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**THIN-WALL HOLLOW CERAMIC SPHERES
FROM SLURRIES**

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Final Report

(ROUGH DRAFT)

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1.0 INTRODUCTION

The overall objective of this effort was to develop a process for economically fabricating thin-wall hollow ceramic spheres from conventional ceramic powders using dispersions. This process resulted in successful production of monosized spheres in the mm size range which were point contact bonded into foams. Thin-wall hollow ceramic spheres of small (one to five millimeter) diameter have novel applications as high-temperature insulation and light structural materials when bonded into monolithic foams.

Other laboratories have fabricated small solid spheres, and in a few cases, even thin-wall hollow spheres of ceramics have been made either from the melt or from sol-gel processes. These approaches have limited the production to either the lower temperature melting ceramics, such as glass, or those that can be made from sol-gel solutions, such as alumina and are expensive. Small diameter spheres of SiC or Si₃N₄ have not been made by other processes but could be made by the process presented here if applications emerge. The basic approach in the present work was to use a patented coaxial nozzle process for formation of hollow spheres from powder dispersions or slurries, permitting the use of virtually any ceramic composition.

This program ran continuously under several contracts from January, 1986 to December 1992. During Phase I of this program the objective was to develop a process for fabricating thin-wall hollow spheres from powder slurries using the coaxial nozzle fabrication method. This objective was successfully met by utilizing alumina powders dispersed in organic liquids, where the individual spheres could be blown at rates between 30 to 100 spheres/second, and dropped into a heated updraft air column to provide time sufficient for drying. The dried spheres had the strength necessary to survive landing and collection on a hard surface. These polymer bonded powder shells were then fired and sintered to dense walls and high strength hollow spheres. The resulting spheres were monosized to $\pm 5\%$ in diameter for fixed process parameters, could be varied in diameter from 1 to 5 mm, and wall thickness could be varied from 50 to 200 microns and could be made uniform in thickness, Figure 1.1.1. By varying diameter and wall thickness, bulk density of sphere beds could be varied from 5 to 50 % of theoretical density (10-100 lb/ft³).

Based on the success during Phase I, Phase II was revised to emphasize the assessment of the potential structural and insulation applications for the spheres and modeling of the sphere formation process was initiated. As more understanding developed, it was clear that to achieve successful structural application, the spheres had to be bonded into monolithic foams and the effort was further expanded to include both bonding into structures and finite element mechanical modeling which

became the basis of Phase III. Successful bonding techniques and mechanical modeling resulted but thermal conductivities were higher than desired for insulating activities. In addition, considerable interest had been expressed by industry for the technology. Thus the final Phase IV concentrated on methods to reduce thermal conductivity by a variety of techniques and technology transfer through individualized visits. This program resulted in three Ph.D. theses and 10 M.S. theses and they are listed in the appropriate technical sections below.

Technically, the program was divided into three distinct areas; (1) processing of hollow spheres including slurry rheology, fluid dynamic modeling, and aqueous gelling technology, (2) mechanical testing and modeling of individual spheres and monolithic foams and (3) thermal conductivity of spheres and foams and efforts to reduce conductivity. In addition, efforts to produce and characterize metal sphere foams were conducted under this program and high permeability applications dictated characterization and control of permeability through the high porosity foams.

Theses completed under this program grouped in each technical area as follows:

Coaxial Nozzle Formation of Hollow Spheres

T.J. Hwang, Ph.D. Thesis, June, 1989, "A Model for Viscosity of Organic Based Oxide Dispersions."

P.R. Chu, Ph.D. Thesis, June, 1991, "A Model for Coaxial Nozzle Formation of Hollow Spheres from Liquids."

C.M. Moore, M.S. Thesis, June, 1991, "Organic Gels from Injection Molding of Powders."

Mechanical Properties of Hollow Spheres and Foams

V. Munne, M.S. Thesis, September, 1988, "Monolithic Structures Foamed from Phosphate Bonded Hollow Microspheres."

M.K. Adicks, M.S. Thesis, March, 1989, "Strength Characterization of Thin-Wall Hollow Ceramic Spheres from Slurries."

J.H. Chung, Ph.D. Thesis, June, 1991, "Compressive Mechanical Behavior of Thin Wall Ceramic Spheres and Sphere Cellular Monoliths."

A.S. Jensen, M.S. Thesis, Dec., 1992, "Phosphate Bonding of Ceramic Hollow Sphere Foams."

Thermal Conductivity of Hollow Spheres and Foams

M.J. Shapiro, M.S. Thesis, March, 1988, "Thermal Conductivity of Thin Wall Hollow Ceramic Spheres."

S.D. Furlong, M.S. Thesis, December, 1990, "Reduction of Radiative Thermal Conductivity in Thin-Wall Hollow Ceramic Spheres Using Scattering Phases."

T.R. Ford, M.S. Thesis, June 1991, "Thermal Conductivity of Bonded Hollow-Sphere Monoliths."

G.E. Carlson, M.S. Thesis, August 1992, "Thermal Conductivity and Infrared Reflectance of Hollow Glass Spheres."

Syntactic Metal and Metal Matrix Foams

S.A. Rickles, M.S. Thesis, March, 1989, "Microstructural and Compressive Properties of Metal/Ceramic Syntactic Foam."

R. Clancy, M.S. Thesis, December, 1991, "Nickel and Nickel Alloy Hollow Spheres."

High Permeability Applications for Hollow Sphere Foams

L.A. Touryan, M.S. Thesis, December, 1992, "Permeability of Point Contact Bonded Hollow Sphere Foams."

2.0 COAXIAL NOZZLE FORMATION OF HOLLOW SPHERES

2.1 HOLLOW SPHERE FORMATION WITH ACETONE SLURRIES

2.1.1 BACKGROUND

Prior to the start of this program, a method to form thin-wall hollow spheres from a variety of conventional ceramic powders dispersed in water had been demonstrated. However, at that time, the liquid spheres were collected on paper, several centimeters below the nozzle and on landing the spheres were distorted into flat bottomed ellipsoids with a wall thickness at the bottom four times greater than the top. This thickness difference was caused by the rapid deceleration on landing resulting in run-off from the top to the bottom. In addition, the fall distance was insufficient to allow spheridization and each ellipsoid was connected to the next by a stringer. The initial project objective therefore was to evaluate means to dry and recover the moisture-laden free-falling spheres, after the stringers had resorbed and the shells had rounded to spheres from surface tension forces. A variety of methods were considered including; microwave drying, hot air furnaces, and direct infrared radiant heating. The microwave drying approach was considered most attractive because the energy would be absorbed directly in the walls of the spheres. Several suppliers of microwave drying equipment were contacted and a series of experiments were performed to assess the feasibility of drying the free-falling, thin-wall spheres with microwave energy. Unfortunately, the small volume occupied by the relatively widely spaced falling spheres resulted in inefficient heating using conventional microwave frequencies and wave guides. Therefore, work on microwave drying was abandoned.

Other drying schemes were considered along with process and changes in slurry composition that would provide faster drying for the free-falling spheres. Dispersion of powders in a high volatility organic fluid was the most attractive alternative for several reasons. For example, acetone has a much larger vapor pressure, smaller heat of vaporization, and a lower surface tension and density than water. Initial testing of Al_2O_3 powders dispersed in acetone demonstrated that a very uniform stream of spheres could be blown for short periods at room temperature, although the high fluid evaporation rate lead to clogging of the coaxial blowing nozzle.

The merits of dispersions made with acetone were readily apparent when, acetone-based shells dried sufficiently to bounce on a soft landing surface after 30 to 40 feet of free-fall, whereas, water-based spheres splattered on impact. Recovery of the partially dried acetone-based bubble streams was attempted using a variety of methods including deflection off inclined surfaces, horizontal air jets to blow spheres for roll-out on flat surface, and heating using an infrared furnace. All of the spheres

collected using these approaches experienced damage on collision with adjacent spheres and/or impact with a solid surface.

Success was achieved by designing an updraft drying and recovery system consisting of a vertical tube tower, approximately 3.2 meters tall and 30 cm in diameter, combined with an air blower and sphere-forming nozzle assembly. The system was constructed and tested. When the updraft air velocity and sphere diameter and weight are properly balanced, the residence time necessary for adequate drying (4 to 5 sec) can be maintained in the tower and a "soft landing" is achieved without visually apparent mechanical damage to the shells. Recent runs using this facility have produced the best defect-free, high strength, thin-walled Al_2O_3 spheres achieved to date.

The major efforts of this part of the program have been 1) analysis of the rheology of alumina/acetone dispersions containing varying amounts of methyl methacrylate which acts as a dispersant and binder, 2) development of a sphere recovery system which provides adequate residence time and a soft landing. The following sections describe the procedures and terminology used to characterize the pseudoplasticity and Newtonian behavior of the acetone-based slips, the influence of the organic binder on slip rheology, and the recovery system that yielded virtually "flaw-free", high strength, thin-walled Al_2O_3 spheres.

2.1.2 RHEOLOGY OF ACETONE-BASED DISPERSIONS

The rheology of alumina/acetone slips has been investigated to provide suitable dispersion for production of hollow polycrystalline spheres. It is necessary that the alumina powder be well dispersed to yield a reproducible process and to permit a high solids volume content which minimizes the quantity of solvent to be removed. In addition, the slips must possess a viscoelastic and film forming character sufficient for blowing and the hollow spheres formed must be strong enough for recovery. For these purposes, methyl methacrylate, Dupont* Elvacite, resins were added to the dispersions. Elvacite 2008 was added as a dispersant and a binder, while Elvacite 2041 served as a binder and a rheology modifier (In the following text, the additives will be simply referred to as "2008" or "2041"). To characterize the rheology of these dispersions, the viscosity was measured with a Brookfield LV Viscometer at shear rate between $0.1\text{-}50\text{ sec}^{-1}$.

Due to the use of organic polymers, the dispersions exhibit pseudoplasticity. This property can be described by the power law (also known as Ostwald-deWaele equation),

$$\tau = K\dot{\gamma}^n \quad (2.1.1)$$

where τ is shear stress, $\dot{\gamma}$ is shear rate, K is the consistency index and n is the flow behavior index. The value of n is less than 1 for pseudoplastic flow, and decreases as the degree of pseudoplasticity increases. If n is close to 1, the liquid is Newtonian. The power law equation can be related to viscosity, η , by:

$$\eta = K\dot{\gamma}^{(n-1)} \quad (2.1.2)$$

Transformed for linear plotting, this equation is rewritten as

$$\log \eta = \log K + (n-1) \log \dot{\gamma} \quad (2.1.3)$$

The value of $\dot{\gamma}$ is not accurately known since $\dot{\gamma}$ varies with distance from the rotating spindle thus causing a variation of η , for non-Newtonian liquids. However, to a first approximation, $\dot{\gamma}$ can be treated as in a Newtonian liquid so that

$$\dot{\gamma} = \frac{2\pi r R}{dr} = 2\pi R, \quad (2.1.4)$$

where r is the radius at which $\dot{\gamma}$ is desired to be known and R is the rotational speed of the spindle. Therefore equation (2.1.3) can be transformed to

$$\log \eta = \log K + (n-1) \log 2\pi + (n-1) \log R. \quad (2.1.5)$$

The rheology of additional alumina/acetone slips as well as additional ceramic materials have been and will be studied by characterizing η and n for various compositions in order to improve the quality of the thin-walled spheres.

As stated above, the materials used for slip preparation were ALCOA* A-3000 Al_2O_3 , acetone, plus Elvacite 2008 and Elvacite 2041. Used as a slip casting alumina, A-3000 Al_2O_3 powder has a mean particle size of $3 \mu\text{m}$, and a broad particle size distribution designed for slips. Elvacite 2008 is a low molecular weight binder and dispersant, which provides low viscosity at high solids content. Elvacite 2041 is a very high molecular weight binder which increases viscosity with small additions. The dispersions investigated had a fixed Al_2O_3 content of 51 v/o based on the acetone plus alumina volumes. The slips were designated according to type of powder, solvent, and weight concentration of polymers based on powder content. For example, A-A-0.6 indicates Al_2O_3 as the powder, acetone as the solvent, and 0.6 w/o of 2008, or A-A-1.2-0.67 indicates the same powder and solvent, but 1.2 w/o of 2008 and 0.67 w/o of 2041.

After weighing, the Al_2O_3 , acetone and 2008 were mixed by rolling with alumina cylinders in a polyethylene jar on a ball mill rack at 70-90 RPM for 24 hours. Elvacite 2041 was added to the slip if needed and the mixture milled for an additional 24 hours. Viscosity was measured with the Brookfield LV viscometer using proper spindles at rotational speeds of 1.5 to 60 RPM.

The viscosities of dispersions were plotted as $\log \eta$ vs. $\log R$ as shown in Figures 2.1.1 to 2.1.4 in accordance with equation 2.1.5. All slips were pseudoplastic as shown by the negative slope, $(n-1)$, in Figures 2.1.1-2.1.4. The flow behavior as indicated by n values, were calculated along with viscosities at 30 RPM. It can be seen that n values increase with 2008 concentration indicating that the slips approach a Newtonian fluid as the powder becomes well dispersed.

The effect of 2008 concentration on viscosity is shown in Figure 2.1.5. These viscosity curves all show minimum viscosity around 1.7-2.0 w/o 2008. This minimum point is indicative of monolayer adsorption of the polymer on the alumina particles. For slips without 2041, the increase of viscosity as the 2008 content was increased beyond the minimum may be due to excess 2008 going into solution. The rate of viscosity increase in this range should be equal to the rate of viscosity increase for a powder free 2008/acetone solution. Therefore, viscosities of 2008/acetone solutions were measured for comparison to slip viscosities. A comparison between slips and solutions was made by converting the 2008 concentration in the slips to a w/o concentration based on solvent content, C . The viscosity increase rate, $[(\log \eta_1 - \log \eta_2)/(C_1 - C_2)]$, for the alumina/acetone slip in the range of 12.21-20.71 w/o 2008 was 0.051 and for the 2008/acetone solutions in the range of 20-30 w/o 2008, the rate was; 0.067. There is reasonable agreement between the two rates which indicates; that after monolayer adsorption on the powder has been achieved, additional 2008 in solution increases the viscosity of slip at the same rate as for powder free acetone.

For fixed 2008 concentrations, the additions of 2041 produced large viscosity increases as would be expected for a high molecular weight polymer, Figure 2.1.6. Addition of 0.67 w/o 2041 to the slips raised viscosity about one order of magnitude, but this effect was not linear as more 2041 polymer was added. If comparison of n for slips at the same 2008 content are made, it is evident that the 2041 also increases the pseudoplasticity along with the viscosity.

2.1.3 SPHERE RECOVERY SYSTEM

This section describes the continuing evaluation of a sphere recovery system capable of high volume collection. The recovery techniques reported below have all utilized

Figure 2.1.1

Viscosity of Alumina/Acetone Slips vs. Rotational Speed for Various PMMA Concentrations of 2008 Polymer.

Figure 2.1.2

Viscosity of Alumina/Acetone Slips vs. Rotational Speed for Various PMMA Concentrations for 2008 Polymer.

Figure 2.1.3 Viscosity of Alumina/Acetone Slops vs. Rotational Speed for Various PMMA 2008 Concentrations at a 2041 Concentration of 0.67 v/o.

Figure 2.1.4

Viscosity of Alumina/Acetone Slips vs. Rotational Speed for Various PMMA 2008 Concentrations at 2041 Concentrations of 1.33 & 1.67 w/o.

Figure 2.1.5

Plot of Viscosity at 30 RPM vs Elvacite 2008 Concentration Based on Solids Content.

Figure 2.1.6

Effect of 2041 Content on Viscosity (304PM) of Alumina/Acetone Dispersions with 2008 Concentration Fixed at 2.3 w/o.

upward flowing air in an effort to increase the residency time for decreasing the free-falling rate of descent to enable a "soft damage-free landing" for the thin-walled product. The most successful design tested consists of a 3.2 meter tall stack of three plexiglass tubes 30 cm in diameter joined on the upper end with a chamber containing the coaxial sphere-forming nozzle, a smaller diameter tube to contain a saturated acetone atmosphere to facilitate sphere-formation and ducting to a high volume air blower. A photograph of the components at the top of the recovery tower is shown in Figure 2.1.7. Air is drawn in at the base of the tower to develop the updraft necessary to retard the decent rate of the free-falling spheres. At the base of the tower the sufficiently dried spheres land on an inclined screen and roll into a collection box. A process diagram describing the major steps for the manufacture of fired hollow ceramic sphere is shown schematically in Figure 2.1.8. The updraft drying and recovery system described above has produced symmetrical, damage-free, thin-walled microspheres. Future modifications planned for this system include (a) a larger capacity blower to increase the updraft air velocity to handle wider ranges of sphere diameters and densities, (b) an improved air intake geometry to provide more laminar flow inside the tube, (c) a larger diameter (low air velocity) chamber between the drying tower and blower to "drop-out" the fine, light weight Al_2O_3 particles carried to the blower and, (d) the evaluation of intake deflectors (wings) at the base of the tower that will generate a mild vortex motion in the raising air to help contain the spheres in the center of the tower.

Figure 2.1.7

Photograph of Components at the Top of the Sphere Recovery Tower.

Figure 2.1.8 Schematic Process Diagram, Incorporating the 3.2 m Tall Sphere Recovery Tower, for the Manufacture of Low Density Ceramic Spheres.

2.2 VISCOSITY-SOLIDS RELATIONSHIP FOR ACETONE SLURRIES

The viscosity-solids concentration relation of alumina and zirconia suspensions in acetone has been investigated because these are the primary sphere forming systems. The addition of poly(methyl methacrylate), PMMA, provided steric stabilization to these slurries. Hence, the effective solids concentration was greatly different from the true solids concentration due to the adsorbed PMMA layer on the solids surface. A model was proposed to account for the thickness of the flexible adsorbed layer by considering the thickness changes with solids concentration. In this study, first, the adsorption behavior of PMMA onto alumina and zirconia surfaces was characterized by the adsorption isotherms. The adsorption isotherms conformed well to the BET and the Langmuir equations. From these isotherms, the monolayer adsorption and the PMMA equilibrium concentration of the liquid phase in the oxide suspensions were calculated. Because a constant layer thickness was found to be inadequate for describing the increase of solids content by the adsorbed PMMA layer, an equation was proposed to account for the variation of the layer thickness with solids content. The viscosity-solids content relationships were compared with Mooney's, Eilers', and Krieger and Dougherty's equations. It was found that viscosity could be expressed by the Eilers and the Krieger and Dougherty equations but not by the Mooney equation. Values for maximum volume fraction and intrinsic viscosity were obtained from the calculations accordingly. The maximum volume fraction values were found to increase with the surface average particle size, whereas the intrinsic viscosities were lowered as the surface area average particle size increased. The deviations of the intrinsic viscosity and the maximum volume fraction from theoretical values were explained by the presence of non-spherical particles and agglomerates.

The objective of this work was to study and model the viscosity of non-aqueous, steric, stabilized dispersions of ceramic powders as a function of solids concentration. The effects of the particle size, the surface area of the solids, the adsorbed polymer layer on ceramic particles, the intrinsic viscosity and the maximum solids concentration of the dispersions were also to be investigated. This study could provide guidelines for the property and viscosity controls of nonaqueous ceramic dispersions.

There have been many studies in the literature pertaining to the viscosity-concentration relation of ceramic suspensions. However these studies investigated the dispersions of uniform spheres, and corrections were made only for monodispersed particles coated with small molecules of constant layer thickness, whereas it was of interest here to examine the viscosity of concentrated suspensions of polydispersed particles. Moreover, a correction model for the apparent solids concentration was proposed to account for a flexible polymer layer adsorbed on the steric stabilized particles, which varies in thickness with crowding. In this study, the ceramic powders used were aluminum oxide and zirconium oxide. Acetone and PMMA

have been chosen for their effectiveness as a volatile solvent and a deflocculant, respectively, in the fabrication process of ceramic thin-wall hollow spheres. The role of PMMA in the oxide-acetone system is as a binder as well as to sterically stabilize the dispersion through adsorption at the solid/liquid interface. Therefore, an investigation of the adsorption isotherms of PMMA on oxides was also conducted to provide the information about the dispersibility of the slurries, and to calculate, indirectly, the apparent solids concentration and the viscosity of liquid phase.

