoxides (14).

In the present work, agglomerate strength distributions and other powder properties of five different yttria stabilized zirconia powders, prepared by coprecipitation in the laboratory from aqueous chloride or nitrate solutions, and of powders of similar composition obtained from two commercial sources were determined. Sintering studies were carried out on these powders and the sintered densities were related to the
powder properties, including agglomerate strength. The effect of differential sintering of agglomerates was shown by using a mixture of two different powders, one with weak agglomerates and one with strong agglomerates.
EXPERIMENTAL

**Powder preparation and characterization**

The five coprecipitated powders prepared in the laboratory each contained 6 mole% $Y_2O_3$. Different precipitation procedures and dewatering techniques were used to produce agglomerates having a variety of characteristic properties (4). Powders Z1 through Z4 were reverse strike powders; the cation solution was added to a solution of the precipitant. This procedure is used in coprecipitation to insure that the solubility products of all of the cations are exceeded simultaneously, so that cation segregation is minimized. A 0.2 M solution of the cations, in the desired mole ratio, was prepared from zirconium tetrachloride and yttrium chloride solutions. It was added slowly to enough 2.5 N NH$_4$OH solution to precipitate the precursor hydroxides. The suspension was filtered and the precipitate resuspended and filtered again three times with pH adjusted distilled water to remove the chlorine ions from the precipitate.

For powder Z1, the precipitate was resuspended in ethanol, filtered, and mixed in ethanol again, using a laboratory blender. This final suspension was filtered through a Buchner funnel by air suction. The cake was dried in a hot mortar and pestle to remove the remaining ethanol, and calcined in air at 800°C for 2 h.

For powder Z2, the water-washed precipitate was dried in an oven overnight at 110°C, and calcined at 800°C for 2 h. To prepare powder Z3, the water-washed precipitate was resuspended, blended in pH adjusted water, spray dried (using Model 190 Mini Spray Dryer, Brinkman/Buchi Instruments Co., Westbury, NY), and calcined at 1000°C for 2 h. For
powder Z4, the precipitate was resuspended in ethanol and filtered three times, dried in air, and calcined at 1000°C for 2 h.

Powder Z5 was a direct strike powder, made by adding a 2.5 N NH₄OH solution to a nitrate solution of the cations. Only one such powder was made this way because of the tendency for segregation of the cations. The initial nitrate solution is strongly acidic; zirconium precipitation begins at a pH of about 3.0, whereas yttrium precipitation does not start until the pH reaches 6.5. The cake was filtered, resuspended and filtered three times in water and two times in acetone. It was then dried in a hot mortar and pestle, and calcined at 1000°C for 2 h.

Powders Z1, Z3 and Z5 passed through a 200 Mesh (74 μm) sieve easily; powders Z2 and Z4 had to be ground with a mortar and pestle to break up the calcined mass.

Powders Z6 and Z7 were experimental powders obtained from a commercial source. Powder Z6 contained 4.5 mol % yttria; powder Z7 had 3 mol % yttria. Powders Z8 and Z9, obtained from a different commercial source, contained 3 mol % yttria and 8 mol % yttria, respectively. These four powders were used as received, without any further conditioning.

Several attempts to prepare powders consisting of submicrometer-size, monodisperse spherical particles by the method described earlier by Fegley et al. (14) were unsuccessful; gel-like precipitates were obtained instead. The only apparent difference in the precipitation conditions was that the yttrium isopropoxide was obtained from a different source. No explanation for this failure could be found, but the process is most likely very sensitive to hydrolysis conditions.

Particle size distributions were measured with a sedimentation-type particle size analyzer (Model 5000ET Sedigraph, Micromeritics Instrument
Corp., Norcross, GA) which had a lower detection limit of 0.2 μm. Surface areas were found by the BET method (using Leeds and Northrup Automatic Surface Area Analyzer, Model 4200, North Wales, PA) using nitrogen as the adsorbate. Samples of each of the powders also were examined with a scanning electron microscope (Model 100 CX, Japan Electron Optics Labs, Tokyo, Japan). Transmission electron microscope pictures of some of the powders were taken. Intrusion pore size distributions for the loose powders and for their compacts (isostatically pressed at 210 MPa) were obtained by mercury porosimetry (using Autoscan Scanning Porosimeter, Model SP-200, Quantachrome Corp., Syosset, NY).