2.2.1 SLURRY PREPARATION AND ADSORPTION/VISCOSITY PROCEDURES

For this study, oxide powder/acetone suspensions of various solids concentrations, were stabilized by the addition of poly(methyl methacrylate) (PMMA), and were prepared for rheological evaluation. In order to examine the effects of particle size and size distribution of the powder on the rheological behavior, two types of commercially available alumina of the same chemical properties but different physical properties were used. Partially stabilized zirconia was also examined for comparison of the effects of the adsorbed PMMA layers at the solids/liquid interface on the rheological behavior of the suspensions. Adsorption experiments for PMMA on powders were conducted in order to provide information on dispersibility of the suspensions and for viscosity modeling.

Materials - The ceramic powders used in this study were aluminum oxide and partially stabilized zirconia (PSZ). Two types of commercially available aluminum oxide, A1000 and A3000 from ALCOA, were chosen. The PSZ powder was HSY3 grade with 5.4 w/o Y_2O_3 as a stabilizer. These powders are described in Table 2.2.1.

The crystallites of Bayer alumina powders are often in the form of thin hexagonal plates in which the basal plane is parallel to the platelet surfaces. However, the powders may lose the plate-like morphology during ball milling subsequent to their calcination. Scanning electron micrographs of A3000 and A1000 alumina showed that the larger particles possess a platey morphology while the shapes of the other particles are irregular. Also from the particle size distributions, Figure 2.2.1, that A3000 has larger particle size and broader size distribution than A1000.

The scanning electron micrograph of HSY3 zirconia, showed many agglomerates consisting of sub-micron particles. These agglomerates may change the shape of the size distribution curve. This may explain why the serigraph curve of HSY3, Figure 2.2.2, does not show a substantial portion of those sub-micron particles, as indicated by the scanning electron micrograph of HSY3.

The polymer used in this study was Elvacite 2008 grade poly(methyl methacrylate) from DU PONT. The molecular weight of Elvacite 2008 is about 25,000, according

Table 2.2.1 Specifications of Alumina and Partially-Stabilized-Zirconia Powders.

Grade	Alumina		PSZ
	XA3000	XA1000	HSY3
Supplier	ALCOA ¹	ALCOA	Zirconia Sales ²
Purity, %	99.7	99.7	99.6 ³
Density, g/cc	3.98	3.98	6.05
Surface Area ⁴ , m ² /g	3.99	9.01	6.52
Average Particle Size ⁵ , μm	3.0	0.5	0.7

¹Aluminum Company of America, Pittsburgh, Pa.

²Zirconia Sales (America), Inc., agent for Daiichi Kigenso, Osaka, Japan

³ $ZrO_2 + Y_2O_3$

⁴Measured by Micromeritics Materials Analysis Lab using FlowSorb II

⁵Sedigraph median, data provided by suppliers

Figure 2.2.1 Particle Size Distribution of XA3000 and XA1000.

Figure 2.2.2 Particle Size Distribution of HSY3.

to the manufacturer's information. It was further analyzed with Gel Permeation Chromatography (GPC) for molecular weight distribution. The results indicated a weight average molecular weight, M_w , of 33,000, a peak molecular weight, W_p , of 41,500, a number average molecular weight, M_n , of 19,000, a Z average molecular weight, M_z , of 48,100, and a polydispersity, M_w/M_n , of 1.74.

The solvent was acetone (CH_3COCH_3). It has a molecular weight of 58.08, a density of 0.79 g/cc at 20°C and a solubility parameter of 10, which makes acetone a good solvent for PMMA (solubility parameter = 9.5) [60]. Acetone was chosen as the solvent for this study because it is used in the production of ceramic thin-wall hollow spheres due to its high evaporation rate (evaporation rate = 1160 relative to n-BuOAc = 100). In the experiments, acetone was obtained in spectroanalyzed grade from Fisher Scientific Co.

Dispersion Preparation - The dispersions were prepared by mixing the batches of materials in 250 ml Nalgene bottles with zirconia mill balls for at least twenty four hours at room temperature. The twenty-four hour milling time was suggested to be sufficient for attaining adsorption equilibrium [44]. The volume of each slurry was about 50-70 ml. All the weighing operations for viscosity experiments were performed with a Sartorius analytical balance (model 1264MP) with an accuracy of 5mg, whereas those for isotherm experiments were performed with an August Sauter analytical balance having an accuracy of ~1 mg.

Adsorption Experiments - In the adsorption experiment, the solids concentrations of dispersions were 30 v/o (volume percent) for A1000 alumina and HSY3 zirconia, and 20 v/o for A3000 alumina. These concentrations were used to allow the slurries to flow easily during mixing. The original PMMA concentrations ranged from 2 w/o to 22 w/o.

After the dispersions were prepared, a typical adsorption experiment was conducted as follows: First, the dispersions were centrifuged at 1000-5000 RPM for a period of time ranging from 10 to 30 minutes depending on the powder property (e.g. finer powders require longer sediment time). The resulting clear supernatant solutions were removed for analysis. Next, the indices of refraction of these solutions were measured with the Abbe refractometer (American Optical, model 10450). For the purpose of quantitative analysis, appropriate calibration curves of refractive index versus PMMA concentration were constructed using a series of Elvacite 2008/acetone solutions of known concentrations. A typical refractive index curve is shown in Figure 2.2.3. The indices of refraction of these standard solutions were measured together with the samples of unknown concentration to eliminate the effects of refractometer and temperature fluctuations. Then, the concentrations of solutions were determined from

Figure 2.2.3

The Calibration Curve of the Refractive Index Versus Solution Concentration for PMMA/Acetone Solution - Used for Adsorption Analysis from HSY3, Temperature = $18.1^{\circ} \pm 0.2^{\circ}\text{C}$.

Figure 2.2.4

The Calibration Curve of the Viscosity of PMMA Solution Versus PMMA Concentration.

that specific calibration curve. These concentrations are the equilibrium concentrations of adsorption. The difference between the equilibrium and the original concentration gives the amount of adsorbed PMMA. Finally, the adsorption isotherm is plotted for the adsorbed amount as a function of equilibrium concentration.

Viscosity Measurements - These experiments were designed with high solids concentration in an attempt to simulate practical ceramic slurry preparation. The lowest concentrations were 29.04 v/o for alumina slurries and 28 v/o for HSY3 zirconia ones. The highest concentrations were 58.88 v/o for XA3000, 43.86 v/o for XA1000 and 39 v/o for HSY3 zirconia dispersions. The high concentration slurries were too thick to provide a reliable viscosity measurement due to the limitation of the viscometer and the poor workability of concentrated slurries. The solids concentration of the dispersions, ϕ , termed the true volume fraction here, was calculated as follows:

$$\phi = \frac{V}{V + V_a + V_p} \quad (2.2.1)$$

where V , V_a and V_p are the volumes of the powder, acetone, and PMMA, respectively. For each composition three dispersions were prepared and measured for viscosity. To determine the viscosity of the equilibrium liquid phase in the ceramic dispersions, a series of PMMA/acetone solutions of known concentration were also prepared for viscosity measurement. From the viscosity measurements of these PMMA solutions, a calibration curve was plotted as solution viscosity versus PMMA concentration, Figure 2.2.4.

The viscometer used here was the HAAKE viscometer. It is a Searle type coaxial cylinder viscometer which provides shear rates up to 2700 1/s and shear stress up to 1200 Pa. A desired measuring range can be set up by selecting an appropriate sensor system (including a sensor and a beaker). The geometry of the sensor (the bob) and the beaker (the cup) are designed to have a very low R_c/R_b ratio (1.02 - 1.14) and to trap air on the bottom of the sensor to eliminate end effect for precision measurements. The process is controlled through a Rotovisco RV20 and an IBM personal computer. This system provided continuous measurement and recording of shear rate, shear stress, viscosity and temperature. In addition, the temperature of the measuring unit was regulated by a HAAKE Circulator, a circulating water bath with thermal elements and a thermal set.

During viscosity measurement, the beaker was covered with a stainless steel plate designed to prevent volatile solvent evaporation. The sensors used here were SV1 for high-viscosity samples ($> 400cp$), MV1 and MV2 for medium-viscosity, and NV for low-viscosity slurries and for all the PMMA/acetone solutions ($< 10cp$). The samples were measured in the following manner: The shear rate was increased at a given rate

from zero to a shear rate at which shear thickening flow behavior was observed. Then the shear rate was returned to zero. All the measurements were performed at $20^{\circ} \pm 0.2^{\circ}\text{C}$.

2.2.2 ADSORPTION ISOTHERMS AND VISCOSITY-SOLIDS MODEL

Adsorption isotherms of PMMA onto alumina and zirconia powders were constructed. From the Langmuir and BET analyses of the isotherms, the conformations of the adsorbed PMMA layers were investigated. Furthermore, analyses of the isotherms provided an estimate of the apparent solids concentration, and allowed calculation of the viscosity of liquid phase, both which were important in viscosity modeling. Results of the viscosity measurements of the alumina and zirconia suspensions are presented as relative viscosity as a function of apparent solids concentration and are compared with the most common viscosity-concentration relationships applied to powder dispersions: the Mooney, the Eilers and the Krieger-Dougherty equations.

Adsorption Isotherms - The isotherms obtained under ambient condition for the adsorption of PMMA from acetone onto alumina and zirconia powders are seen in Figures 2.2.5 and 2.2.6. They are plotted as weight of PMMA adsorbed on per 100 grams of powder, N , versus equilibrium PMMA concentration, C .

A generalized form of the Langmuir adsorption model was developed by Brunauer, Emmett, and Teller in 1938 to include multilayer adsorption [59]. Basically, the BET model is a Langmuir adsorption in the first layer with liquid-like condensation on molecules adsorbed in the first layer. The assumptions made were:

1. in all layers except the first, the heat of adsorption is equal to the molar heat of condensation qL ;
2. in all layer except the first, the evaporation-condensation conditions are identical;
3. when the concentration becomes equal to the saturation concentration, the adsorbate condenses to a bulk liquid on the surface of the solid, i.e. the number of layers becomes infinite.

Hence, a linear form of the BET equation for polymer adsorption on solid surface is given as

$$\frac{C}{N(1-K)} = \frac{1}{N_m K} + \left(\frac{K-1}{N_m K} \right) C \quad (2.2.2)$$

Figure 2.2.5

Adsorption Isotherms of PMMA onto XA1000 and XA3000 Alumina from Acetone.

Figure 2.2.6

Adsorption Isotherm of PMMA onto HSY3 Zirconia from Acetone.

where C is the equilibrium solute contraction, N is the amount adsorbed per unit weight of solid, N_m is amount absorbed in a monolayer, and K is a system constant.

Likewise, the values of N_m and K can be calculated from the plot of the left hand side of Eq. (2.2.2) versus concentration C . The parameter K is practically taken as $K = \exp[(q^{st} - q_L)/RT]$, where $(q^{st} - q_L)$ is the net heat of adsorption; q_L the heat of condensation for gas; q^{st} the differential heat of adsorption of the monolayer on solid surfaces. In addition, an important factor for successful application of the BET equation is that the K value should be high enough to ensure the separation of monolayer and multilayer formation [59]. On the other hand, it should be low enough to eliminate appreciable localization of the adsorbate molecules. The net result of these two opposing requirements for K value is that K should have an optimum value.

In gaseous adsorption, the BET equation fails in the low pressure region. Brunauer et al adduce energetical non-uniformity as the reason[59]. In adsorption from solutions, however, a smoothing out of the surface non-uniformity occurs[57] when the solid surface is covered with solvent because the high energy regions are made relatively inaccessible to solute by their firm retention of solvent molecules. Consequently, the values of N_m may not be representative of a close packed solute monolayer.

BET Analysis of Adsorption Isotherms - BET plots of adsorption of PMMA onto A1000, A3000 and HSY3 are shown in Figure 2.2.7. They were plotted as $C/N(1-K)$ versus C and least squares lines, which are described in Table 2.2.2, were drawn through the data points. From the slopes (s) and intercepts (i) of these straight lines, the monolayer adsorption capacity N_m and the constant K were determined;

$$N_m = \frac{1}{s + i} \quad (2.2.3)$$

$$K = \frac{s}{i} + 1 \quad (2.2.4)$$

and listed in Table 2.2.2.

The N_m values for A1000 and A3000 agree well with the plateau level adsorption in their isotherms. However, the N_m for HSY3 is much lower than the plateau adsorption. This deviation may have resulted from experimental errors. Furthermore, in the analysis on the relation between N_B from the "Point B"¹ and N_m from the BET equation, several workers have noted that *satisfactory agreement between the two quantities may not be achieved unless the BET equation is applied over a range of the isotherm*

Figure 2.2.7

BET Plot for the Adsorption of PMMA onto XA1000, XA3000 and HSY3.

Table 2.2.2 Analysis of Adsorption Isotherms by BET Theory.

(a) Fitting of Experimental Data to the BET Equation

Oxides	Best fit equation	R
XA1000	$\frac{C}{N(1-C)} = 0.427C + 3.50 \times 10^{-3}$	0.992
XA3000	$\frac{C}{N(1-C)} = 0.948C + 4.19 \times 10^{-3}$	0.992
HSY3	$\frac{C}{N(1-C)} = 1.032C + 0.53 \times 10^{-3}$	0.999

(b) Adsorption Analysis Using the BET Equation

Oxides	N_m , g/100g oxide	K
XA1000	2.323	123.14
XA3000	1.050	227.31
HSY3	0.968	1948.17

(c) Heat of Adsorption and $N_{m,area}$

Oxides	Heat of adsorption, cal/mol	$N_{m,area}$, mg/m ²
XA1000	2850.0	2.58
XA3000	3213.1	2.63
HSY3	4485.1	1.48

(d) Area Occupied by One PMMA Molecule Adsorbed on Oxide Surface

Oxides	$a_{m,BET}$, Å ²	$a_{m,L}$, Å ²
XA1000	1610.27	1308.05
XA3000	1577.43	1308.05
HSY3	2790.67	1308.05

which contains Point B[59]. Therefore, insufficient data points in the isotherm might cause the deviation of N_m from N_B in this study.

'Point B: the point of inflection in the Langmuir type of adsorption isotherm, that is, the point at which the linear plateau portion begins. It is sometimes used as an indicator of the completion of the monolayer.'

Furthermore, an estimate of the net heat of adsorption, $(q^{st} - q_L)$, was obtained by the following equation:

$$q^{st} - q_L = RT \ln K \quad (2.2.5)$$

by using $R = 1.987 \text{ calK}^{-1}\text{mol}^{-1}$, $T = 298^\circ\text{K}$ and each K in Table 2.2.2. The results were listed in Table 2.2.2 along with the $N_{m,area}$ values. The values for heat of adsorption of PMMA on alumina and zirconia range from 2.9 kcal/mol to 4.5 kcal/mol. In the literature, values of heat of adsorption of 2.0 and 1.7 kcal/mol have been found for adsorption of naphthalene and α -methyl naphthalene onto silica gel from n-heptane[58]. Higher values of 5-10 kcal/mol were also found for the heat of adsorption of aliphatic alcohols from benzene onto alumina. Therefore, equation (2.2.5) is considered to be able to provide a feasible computation of the heat of adsorption. The $N_{m,area}$ value for the adsorption on HSY3 was lower than those on alumina. Again, it may result from either one of the following two phenomena. First, the area occupied by one PMMA molecule on the HSY3 surface is larger than on the alumina surface; or the surface coverage on the former is lower than the latter. Since the heat of adsorption for PMMA adsorbed by HSY3 zirconia is considerably higher (indicating a stronger affinity of PMMA molecules for HSY3 zirconia than for alumina), more segments in one polymer molecule may lie on the zirconia surface than extend into the liquid. Consequently, each molecule occupies more surface area, that is, fewer PMMA molecules are adsorbed per unit surface area of zirconia-yielding lower $N_{m,area}$.

Since the poly(methyl methacrylate) may attach on basic sites of oxides by acidic methacrylate groups, the PMMA molecules are adsorbed on solids at multiple points of attachment. Parts of PMMA segments may lie in the layer immediately adjacent to the surface, which are called "trains", and other segments may extend into the bulk solution, called "loops" or "tails" [39]. It was suggested that as polymer concentration increases, the fraction of segments in "trains" should decrease and cross-linking of polymers occurs[36,39]. Since the PMMA concentration ranges are high in this study, there may be more segments in "trains" on zirconia than on alumina, and the polymer molecules may be more highly entangled.

The average area occupied by a molecule of adsorbate in the completed monolayer, a_m , can be estimated from the monolayer adsorption or from the geometrical

calculation of the molecules. By comparing the results from these two different computations, one can approximate the conformation of the adsorbed layer.

The values of a_m from the monolayer adsorption, termed $a_{m,BET}$ here, were calculated by

$$a_{m,BET} = A \times \frac{M}{N_m} \times \frac{1}{L} \times 20^{20} \quad (2.2.6)$$

where A is the specific N_2 surface area of the adsorbent in m^2/g , M is the molecular weight of the polymer, N_m is in grams of polymer per gram of solid, and L is the Avogadro constant. For M , the average molecular weight of 25,000 was used. The resultant $a_{m,BET}$ values, in $\text{\AA}^2$, are listed in Table 2.2.2.

The a_m value was also obtained by assuming that the arrangement of the adsorbed molecules on the surface is the same as it would be on a plane surface immersed in the bulk liquid of the adsorbate without disturbing the pre-existing arrangement. Therefore, the area occupied by one PMMA molecule of density of 1 g/cc, termed $a_{m,L}$, is

$$a_{m,L} = 1.091 \left(\frac{M}{\rho L} \right)^{2/3} \times 10^{16} \quad (2.2.7)$$

$$= 1308.05 \text{\AA}^2$$

where 1.091 is the packing factor for 12 nearest neighbors in the bulk and six on the plane surface[59]. Since the $a_{m,L}$ value represents the area of adsorbent occupied by a molecule with a cubic form, the divergence between $a_{m,BET}$ and $a_{m,L}$ indicates that the shape of the adsorbed molecule is deviated from cubic. The $a_{m,BET}$ value of each PMMA/oxide system are higher than the $a_{m,L}$ value. Hence, more of the segments in the adsorbed polymer molecule apparently lie on the surface of the solid than are solvated into the liquid medium. The higher $a_{m,BET}$ value for HSY3 compared to those for alumina further prove that the stronger affinity of PMMA for HSY3 zirconia results in a thinner layer of the adsorbed molecules on the HSY3 surface.

Viscosity-Solids Content Relation of Slurry - In general the dispersions prepared in this study exhibited Newtonian flow behavior at low solids content. As the concentration increased, the flow behavior became strongly dependent on the shear rate. A typical viscosity-shear rate flow curve in this analysis could be divided into three continuous stages: pseudoplastic (shear thinning) flow at low shear rates, Newtonian flow at medium shear rates, and shear thickening (dilatant) flow at high shear rates. At low solids content, the Newtonian range extended to high shear rate. As solids content increased, the Newtonian portion became progressively narrower and finally disappeared producing a minimum in the flow curve.

Although it was not shown in the flow curve here, the presence of Newtonian behavior at sufficiently low shear rate was of little doubt. This low-shear Newtonian behavior occurs due to the absence of sufficient forces to break up agglomerates or affect particle alignment[63]. In the range of slightly higher shear rates, the flowing particles either align or weak agglomerates are progressively broken due to the imposed shear[63]. Therefore, shear-thinning flow behavior emerges. As the shear stresses increase to levels at which the size of the aggregates has been reduced to a minimum, the flow should become Newtonian (constant viscosity). Above a particular shear rate, the flow becomes dilatant. This is due to the hindered rotation and mutual particle interference[6]. The dilatant behavior might also result from the turbulent flow in the viscometer at high shear rate[7]. Above the turbulent point, the kinetic energy of flow is diverted to nonstreamline phenomena so that more stress is required for an arbitrary increase in the shear rate than for laminar flow. This phenomenon may be misinterpreted as dilatancy.

According to the mechanisms explained above, one can conclude that the Newtonian range in the viscosity-shear rate curve indicates minimal particle-particle interaction in the sheared suspensions. Therefore, the minimum viscosity in the flow curve was recorded and used in modeling viscosity relationships. The results are seen in Tables 2.2.3 to 2.2.5.

To compute the relative viscosity of the suspension, first, the BET equation obtained previously, Table 2.2.2, was used to calculate the PMMA equilibrium concentration in the liquid phase in the suspension, as shown in the third column in Tables 2.2.3-2.2.5. Then, the viscosity of the liquid phase (PMMA/acetone solution) was determined by interpolating from a calibration curve of solution viscosity versus PMMA concentration, Figure 2.2.4, and the solution viscosity was listed in the fourth column in Tables 2.2.3-2.2.5. Finally, the relative viscosity, η_r , was obtained as the ratio of the viscosity of the suspension to that of the equilibrium liquid medium, Tables 2.2.3-2.2.5. Furthermore, the standard deviation of the relative viscosity, σ_{n-1} was calculated from multiple samples and the results are listed in Table 2.2.6 along with the average relative viscosity. In general, standard deviations for relative viscosity were less than 9% of the average viscosity.

Comparison of Viscosity Results with Classic Equations - The simple viscosity-concentration functions were tested by fitting them to the data of Tables 2.2.3-2.2.5, by adjustment of the parameters $[\eta]_0$ and ϕ_{max} . These three equations are:

Table 2.2.3

Viscosity of XA1000 Dispersion and Calculation of the Relative Viscosity

Volume fraction	Viscosity, cp	Liquid phase		η_r
		conc., g/g	viscosity, cp	
.2904	15.45	.0851	1.095	14.1
.3396	28.29	.0824	1.018	27.80
.3889	80.38	.0861	1.124	71.51
40.87	110.82	.0808	.972	114.02
41.87	138.44	.0838	1.058	130.84
43.86	259.09	.0812	.983	253.45

Table 2.2.4

Viscosity of XA3000 Dispersion and Calculation of the Relative Viscosity

Volume fraction	Viscosity, cp	Liquid phase		η_r
		conc., g/g	viscosity, cp	
.2904	4.13	.05032	.763	5.42
.3395	5.54	.05062	.764	7.24
.3889	10.77	.06186	.827	13.02
.4885	36.75	.0904	1.247	33.14
.5386	84.57	.1090	1.7813	51.7
.5587	196.2	.1175	2.025	91.5
.5888	584.69	.1316	2.254	269.8

Table 2.2.5

Viscosity of HSY3 Dispersion and Calculation of the Relative Viscosity

Volume fraction	Viscosity, cp	Liquid phase		η_r
		conc., g/g	viscosity, cp	
.28	11.85	.0330	.4867	24.35
.30	15.25	.0332	.4874	31.375
.33	34.46	.0379	.4940	69.755
.35	50.75	.0336	.4894	103.70
.37	68.39	.0365	.4923	138.91
.39	115.28	.0396	.5174	222.81

Table 2.2.6

Mean and Standard Deviation of the Relative Viscosity of XA1000, XA3000 and HSY3 Dispersions

XA3000			XA1000			HSY3		
ϕ	$\bar{\eta}_r$	σ_{n-1}	ϕ	$\bar{\eta}_r$	σ_{n-1}	ϕ	$\bar{\eta}_r$	σ_{n-1}
.2904	5.42	.799	.2904	14.10	.213	.28	24.35	.0849
.3395	7.24	1.937	.3396	27.80	.431	.30	31.375	.1626
.3889	13.02	1.890	.3889	71.51	.389	.33	69.755	9.27
.4885	33.14	1.690	.4087	114.02	4.476	.35	103.7	.0283
.5386	51.70	3.224	.4187	130.84	3.366	.37	138.91	7.76
.5587	91.50	2.793	.4386	263.45	8.754	.39	222.81	77.35
.5888	214.69	26.98						

Eilers' equation:

$$\eta_r = \left(1 + \frac{[\eta]_f \phi}{2 \left(1 - \frac{\phi}{\phi_{max}} \right)} \right)^2 \quad (2.2.8)$$

Mooney's equation:

$$\eta_r = \exp \left(\frac{[\eta]_f \phi}{1 - \frac{\phi}{\phi_{max}}} \right) \quad (2.2.9)$$

and Krieger-Dougherty's equation:

$$\eta_r = \left(1 - \frac{\phi}{\phi_{max}} \right)^{-[\eta]_f \phi_{max}} \quad (2.2.10)$$

Here ϕ is the solids content, $[\eta]_f$ is the intrinsic viscosity, and ϕ_{max} is the maximum solid volume fraction at which $\eta \rightarrow \infty$. It was not unexpected that the experimental results did not agree with any of the equations above because of the increase in the effective solids content from adsorption of PMMA on the oxide surface. To provide a realistic solids load effect, the solids content had to be corrected for the thickness of the adsorbed PMMA layer.

Traditionally, the apparent volume fraction, ϕ_{app} , is calculated from the original volume fraction ϕ_o , the diameter of the suspension particle D , and the thickness of the adsorbed layer Δ by [22,64].

$$\phi_{app} = \phi_o \left(1 + 6 \frac{\Delta}{D} \right) \quad (2.2.11)$$

Equations 2.2.8, 2.2.9, and 2.2.10 can then be modified by substituting ϕ_{app} for ϕ using Eq. (2.2.11).

Usually, when ϕ is corrected to ϕ_{app} with Eq. (2.2.11), the layer thickness is considered a constant for a given powder/dispersant system. For sterically stabilized dispersions, the adsorbed layer thickness, Δ , can be estimated from the monolayer adsorption and from the radius of gyration of PMMA in acetone. These two methods are described in the following.

Calculation of δ_1 from Monolayer Adsorption - For a close packed monolayer, the layer thickness, denoted δ_1 here, can be calculated from monolayer adsorption, $N_{m,area}$ (listed in Table 2.2.2), and the density of PMMA in the adsorbed layer, ρ , by

$$\delta_1 = \frac{N_{m,area}}{0.94\rho} \quad (2.2.12)$$

where 0.94 is the close packing factor. The density of PMMA in the adsorbed layer is not known and thus it was assumed to be 1 g/cc, which is the density of the PMMA powder. Accordingly, the δ_1 values for PMMA on A1000, A3000, and HSY3 are calculated to be 27.4 Å, 28.0 Å and 15.8 Å respectively.

Calculation of δ_2 from Radius of Gyration - In many cases, the thickness of the adsorbed polymer layer is generally of the order of the diameter of the free coil in solution[39,48,49,50], and computation of the radius of gyration will yield an estimate of the thickness of the layer. The radius of gyration, which is a statistical approach to polymer chain dimensions, is calculated from the Flory-Fox relation[49]

$$(\overline{S^2})^{1/2} = \left(\frac{M_w[\eta]}{\Phi} \right)^{1/3} \quad (2.2.13)$$

where M_w , is the weight molecular weight of polymer, $[\eta]$ is intrinsic viscosity, and Φ , the Flory-fox hydrodynamic parameter, is equal to $3.2 \times 10^{23} \text{ ml/mole.cm}^3$. The intrinsic viscosity of Elvacite 2008 in acetone was calculated from two parameters, K and a , by

$$[\eta] = KM_w^a \quad (2.2.14)$$

According to the *Polymer Handbook*[65], at 25°C, the average values of K and a for PMMA at a molecular weight of $2 \sim 740 \times 10^4$ are $6.77 \times 10^{-3} \text{ ml/g}$ and 0.71 respectively - measured with light scattering method. Therefore, the $[\eta]$ value is equal to 10.928 ml/g for $M_w = 33,000$, and the radius of gyration is calculated to be 104Å. In this case, the adsorbed PMMA layer, denoted δ_2 , was approximated as $2 \times (\text{radius of gyration})$, which becomes 208Å. The particle sizes of A1000, A3000, and HSY3 powder used in Eq. (2.2.11) were the surface area average diameter, D . They were calculated by

$$D = \frac{6}{\rho_p A} \quad (2.2.15)$$

where ρ_p is the density of the powder and A is the specific surface area of the powder. The resultant diameter values for XA1000, XA3000, and HSY3 are 1673.1A,

3778.6Å and 1521.1Å. Using both δ_1 and δ_2 for Δ and the D values obtained above, the solids content was modified by using ϕ_{app} from Eq. (2.2.11) and the viscosity was again fit to the Eilers, Mooney, and Krieger-Dougherty equations. It was found that the modified data using a constant layer thickness correction did not agree with any of the equations. Examples are shown in Figure 2.2.8 for A3000 dispersions. Furthermore, it was noted that for Δ values varying between δ_1 and δ_2 , the experimental data would not fit either the Eilers, the Mooney, or the Krieger-Dougherty functions simply by employing the correction made with Eq. (2.2.11). The curves also showed that the increases of ϕ from ϕ_0 to ϕ_{app} were less at high solids content than at low solids content in order to fit those viscosity-concentration functions. This indicates that the adsorbed layer may not be of constant thickness as ϕ increases. Therefore, a model considering varying layer thickness was developed and is described in the following section.

Model For Calculation of Apparent Volume Fraction - The basic concept of the model for modification of the apparent volume fraction is that the thickness of the adsorbed polymer layer is not constant but varies with the solids concentration. Since the PMMA chain molecule is flexible and of a rather high molecular weight, its effective dimension in acetone can be greatly decreased under compression which probably occurs at high solids content where interparticle space is smaller than the double PMMA dimension (freely extending) in acetone. Therefore, the adsorbed PMMA layer was considered to extend fully into the liquid medium in dilute suspensions, and to be progressively compressed toward the solids surface as the solids concentration increases.

Based on the concept described above, the thickness of the adsorbed layer has two limits. The upper limit, δ_{max} exists when the adsorbed polymer chain can extend freely into the liquid phase. This can be approximated by the radius of gyration of PMMA in acetone, i.e. $\delta_{max} = \delta_2$ as calculated in the previous section. The lower limit of the layer thickness, δ_{min} , would be reached when the adsorbed polymer molecules coil or lie on the solids surface. This occurs as the solids fraction ϕ reaches ϕ_{max} . This thickness can be calculated from the monolayer adsorption for complete surface coverage, that is, $\delta_{min} = \delta_1$. As a summary, the boundary conditions are: when the solids fraction ϕ equals ϕ_{max} , the layer thickness becomes δ_{min} ; as ϕ decreases, the layer thickness approaches δ_{max} and after ϕ is lower than an arbitrary solids fraction, the layer thickness becomes constant and is equal to δ_{max} .

According to the boundary conditions above, an equation was developed to modify the solids concentration for the layer thickness between δ_{max} and δ_{min} :

Figure 2.2.8

Comparison of the experimental results with the Eilers equation for $[\eta]_t = 2.5$, $\phi_{\max} = 0.7$ (curve 1) $\phi_{\max} = 0.65$ (curve 2), and $\phi_{\max} = 0.6$ (curve 3); the volume fraction of XA3000 slurry was corrected for the thickness of the adsorbed layer for $\Delta = 28\text{\AA}$ and $\Delta = 208.13\text{\AA}$, using Eq. 2.2.8.

Figure 2.2.9

Thickness of Adsorbed Polymer Layer Versus Solids Volume Fraction.

$$\phi_{app} = \phi \left\{ \frac{D + 2 \left[\left(1 - \ln \left(\frac{\phi_{max}}{\phi} \right) \right) \delta_{min} + \ln \left(\frac{\phi_{max}}{\phi} \right) \delta_{max} \right]}{D} \right\}^3 \quad (2.2.16)$$

Equation (2.2.16) reduces to $\phi_{app} = \phi(1 + 2\delta_{min}/D)^3$ at $\phi = \phi_{max}$, and becomes $\phi_{app} = \phi(1 + 2\delta_{max}/D)^3$ when $\ln(\phi_{max}/\phi) \geq 1$ (i.e. $\phi \leq \phi_{max}/e$). In other words, the layer thickness is a constant, δ_{max} , when solids content, ϕ , is no greater than an arbitrary solids content, ϕ_{max}/e . This arbitrary solids content is believed to be a function of the nature of the suspension powders, as is implied by ϕ_{max}/e . Because the value of ϕ_{max} is not readily available, the solids content corresponding to the onset of the compression of adsorbed PMMA layer can not be known in advance.

The proposed variation of layer thickness with solids content, Figure 2.2.9, suggests that the compression rate of the adsorbed layer is decreasing as solids content increases. This is explained physically by the increasing difficulty in compressing the adsorbed layer as the adsorbed layer becomes denser.

Experimental Result Modified with Flexible Layer Model - The experimental data was fit to Eq. (2.2.16) and one of the viscosity-concentration functions simultaneously. This process provided unique values for $[\eta]_t$ and ϕ_{max} .

For the best fit Mooney equation the resultant $[\eta]_t$ and ϕ_{max} values were not reasonable. For example, the data required $[\eta]_t = 2.0$ and $\phi_{max} = 0.96$ for XA3000 suspensions with a standard deviation of 10.64. Since the upper limit on ϕ_{max} is 0.74 (for uniform spheres, whereas for polydisperse particles, the highest ϕ_{max} ever reported is 0.82) and the lower limit on $[\eta]_t$ is 2.5 (for rigid particles), it must be concluded that the Mooney equation is unsuitable here. However, both the Eilers equation and the Krieger-Dougherty equation fit the data with realistic values of $[\eta]_t$ and ϕ_{max} . The $[\eta]_t$, ϕ_{max} values and the standard deviation from the best fit, δ , are listed in Table 2.2.7. The experimental data with the solids fraction modified by Eq. (2.2.16) are plotted in Figures 2.2.10 and 2.2.11. The curve drawn through the data points are the Eilers equation and the Krieger-Dougherty equation using the $[\eta]_t$ and ϕ_{max} values in Table 2.2.7.

Both the Eilers and Krieger-Dougherty equations provide equally good agreement (almost the same δ) with the experimental data. One should bear in mind that the Krieger-Dougherty equation was derived as a modification of Mooney's functional analysis while Eilers obtained his equation empirically. Furthermore, the $[\eta]_t$ and ϕ_{max} values obtained from the Eilers equation are, generally, very close to those from the Krieger-Dougherty equation.

Figure 2.2.10 Relative Viscosity Versus Apparent Viscosity Calculated from Eq. 2.2.16 and the Eilers Equation.

Figure 2.2.11 Relative Viscosity Versus Apparent Viscosity Calculated from Eq. 2.2.16 and the Krieger-Dougherty Equation.

Table 2.2.7

The values of $[\eta]_f$, ϕ_{max} and σ for XA1000, XA3000 and HSY3 for the Eilers and the Krieger-Dougherty Equations.

Oxides	Eilers'			Krieger-Dougherty's		
	$[\eta]_f$	ϕ_{max}	σ	$[\eta]_f$	ϕ_{max}	σ
XA3000	2.68	0.685	4.64	2.80	0.682	4.55
XA1000	2.42	0.634	5.73	2.81	0.624	5.69
HSY3	3.05	0.597	8.18	3.22	0.592	8.36

For the A1000 system, the reason that the $[\eta]_t$ values from the Eilers equation are a little lower than 2.5 and greatly different from that of the Krieger-Dougherty equation is not clear. However, two possibilities were considered: ϕ_{max} and experimental error in viscosity. Since the quantity of ϕ_{max} used in correcting the solids content has a greater effect on ϕ_{app} at low solids concentration than at high solids concentration, an error in ϕ_{max} will result in an aberration in $[\eta]_t$, but would have little effect on ϕ_{max} . Therefore, a better estimate of ϕ_{max} would likely yield a more reliable $[\eta]_t$ value. In addition, there is a distinct possibility that the deviation might be attributed to experimental error, which was relatively more significant at low viscosities (low solids content) than at high viscosities. The errors in viscosity at low solids content affect regression and thus generate errors in $[\eta]_t$.

Theoretically, $[\eta]_t$ is equal to 2.5 for dilute suspension of spherical particles. By examining the SEM photographs of the alumina and zirconia powders, it was clear that most of the particles were not spheres and that there were noticeable quantities of aggregated fine particles in the HSY3 zirconia powders. The non-spherical particles and particle agglomeration both contribute to the higher $[\eta]_t$ values here. The extraordinarily high $[\eta]_t$ for HSY3 zirconia may be mainly the result of the presence of the hard agglomerates which were not broken down during milling.

2.2.3 CONCLUSIONS

Poly(methyl methacrylate) contributes to the dispersibility of alumina and zirconia powders in acetone by adsorbing at the solids/liquid interface. Both the BET and Langmuir equations could adequately describe the adsorption isotherms of PMAA on alumina and zirconia. By calculating the monolayer adsorption, N_m from the BET or the Langmuir equations, the conformations of the adsorbed PMMA layer can be compared between alumina and zirconia. The analysis of adsorption isotherms of PMMA on A1000, A3000 and HSY3 provided an estimation of the adsorbed layer thickness and allowed calculation of the PMMA concentration in the equilibrium liquid phase in suspensions. Instead of the true solids concentration, the apparent solids concentration should be used to account for the adsorbed PMMA layer during viscosity-concentration modeling. The traditional equation $\phi_{app} = \phi(1 + 6\Delta/D)$ is not sufficient in describing the volume change of the solids due to the adsorption of the flexible PMMA on powders. Therefore, an equation which considers the layer thickness varying with the solids concentration was used:

$$\phi_{app} = \phi \left\{ \frac{D + 2 \left[\left(1 - \ln \left(\frac{\phi_{max}}{\phi} \right) \right) \delta_{min} + \ln \left(\frac{\phi_{max}}{\phi} \right) \delta_{max} \right]}{D} \right\}^3 \quad (2.2.17)$$

The layer thickness at $\phi = \phi_{max}$ is ϕ_{min} which can be calculated from the monolayer adsorption assuming complete surface coverage of solids by PMMA. The maximum layer thickness, ϕ_{max} is that which results when the polymer chains extend freely into the liquid medium. It was approximated by the radius of gyration of PMMA in acetone. The Mooney equation could not describe the viscosity-solids concentration relation of these PMMA/acetone/oxide slurries, with or without the correction for the thickness of the adsorbed layer. Both the Eilers equation, $\eta_r = [1 + [\eta]_i \phi / 2(1 - \phi/\phi_{max})]^2$, and the Krieger-Dougherty equation, $\eta_r = (1 - \phi/\phi_{max})^{[\eta] \phi_{max}}$, were found to agree with the experimental data by correcting the apparent solids volume fraction with an equation which takes into account the variation in adsorbed layer thickness with solids content. The average intrinsic viscosity values for XA1000, XA3000, and HSY3 are all higher than 2.5, the intrinsic viscosity of dilute suspensions of spheres. This is likely due to the non-spherical shape of the particles and the presence of agglomerates in the suspensions. The values of apparent maximum volume fraction increases as the surface average particle size increases. They are apparently irrelevant to specific surface area alone or serigraph medium particle size. The effective volume fraction, the solids content plus adsorbed PMMA layer plus particle interaction range, can be computed as a function of the particle interaction distance, d .