The strength distributions of the agglomerates in each of the nine powders were calculated from particle distributions measured after dispersing samples of the powders in an aqueous medium (a dilute sodium pyrophosphate–water solution) and subjecting them to consecutively higher ultrasonic breaking pressures from 1 MPa to 76 MPa using an ultrasonic probe (Model TSD500 Sonic Disruptor, Tekmar Co., Cincinnati, OH) calibrated in a manner described earlier (4,5).

**Sintering studies**

For the sintering experiments, 0.8 g powder samples were dry-pressed to 35 MPa in a 9.5 mm tungsten carbide-lined die lubricated with stearic acid, and then pressed isostatically to 210 MPa. The pressed pellets were sintered in air for 2 h at various temperatures from 1200 to 1400°C. Sintered densities were measured using a water displacement method and compared with the theoretical densities given by Ingel and Lewis (15). Scanning electron microscope pictures of the fracture surfaces of the
sintered pellets prepared by mixing powders Z7 and Z8 were taken to show differential sintering effects.
RESULTS

**Powder characterization**

Scanning electron micrographs of typical particles are shown in Figures 1a, 1b, and 1c. The agglomerates found in those powders (Z1-Z5) prepared in the laboratory had the three-particle structure typical of hydroxides or hydrous oxides made by chemical precipitation from solution (4). In the precursor precipitate, one finds very small primary particles of the order of a few tens of Angstroms; these are the particles formed, either by nucleation or by polymerization, as a result of chemical reaction. These primary particles coagulate to form dense aggregates, usually of the order of 0.1 to 0.3 micrometer in size. The aggregates, in turn, combine to form more porous and less tightly bonded agglomerates up to a few tens of micrometer in size. This structure, formed during precipitation and washing of the precursor, remains largely intact after calcination. When the precursor precipitate is calcined, the aggregates are converted to polycrystalline material; these dense polycrystalline particles are the small sub-units visible in the calcined agglomerates shown in Figure 1a, parts A, B, and D, and in Figure 1c, part D. Under ultrasonic irradiation, the agglomerates may be broken into the dense polycrystalline aggregates, but the aggregates are usually too strong to be affected.

Particle size distributions, before and after ultrasonic treatment of the powder samples, are shown in Figures 2a, 2b, and 2c. They were measured with the sedimentation type particle size analyzer. Since the agglomerates were porous, a sedimentation density was found by assuming that the intraagglomerate pores were filled with water during the
Figure 1a. Scanning electron photomicrographs of agglomerated yttria stabilized zirconia powders: (A) powder Z1 (bar=2 μm); (B) powder Z2 (bar=4 μm); (C) powder Z3 (bar=5 μm); (D) powder Z4 (bar=2 μm).
Figure 1b. Scanning electron photomicrographs of agglomerated yttria stabilized zirconia powders: (A) powder Z6 (bar=50 μm); (B) powder Z7 (bar=20 μm); (C) powder Z7 (bar=5 μm); (D) powder Z7 (bar=2 μm)
Figure 1c. Scanning electron photomicrographs of agglomerated yttria stabilized zirconia powders: (A) powder Z9 (bar=100 μm); (B) powder Z3 (bar=50 μm); (C) powder Z9 (bar=10 μm); (D) powder Z9 (bar=1 μm)
Figure 2a. Particle size distribution curves for powders Z1-Z4 before treatment and after exposure to ultrasonic breaking pressures of 1 MPa and 76 MPa
Figure 2b. Particle size distribution curves for powders Z6 and Z7 before treatment and after exposure to ultrasonic breaking pressure 76 MPa.
Figure 2c. Particle size distribution curves for powders Z8 and Z9 before treatment and after exposure to ultrasonic breaking pressures of 1 MPa and 76 MPa.
Comparison of the curves in these figures show readily that the powders behaved differently when subjected to the same ultrasonic sound fields. Except for powders 28 and 29, which consisted of very large (52 μm) spherical agglomerates produced by spray drying, the agglomerates in the untreated powders had size distribution curves which peaked in the 20-30 μm size range.

The mercury intrusion curves for the loose powders and for their pressed compacts are shown in Figure 3a through 3e. These curves were all bimodal for the loose powders; some remained bimodal for the pressed compacts. The pressure-volume curves obtained from the mercury porosimeter were separated in two portions— the interagglomerate pore volume and the intraagglomerate pore volume. From this information, agglomerate densities were calculated.

The agglomerate strength curves were calculated as described in earlier work (4,5). The aggregates were assumed to be spherical, 0.1 μm in diameter, for all of the powders. This size was taken from the photomicrographs in Figures 1a through 1c. The powder suspensions were treated in the ultrasonic media at five different settings corresponding to breaking pressures between 1 MPa and 76 MPa. The fraction of treated powder which was reduced to particle sizes below 0.2 μm (the detection limit of the particle size analyzer), was assumed to consist of individual aggregates. The particle size distribution of the untreated powder was divided into ten size intervals and the size at the midpoint was used as the size of the agglomerates in that size fraction. After finding the number of bonds in the original powder, using one hundred aggregates as a basis of calculation, the calculations were then repeated for the particle size distributions obtained for each breaking pressure.
Figure 3a. Intrusion pore size distribution curves for powder Z1
Figure 3b. Intrusion pore size distribution curves for powders Z2 and Z3.
Figure 3c. Intrusion pore size distribution curves for powders Z4 and Z5
Figure 3d. Intrusion pore size distribution curves for powders Z6 and Z7
Figure 3e. Intrusion pore size distribution curves for powders Z8 and Z9
The resulting agglomerate strength distribution curves are shown in Figure 4.

A summary of the data derived from the various particle characterization techniques is given in Tables I and II. The powder characterization tests gave a clear picture of the differences among nine powders. They could be easily separated into three groups.

Powders Z1, Z8, and Z9 all contained weak agglomerates which broke easily in the ultrasonic sound field, even at a low breaking pressure of 1 MPa. At 76 MPa, 88%, 92%, and 90% of the interagglomerate bonds were broken. The loose powders had bimodal pore size distributions, but when they were pressed all interagglomerate porosity was eliminated. The remaining pores had narrow size distributions with peaks at sizes slightly smaller than the intraagglomerate pores in the loose powders. None of the other powders showed this behavior. All of the characterization data for powders Z8 and Z9 were very nearly the same. They had obviously been prepared in the same way, differing only in yttria content. Powder Z1 was less dense than any of the other powders. It had a higher surface area and a lower tap density than any of the other powders, and the agglomerates were more porous. This latter conclusion, which is based on properties of the loose powders, should be viewed with caution when powder Z1 is compared with spray-dried powders Z8 and Z9. Comparisons with data on the pressed pellets are more meaningful for these three powders, and the looser structure of powder Z1 is still evident in the green densities of the pellets.

Powders Z2 and Z4 contained stronger agglomerates than were present in powders Z1, Z8, and Z9. For powders Z2 and Z4, the agglomerates broke less easily under ultrasonic irradiation. At breaking pressures of 76
Table I: Distribution of interagglomerate and intraagglomerate porosity
for loose powders and for pressed compacts

<table>
<thead>
<tr>
<th>Powder</th>
<th>Loose Powder</th>
<th>210 MPa Compact</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intruded Volume cm³/gm</td>
<td>Interaggl. a Porosity cm³/gm</td>
</tr>
<tr>
<td>Z1</td>
<td>1.095</td>
<td>0.655</td>
</tr>
<tr>
<td>Z2</td>
<td>0.325</td>
<td>0.198</td>
</tr>
<tr>
<td>Z3</td>
<td>0.409</td>
<td>0.350</td>
</tr>
<tr>
<td>Z4</td>
<td>0.325</td>
<td>0.165</td>
</tr>
<tr>
<td>Z5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Z6</td>
<td>0.220</td>
<td>0.180</td>
</tr>
<tr>
<td>Z7</td>
<td>0.145</td>
<td>0.110</td>
</tr>
<tr>
<td>Z8</td>
<td>0.335</td>
<td>0.090</td>
</tr>
<tr>
<td>Z9</td>
<td>0.375</td>
<td>0.142</td>
</tr>
</tbody>
</table>