2.2.4 BIBLIOGRAPHY

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2.3 MODEL FOR FORMATION OF HOLLOW SPHERES

Thin wall hollow liquid spheres are fabricated by the coaxial nozzle process by extruding a liquid through an annular-cross-section nozzle with a gas jet providing a ballooning effect. This process produces monosized hollow spheres at constant, precise rates or frequencies for a fixed set of conditions. A model based on fluid continuum concepts and dynamic equations (equations of motion) was derived to describe liquid hollow sphere formation. This model resulted in mathematical expressions to calculate hollow sphere formation frequency, based on liquid and gas flow rates, liquid viscosity, surface tension, density, and jet dimensions. At high liquid flow rates, a critical condition for hollow sphere closure was postulated which permitted prediction of the sphere formation cycle. At higher liquid flow rates, the model frequencies agree with experimental frequencies reasonably well. However the model was insufficient to predict frequencies at lower liquid flow rate because the critical condition of bubble formation could not be clearly defined for the lower liquid flow rate situation.

The coaxial nozzle is named because the nozzle consists of two coaxial tubes where the inner tube injects gas (this is termed inner jet) and a slurry flows in the annular opening between the inner jet and outer tube, as shown in Figure 2.3.1(a). Figure 2.3.1(b) shows sphere formation with a coaxial nozzle from a 55 v/o alumina slurry. The hollow spheres manufactured by coaxial nozzle technique have very narrow size distribution, Figure 2.3.2(a). This technique is unique in that not only does it accommodate any composition because it is a powder process, but it also allows tailoring of thermal conductivities using additives such as pores and pacifiers in the sphere walls^{1,4}. The process is practical in that over 300 tons of ceramic spheres have been made by the process for several applications over the last few years. For practical reasons, high quality spheres, i.e. monosized with uniform wall thickness, are desired because increased perfection enhances both mechanical and insulation performance. Uniformity in the sphere wall thickness also eliminates anisotropic mechanical and thermal properties. Unfortunately, this process has not been shown to produce sphere with a uniform wall thickness² (Figure 2.3.2(b)) and therefore improvements are desired. Improved sphere quality is probable when the sphere forming process is fully understood. Therefore, the objective of this study was to investigate the mechanism of hollow liquid sphere formation using a coaxial nozzle technique.

Two models for sphere formation from liquid existed previously. The earliest model, the capillary model⁹⁻¹², was based on capillary waves developed on a liquid jet surface due to surface tension of the liquid. This was used to describe solid liquid sphere formation as early as the end of the last century. More recently, research conducted in the Jet Propulsion Laboratory, California Institute of Technology resulted in a hollow

Figure 2.3.1 (a) Cross Section of a Coaxial Nozzle. (b) Hollow Alumina Spheres Formation with Coaxial Nozzle from Alumina Slurry.

(a)

(b)

Figure 2.3.2

(a) Hollow Ceramic Spheres with Narrow size Distribution. (b) Sphere Wall Thickness Variation.

sphere formation scheme¹³. This model started with the continuity equation and kinematic relations, and incorporated the assumption of capillary waves growing on the liquid jet surface.

An easily applied model, involving few assumptions, was established in this study. In the model, a balance is established between the interior gas pressure, the viscous stress in the liquid shell, and surface tension. The sphere formation process was divided into two regions, high and low, based on liquid flow rate. As can be seen later, the model predictions agreed with experimental results reasonably well at high liquid flow rates. At low liquid flow rates, sphere formation was not predicable by this model because the critical closure mechanism postulated here must not be valid at low liquid flow rates.

2.3.1 EXPERIMENTAL SPHERE FORMATION

To test the model derived below, hollow spheres were formed by flowing silicone fluid through the annular opening of a coaxial nozzle and the ballooning effect was provided by a N_2 gas jet flow through the center tube in the nozzle. The liquid flow rate was controlled by gas pressure, which will be termed cell pressure, in a liquid reservoir connected to the nozzle. The liquid exited the nozzle with the configuration shown in Figure 2.3.3. The hollow liquid jet initially forms a cylindrical liquid tube with a inner radius, $R_o = 0.014$ in., equal to nozzle inner radius and a thickness, $\delta = R_i - R_o = 0.012$ in., equal to the width of the annular opening of the nozzle. Due to the flowing N_2 gas jet, the cylindrical liquid shell gradually expands into a spherical shell at the end of the liquid tube. The sphere formation frequency (number of hollow liquid spheres formed per minute) was measured by a Ametec stroboscope. Cell pressure (or liquid flow rate Q_l) and inner jet flow rate Q_g were varied to obtain diverse sphere formation frequencies. Silicone viscosity standard fluid was used in the preliminary hollow liquid sphere formation experiments. The silicone oil was purchased from Brookfield Engineering Laboratories, Inc. and exhibit newtonian behavior with a viscosity of 0.993 poise and a surface tension of 23 dyne/cm.

2.3.2 MODEL OF HOLLOW SPHERE FORMATION

Liquid hollow sphere formation from a coaxial nozzle usually follows the sequence described in Figure 2.3.4. A hollow cylindrical liquid tube produced by flow of the liquid through the nozzle closes at a distance below the nozzle at which point a spherical shell is generated due to the inflation pressure of the gas jet. The length of the cylinder appears to be controlled partially by liquid flow rate Q_l . Longer cylindrical cavities were observed at higher liquid flow rates, as shown in Figure 2.3.4(a). As Q_l decreased, cylindrical cavities became shorter and eventually disappeared, Figure 2.3.4(b). Similar phenomena were also found by Bennie and Squire¹⁹ and Baird and

(a) at higher liquid flow rates

(b) at lower liquid flow rates

Figure 2.3.4.

Schematic Description of Sphere Formation for (a) Higher and (b) Lower Liquid Flow Rates.

Davison²⁰. They attributed this to the fact that the length of the center cavities was affected by the vertical curvatures of the cavities which could be altered by the velocities of the liquid jet.

In addition to the different forming configuration, sphere formation frequencies were also influenced distinctly by liquid flow rate. As can be seen from Figure 2.3.5, at higher liquid flow rates, for example $Q_l \geq 1.25$ cc/s, the dependency of frequency on gas flow rate is more dominant than at lower liquid flow rates. The variations in sphere formation configuration and frequency vs. flow rate tendency suggested that separate sphere formation mechanisms should be considered for higher Q_l and lower Q_l .

Model - The driving force for growth of a liquid hollow sphere comes from the gas pressure inside the sphere. Expansion rate of the shell is controlled by the balance between the stresses caused by the gas pressure inside the shell, the viscous stress due to the liquid motion, and the surface tension. By establishing and solving stress balance equations, the expansion rate (or radius vs time relationship) of the hollow sphere can be determined.

To simplify the problem, the system was decoupled into two parts, a cylindrical and a spherical cavity, Figure 2.3.3. The cylindrical cavity appeared to maintain approximately the same configuration and dimensions during sphere formation and thus was independent of time as will be presented later. This implied that the amount of liquid in the sphere was constant during the expansion and as the spheres increase in size, the sphere wall thickness became thinner due to stretching. However, in actuality, the boundary between the cylinder and the sphere cannot be distinct. As the sphere grows, the center of the sphere must move toward the cylinder and incorporate some of the liquid from the cylinder (meaning the amount of the liquid in the sphere did not remain constant). This variation in the amount of liquid in the sphere was not considered in the model because the sphere expands at such a fast rate that radial expansion and the thinning of the wall thickness is assumed to be the dominate mechanism, and the effects of increasing the amount of the liquid in the sphere is assumed negligible. The motion of liquid shell can be expressed in terms of the following velocity tensor²¹, v_i ,

$$v_i \rightarrow (v_r, v_\theta, v_\phi) \rightarrow (v_r, 0, 0) \quad (2.3.1)$$

Because the sphere only grows in the r direction, $v_\theta = v_\phi = 0$. The sphere was assumed to be symmetric about the θ and ϕ axes, therefore $v_r = f(r) \neq f(\theta, \phi)$. This assumption idealized the process and assumed a spherical geometry from the initiation of sphere formation. In the actual sphere formation process, the bubbles appear as ellipsoids

Figure 2.3.5.

Frequency vs. Inner Jet Gas Flow Rate for Silicone Fluid ($\mu = 0.993$ poise, $\alpha = 23$ dyne/cm, $\rho = 0.97$ g/cm³) at a Variety of Liquid Flow Rates.

rather than spheres and v_r would be a function of r and θ . As bubbles increased in size, the non-symmetry of v_r about θ appeared to be gradually eliminated and the assumption that $v_r = f(r)$ only became more valid. Hence the assumption that v_r was symmetric about both θ and ϕ seemed acceptable and allowed an idealized and less complicated sphere formation model.

By applying the following continuity equation²¹ and boundary conditions,

$$\text{Continuity Equation: } \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 v_r) = 0 \quad (2.3.2)$$

where R was instantaneous sphere inner radius, v_r can be solved as,

$$\text{Boundary Condition: } v_r|_{r=R} = \frac{dR}{dt} = \dot{R} ; \quad \text{at } r=R \quad (2.3.3)$$

$$v_r = \frac{\dot{R} R^2}{r^2} \quad (2.3.4)$$

Equation (2.3.4) was valid for r ranges from the sphere inner radius, R , to an outer surface radius, $R+w$. Therefore the velocity tensor for a growing hollow sphere, equation (2.3.1), could be rewritten as,

$$v_i \rightarrow \left(\frac{\dot{R} R^2}{r^2}, 0, 0 \right) \quad (2.3.5)$$

Stress Balance - Figure 3 indicates that stresses on the spherical shell included hydrostatic pressures, P , normal viscous stress, τ , and stresses caused by surface tension, α . The balance between the these stresses for inner and outer surfaces can be presented as:

$$\text{Inner Surface: } -P_{liq,R} + \tau_{rr}|_{liq,R} + P_{gas,R} = \alpha \frac{2}{R} \quad (2.3.6)$$

$$\text{Outer Surface: } -P_A + P_{liq,R+w} - \tau_{rr}|_{liq,R+w} = \alpha \left(\frac{2}{R+w} \right) \quad (2.3.7)$$

The total stress balance is the summation of equation (2.3.6) and

$$\Delta P + (P_{liq,R+w} - P_{liq,R}) + (\tau_{rr}|_{liq,R} - \tau_{rr}|_{liq,R+w}) = 2\alpha \left(\frac{1}{R} + \frac{1}{R+w} \right) \quad (2.3.8)$$

(2.3.7), where ΔP replaced $(P_{gas,R} - P_A)$ and is the pressure difference inside and outside the shell. Liquid hydrostatic pressure difference, $(P_{liq,R+w} - P_{liq,R})$, and liquid viscous stress difference, $(\tau_{rr}|_{liq,R} - \tau_{rr}|_{liq,R+w})$, are solved from the rate-of-deformation tensor, the viscous stress, and the dynamic equation^{21,22} as presented below.

For a bubble expanding according to the velocity vector of equation (2.3.5), the rate-of-deformation tensor is derived as,

$$\Delta_{ij} \rightarrow \begin{vmatrix} -4\frac{\dot{R}R^2}{r^3} & 0 & 0 \\ 0 & 2\frac{\dot{R}R^2}{r^3} & 0 \\ 0 & 0 & 2\frac{\dot{R}R^2}{r^3} \end{vmatrix} \quad (2.3.9)$$

The general expression for viscous stress tensor is $\tau_{ij} \Rightarrow \eta(\Delta_{ij} + \Delta_{ji})$. For a newtonian fluid the coefficient, $\eta(\Delta_{ij})$, does not depends on Δ_{ij} and viscosity, μ , is constant. Thus the viscous stress tensor becomes,

$$\tau_{ij} \rightarrow \begin{vmatrix} -4\mu\frac{\dot{R}R^2}{r^3} & 0 & 0 \\ 0 & 2\mu\frac{\dot{R}R^2}{r^3} & 0 \\ 0 & 0 & 2\mu\frac{\dot{R}R^2}{r^3} \end{vmatrix} \quad (2.3.10)$$

Using τ_{rr} component and replacing r with R and $R + w$, the viscous stress difference in equation (2.3.8) could be solved,

$$\tau_{rr}|_{liq,R} - \tau_{rr}|_{liq,R+w} = -4\mu \frac{\dot{R}}{R} \left(1 - \frac{R^3}{(R+w)^3} \right) \quad (2.3.11)$$

The liquid hydrostatic pressure difference, $(P_{liq,R+w} - P_{liq,R})$, is acquired by solving the r -component dynamic equation^{19,20},

$$\rho \left(\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} \right) = -\frac{\partial P}{\partial r} + \left(\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \tau_{rr}) - \frac{\tau_{\theta\theta} + \tau_{\phi\phi}}{r} \right) \quad (2.3.12)$$

and for a newtonian fluid,

$$P_{liq,R+w} - P_{liq,R} = -\rho \left[(\ddot{R}R + 2\dot{R}^2) \left(1 - \frac{R}{R+w} \right) - \frac{\dot{R}^2}{2} \left(1 - \frac{R^4}{(R+w)^4} \right) \right] \quad (2.3.13)$$

where ρ was the liquid density. The sphere inner radius inflation rate, $\dot{R}$, depends on the volumetric flow rate of the gas into the sphere which is dependent on the instantaneous pressure inside the sphere. Because the pressure difference inside and outside the cavity was on the order of less than a few percent of the atmosphere pressure (the pressure outside the cavity), it should be reasonable to assume the gas volume flow rate into the sphere was equal to the metered inner jet gas flow rate which was calibrated at atmosphere pressure. Therefore the sphere inner radius inflation rate, $\dot{R}$, was related to inner jet flow rate, Q_g , in the following fashion,

$$\dot{R} = \frac{Q_g}{4\pi R^2} \quad (2.3.14)$$

Combining equation (2.3.8), (2.3.11), (2.3.13), and (2.3.14), the stress balance in a growing liquid shell becomes,

$$\Delta P + \frac{\rho Q_g^2}{32\pi^2 R^4} \left[1 - \left(\frac{R}{R+w} \right)^4 \right] - \mu \frac{Q_g}{\pi R^3} \left[1 - \left(\frac{R}{R+w} \right)^3 \right] = \frac{2\alpha}{R} \left(1 + \frac{R}{R+w} \right) \quad (2.3.15)$$

Critical Condition - The stress balance in, equation (2.3.15), presents the relationship between the pressure inside the hollow sphere (which was expressed as pressure difference across the spherical shell, ΔP) and instantaneous inner sphere radius, R .

Equation (2.3.15) can also be rearranged to predict ΔP vs time, t , if R is expressed by the following relationship,

$$t = \frac{4/3\pi R^3}{Q_g} \quad (2.3.16)$$

Once the pressure drop across the shell, ΔP , is known as a function of time, a mechanism can be proposed based on the pressure distribution inside the spherical cylindrical which leads to the closing of the separation at the neck between the cylinder and the sphere. As shown in Figure 2.3.6, between the two pressures in the cylinder, ΔP_{cav} (which is approximately constant due to the unchanged cylindrical configuration) and in the sphere, ΔP , there should exist a transition zone to allow the pressure to change gradually from ΔP_{cav} to ΔP . Therefore the pressure in the transition zone, ΔP_{tran} , would range between ΔP_{cav} and ΔP at any point of time. The pressure ΔP_{tran} must determine the two curvatures and thus the shape of this neck area. When ΔP and consequently ΔP_{tran} become smaller than ΔP_{cav} , the liquid shell at the transition area should exhibit a neck because negative curvature develops. The necking effect increases with decreasing ΔP and ΔP_{tran} because of increased negative curvature until the neck collapses. This argument suggests that the critical condition $\Delta P_{cav} = \Delta P_{tran} = \Delta P$ triggers the development of the neck and the collapse of the neck. Because the collapse is observed to occur very rapidly, it is reasonable to assume that bubbles stop growing when the following critical condition is satisfied, where δ is the annular width of nozzle between the inner and outer radii or the thickness of the cylindrical tube. If ΔP_{cav} from equations (2.3.17) and ΔP from equation (2.3.15) are plotted vs time, Figure 2.3.7, the intersection defines the critical condition for sphere closure, and t_b defines the time period for sphere formation. Please note that sphere formation frequency is the reciprocal of the critical time, $f = 1/t_b$.

$$\Delta P = \Delta P_{cav} = \alpha \left(\frac{1}{R_o} + \frac{1}{R_o + \delta} \right) \quad (2.3.17)$$

Most of the variables involved in the process of determining ΔP vs R , equation (2.3.15), can be experimentally measured, such as liquid density ρ , liquid viscosity μ , liquid surface tension α , and inner gas flow rate Q_g . The instantaneous spherical shell thickness, w , however can only be calculated from liquid flow rate, Q_l , when sphere formation frequency ($1/t_b$) is known. Thus, calculation of Q_l and t_b must be resolved by a iterative method. Assuming that the volume of liquid per sphere is constant during the sphere formation, the spherical shell thickness, w , is approximately equal to volume of liquid per bubble, $Q/f_{assumed}$, divided by surface area of the spheres, or,

(a) $\Delta P_{\text{cav}} < \Delta P_{\text{tran}} < \Delta P$

(b) $\Delta P_{\text{cav}} > \Delta P_{\text{tran}} > \Delta P$

Figure 2.3.6. The Pressure in the Transition Zone of the Cavity Affect the Magnitude of the Negative Curvature.

Figure 2.3.7. The Pressure Inside the Cavities as a Function of Time and the Critical Condition.

$$w = \frac{Q_i}{4\pi R^2 f_{\text{assumed}}} \quad (2.3.18)$$

This w , calculated by a assumed frequency, was then used to calculate ΔP , equation (2.3.15), and obtain the calculated frequency $1/t_b$. If the assumed frequency, f_{assumed} , and calculated frequency, f , did not agree, the calculation is repeated with another assumed frequency. An appropriate number of iterations are completed until an acceptable agreement between the assumed and calculated frequencies is achieved. A sample demonstration of this operation is shown in Figure 2.3.8.

One concern presented by this model centered on the flow of inner jet gas. From Figure 2.3.7, it is obvious that at initiation of hollow sphere formation, the pressure in the spherical cavity is greater than that in the cylindrical cavity. This required the inner jet gas to flow from a low pressure region (cylindrical tube) to a high pressure region (hollow sphere). It is possible that the inner jet possesses enough momentum to carry the gas down stream in the hollow cylinder until hindered by an obstacle, in this situation the closed end of the cylindrical liquid shell. The accumulation of the inner jet gas caused the expansion at the closed end. In addition, the momentum of the annular liquid jet provides a retarding force to prevent expansion of the cylindrical tube, particularly near the nozzle and at high liquid flow rates as demonstrated by Baird and Davidson²⁰.

In addition to the momentum of both the inner jet gas and the annular liquid jet, equilibrium of pressures in the cavities must be considered. Although the system was divided into two cavities when the model was derived, the two cavities were physically connected and the pressures inside the two must have the tendency to reach an equilibrium. Either the cylindrical cavity must decrease in size to raise ΔP_{cav} or the spherical cavity must increase in size to reduce ΔP . The former was not possible because of the continuous feeding of the inner jet gas. Therefore the spherical cavity would have to grow to reduce the pressure inside the sphere and consequently to eliminate the difference between ΔP_{cav} and ΔP . Consequently, the sphere formation process is basically the competition between the inner jet momentum which carries the gas down stream and the pressure distribution in the cavities which retard the gas flow toward the closed end. If the pressure distribution was the energy barrier for a reaction (growth of bubbles), inner jet must have enough energy (*i.e.* velocity) to overcome the energy barrier to activate the reaction. This might help to explain the observation that when Q_g was too low there would be no hollow spheres produced.

	Assumed Frequency (bubbles/min)	Calculated Time Period (sec/bubble)	Calculated Frequency (Bubbles/min)
First Trial	$f_1 = 15000$	$t_1 = 0.0061$	9800
Second Trial	$f_2 = 5000$	$t_2 = 0.0067$	9000
Third Trial	$f_3 = 9200$	$t_3 = 0.0064$	9300

Figure 2.3.8. Iterative Method Used to Calculate Correct Frequency.