aInteragglomerate porosity between the agglomerates.
bIntraagglomerate porosity within the agglomerates.
| Powder | Surface Area $^a$ m$^2$/g | $d_{BET}$ μm | Tap Density gm/cm$^3$ | Green Density$^b$ %TD$^a$ | %Agglomerate Bonds Broken 1400°C at 76 MPa | Sintered Densities of Pellets$^c$ 1300°C | 1250°C | 1200°C |
|--------|---------------------------|-------------|-----------------|------------------|---------------------------------|----------------|--------|--------|--------|
| Z1     | 66.05                     | 0.01506     | 9.70            | 43.33            | 88                              | 87.78          | 98.06  | 97.49  | 95.39  |
| Z2     | 34.37                     | 0.02895     | 25.52           | 51.07            | 35                              | 86.73          | 86.55  | 85.74  | -      |
| Z3     | 6.32                      | 0.15740     | 18.95           | 46.45            | 0                               | 78.96          | 76.21  | 71.14  | -      |
| Z4     | 18.52                     | 0.05373     | 23.95           | 46.85            | 31                              | 83.00          | 81.38  | 80.76  | -      |
| Z5     | 4.00                      | 0.24870     | 19.17           | 52.82            | 0                               | 70.93          | 59.26  | 66.44  | -      |
| Z6     | 3.81                      | 0.25980     | 39.32           | 47.10            | 0                               | 57.59          | 55.99  | 56.44  | -      |
| Z7     | 5.18                      | 0.19050     | 36.16           | 49.56            | 9                               | 57.59          | 55.31  | 54.97  | -      |
| Z8     | 19.21                     | 0.05140     | 22.84           | 49.74            | 92                              | 99.14          | 98.55  | 96.67  | 89.72  |
| Z9     | 15.90                     | 0.06290     | 22.50           | 48.87            | 90                              | 98.86          | 95.01  | 92.39  | 75.47  |

$^a$Percent of theoretical density.

$^b$Heating rates are 11.7°C/min for 1400°C and about 1.7°C/min for other sintering tests.

$^c$Isoostatically pressed at 210 MPa final pressure.
Figure 4. Agglomerate strength distribution curves for yttria stabilized zirconia powders.
MPa, about the same number of intraagglomerate bonds were broken in both powders—35% in powder Z2 and 31% in powder Z4. The bimodal pore size distributions in the loose powders could still be seen in the pressed compacts. All of the characterization data were so similar that no useful conclusions could be drawn about differences between these two powders. It is useful, however, to compare the results with those obtained for powder Z1. The effects of eliminating the final alcohol washes for powder Z2 produced about the same effect as calcining the ethanol-washed powder Z4 at 1000°C instead of 800°C. In both cases the quality of the powder was substantially lower than for powder Z1.

The agglomerates in powders Z3, Z5, and Z6 were too strong to be broken at the highest ultrasonic pressure available (76 MPa); it was not possible to rank these powders according to the strength of their agglomerates. For powder Z7, only 9% of the intraagglomerate bonds could be broken. All of these powders had very low BET surface areas. The pore size distribution curves for the pressed compacts were bimodal, with very little intraagglomerate porosity. Most of the porosity was found in pores among unbroken agglomerates.

The agglomerates in powders Z6 and Z7 were unique among the nine powders tested. This is immediately apparent in the SEM photomicrographs in Figure 1b. They appear to have a narrow size distribution, an observation which is confirmed by the particle size distribution curves in Figure 2b. It is difficult to imagine that powders Z6 and Z7 were made by precipitating the hydrous oxide. Since zirconium obtained by the caustic treatment of zircon sands is sometimes purified by a sulphuric acid leaching process, it is more likely that the precursor of these powders was a basic zirconium sulfate. Larsen and Gammill (16) have
described such a precipitation, indicating that the precipitate was very granular and dense in nature compared to the gelatinous precipitates obtained by precipitation of hydrous zirconia from chloride and nitrate solutions.

Sintering tests

The densities of the sintered pellets are given in Table II. Except for agglomerate strength, there was no consistent correlation of sintered density with any of the powder properties listed in Table II. The relation of agglomerate strength to sintered density is shown in Figure 5. Powders Z1, Z8, and Z9, which had the weakest agglomerates among the nine powders, sintered to the highest densities. The percent of intraagglomerate bonds broken at 76 MPa was almost the same for these three powders. For powders Z8 and Z9 the difference was only 2%, yet the powder (Z9) with the slightly stronger agglomerates sintered to the lower density at all sintering temperatures. Sintered densities for powder Z1, which had the strongest agglomerates among these three powders by a margin of only another 2%, did not produce a consistent correlation with the densities of the other two powders. At 1200°C and 1250°C, it sintered to the highest density. At 1300°C it reached a density slightly lower than that of powder Z8, and at 1400°C the density of the Z1 pellets were substantially lower than those of both powders Z8 and Z9.

The reason for the seemingly anomalous behavior of powder Z1 can be seen in the TEM photomicrographs in Figure 6. The polycrystalline aggregates in the Z1 powder are much smaller (~150-200Å) than those in powder Z8 (~800-1000Å); powder Z1 is a highly active powder. It therefore begins to sinter to high density at a lower temperature, as
Figure 5. Sintered density of powder pellets vs interagglomerate bonds broken during ultrasonic irradiation of loose powder at a breaking pressure of 76 MPa
Figure 6. Transmission electron photomicrographs showing the polycrystalline aggregates in agglomerates of (A) powder Z1; (B) powder Z4; (C) powder Z8 (Bars= 0.3 μm)
shown in Table II. However, when such powders are sintered at too high a temperature and too rapid a heating rate, closed porosity can develop in the pellet and the full sintering potential of the fine particles is not realized. This occurred for powder Z1 when it was sintered at 1400°C.

Powders Z2 and Z4 also had agglomerates of nearly the same strength, but they were stronger than those in powders Z1, Z8, and Z9. For powder Z2, 35% of the intraagglomerate bonds were broken at 76 MPa and 31% were broken for powder Z4—a difference of only 4%. However, the powder with the slightly stronger agglomerates, as measured by the agglomerate strength calculations, again sintered to the lowest density at all temperatures employed.

Except for powder Z7, all of the remaining powders contained agglomerates that were too strong to be broken at even the highest setting of the ultrasonic probe. Thus no comparison of the sintered densities of these powders with the strength of their agglomerates was possible. The agglomerate strength calculations for powder Z7 showed that 9% of the intraagglomerate bonds were broken at 76 MPa, but the sintered densities of the pellets were the lowest values obtained for any of the powders. There is a probable reason for this inconsistency in an agglomerate strength measurement technique that had consistently been able to show differences in sintered density for powders with only a few percent difference in the strength of their agglomerates. The agglomerates in powder Z7 had cracks in them. These cracks are clearly visible in the photomicrographs in Figure 1. Irradiation of suspensions of this powder by the ultrasonic probe may simply have fractured these agglomerates along the pre-existing cracks. The resulting changes in the particle size distributions, from which the agglomerate strength was
calculated, would not have been a true measure of the strength of the intraagglomerate bonds.

Examples of differential sintering caused by the presence of strong agglomerates in a matrix of highly sinterable powder are shown in Figure 7. The internal crack-like pores caused by the difference in sintering rates between the agglomerates and the surrounding matrix are clearly visible. The pellets were sintered in air at 1400°C, under the same conditions given in Table II for pellets of pure powder Z8. For pellets containing 5% and 10% powder Z7, the sintered density dropped from 99.14% to 96.39% and 93.395 respectively. These results show very clearly the detrimental effect of strong agglomerates in ceramic powders.
Figure 7. Scanning electron photomicrographs of fracture surfaces for pellets of powder Z8 to which small amounts of powder Z7 had been added: (A) 10% Z7 (bar=25 μm); (B) 10% Z7 (bar= 10 μm); (C) 5% Z7 (bar=50 μm); (D) 5% Z7 (bar=20 μm)
DISCUSSION

As was shown in earlier work on yttria powders (4,5), a direct correlation was found between agglomerate strength and sintered density for the yttria-stabilized zirconia powders. Sufficient data on agglomerate strength measurement using the calibrated ultrasonic probe, and on the relation of these measurements to sintered density have been accumulated, that some tentative generalizations about the method can be made. For powders of the same material, pressed and sintered under the same conditions, the sintered densities can be ordered according to the measured strength of the agglomerates in the loose powders, even though the morphology of the particles in the various powders may be substantially different. This correlation has been found consistently when such powders showed no correlation whatever between sintered density and other common powder properties such as BET surface area, tap density, pressed density, or compaction data. Other than agglomerate strength measurements, mercury porosimetry curves for the loose powder and the pressed compact appear to supply the best data on potential sintering behavior; but mercury porosimetry curves of similar powders rarely enable one to actually arrange the compacts in order of their sintered density.