2.3.3 PREDICTION OF SPHERE DIMENSIONS AND VERIFICATION

One purpose of an accurate hollow sphere formation model is that, by predicting sphere formation frequency, f , one can predict other characteristics of the hollow spheres such as diameter, d , wall thickness, th , and liquid sphere density, ρ , with the following relationships,

$$d = 2 \left[\frac{3(Q_l + Q_g)}{4\pi f} \right]^{\frac{1}{3}} \quad (2.3.19)$$

$$th = \left[\frac{3(Q_l + Q_g)}{4\pi f} \right]^{\frac{1}{3}} - \left[\frac{3Q_g}{4\pi f} \right]^{\frac{1}{3}} \quad (2.3.20)$$

$$\rho_{bubble} = \frac{Q_l/f}{(Q_l + Q_g)/f} \cdot \rho = \frac{Q_l}{Q_l + Q_g} \cdot \rho \quad (2.3.21)$$

These parameters have been intensively addressed and it was demonstrated²³ that the establishment of the model allows for tailoring of the process to meet the specification requirements of the final products.

Verification of the model is shown in Figure 2.3.9. The model (solid curves) agree well with experimental data for higher liquid flow rate ($Q_l \geq 1.25$ cc/s). However, at lower Q_l , or lower Q_l/Q_g ratios, model calculations deviates from the experimental frequencies. This deviation might be explained by the fact that at lower Q_l , or lower Q_l/Q_g ratios, the cylindrical part of the cavity became less obvious or even disappeared. Consequently the definition of critical condition (which was closely related to the existence of the cylindrical cavity) became ambiguous and eventually led to invalidity of the model.

2.3.4 CONCLUSIONS

The experiments presented here with newtonian silicone oil have shown that coaxial nozzle hollow sphere formation was divided into high Q_l region and low Q_l region. At high Q_l region inner jet gas flow rate dominated the process. Sphere formation frequency increased with increasing inner jet gas flow rate. At low Q_l region the influence of inner jet gas flow rate on frequency disappeared. Frequency remain approximately the same in spite of changing inner jet flow rate. A mathematic model was derived which predicted newtonian liquid hollow sphere formation to a reasonable

Figure 2.3.9. Comparison of Experimental Results and Model Calculations of Frequency vs. Inner Jet Flow Rate for Silicone Fluid ($\mu = 0.993$ poise, $\alpha = 23$ dyne/cm, $\rho = 0.97$ g/cm³) for High Liquid Flow Rates.

extend at high Q , region. The current model does not predict the sphere formation frequency at lower liquid flow rate range because the critical condition for the hollow sphere formation could not be defined at low liquid flow rates. It should be noted that experiments were also conducted with high solids loaded alumina slurries and experimental testing confirmed that the model presented here has the same accuracy as for the silicon oil data.

Thus, the model appears to describe the process accurate over the regions where it applies.

2.3.5 GLOSSARY

R_o	: inner radius of cylindrical cavity
δ	: wall thickness of cylindrical cavity
R	: instantaneous inner radius of the hollow sphere
w	: spherical shell thickness
$\dot{R}$	: expansion rate of inner radius of sphere, $= \partial R / \partial t$
R^*	: sphere inner radius at critical condition
Q_g	: gas flow rate
Q_l	: liquid flow rate
ρ	: liquid density
α	: liquid surface tension
μ	: liquid viscosity
t_b	: time period of sphere formation
f	: hollow sphere formation frequency
P_A	$= P_{air, R+w}$
$P_{air, R+w}$	: hydrostatic pressure of atmospheric air
$P_{liq, R+w}$	: hydrostatic pressure of liquid at outer surface of sphere
$P_{liq, R}$	: hydrostatic pressure of liquid at inner surface of sphere
$P_{gas, R}$	: hydrostatic pressure of gas inside the sphere
$\tau_{rr} _{air, R+w}$	: viscous stress due to atmospheric air
$\tau_{rr} _{liq, R+w}$	: viscous stress due to liquid at outer surface of sphere
$\tau_{rr} _{liq, R}$	: viscous stress due to liquid at inner surface of sphere
$\tau_{rr} _{gas, R}$	: viscous stress due to gas inside the sphere
ΔP	: pressure difference across the spherical shell
ΔP_{cav}	: pressure difference across the cylindrical shell
ΔP_{tran}	: pressure difference across the liquid shell at the transition zone.

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2.4 GEOMETRICAL CHARACTERISTICS OF THIN WALL HOLLOW SPHERES

This section characterizes the sphere geometry from the coaxial nozzle process and demonstrates that this produces thin-wall hollow spheres which have a size uniformity seldom achieved by high volume manufacturing processes. To demonstrate the capabilities of the process, spheres were blown from the same slip under two sets of conditions; (1) 40 psi on the slip and 20 cc/min blowing gas flow rate (40-20) and (2) 20 psi with a blowing gas rate of 40 cc/min (20-40). Note that the ranges for both these variables are much greater than those values used here. The hollow sphere parameters presented below, Table 2.4.1, are not the limitation of the process but are presented to demonstrate the degree of perfection of size distribution and sphericity achievable at this time. As the process continues to improve, degree of perfection will increase. The measurements and distributions presented are for randomly selected spheres from the two conditions.

Table 2.4.1. Characteristics of Thin Wall Hollow Spheres Fabricated Under Two Blowing Conditions.

Parameter	<u>Blowing Conditions</u>	
	40-20	20-40
Green Bulk Density (g/cc)	0.51	0.20
Fired Bulk Density (g/cc)	0.61	0.25
Fired Sphere Density (g/cc)	1.07	0.41
Wall Thickness Fired (μm)	112	56
Diameter (μm)	2502 ± 71	3169 ± 83
Aspect Ratio a	1.11 ± 0.05	1.08 ± 0.02
Shape Factor b	1.04 ± 0.02	1.03 ± 0.02

a Due to measurement error, the aspect ratio (max dia/min dia) for perfect spheres was 1.05 for 40-20 and 1.04 for 20-40.

b Shape Factor = $P^2/4\pi A$ where P = perimeter and A = area.
Shape Factor for Spheres = 1.00, Hexagons = 1.10, Squares = 1.27 and Triangles 1.65.

For the higher slip pressure (or liquid flow rate) and lower blowing gas flow rate (40-20), spheres of smaller size were produced compared to a lower slip flow rate and higher gas flow rate (20-40) as shown in Figure 2.4.1. As the ratio of gas to slip flow rate increased, spheres were larger and had a smaller wall thickness as would be expected, Figure 2.4.2. After recovery and drying, the bulk density of the green product as measured by weighing ~ 100 cc of tapped spheres was 0.51 and 0.20 g/cc (31.8 and 12.5 lb/ft³), respectively. After firing at 1650°C for 2 hours, the A-3000 alumina sphere walls were impervious as indicated by boiling in water and the spheres increased in bulk density to 0.61 and 0.25 g/cc (38.1 and 15.6 lb/ft³), respectively.

Sphere diameters, aspect ratios, and shape factors were measured using a video camera interfaced to an image analyzer. At a magnification of 11x, four spheres at a time could be measured. For each sphere, the diameter in eight directions, the perimeter, and the cross sectional area were recorded. For each blowing condition, 64 randomly selected spheres were quantified. As reported in Table 2.4.1 and shown in Figure 2.4.3, the average diameters for the two conditions were 2.50 and 3.17 mm with one standard deviation for the distributions of 2.8% and 2.6%, respectively. This provides a 3 σ limit of ~8% which is well under the 10% target for diameter variation suggested in the work statement.

Spherodicity was measured with two techniques, aspect ratio and shape factor, by the image analyzer. The aspect ratio measured for each sphere was the maximum of the eight diameters divided by the minimum diameter. Because the sphere image was digitized from a video camera, the viewed area was divided into 256 x 256 pixels. Each diameter measurement had an error of ± 1 pixel. This provided a diameter measurement error of 2.5% for the small spheres and 2.0% for the large spheres. Because of the error, perfect spheres would have average aspect ratios of 1.05 and 1.04 for the small and large spheres, respectively. The measured average aspect ratios for 40-20 and 20-40 were 1.11 and 1.08, respectively (Figure 2.4.4) which provided deviations of 6% and 4% from spherodicity, respectively. Although, the 6% and 4% deviations are above the desired value of 2%, it must be noted that aspect ratio is the most severe measurement of spherodicity that can be applied. As residence time in the recovery tower is increased, so also should spherodicity. A more moderate measure of spherodicity was the shape factor which is $P^2/4\pi A$ where P is the measured perimeter and A the cross sectional area of the projected sphere. Shape factor for a perfect sphere is 1.00; for a hexagon, it is 1.10; and a square has a factor of 1.27. Shape factors on average were 1.04 and 1.03 for the small and large spheres, respectively. Standard deviations for the shape factors were only 2%. By this techniques, deviations from spherodicity were minimal.

Using the average diameter for each distribution to calculate individual sphere volume and the average individual sphere weight from 100 spheres, the true sphere density

Figure 2.4.1

Photographs of Fired, Thin-Wall, Alumina, Spheres Formed at Blowing Conditions (a) 40-20 and (b) 20-40.

Figure 2.4.2

Cross-section of Sphere Walls for Polycrystalline Alumina Spheres Fired at 1650°C, (a) 40-20 and (b) 20-40.

(a) Blowing Condition 40-20

(b) Blowing Condition 20-40

Figure 2.4.3

Diameter Distributions for 64 Randomly Selected Thin Wall Hollow Alumina Spheres.

(a) Blowing Conditions 40-20

(b) Blowing Condition 20-40

Figure 2.4.4

Aspect Ratio Distributions for 64 Randomly Selected Thin Wall Hollow Alumina Spheres.

was calculated to be 1.07 and 0.41 g/cc for the small and large spheres, Table 2.4.1. Based on an alumina wall density of 3.98, the average wall thicknesses were calculated to be 112 and 56 μ m, respectively, see Table 2.4.1. The thicknesses from the wall cross section micrographs of Figure 2.4.2 agree well with these values. Statistical analysis of wall thickness variation has not yet been completed but techniques using the image analyzer are under development.

From the above analysis, it can be seen that the thin walled spheres being produced by the coaxial nozzle process have a uniformity seldom achieved by a bulk production process. As process controls are varied and improved, not only will the range of diameter and densities increase but distributions and deviations from sphericity will approach a true monodispersed state.

2.5 FORMING SPHERES FROM AQUEOUS SLURRIES

Formation of hollow spheres from acetone based slurries has been very successful and at the time of this report over 300,000 lbs of spheres/year are being manufactured for automotive applications. However, because of concerns for organic emissions and the limitations that are legislated, a real need exist to convert the process to water based operation. A major effort has been made to use naturally occurring gums to gel the slurry systems and provide the necessary rigidity in the free falling spheres to survive a landing on a hard surface. Carrageenan was identified as the gum possessing the optimum properties for the sphere forming and collecting process. The typical gelling and melting characteristics of this class of material is shown in Figure 2.5.1 where the viscosity versus cycling temperature are plotted. After the initial gum solution and slurry processing, the dispersions containing the gelling agent are heated to high temperature ($\sim 80^{\circ}\text{C}$) to provide a low viscosity slurry for forming the sphere. Once the spheres are formed by the coaxial nozzle technique, they are rapidly cooled to below 50°C to initiate the gelling process. Most encouraging was the demonstration that, indeed, the aqueous-based systems could be gelled during the 3 to 5 second free-fall residence time and the sphere wall developed adequate strength to maintain a "sphere-like" geometry during landing.

At present the sphere forming characteristics of the aqueous slurries have not matched the quality or low densities of acetone-based systems. For example, the slurries containing carrageenan must employ 3 to 4 w/o of the gum to provide enough gel strength to maintain the shape during free-fall and survive the landing. Unfortunately these slurries, with a high volume loading of solids (Al_2O_3 powder), are very viscous and do not possess the film-forming capacity of the organic systems. As a result the typical density of the aqueous processed spheres is 40-50 lbs/ft³ compared to 20-30 lbs/ft³ for the acetone derived spheres. Photographs comparing spheres formed from both acetone and aqueous/carrageenan slurries are showing the raisin like surface of the aqueous spheres, Figure 2.5.2. Because of the softer wall and landing damage, the sphericity of the aqueous spheres do not match that of the organic base spheres. Work should be continued on aqueous systems and the gelling concept because of the economic attractiveness of the water-based systems.

2.5.1 PROPERTIES OF POLYSACCHARIDES

Polysaccharides exhibit a behavior known as gel thermoreversibility [5], Figure 2.5.1. To gel a polysaccharide, it is first dispersed in water. The dispersion is brought to an elevated temperature and, just prior to boiling, the polysaccharide goes into solution. The solution exhibits a relatively low apparent viscosity. On cooling, the polysaccharide solution gels. This gel can be reheated and put back into solution, resulting again in a low apparent viscosity. The cycle of converting gel to fluid and

Figure 2.5.1

Gel Thermoreversibility, Describes Repeated Low Viscosity Solutions at High Temperatures and Solid Gels at Low Temperatures

Organic Based Alumina Aerospheres

Water based Alumina Aerospheres

Figure 2.5.2

Comparison of Hollow Spheres From (A) Acetone Based Slurries and (B) Aqueous Based Slurries Using Carrogenan as the Gelling Agent

fluid to gel can be repeated many times. The average molecular weights of two most used polysaccharides, agar and carrageenan, are on the order of 100,000 [2] and 250,000 [22], respectively. The viscosity of the polysaccharides are very high due to their unbranched linear polymer structure and the negative repulsion that is produced along the chain by the ester sulfate groups. For carrageenan, this repulsion keeps the polymer rigid. The hydrophilic nature of the polymer causes a layer of immobilized water to be maintained [3] which results in a viscous fluid. Addition of cations, in the form of salts, decrease the viscosity of carrageenan at elevated temperatures, by reducing the effect of the negative charge by the sulfate group [3]. Polysaccharides exhibit a characteristic that is termed "pseudoplastic" and often referred to as shear thinning [5,23]. Pseudoplasticity in polysaccharides is due to the alignment of the polymer molecules in a manner that reduces the resistance of flow [8]. This results in an apparent decrease in viscosity as shear is increased.

After identifying the "idealized" structure of agar, it was determined that the fraction of agar with the greatest gelling capacity could be separated from a normal distribution of the product. This "high gelling" fraction was termed agarose [17], Figure 2.5.3(A) [1,2,24]. Carrageenan also can be separated by precipitation and centrifuge methods. To date, six different types, of carrageenan have been identified, three of which, kappa, iota and lambda, are available commercially [3,17,22,25]. Lambda carrageenan does not gel but proves to be an excellent dispersant for heavy particles [5,22]. Iota carrageenan forms elastic syneresis free gels, that is, a gel that does not weep or exude water upon gelation [4,5,26]. Kappa carrageenan, which usually has traces of calcium ions, form rigid or, as commonly referred to in the industry, brittle gels [5,22,26], Figure 2.5.3(B) [3,22,24,27]. Kappa carrageenan also exhibits syneresis. Iota gels are the only ones that have "rehealing" properties; if the gel is broken, the polymer molecules can eventually reform. Reformation of a gel is referred to as thixotropy [3, 26] .

The process of gelation for kappa carrageenan and agarose has been drawn from the verbal description in reference [17]. The differences between the two may seem slight, but actually are of major influence to final gel strength. For kappa carrageenan, small levels of masking residue from the production process cause portions of the molecular chain to kink. Therefore, a double helix formation produced by two polymer chains is interrupted at the kink, allowing the polymers to form additional double helices with other chains [3,17]. Agarose, on the other hand, can only form single pairs of double helices [17]. The formation of the double helices are the result of hydrogen bonding between the two polymer chains [4]. In both cases, the helices "trap" water and hold it in place forming the gel.

Kappa carrageenan has the added ability to trap water through aggregation. Aggregation is the formation of "super junctions" [24] between two or more helices,

(A)

(B)

Figure 2.5.3 Idealized Molecular Structure of (A) Agarose and (B) Kappa Carrageenan

due to the attraction caused by the potassium and calcium ions, which are usually present in the carrageenan. The ester sulfates along the kappa carrageenan molecule provide attachment points for the calcium ions. This aggregation of the polymer helices causes syneresis and contributes to dramatically increasing the gel strength. The process of aggregation can be enhanced through further addition of calcium ions and certain other types of cations in the solution [4,5,26,27]. Cesium ions are more efficient than sodium ions in their ability to form junction zones. This is apparently due to an observed selectivity by the molecule, which results in more bonding sites [29,30]. Agar's gel strength is not affected by ions dispersed in the water; hence its helices cannot be aggregated. The inability to aggregate the agar helices is most likely due to the lack of sulphates associated with the molecule. The sulfates are theorized to be points of attachment for the cations in kappa carrageenan [27].

2.5.2 MEASUREMENT OF GEL STRENGTH AND VISCOSITY

A comparison of the most promising polysaccharides were tested for gel strength and fluid viscosity. It should be noted that there is no standard for measuring gel strengths [26]. This is probably due to the fact that the principal consumer of gels is the foods industry which is more interested in the texture as felt by the mouth, rather than in the actual strength of the gel in engineering terms. The most common form of measuring gel strengths is to impinge the gel surface with a 1 cm² diameter plunger, which is subsequently forced into the gel. The force required to break the gel at room temperature is measured in units of grams/cm² [1,23].

Preparation of Gels - The polysaccharide test samples to be measured for their gel strength were made in the following manner. Polyethylene containers, 250 ml, with air tight threaded caps were filled with 200 grams of tap water. Specified weights of ion species, such as K₂CO₃, were added to the water. The polysaccharide was weighed and added to the solution and, after sealing the container, was shaken vigorously. The container was placed into a boiling water bath and agitated occasionally until all the gel powder had gone into solution. It was determined the polysaccharide had gone into solution when there were no visible clumps and the viscosity had decreased dramatically. The solution was poured into 250 ml sealable molds (cups with lids) and was allowed to gel on cooling to room temperature. For kappa carrageenan, the gel temperature is dependent on the concentration of cation species in solution and to a lesser degree the concentration of kappa carrageenan in solution. The larger the concentration of cations and kappa carrageenan, the higher the gelation temperature. Usual gelation temperatures for kappa carrageenan fall in the range of 20 to 80°C [3]. For agarose, the gel temperature is dependent on the concentration of agarose in solution. The higher the concentration of agarose, the higher the gel temperature. Usual gelation temperatures for agarose fall in the range of 30 to 45°C [2].

Gel Strength Measurements - A Universal Instron Testing machine, used in compressive mode was used to test gel strengths. The gels were placed on a precalibrated load cell, usually in the cup, unless the surface of the gel was defective. If there was entrained air at the surface due to an accelerated gelation rate, the gel was removed from the cup and set inverted, on the load cell. The force required to break the gels was read off of a strip chart in g/cm² using a cross head speed of 0.1 cm/min and a plunger with 1 cm² surface area. The edges of the plunger were polished to eliminate sharp edges to prevent prematurely rupturing the gel. Gel strength tests were conducted on agar (S-100 [31]) and kappa carrageenan (Gelcarin® GP 911 [28]). A series of tests were conducted on kappa carrageenan (911) with varying concentrations of specific cations to determine cation effect on gel strength. Note, there is no increase of gel strength on agar when cations are added because of the lack of ester sulfate groups. Hence, many more tests were conducted on kappa carrageenan than on agar.

Gel Viscosity Measurements - To measure viscosities of gel solutions, the same steps were repeated in preparation of the gels, up to the point that the dispersed polysaccharide went into solution in the hot water bath. Samples were placed directly into a preheated HAAKE viscometer of the Searle coaxial cylinder type. The viscometer was controlled through a Rotoviscometer RV20 and an IBM personal computer [32]. Solutions with low viscosities and high viscosities were measured with spindles NV and MVII, respectively. It was recommended that viscosity measurements of polysaccharides be conducted at temperatures greater than 75 °C [3] to stay well above solution temperatures. Hence, the temperature of the samples was maintained at 90°C +/-0.4 during these measurements. Temperature of the gel solution samples was controlled by a HAAKE circulator, a circulating water bath with thermal elements, and a temperature control monitor [32]. During viscosity measurements, the samples were covered with a stainless steel disc which had a hole in the center for the spindle and a rubber ring that fit close to the spindle to prevent evaporation of the water. Evaporation had to be prevented in order to maintain the proper concentration of the polysaccharide in solution. The shear rate was increased at a predetermined rate from zero to 1100 1/sec for spindle NV, zero to 450 1/sec for spindle MVI 1.