The agglomerate strength measurement technique appears to be a quite sensitive method of predicting sinterability, in terms of sintered density. For the yttria-stabilized zirconia powders, two cases were found where a difference of only 2% in the number of intraagglomerate bonds broken during ultrasonic irradiation of the powders permitted the pellets to be ordered correctly in terms of their sintered densities. These were powders Z2 and Z4, and powders Z8 and Z9. In previous work on yttria powders, two examples were found where a 4.5% and a 6% difference,
respectively, gave the correct correlation between agglomerate strength and sintered density. From this, one may conclude that a difference of 6%, or more conservatively, 10%, in the number of intraagglomerate bonds broken in the agglomerate strength test will permit ranking two powders, pressed and sintered under the same conditions, in order of their sintered density.

A notable exception to these generalizations was found when powder Z1 was compared with powders Z8 and Z9, all of which sintered to very high densities. When such active powders are compared, very small differences in agglomerate strength may be overshadowed by an improper choice of sintering temperature and/or heating rate.

One other interesting observation should be made. In all of the agglomerate strength curves measured to date on powders of the same material, the curves have never crossed each other. For the powders measured so far, the relative agglomerate strength of the powders seems to be established at low breaking pressures and does not change at higher breaking pressures.
CONCLUSIONS

The sintered densities of the yttria-stabilized zirconia pellets correlated directly with the measured strength of the agglomerates in the loose powders. Only one exception was found, for the case where very active powders were compared. In such cases, very small differences in agglomerate strength may be overshadowed by the enhanced sinterability of smaller crystallites. Otherwise, even small differences—of the order of a few percent—in the agglomerate strength of the powders correlate with the sintered densities of the pellets over a temperature range of 1200°C to 1400°C.
ACKNOWLEDGEMENT

This work was conducted through the Ames Laboratory which is operated by Iowa State University for the U.S. Department of Energy under contract No. W-7405-Eng-82. This work was supported by the Director of Energy Research, Office of Basic Energy Sciences.
REFERENCES


Summary

The need for more reliable structural and electronic ceramics, with reproducible properties, created a corresponding need for higher sintered densities with commensurate increases in mechanical strength and homogeneous electrical properties. One of the major impediments to achieving these goals has been the detrimental effects of agglomerated particles in ceramic powders. Although the effects of agglomerates were reported as early as 1957, the problem was not fully appreciated until the late 1970s—probably because this date corresponded with the miniaturization of solid-state electronic devices and the need for structural materials that could withstand the harsh environments encountered in advanced energy conversion systems.

In more recent years, much research effort has been placed on eliminating or controlling agglomeration in ceramic powders. However, as time passed, the typical particle size found in high-quality powders steadily decreased. It is now well into the sub-micrometer range, where the tendency toward agglomeration is very great because of the dominant roles by surface forces in determining the behavior of such small particles. Despite the substantial effort devoted to studying the effect of agglomerates, there has been no way of measuring, quantitatively, the strength of agglomerates in fine powders. This research was aimed at filling that need.

In Part I of this work, a means of determining the strength distributions of hollow glass microspheres by using mercury porosimetry was developed. These bubbles were then used for determining the breaking
pressure of the pressure waves in an ultrasonic sound field.

In Part II, an ultrasonic probe with a variable power output—calibrated by using the bubbles described in Part I, was used to irradiate various ceramic powders. The data so obtained were used, in combination with the classical Rumpf equation for calculating the strength of bonds between particles, to find the agglomerate strength distributions of a variety of different yttria powders. The measured strength of the agglomerates in the loose powders were shown to correlate directly with the densities of pressed and sintered pellets. Significantly, there was no correlation of sintered density with any other commonly used powder characterization data such as BET surface area, tap density, agglomerate size distribution, or green density. This is the first time that any powder characterization parameter has been measured which could actually rank a series of powders of the same material, pressed and sintered under the same conditions, in order of their sintered densities. It shows, quantitatively, the overwhelming importance of agglomerate strength in ceramic powders.