Slurry Preparation - Kappa carrageenan was chosen as the binder for attempts to fabricate aqueous based hollow spheres. Slurry preparation entailed weighing the water, adding 0.5 wt% of a dispersant (Darvan 811 a 43% solution sodium polyacrylate), based on powder weight, and adding potassium ions, in the form of K₂CO₃, based on weight percent in the water. The mixture was shaken to place the potassium ions into solution. Alumina, A3000 from Alcoa, with a particle density of 3.98 g/cm³, was weighed to produce a known solids volume in water. The slip was ball milled overnight using 2 cm zirconia cylinders. After milling, kappa carrageenan

(911) was added to the slip at a specific percent weight in water. The slip was mixed with a high shear blender to promote dispersion of the carrageenan particles. The sealed container was placed in a boiling water bath. The container was removed and shaken periodically for verification of polysaccharide solution.

2.5.3 GEL STRENGTH AND VISCOSITY OF CARRAGEENAN SLURRIES

Gel strength tests and viscosity measurements were conducted on agar and kappa carrageenan. Data and results for agar gels will not be presented here since carrageenan was selected for sphere formation. Kappa carrageenan was tailored, through the use of specific cations, for optimum strength and viscosity properties. The kappa carrageenan was then used as the binder for slurries in the formation in wall hollow spheres.

Gel Strength Comparison - Agar's gel strength of 1500 g/cm², at 3 wt% concentration, was consistent with Fanelli et al. [1]. In an effort to produce stronger gels, the gel strength of agar (S-100) was measured as a function of concentration. Agar reached a strength of 2600 g/cm² at 5 wt% and the strength was approximately linear with concentration. Extrapolating to zero strength indicates that 0.5 wt% of agar is required to form a gel. For use as a binder, agar's gel strength was only half that of kappa carrageenan samples gelled with K⁺ and Cs⁺ at high concentrations. Therefore, agar was abandoned as a hollow sphere binder.

Optimization of Kappa Carrageenan's Gel Strength - Unlike agar, it is known that kappa carrageenan's gel strength can be enhanced through the use of certain cations. A list of suitable cations can be found in the foods industry literature. The list includes: potassium (K⁺), calcium (Ca⁺⁺), sodium (Na⁺), and ammonia (NH₄⁺) [5,26,39]. One reference noted additional cations, Sr⁺⁺, and Ba⁺⁺, but did not say how effective they were in increasing the gel strength [3]. Therefore, varying concentrations of certain cations were put into solution and 3 wt% kappa carrageenan (911) was added to the solution. After going through the procedure outlined above, the solutions were gelled and strength determined, Figure 2.5.4. It was readily apparent that monovalent cations, in particular K⁺ and Cs⁺, were superior in terms of improving gel strength. The monovalent cations are dimensionally larger than the divalent cations because the divalent nucleus has a larger contraction effect on the electron cloud, thereby making the cation dimensionally smaller. It is thought that the larger cations can be positioned between the helices more favorable and therefore are able to promote a larger aggregation effect. The gel strength difference between K⁺ and Cs⁺ were not very different, with K⁺ having the slightly higher peak value at 0.42 molarity. A larger K⁺ concentration was required to match the same strength produced by Cs⁺. For divalent cations at low concentrations (<0.1 M), Ba⁺⁺ exhibited the largest gel strength.

Figure 2.5.4

Monovalent Cations Dissolved at Specific Molarities in Water with 3 wt% Kappa Carrageenan

Again, cation size may be contributing because Ba^{++} was the largest of all the divalent cations tested. It was thought that a composition of Ba^{++} and K^+ together would result in an increased gel strength. However, the effect was not statistically significant from K^+ by itself. Therefore, potassium cations, due to their excellent gel strength properties, were used for the rest of the experiments involving kappa carrageenan.

In order to find the amount of potassium in kappa carrageenan that will produce optimum gel strengths, various weight percentages of K^+ , based on water weight, were produced by dissolving the solid dry form of K_2CO_3 . Weight percentages of kappa carrageenan (911), based on water weight, were dispersed in the water. As was expected, an increase in the amount of potassium, resulted in an increase in gel strength. Above some critical value of potassium, or any cation species, there is a decrease in gel strength, as can be seen in Figure 2.5.5. The drop in gel strength at 2% potassium, is due to a "salting out" [26] of the polysaccharide; that is, a major portion of the polysaccharide is prevented from going into solution at high salt concentrations. The maximum gel strength occurs in the range of 1.5% potassium; but this value exhibits the largest error, which means the predictability of the gel strength is not very good. It has been surmised that the quantity of potassium cations (1.5 wt% K^+) is near the critical juncture. Some specimens were just beginning to salt out at 1.5 wt% K^+ , while others were experiencing maximum strength. As a result of the unpredictability at 1.5% potassium, all tests conducted after this observation used 1% potassium. This provided sufficient gel strengths which could be expected with some certainty, without having to be tested.

A general trend of the gel strength versus kappa carrageenan concentration is also apparent in Figure 2.5.5 in addition to the K^+ concentration effect. The gel strength was first examined using regression analysis at each carrageenan concentration curve based on the effect of K^+ concentration. The potassium was thought to have a volume effect; and the K^+ concentration raised to the 1/3 power provided a reasonable fit for all five carrageenan contents resulting in the general Equation (2.5.1), where n is equivalent to 1/3.

$$\sigma_g = C [K^+]^n \quad (2.5.1)$$

Where s_g is gel strength, C is a constant, $[K^+]$ is potassium concentration, and n was 0.333. Similarly, the amount of kappa carrageenan (911) was expected to be related directly to gel strength and when C, in Equation (2.5.1), was analyzed versus carrageenan content, C could be approximated by 900(wt% carrageenan). Therefore, the combined effect of carrageenan and potassium concentration could be expressed as:

Figure 2.5.5

Gel Strength at Varying Concentrations of Potassium Ions in Aqueous Kappa Carrageenan Gels

$$\sigma_g = 900(\text{wt\% kappa carrageenan})(K^+)^{0.33} \quad (2.5.2)$$

The degree of fit can be seen in Figure 2.5.6, where Equation (2.5.2) is seen to slightly underestimate strengths at high carrageenan contents and overestimate at lower contents. The salting out occurred near the same level for all weight percentages of kappa carrageenan. Therefore, data points were eliminated at K^+ concentrations above the maximum strength and not considered in arriving at this formulation.

Viscosity of Carrageenan Solutions and Slurries - The viscosity of kappa carrageenan was measured at two concentrations: 3, and 5 wt% in water, Figure 2.5.7. As anticipated, the addition of agar into water increased in viscosity as a function of the carrageenan concentration. This increase in viscosity was from ~ 30 mPa.sec at 3 wt% to ~ 120 mPa.sec at 5 wt%. Note the shear thinning as the shear rate is increased. This has been attributed to the breaking of bonds between the polymeric chains and alignment of chains with increased shear, which provides less resistance to flow [12]. As polymers get shorter, the molecular weight decreases. This results in an exponential decrease in viscosity [3] as expressed in power law rheology [12].

According to the manufacture [3], viscosity of carrageenan solutions can be decreased through the addition of cations into the polymer solution. A decrease in viscosity is due to a screening of the effective negative charge of the sulfur groups along the polymer chain which in turn, decreases the repulsive forces between neighboring chains, allowing them to slide by each other more easily. An increase in the amount of cations did not necessarily translate into a specific decrease in viscosity, as is shown in Figure 2.5.7.

There is an effect by the potassium cations on the viscosity, but it does not seem to be precisely predictable. For example, Figure 2.5.7(A), the 3 wt% carrageenan (911) has an expected maximum viscosity when no extra cations are introduced into the solution (0 wt% potassium). In Figure 2.5.7(B), at 5 wt% carrageenan (911) 1% K^+ produces the minimum viscosity over the entire applied shear. Except for the decrease in viscosity shown for 3% kappa carrageenan, Figure 2.5.7(A), when K^+ is added, the suggestion that K^+ reduces viscosity was not observed. There appears to be no predictability for viscosity with K^+ concentration. Agar and kappa carrageenan have approximately the same viscosity. Unlike agar, kappa carrageenan's viscosity can be affected, or possibly engineered upon further study, with variations in cation concentration.

Another test was conducted to see if the polysaccharide maintained a constant viscosity after repeated solution and gelling cycles. The viscosity was suggested not to change as thermoreversibility, the cycle of heating and cooling the gel, proceeds

Figure 2.5.6

Curve-Fitting of Kappa Carrageenan Gel-Strengths in Figure (3.5.5), According to the Equation 2.5.2.

Figure 2.5.7

Viscosity of (A) 3 Weight % and (B) 5 Weight % Kappa Carrageenan in Water, with Specific Concentrations of K^+ Measured at 90 Degrees C.

[5]. But in fact, viscosity did vary based on a number of cycles of thermoreversibility for kappa carrageenan. A container of the polysaccharide was prepared and a small portion of it was used for one viscosity measurement. The container was immediately resealed, allowed to gel, and then reheated whereupon another sample was withdrawn for testing. A minimum amount of shaking was done from cycle to cycle. A decrease in viscosity of 25% measured at a shear rate of 600 1/sec for kappa carrageenan at 3, 4, and 5 wt% in water at 90 °C. Gel strength exhibited an approximate decrease of only 7%, measured from cycle to cycle. Thus, repeated cycling could be used for viscosity reduction without sacrificing strength in the gelled state.

Kappa carrageenan was selected over agar for slurry binder studies because of its superior gel strength and similar viscosities. Slips were prepared and viscosities were measured at 90 °C, Figure 2.5.8. Relative viscosities, comparing slurry to carrageenan solution viscosities, were low, and ranged from 4 to 8. Relative viscosity is defined as viscosity of the slip (solution containing the alumina particles) divided by the viscosity of the solution (kappa carrageenan, water, and cations). A low relative viscosity implies a negligible interaction between the alumina particles and the kappa carrageenan molecules. Therefore, high solids contents can be used with relatively high kappa carrageenan contents.

2.5.4 CONCLUSIONS AND RECOMMENDATIONS

Viscosities of kappa carrageenan solutions have been shown to be low enough to allow 40 vol% solids to be used for formation of hollow spheres, Figure 2.5.2. This demonstrates that powders can be readily dispersed in the system. Kappa carrageenan when tailored correctly, has greater gel strength than either agarose or agar, for the same concentration. In addition the much higher resolution temperature of carrageenan (70°C) compared to agar (50°C) allows gelled carrageenan slurries to be dried in a reasonable time period with out melting the gel. Manufacturers interested in the polysaccharides should investigate the potential of multiple gelation cycles to dramatically decrease slip viscosity without a significant decrease in gel strength. This would allow increased solid loads. Also the concentration of kappa carrageenan, and the effect of pH on the slip system, needs to be investigated further to obtain insight on the dispersiveness of ceramic particles to higher solids loading.

2.5.5 FOOTNOTES AND BIBLIOGRAPHY

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3.0 MECHANICAL BEHAVIOR OF HOLLOW SPHERES AND FOAMS

3.1 UNIAXIAL COMPRESSIVE BEHAVIOR OF BRITTLE HOLLOW SPHERES

Mechanical behavior of hollow spheres was evaluated using finite element analysis. Failure mode and strength of spheres were determined from stress analysis. A parametric study of strength as a function of wall thickness to sphere diameter ratios indicated that strength is a function of relative density squared. Strength of aluminum oxide hollow spheres made by the coaxial nozzle powder process agreed reasonably with the finite element parametric model.

This research was done primarily to investigate the compressive strengths of individual hollow spheres. Sphere strength was defined for this research as the critical force exerted on a sphere at failure per maximum cross-sectional area of the sphere to represent a load bearing capacity of the sphere. Finite element analyses were used to calculate the sphere strengths for various sphere geometries. Stress distributions and the mode of failure of a sphere under compression were investigated. Parametric analyses were carried out to obtain the sphere strength as a function of sphere properties. Compressive strengths for hollow alumina spheres were measured experimentally and the finite element analyses results were compared with the empirical results.

3.1.1 PREVIOUS MODELS

Compressive contact loading problems on a brittle solid sphere have well-established theoretical solutions¹. However, contact loading on a hollow sphere does not have a widely accepted solution. Two of the few proposed models are reviewed.

Bratt, Cunnion, and Spivack Model - Bratt et al.² investigated the mechanical properties of thin-wall glass spheres. They proposed that under an uniaxial compressive force, a hollow sphere experiences a compressive stress on the axis and a tensile stress on the sphere surface at the equator. When the tensile stress exceeds the tensile strength of the wall material, fracture occurs and a circumferential crack forms around the equator splitting the sphere into two hemispheres. The tensile stress σ , on the surface was calculated as,

$$\sigma = \frac{3F(D/3)}{2(\pi D)t^2} = \frac{F}{2\pi t^2} \quad (3.1.1)$$

where F is the uniaxial compressive force. D is the diameter, and t is the wall thickness of the sphere. Sphere strength, σ_c , was defined as the stress on the sphere at failure. The sphere strength, according to the model, is equal to the tensile strength of the wall material, σ_w , and therefore is a constant for spheres made of the same material regardless of diameter. They argued that the critical force, F_c , at which a sphere fails was only related to the wall thickness, t , of the sphere and is independent of the size of the sphere as in equation (3.1.3).

The hollow glass spheres were tested by compressing a sphere between a flat tipped, conical rod and a stationary platen, which is a contact loading case. The experimental results for the uniaxial compression of the spheres were plotted as F_c versus t , which showed the critical force is a square function of the wall thickness.

Swanson and Cutler Model - Swanson et al³. investigated the stress and strength of hollow ceramic spheres as possible proppants, which are small particles mixed with fluid in hydraulic fracturing treatments of petroleum wells to stimulate production. They modeled the arrangement of spheres with uniform diameters in a hydraulic fracture cavity as a cubic close packed structure, each sphere contacting twelve neighbors in six pairs of diametral contact loadings. The overall loading on proppants is caused by the closure pressure, P , which is defined as the lithostatic confining pressure minus the pore pressure. Assuming that each of the twelve surrounding spheres exert the same contact force F on a sphere, F is given by

$$F = bP\pi r^2 \quad (3.1.2)$$

where b is a constant that depends on the packing geometry and r is the radius of the sphere. For the close packing with the packing factor of 0.74, b is $4/(12 \times 0.74^{2/3}) = 0.41$. Other packing geometries produce higher values of b .

The stress at the inner surface σ , could become critical for the failure of the sphere, and was calculated to be

$$\sigma = 1.243 \left(\frac{P}{1-2\xi+\xi^2} \right) \ln \left\{ \frac{33.61}{(1-\xi)} \left[\frac{2+\xi^3}{1-\xi^3} + 0.667 \right] \right\} \quad (3.1.3)$$

where ξ is (r_i/r_o) , the ratio of the sphere inner and outer radii, and P is the closure pressure. The stress, σ , has a linear relationship with the closure stress and when the closure stress exceeds a critical stress P_c , σ exceeds the bend strength of the wall material, σ_w , leading to the failure of the sphere. The fracture strength of the sphere can be defined as the critical closure stress, P_c , which causes the diametral failure loading, F_c , on the sphere. The sphere inside to outside ratio, ξ , can be substituted

by $(1-t/r)$, and Equation (3.3.3) suggests that the fracture strength of a hollow sphere under diametral concentrated loading is a function of the aspect ratio, and is not governed by a single factor of the wall thickness or the diameter of a sphere alone.

Sphere Strength - Sphere strength was defined for this research based on total cross-sectional area. When a sphere fails under a fracture load F_c , the sphere strength, σ_s , can be defined as the fracture load per maximum cross-sectional area of the sphere regardless of the deformation mode to represent the load bearing capacity of the sphere:

$$\sigma_s = \frac{F_c}{\pi r^2} \quad (3.1.4)$$

3.1.2 FINITE ELEMENT PROCEDURES AND LOAD CONDITIONS

Finite element model analyses were carried out to investigate the compressive behavior of hollow ceramic spheres and bonded-sphere foams. The MSC/NASTRAN V66A program was used on a Cyber 990 and a Vax 6440 main frame computers for the finite element model calculations. Linear elastic static analyses were performed because the primary concern of this research was in hollow brittle spheres.

Compressive behavior of a hollow sphere under uniaxial concentrated loading was calculated first for various aspect ratios (wall thickness to sphere radius ratios). Membrane forces, bending moments, deformations, transverse shear forces, and stresses on the spheres were analyzed. From the stress analysis, the critical loads required for the failure of the spheres were calculated. Secondly, compressive strength of hollow spheres under diametral contact loading by platens were simulated for comparison with the experimental results.

Finite element analyses were performed for a range of ideal alumina spheres with varying dimensions. The relative density of the sphere, (ρ_s/ρ_o) , can be expressed as a function of the aspect ratio, (t/r) ,

$$\frac{\rho_s}{\rho_o} = \frac{3\left(\frac{3}{r}\right) + \frac{1}{4}\left(\frac{t}{r}\right)^3}{1 + \frac{3}{2}\left(\frac{t}{r}\right) + \frac{e}{4}\left(\frac{t}{r}\right)^2 + \frac{1}{8}\left(\frac{t}{r}\right)^3} \quad (3.1.5)$$

where ρ_s is the sphere density and ρ_o is the wall material density. The radius of a sphere, r , used in this study is the distance from the center of a sphere to the midplane of the shell.

In these linear elastic analyses, only one set of load and sphere dimensions for an aspect ratio is necessary for the investigation. A uniaxial compressive force on the spheres of 2.45 N was simulated to evaluate the force and stress distributions on the spheres under the same load and to calculate sphere strengths. The material properties of ideal alumina, Al_2O_3 , with Young's modulus, poisson's ratio, ν , tensile strength, and compressive strength of 380 GPa, 0.26, 300 MPa, and 3450 MPa, respectively, were used in the finite element analyses.

Parametric studies were carried out to investigate the relationship between the sphere strength, σ_s , and the geometrical parameters of a hollow sphere. Fracture of a hollow sphere was determined from the stress analysis using the Griffith criterion. When a set of principal stress coordinates, (σ_1, σ_2) , at a point on the sphere is outside the criterion boundary, failure starts from that location. Accordingly, tensile stresses are far more critical for failure of the sphere than compressive stresses. When both principal stresses are tensile, the fracture criterion shows that failure will take place when the major principal stress exceeds the tensile fracture strength.

Concentrated Loading - The stress analyses and the fracture criterion dictates that under uniaxial concentrated loading, hollow brittle spheres should fail at the loading point inside the shell due to tensile stress. The sphere strengths were calculated from the critical stresses at the closest location to the loading point where stresses were calculated. The sphere strength was found to be a linear function of the relative density squared, $(\rho_s/\rho_o)^2$, as shown in Figure 3.1.1. The linear relationship in the figure is valid for spheres with relative densities up to about 40%. This encompasses the entire density range of actual spheres produced to date. The correlation coefficient squared, R^2 , of the relationship is 0.99976. Rewriting the linear regression equation in the figure to include the strength of the wall material, the sphere strength is given by:

$$\sigma_s = 0.0275\sigma_o \left(\frac{\rho_s}{\rho_o} \right)^2 \quad (3.1.6)$$

The linear relationship between the sphere strength and the relative density squared holds true independent of the coefficients. Strength models developed in this research are valid for all ceramic materials with poisson's ratio of 0.26, although the finite element analyses were performed for ideal alumina spheres. This is because of the definition of the sphere strength as mentioned above and linear elasticity.

Figure 3.1.1

Sphere Strength σ_s , vs. Relative Density Squared, $(\rho_s/\rho_o)^2$, Under Uniaxial Concentrated Loading.