In Part III, the importance of agglomerate strength alone, when all other properties of the powders were equal, was shown. This was accomplished by preparing 0.1 μm spherical, monosize particles by homogeneous precipitation and intentionally agglomerating them. This is the first time that agglomerate strength has been isolated from all other properties of two ceramic powders and its effect on sintered density actually demonstrated experimentally.

In Part IV, investigation of the relationship between agglomerate strength and sintered density was extended to yttria-stabilized zirconia powders. The same correlation held for these powders. Their sintered
densities could be ranked according to the strength of the agglomerates in the loose powders. It was further found that differences of only 2% in the strength of two powders was sufficient, in the case studied, to predict which powder would sinter to the highest density under the same conditions. In earlier work, agglomerate strength differences of 4.5% and 6% were sufficient to order two powders according to their sintered densities. Cumulatively, the results mean that the technique, developed in this work, for measuring agglomerate strength distributions provides a sensitive means of differentiating the quality of two similar ceramic powders.

Recommendations for future work

The use of the calibrated ultrasonic probe has proved to be useful in the determination of agglomerate strength distributions. Useful data have been obtained, which gave significant insight into the role played by the strength of agglomerates in the processing of ceramics. Further refinement of the calculation procedures would be helpful. The following are some specific suggestions on the use of ultrasonic forces for agglomerate strength determination and on the use of model spherical powders.

1. The calibrated ultrasonic field used in this work was applied to inorganic powders. The same system should be used for the strength determination of organic based flocs or cells.

2. The ultrasonic system had a breaking pressure range of 1 to 76 MPa in this work. This range should be enlarged by an appropriate ultrasonic disruptor design which can yield valuable information for very strong bonds in ceramic powders.
3. The low strength end of the calibration should be worked out in more detail to differentiate between a series of powders having weak agglomerates. This area of work becomes increasingly important as better powders are developed to yield very high sintered densities.

4. The relation between strength values and the neck sizes between monodisperse spheres should be investigated, possibly through careful TEM examination and neck size measurements from the photomicrographs. This can yield valuable information which can be related to theoretical calculations of the strengths of interparticle bonds and solid bridges.

5. More differential sintering studies should be done by adding a series of hard agglomerates with varying agglomerate strengths to a highly sinterable powder matrix. Actual strength measurements on ceramic pieces fabricated from these powders should be tied to the differential sintering results.

6. The studies in this work were mostly on calcined ceramic oxide powders. Similar studies on precursor agglomerates would be valuable. This may produce information that could help to differentiate between alternate processing routes for producing weak precursor flocculates.

7. A better way of estimating coordination number distribution in randomly packed or ordered monosize particle packings would be helpful in making more accurate agglomerate strength calculations. X-ray diffraction methods involving the use of radial distribution functions may be useful in this area.

8. Pore structure characterization of ordered compacts of monodisperse particles by using mercury porosimetry should be done.
9. Studies on agglomerate strength determination should be done on agglomerates formed from monosize powders of materials other than yttria; both randomly packed agglomerates and agglomerates with ordered structures should be studied.
ADDITIONAL LITERATURE CITED


ACKNOWLEDGEMENT

I would like to thank Dr. L. E. Burkhart for his advice, guidance and understanding throughout the work. He taught me, along the way, a great deal about how to be a better researcher. I will try to make the best use of the knowledge he has given me.

I would like to express my deepest gratitude to Dr. M. Akinc, to whom I owe the opportunity for carrying out my research at Iowa State, for his guidance, understanding, and friendship during the course of the work. I have learned a lot from him.

I would like to thank Dr. M. F. Berard, Dr. C. E. Glatz, Dr. M. A. Larson and Dr. B. R. Munson for their valuable contributions.

I also would like to thank all my friends both here and back in my own country, who encouraged and helped me throughout the work.

Special thanks are to Glen Oren, KwangSoo No, Ray Jouett, Harlan Baker, Randy Keisler and Jerry Amenson for their help during various stages of the work.

Finally, I would like to thank my best friend in life, my wife Rukiye, for her love, patience, encouragement and understanding. Her support made it all possible.