Contact Loading - In actual applications, the spheres will likely experience distributed or contact loading instead of concentrated loading. When a hollow brittle sphere is diametrically compressed between a pair of rigid platens, the sphere contacts the platens at the loading points initially. As soon as a load is applied to the sphere, however, it will start to deform by flattening at the contact area as illustrated in Figure 3.1.2. The critical region for failure was thought to be around the perimeter of the surface of contact. A failure criterion for contact loading situation was postulated to predict the sphere strength based on the uniaxial concentrated loading results and the above assumption. It was found that the location of minimum bending moment in the direction tangential to the latitude, M_y , is where the deformation of a hollow sphere wall starts to be significant under a uniaxial concentrated loading. The region where M_y is minimum under a concentrated loading was assumed to be the critical region in the contact loading situation. Thus, the principal stresses on the elements that lie at that region became important for the failure analysis.

When the normal- x stress, σ_x , which is also a major principal stress, on the inner surface of an element in the critical region exceeds the tensile strength of the wall material, failure occurs at the inner surface of that element. The hollow sphere will break parallel to the loading axis into two hemispheres. From this failure model, sphere strengths of hollow brittle spheres under uniaxial compression between rigid platens were calculated for various aspect ratios. Parametric studies showed that the sphere strength under the contact loading is also a linear function of the relative density squared as shown in Figure 3.1.3. From the linear relationship the sphere strength is given by:

$$\sigma_s = 0.774\sigma_o \left(\frac{\rho_s}{\sigma_o} \right)^2 \quad (3.1.7)$$

The coefficient in Equation (3.1.7) is an order of magnitude larger than the one in Equation (3.1.6) which predicts that the sphere strength under a uniaxial contact loading between a pair of rigid platens will be much higher than under uniaxial concentrated loading.

To confirm the validity of the failure model for the contact loading, finite element analyses were performed for three aspect ratios, 0.015, 0.05, and 0.075. Instead of applying loads, displacements of grid points were forced to simulate a deformed contact area. Since this was a varying boundary condition problem, numerous simulations were iterated to find a situation when the sphere would fail. The coefficient in Equation (3.1.7) obtained from these analyses was in the range of 0.4 to 0.8 because simulating and determining the exact degree of deformation at failure

Figure 3.1.2 Deformation Mode of a Hollow Sphere under Contact Loading.

Figure 3.1.3

Sphere Strength σ_s , vs. Relative Density Squared, $(\rho_s/\rho_o)^2$, Under Contact Loading by Rigid Platens.

were difficult. However, this simulation of contact loading confirmed that the coefficient in Equation (3.1.7) is of a reasonable order.

3.1.3 EXPERIMENTAL RESULTS AND DISCUSSIONS

Hollow alumina spheres were produced by the coaxial nozzle technology using Alcoa XA-3000 alumina powder. The process can be controlled to produce monosized hollow spheres with predetermined size and wall thickness for the application. These hollow alumina spheres had densified walls after being sintered, typically at 1600°C for 3 hours.

The hollow alumina spheres were loaded on an Instron testing machine using a 50 kg load cell. A sphere was tested between a pair of polished, hardened steel platens using a crosshead speed of 0.1 inches per minute. Twenty-five to thirty spheres were tested for each batch of spheres. Fracture load, F_c , was recorded for each sphere. Sphere strength, σ_s , for each sphere was calculated from the fracture load and the diameter of the sphere.

The hollow spheres under uniaxial loading failed in several modes. Many spheres failed leaving two hemispheres as predicted by the finite element model. For small spheres, vertical or horizontal failure was not easily observed because failure was instantaneous and the objects were small. Large spheres with thick walls broke vertically into two hemispheres. Thus, the small spheres are also believed to have failed vertical because the finite element model predicts this failure mode for all spheres.

Some spheres failed leaving small holes at contact areas. The size of a hole varied from a very small hole to a large hole for various spheres. This can be explained by the fact that σ_s is close to σ_x inside a sphere near the loading axis, although σ_x is the critical stress for ideal hollow spheres. Considering the imperfect geometry of the spheres, it can be assumed that for some spheres, σ_y becomes the critical stress thus leaving a hole around the loading axis.

Other spheres failed leaving randomly shaped fragments of spheres. This can be also contributed to the imperfect sphere geometries. Once the fracture was initiated at the critically stressed region, the crack may propagate along the weakest path, *e.g.*, the thin part of the sphere, etc.

The hollow alumina sphere strength versus relative density squared is plotted in Figure 3.1.4. The experimental results show a strong linear relationship with the relative density squared as predicted by the finite element model analysis. The coefficient obtained from the linear regression of the experimental data is 0.252 whereas the

Figure 3.1.4

Sphere Strength vs. Relative Density Squared for Alumina Spheres.

coefficient in Equation (3.1.7) calculated from the finite element analysis is 0.774. The finite element model predicts about three times higher sphere strength than the actual sphere strength. However, the real spheres have imperfections such as non-uniform wall thickness, imperfect sphere geometry, flaws, small tials, etc. Considering these facts, the finite element model provides a respectable strength model for the hollow spheres. More important than the coefficient, the linear relationship between the sphere strength and the relative density squared predicted by the finite element model was confirmed by the experimental results.

Model Comparisons - Finite element methods were used to model the mechanical behavior of hollow ceramic spheres because satisfactory theoretical solutions could not be found. However, a comparison of the finite element model can be made to the existing model by Swanson and Cutler for the uniaxial concentrated loading condition. The concept of the closure stress in Equation (3.1.2) can be extended to describe the strength of a sphere under uniaxial compression. When sphere is loaded by only one set of diametral loading, the constant, b , in the equation can be replace by unity, and the closure pressure, P , can be replaced by σ , which represents the macroscopic overall stress state of the sphere:

$$\sigma = \frac{F}{\pi r^2} \quad (3.1.8)$$

Substituting the sphere strength for the closure stress in Equation (3.1.3), the sphere strength of a hollow sphere under a diametral concentrated loading is

$$\sigma_s = 0.805 \sigma_o \frac{(1-\xi)^2}{\ln \left\{ \frac{33.61}{(1-\xi)} \left[\frac{(2+\xi^3)}{(1-\xi^3)} + 0.667 \right] \right\}} \quad (3.1.9)$$

Equation (3.1.9) predicts unreasonably low sphere strengths values, especially for thin-wall spheres, because it was derived on a thick plate foundation and for concentrated loading. While Equation (3.1.9) cannot be directly compared with Equation (3.1.6), rearranging Equation (3.1.9) by substituting $(1-t/r)$ for ξ and then making the further substitution of $t/r = (\rho_s/\rho_o)/3$ for small aspect rations places the equation in a form similar to that of Equation (3.1.6), and results in Equation (3.1.10)

$$\sigma_s = (0.006 \text{ } 0.01) \sigma_o \left(\frac{\rho_s}{\rho_o} \right)^2 \quad (3.1.10)$$

for the relative density range from 0.03 to 0.4 Equation (3.1.10) has the same form as Equation (3.1.6) except for the magnitude of the constant. The constant in Equation (3.1.6) depends on the size of the meshes around the loading point. Even if the meshes were refined until good convergence was observed as explained previously, precise stresses could not be expected near the loading point because the meshes could not be reduced infinitely. If the meshes are refined too small, a greater calculation error can result. Also, Equation (3.1.9) was divided by approximation and by substituting actual values for the aspect ratio. However, Equation (3.1.6) and Equation (3.1.10) agree well qualitatively, and the constants are of a same order of magnitude.

3.1.4 CONCLUSIONS

The mechanical behavior of hollow spheres with various aspect ratios under uniaxial concentrated loading was investigated using the finite element methods. The distributions of membrane forces, bending moments, and transverse shear forces on the hollow spheres were studied and the failure of the spheres was determined from the stress analysis using Griffith criterion for the failure of a brittle material for plane stress. Parametric studies were carried out and sphere strength under uniaxial concentrated loading was predicted to be a linear function of relative sphere density squared.

A failure model of a hollow sphere under a contact loading by platens was proposed to predict the sphere strength based on failure analysis of the sphere under uniaxial concentrated loading. The sphere strength under contact loading was also predicted to have a linear relationship with the relative sphere density squared.

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3.2 COMPRESSIVE STRENGTH OF HOLLOW SPHERE FOAMS

As in any engineering design, mechanical properties of bonded sphere foams could be a limiting factor in their applications. Especially for use as a light structural material, the strengths of the spheres and the spheres foams need to be maximized. The factors governing the strengths must be understood and strength models need to be developed to achieve maximum strengths of the materials for given application conditions. There has been a few publications proposing strength models of ideal hollow elastic spheres and there are no models dealing directly with hollow sphere foams. The mechanical properties of cellular materials have been summarized by Ashby and are described below.

This research was performed primarily to investigate the compressive strengths of sphere foams. A model of basic unit structure in a spheres foam was proposed, and finite element analyses were performed to calculate the strength of the foam. A bonding technique was developed to form bonded spheres foams and the compressive strengths of the foams were measured. The finite element analyses results were compared with the empirical results and agreement reasonable.

3.2.1 COMPRESSIVE STRENGTH OF CELLULAR SOLIDS

Ashby has summarized the mechanical properties of general cellular solids based on an open-cell and a closed-cell models as geometric foundations of cellular solids. An open-cell foam was modeled as a cubic array of members of length l and square section of side t which were arranged that adjoining cells meet at mid-points. In the open-cell model, the relative density of the cell, ρ_f/ρ_o , is given by

$$\frac{\rho_f}{\rho_o} \propto \left(\frac{t}{l}\right)^2 \quad (3.2.1)$$

where ρ_f is the density of the foam, and ρ_o is the density of the wall material. The second moment of the section of a member from the geometry is given by

$$I = \frac{t^4}{12} \quad (3.2.2)$$

A closed-cell foam was modeled as a cubic array of square plates of side l and thickness t . Adjoining cells were staggered similar to the open-cell model. The relative density of the closed-cell foam is given by

$$\frac{\rho_f}{\rho_o} \propto \frac{t}{l} \quad (3.2.3)$$

and the second moment of the section of a plate is given by

$$I = \frac{lt^3}{12} \quad (3.2.4)$$

Most artificial foams behave like open-cell foams because most of the solid material is concentrated into the cell edges due to the surface tension during the manufacturing process even if they have closed-cell faces.

For the analyses of the mechanical properties of the foams, a two-dimensional model of hexagonal cells, which is shown in Figure 3.2.1, was used. When a foam is under a compressive loading as shown in the figure, the cell walls which experience force components normal to them bend. A brittle foam shows a linear elastic deformation until it fails. Brittle foams fail by brittle crushing in compression and brittle fracture in tension. The brittle foam modeled in the figure will fail due to the bending fracture near the hinges. A force F exerts a moment which is proportional to Fl to the wall of length l . The stress on the foam, σ , is proportional to F/l^2 . The bending moment, M_c , exerted by the force F_c acting on an open-cell at failure is given by

$$M_c = \frac{1}{6} \sigma_c t^3 \quad (3.2.5)$$

where σ_c is the modulus of rupture of the cell-wall material. Thus the brittle crushing strength of the foam, σ_f , is given by

$$\sigma_f \propto \frac{F_c}{l^2} \propto \frac{M_c}{l^3} \propto \sigma_c \left(\frac{t}{l} \right)^3 \quad (3.2.6)$$

and by substituting Equation (3.2.1) into Equation (3.2.6), σ_f for an open-cell foam is given by

$$\sigma_f = C_1 \sigma_c \left(\frac{\rho_f}{\rho_o} \right)^{\frac{3}{2}} \quad (3.2.7)$$

where C_1 is a constant which is approximately 0.65 as given by Ashby. Equation (3.2.7) indicates that the compressive strength of a brittle open-cell foam is governed by the modulus of rupture of the cell-wall material, which is close to the tensile strength for a brittle solid, and has a linear relationship with $(\rho_f/\rho_o)^{3/2}$.

Figure 3.2.1 Two-Dimensional Model of Hexagonal Cells.

Compressive strength of a true closed-cell brittle foam with no thickening of the cell edges was calculated similarly using Equations (3.2.3) and (3.2.4) instead of Equations (3.2.1) and (3.2.2) as

$$\sigma_f = C_2 \sigma_c \left(\frac{\rho_f}{\rho_o} \right)^2 \quad (3.2.8)$$

where C_2 is a dimensionless constant which needs to be determined experimentally. The compressive strength of a closed-cell brittle foam is a square function of the relative density of the foam.

It was suggested that even though the relationships were developed based on the three-dimensional structural models of the members and the plates, and the two-dimensional deformation model as shown in Figure 3.2.1, the relationships could be applied to general isotropic foams.

3.2.2 FINITE ELEMENT MODEL OF FOAM COMPRESSIVE STRENGTH

A closed-cell ceramic foam can be fabricated by bonding hollow ceramic spheres together. Most of the bonding material fills in the spaces around the contact points between spheres during the bonding process due to capillary forces, forming neck areas as shown in Figure 3.2.2. After drying and firing, the spheres in the bonded sphere foam transfer loads through the solid neck areas. Thus a sphere in the bonded sphere foam experiences distributed loadings at the neck areas instead of concentrated loadings or contact loadings. Compressive behavior of a hollow sphere under uniaxial distributed loading was investigated for comparison with the concentrated loading case. The solid angle ϕ in Figure 3.2.2 was defined as the contact angle and used to describe the area of loading on a sphere. Finite element analyses were performed for the contact angles $\phi = 10^\circ$, 20° , and 30° to study the effect of the size of the bonding area. Finally loading on a sphere in a bonded-sphere foam was modeled as three pairs of diametral distributed loading and finite element analyses were carried out also for various aspect ratios and contact angles.

Sphere Strength under Uniaxial Distributed Load - Failure of a hollow sphere under uniaxial distributed loading was investigated using the Griffith criterion¹⁵ for the plane stress. Failure mode and location on a hollow sphere were determined from the stress analysis results. Table 3.2.1 shows the failure location in terms of θ for spheres of different wall thicknesses and contact angle of 10° , 20° , and 30° . Fracture would occur at 12.5° away from the loading axis on the outer surface of the sphere with 1 mm radius and 5 μ m wall thickness under a uniaxial distributed load with the contact

Figure 3.2.2

Neck Area Between Spheres and Contact Angle of a Distributed Load Produced by Point Contact Bonding.

Table 3.2.1

Failure Locations on Hollow Spheres under Uniaxial Distributed Loading.

t (μm)	$\phi = 10^\circ$		$\phi = 20^\circ$		$\phi = 30^\circ$	
	$\theta (^\circ)$	Surface	$\theta (^\circ)$	Surface	$\theta (^\circ)$	Surface
5	12.5	Outside	17.5	Outside	22.5	Outside
15	2.5	Inside	17.5	Outside	22.5	Outside
25	2.5	Inside	2.5	Inside	27.5	Outside
35	2.5	Inside	2.5	Inside	27.5	Outside
50	2.5	Inside	2.5	Inside	32.5	Outside
75	2.5	Inside	2.5	Inside	2.5	Inside
100	2.5	Inside	2.5	Inside	2.5	Inside

angle of 10° due to a tensile normal stress σ_x . A hollow alumina sphere with the same aspect ratio, t/r , of 0.005 or the same relative density of 0.01489 would fail in the same way. A hollow alumina sphere with the aspect ratio of 0.075 would fail in the immediate vicinity of the loading axis on the inner surface of the sphere when the contact angle is 30° also due to a tensile normal stress σ_x . The failure locations represented by θ of 2.5° in Table 3.2.1 may actually be on the loading axis. In all cases the spheres would fail because of tensile normal stresses in the element- x direction, which are major principal stresses.

Table 3.2.1 suggests that a sphere with a small aspect ratio may fail some distance away from the loading axis outside the loading area on the outer surface of the sphere. As the aspect ratio increases for the same contact angle, the failure location will move farther away from the loading axis on the outer surface which is the pattern for $\phi = 30^\circ$ shown in the table. Spheres with larger aspect ratios would fail inside the loading area on the inner surface of the sphere. For a given aspect ratio, the failure location will move farther away from the loading axis as the contact angle increases. The above failure modes and the locations were determined using the Griffith criterion for the finite element stress analysis results. A load was applied to an area on a sphere as an uniform uniaxial distributed load parallel to the loading axis in the finite element model. In the actual loading situation, however, the load is applied on a sphere by solid material that bonds spheres together at neck areas as shown in Figure 3.2.2.

An assumption was made to determine failure modes, failure locations, and sphere strengths for the real case using the stress data obtained from the finite element model. It was assumed that the stress distribution on a sphere would be valid for the real loading situation and failure could be then determined using the Griffith criterion for the stress data except at the loading area. Failure of a sphere was assumed not to take place in the loading area because the area is reinforced by the solid bonding material and the failure criterion for plane stress may not be applicable to the neck area. When failure occurred inside a loading area from the previous failure analysis, it was excluded and another failure location was determined outside the loading area. Sphere strength was calculated from the critical stress at the failure location.

Table 3.2.2 shows the failure locations on hollow spheres determined by forcing failure outside the loading area. For $\phi = 10^\circ$, the spheres with wall thicknesses equal to or greater than $15 \mu\text{m}$ in the table would fail right outside the loading area on the inner surface. For $\phi = 20^\circ$, the sphere with $25 \mu\text{m}$ wall thickness would fail at $\theta = 22.5^\circ$ on the inner surface, further away from the loading axis than the spheres with $5 \mu\text{m}$ and $15 \mu\text{m}$ wall thickness, which fail at $\theta = 17.5^\circ$. As the wall thickness increases to $35 \mu\text{m}$, the failure location moves further away from the loading axis to $\theta = 27.5^\circ$. Further increases in wall thickness brings the failure location to just outside

Table 3.2.2

Failure Locations on Hollow Alumina Spheres under Uniaxial Distributed Loading when Failure is Determined Outside the Loading Area.

t (μm)	$\phi = 10^\circ$		$\phi = 20^\circ$		$\phi = 30^\circ$	
	$\theta (^\circ)$	Surface	$\theta (^\circ)$	Surface	$\theta (^\circ)$	Surface
5	12.5	Outside	17.5	Outside	22.5	Outside
15	7.5	Inside	17.5	Outside	22.5	Outside
25	7.5	Inside	22.5	Inside	27.5	Outside
35	7.5	Inside	27.5	Inside	27.5	Outside
50	7.5	Inside	12.5	Inside	32.5	Outside
75	7.5	Inside	12.5	Inside	17.5	Inside
100	7.5	Inside	12.5	Inside	17.5	Inside

the loading area at $\theta = 12.5^\circ$. When the contact angle is 30° , the spheres with wall thicknesses of $75 \mu\text{m}$ and $100 \mu\text{m}$ would fail just outside of the loading area on the inner surface instead of near the loading axis as shown in Table 3.2.1. The failure mode in all cases would be a tensile failure due to the normal tensile stress σ_x at the failure location.

Sphere strength under uniaxial distributed loading was calculated from the critical stress determined from the failure analysis. Parametric analysis was performed to characterize the sphere strength as a function of parameters such as sphere radius, wall thickness, or sphere density. As in the previous cases of the sphere strength under uniaxial concentrated loading and stiffness of sphere, the sphere strength under uniaxial distributed loading turned out not to be a function of either sphere radius or wall thickness. The parametric study revealed that the sphere strength could be reduced to linear relationships with the relative density squared, which is shown in Figure 3.2.3. The relationships between the sphere strength under uniaxial distributed loading and the relative density squared for each contact angle in the figure consist of two linear portions. For $\phi = 10^\circ$, the first linear portion is the line defined by the first two data points from the Y-axis, which represent two spheres with aspect ratios of 0.005 and 0.015. The second linear portion is defined by the data points with aspect ratios of 0.015 and higher. The first linear portion for $\phi = 20^\circ$ is defined by the first four data points from the Y-axis and the second linear portion is defined by the fourth and successive data points from the axis. When the contact angle is 30° , the first linear portion of the relationship consists of the first six data points from the Y-axis and the second linear portion could be defined by the sixth and the seventh data points. Interestingly these linear portions have a pattern. The first linear portions represent spheres that fail away from the loading areas. The second linear portions represent the spheres which fail just outside the loading areas.

The sphere strength under uniaxial distributed loading can be expressed as a linear function of the relative density squared given by

$$\sigma_s = C_1 \sigma_o \left(\frac{\rho_s}{\rho_o} \right)^2 \quad (3.2.9)$$

for the initial linear portion and

$$\sigma_s = C_o + C_2 \sigma_o \left(\frac{\rho_s}{\rho_o} \right)^2 \quad (3.2.10)$$

for the second linear portion. The constants in Equation 3.2.9 and Equation 3.2.10

Figure 3.2.3

Sphere Strength, σ_s , vs. Relative Density Squared, $(\rho_s/\rho_o)^2$, under Uniaxial Distributed Loading.

were obtained from linear regression of the data in Figure 3.2.3. The constant C_1 in Equation 3.3.9 was calculated by forcing the linear regression line to pass zero. C_1 , C_o , and C_2 for $\phi = 10^\circ$ were calculated as 0.843, 0.545, and 0.152, and the correlation coefficients squared were 0.9687 and 0.9929 for the first and the second linear portions respectively. When the contact angle is 20° , the constants were calculated to be 1.18, 2.69, and 0.271, and the correlation coefficients squared to be 0.9862 and 0.9982 in the same order. For $\phi = 30^\circ$ the constants are 1.12, 7.53, and 0.443, and R^2 for the first portion is 0.9663.

Bonded Sphere Foam Model with Six-Directional Distributed Loading -When a closed-cell ceramic foam is fabricated by bonding hollow ceramic spheres together, the spheres in the foam experience compressive loadings from many directions. Spheres inside the bonded sphere foam fabricated to date tend to be randomly packed. In such a random pack, a sphere contacts about six to eight spheres. The basic unit of the structure was proposed to be a sphere surrounded by six spheres as illustrated in Figure 3.2.4. The unit structure is an octahedron where the center sphere is diametrically bonded to three pairs of spheres at right angles. The foam structure then may be described as consisting of randomly oriented basic unit structures.

It was assumed that a bonded sphere foam would start to fail when the sphere in a basic unit structure fails. The load transfer to the center sphere by the surrounding spheres was assumed to be in the axial directions. Thus the center sphere would experience three pairs of diametral compressive loadings of equal magnitude when the bonded sphere foam is under a compressive loading. A finite element model of the center sphere in the unit structure developed. Loading areas which are represented by the contact angle, ϕ , were again varied for $\phi = 10^\circ$, 20° , and 30° . Uniformly distributed loads were applied to the loading areas parallel to the loading axes. Distributions of membrane forces, bending moments, transverse shear forces, and stresses were investigated. Despite the non-axisymmetry of the loading situation around a loading axis, the distributions of those parameters exhibited similar patterns as in the uniaxial distributed loading case with more or less axisymmetry around a loading area, especially for small contact angle, up to some distance away from the loading axis. The axisymmetry began to be disturbed past this distance because of effects from adjacent loading areas.

Sphere Strength under Six-Directional Loading - Sphere strength was calculated from the finite element stress data in the same way as in the uniaxial distributed loading case. The sphere strength versus the relative density squared is plotted in Figure 3.2.5. The linear relationships between the sphere strength and the relative density squared for different contact angles are similar to those in the uniaxial distributed loading case. The linear relationships for $\phi = 10^\circ$ and 30° can be described by one line for each for practical purposes. For $\phi = 10^\circ$, the linear relationship can be given by

Figure 3.2.4 Basic Unit Structure of Random-Packed Bonded Sphere Foam.

Figure 3.2.5

Sphere Strength σ_s , vs. Relative Density Squared, $(\rho_s/\rho_o)^2$, under Six-Directional Distributed Loading.

Equation 3.2.10 with $C_0 = 2.84$, $C_2 = 0.786$, and $R^2 = 0.9925$. For $\phi = 30^\circ$, the linear relationship can be expressed by Equation 3.2.9 with $C_1 = 5.40$ and $R^2 = 0.9805$. The first linear portion for $\phi = 20^\circ$ has C_1 of 5.67 and R^2 of 0.9676 and the second linear portion has $C_0 = 12.9$, $C_2 = 1.46$, and $R^2 = 0.9909$.

3.2.3 EXPERIMENTAL VERIFICATION OF FINITE ELEMENT MODEL

Bonded Sphere Foam Fabrication - Hollow alumina spheres were bonded mixing with a small quantity of slurry, which consisted of alumina, organic binder, and water. Precise control of the viscosity of the slurry as well as the batch composition of the ingredients was necessary to achieve strong bonds at points of contact and to maintain a low foam density. When the viscosity of the slip was too low, the bonding angle was usually small and the bonds between spheres did not have adequate strength resulting in the failure through the bonds. When the viscosity was too high the bonding material coated the spheres relatively evenly rather than concentrating at the neck areas thus increasing the density of the foam greatly and also resulting in low strength of the bonds. The spheres coated with slip were cast into a mold applying vibration and pressure to achieve better packing of the spheres. The casting was dried at room temperature and removed from the mold. The green foam was then fired at 1600°C for 4 hours to sinter the bonding material. Mullite spheres were also bonded into mullite foams using mullite slip to investigate the compressive strengths of mullite foams, Figure 3.2.6 shows a bonded alumina sphere foam after firing. The spheres at the surface of the foam show some degree of hexagonal packing because of mold wall forces. However, the spheres inside the foam are packed randomly as shown in Figure 3.2.7. Figure 3.2.7 shows a point contact bonded mullite sphere foam made of mullite spheres with 3.5 mm average diameter. Note that the fillets produce a distributed load with contact angle of $\sim 20^\circ$.

Compression Testing of Bonded Sphere Foams - For compressive testing of the bonded sphere foams, epoxy end caps were cast on the loading faces to transfer the load uniformly. Some foams were tested without epoxy caps but load was distributed using polyurethane pads and steel caps. The polyurethane pad was placed between the loading face of the foam and the steel cap. Bonded sphere foams were tested under compressive loading on an Instron testing machine. Swivel heads were used to transfer the load uniformly to the loading faces of the foam. The foam strength was calculated as the load at fracture per cross-sectional area of the foam.

Bonded Sphere Foam Compressive Strength - The bonded sphere foams with epoxy end caps failed horizontally across the foams in most cases. As the load increased some spheres began to pop out from the surface of the foam without apparent

Figure 3.2.6

A Bonded Alumina Sphere Foam to be Tested under Compressive Load.

Figure 3.2.7

Cross Section of Bonded Mullite Sphere Foam Showing Random Packing and Point Contact Bonding.

catastrophic. The failures were almost explosive as in the typical crushing of a solid brittle material. Most of the foams tested with the polyurethane pads and the steel caps failed vertically indicating non-uniform loading on the foams.

The compressive strengths of the foams versus the foam densities are plotted in Figure 3.2.8. The experimental results are also compared with commercial ceramic foam (insulating fire brick) strength data. At comparable densities the bonded sphere foams have compressive strengths five to eight times higher than the insulating fire brick foams. The bonded-sphere foams with the epoxy end caps show higher strength than the same foams tested with the polyurethane pads and the steel caps because of the uniform load transfer.

The foam strengths data in Figure 3.2.8 were plotted again in Figure 3.2.9 based on the corresponding sphere density to evaluate the effect of the contact angle on the strength of foam. The alumina foams with densities of 43 lb./ft^3 and 54 lb./ft^3 shown in Figure 3.2.8 were made of same alumina spheres with a relative density squared of 0.02. Assuming packing factors are same for both foams, it is obvious from the two alumina samples with epoxy end caps in Figure 3.2.9 that the amount of bonding material affects the foam strength. There can be two possible reasons for this. If the bonds between the spheres do not have adequate strength, the foam fails at the bonds before the spheres fail thus not fully utilizing the sphere strength. If bonds have proper strength, the amount of bonding material will control the contact angle and will be a governing factor of foam strength as predicted by the finite element analysis. The difference in increased sphere wall thickness due to the coating of the spheres with bonding material was assumed to be negligible regardless of the amount of the bonding material, because most bonding material migrates to the neck area with the use of a proper bonding technique. Fracture surface of the samples showed that both foams failed through the sphere walls, not at the bonds. Accordingly the difference in the foam strength exhibited by these two samples can be adequately explained by contact angle. Since the sphere strength for various loading conditions has a linear relationship with relative density squared as determined previously, increasing the strength a factor of two requires that the relative sphere density squared should also increase by two, if bond angles (contact angles) are the same. In this case, the relative density squared of the two foams, however, increased only 63 %, while the foam strength increased approximately 100 %. Again, increased bond angle appears to have a larger effect than density increases as predicted by the model.

Mullite spheres and alumina spheres used in this research have similar wall material strength. Thus they can be compared with each other in Figure 3.2.9. The contact angles for the foams were not precisely determined. Calculation of the contact angle from the sphere density, the sphere size, and the foam density based on the basic unit structure model of the random packed monolith is proposed as future research.

Figure 3.2.8

Bonded Sphere Foam Compressive Strength (psi) vs. Foam Density (lb/ft³).

Figure 3.2.9

Foam Strength vs. Relative Sphere Density Squared.

decrease in the load at the constant crosshead speed and failure was sudden and catastrophic. The failures were almost explosive as in the typical crushing of a solid brittle material. Most of the foams tested with the polyurethane pads and the steel caps failed vertically indicating non-uniform loading on the foams.

The compressive strengths of the foams versus the foam densities are plotted in Figure 3.2.8. The experimental results are also compared with commercial ceramic foam (insulating fire brick) strength data. At comparable densities the bonded sphere foams have compressive strengths five to eight times higher than the insulating fire brick foams. The bonded-sphere foams with the epoxy end caps show higher strength than the same foams tested with the polyurethane pads and the steel caps because of the uniform load transfer.

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Mullite spheres and alumina spheres used in this research have similar wall material strength. Thus they can be compared with each other in Figure 3.2.9. The contact angles for the foams were not precisely determined. Calculation of the contact angle from the sphere density, the sphere size, and the foam density based on the basic unit

structure model of the random packed monolith is proposed as future research. However, assuming the increase in density from sphere density to foam density translates to the bond angle, the mullite foams tested with epoxy end caps, which relative sphere density squared are 0.0028 and 0.0113 in Figure 3.2.9 have similar bond angles. Also, the alumina foam with epoxy end cap, which relative sphere density squared and strength are 0.02 and 9 MPa, has a similar bond angle. These three foams lie within experimental error on the finite element analysis prediction for $\phi = 10^\circ$. It has already been shown that experimental sphere strength under contact loading provided one third the strength predicted by finite element model due to defects and the same is probably true here. The three data points should probably multiplied by three which would place them between the lines for $\theta = 20^\circ$ and 30° . The bonds in the bonded-sphere foams had contact angles in that range. Thus the finite element prediction agrees reasonably with the only available data for comparisons.

3.3 ISOSTATIC COMPRESSIVE STRENGTH

Potential uses for hollow ceramic spheres include bonding together to form monoliths for high-temperature insulation or light structural materials in syntactic foams. They might also be introduced into various matrix materials to form light weight composites. Stresses on individual spheres would then be more uniformly distributed, rather than resulting from a simple uniaxial load. In such situations the isostatic compressive strength would serve as a better approximation of the mechanical properties of the sphere.

There are several methods described in the literature for determining the isostatic strength of small hollow spheres, specifically glass spheres. One method, the ASTM Standard Method of Test D3102⁵, is an isostatic compression test. However, it requires a special, costly set-up and reportedly⁶ is seldom used. Another technique was described by Milewsky and Marsters⁷. In their technique, a pressure differential is created between the inside and the outside of the sphere and thus the sphere fails in tension. The problem with this method are that it also requires a special, costly set-up, it is only useful for relatively large spheres, and only one sphere at a time can be tested. The preferred method, described by Ciftcioglu and Akinc⁶, used a scanning mercury porosimeter.

The mercury porosimeter method allows a relatively large number of spheres to be tested at one time. The primary disadvantage is that individual sphere strengths cannot be determined. In this method, spheres are placed in the sample cell of the mercury porosimeter and the cell is filled with mercury. The pressure is gradually increased and as the spheres break, the void within each is filled with mercury and the change in volume is recorded. From the pressure-volume data, the distribution of the isostatic compression strengths is generated. Since values for individual spheres are not available, numbers such as the strength at twenty percent (20%) volume reduction or strength at fifty percent (50%) volume reduction are reported.

3.3.1 BACKGROUND

When a thin wall spherical shell is placed in isostatic compression it may fail by one of two different modes, compressive wall failure or thin shell buckling. If a spherical shell is subjected to uniform external pressure in which it maintains its shape then the magnitude of the compressive stress is:

$$\sigma = \frac{Pr}{2t} \quad (3.3.1)$$

For r/t values less than 20, it is predicted³ that the spheres should fail by crushing. Substituting from Equation (3.3.2),

$$\left(\frac{\rho_s}{\rho_o} \right) = \frac{3t}{r} \quad (3.3.2)$$

and rearranging gives the predicted critical crushing pressure:

$$P_c = \frac{2}{3} \sigma_{ultc} \frac{\rho_s}{\rho_o} \quad (3.3.3)$$

where σ_{ultc} is the ultimate compressive strength of the wall material. For the case of $r/t > 20$, as the pressure increases, the spherical form of equilibrium may become unstable and buckling then occurs⁸. Timoshenko and Gere⁸ derived the equation for the classical critical stress in a sphere which fails by thin shell buckling. It is given by

$$\sigma_{cl} = \frac{Et}{r [3(1 - \nu^2)]^{1/2}} \quad (3.3.4)$$

where ν is Poisson's ratio for the wall material. Rearranging gives the predicted critical pressure when failure occurs by thin shell buckling:

$$P_{cl} = \frac{2E}{9 [3(1 - \nu^2)]^{1/2}} \left(\frac{\rho_s}{\rho_o} \right)^2 \quad (3.3.5)$$

As was the case for uniaxial loading, these solutions depend on wall thickness uniformity. Ciftcioglu and Akinc⁶ found the theoretical critical buckling pressure to be approximately twenty (20) times higher than the experimentally determined pressure for low-strength spheres and approximately four (4) times higher for high-strength spheres. The authors concluded that the degree of deviation from theoretical strength is a measure of perfection of the spheres. Because of the geometry of the spheres used in this investigation, they would probably fail at the thinnest spot yielding lower than expected values. Timoshenko and Gere⁸ point out that "in the vicinity of the spherical shape of equilibrium of a compressed shell there exist forms of equilibrium slightly deviated from the spherical shape which require pressures much smaller [than predicted by Equation (3.3.5)]." Therefore a small disturbance during loading might result in failure at a much lower pressure than expected. This might partially explain the results obtained by Ciftcioglu and Akinc as the failure of one sphere within the sample cell might disturb the spheres around it and cause them to fail as well. This also helps to explain the wide scatter of the experimental results.

3.3.2 ISOSTATIC TESTING

Testing the isostatic strength of select groups of spheres was performed using mercury porosimetry by two independent laboratories. Batches 11186, 02057, and 03247 were tested by Micromeritics Corporation in Norcross, Georgia. Batches 05077 30/30, 05287 31/10, 05287 60/40, and 08267 70/40 were tested by PQ Corporation in Lafayette Hill, Pennsylvania.

The data received from the isostatic testing was in two different forms. The data from Micromeritics Corporation was tabulated as pressure and cumulative volume intruded. The data from PQ Corporation was in the form of graphs of percent volume loss versus log pressure. All data was retabulated and is plotted as percent volume loss versus log pressure in Figures 3.3.1 and 3.3.2. Table 3.3.1 tabulates pressures at 20, 50, and 80 percent volume loss (P_{20} , P_{50} , P_{80}) as well as relative density for each batch tested.

Both labs reported problems associated with the penetrometer. The penetrometer is the part of the porosimeter which holds the sample and is made of glass. For an unknown reason it frequently broke during testing of the spheres. Some of the data was rendered unusable because of this. Other data could still be used when this happened but had to be adjusted to account for the volume intruded as a result of the breakage. The remainder of the data was quite satisfactory.

3.3.3 THEORETICAL STRENGTH

Under isostatic compression the spheres were expected to fail either by compressive wall failure or thin shell buckling depending on the radius to wall thickness (r/t) ratio. If r/t is less than 20 [$\rho_s/\rho_o > 0.150$] then crushing is predicted and Equation (3.3.3) applies. For the case of r/t greater than 20 [$\rho_s/\rho_o < 0.150$] thin shell buckling is predicted and Equation (3.3.5) applies. However experimental results usually indicated that the buckling pressure is considerably smaller than the analytically predicted critical pressure⁸. Because thin spherical shells are imperfection sensitive⁹, a factor is used to relate the predicted to experimental results along with Equation 11:

$$P_{cv} = \Lambda P_d \quad (3.3.6)$$

where Λ is a factor known as the "knockdown factor." This factor is dependent on parameters such as the radius to thickness ratio and for the spheres used in this investigation a reasonable value to use is $0.6^{8,9,10}$. The values which were used for the relevant material properties were:

$$\sigma_{ultc} = 3447 \text{ Mpa} = 5 \times 10^5 \text{ psi}$$

Figure 3.3.1 Isostatic Compressive Strength Distributions for Alumina Hollow Spheres from Hg Porosimetry

Figure 3.3.2 Isostatic Compressive Strength Distributions for Alumina Hollow Spheres from Hg Porosimetry

Table 3.3.1

Isostatic Strength (psi) of Alumina Hollow Spheres at 20, 50, and 80 Percent Volume Loss and Relative Density

Batch	P ₂₀	P ₅₀	P ₈₀	ρ_s / ρ_o
11186	395	1009	2485	0.100
08267 70/40	661	1000	1349	0.111
02057	799	1004	1904	0.214
05287 31/10	832	933	1230	0.230
05287 60/40	1175	1738	2291	0.213
05077 30/30	1175	1950	3981	0.204
03247	4775	13145	18402	0.159

$$E = 380 \times 10^9 \text{ Pa} = 55.1 \times 10^6 \text{ psi}$$

$$\nu = 0.26$$

The results of the theoretical calculations of P_{fail} are summarized in Table 3.3.2. Clearly, the predicted failure pressures, even with the knockdown factor, are still much higher than the experimental results even when compared to the P_{80} values. Figure 3.3.3 further illustrates this point where isostatic pressure is plotted versus relative density. The area shown represents a range for σ_{ultc} from 280,000 to 540,000 psi and for E from 50 to 55 $\times 10^6$ psi with the knockdown factor not included. These values are typical for fine grained polycrystalline alumina, such as produced here. This range represents a maximum range where the spheres might be expected to fall. The probable cause of the difference between theoretical and experimental results, as in the uniaxial case, is the variable wall thickness. In addition, nonsphericity can cause an appreciable reduction in the predicted critical pressures. Across all batches of spheres it was found that the average aspect ratio is approximately 1.02.

Obviously, the main improvements to isostatic compressive strengths would be produced by decreases in wall thickness variation. This is more dramatically illustrated when isostatic failure is compared to relative density. No correlation is present and, in fact, the strongest spheres had a density significantly less than four other much weaker groups of spheres. The theoretical limits for compressive strength are an order of magnitude greater than observed and improvements in sphere perfection could provide significant increases with no increase in density.

Table 3.3.2. Predicted Isostatic Failure Loads.

Batch	ρ_s ----- ρ_o	Predicted Failure Mode	P_{fail} ----- Mpa	P_{fail} ----- psi
11186	0.100	Buckling	303	43,927
02057	0.214	Crushing	492	71,333
03247	0.159	Crushing	365	53,000
05077-30/30	0.204	Crushing	469	68,000
05287-31/10	0.230	Crushing	529	76,667
05287-60/40	0.213	Crushing	490	71,000
08267-70/40	0.111	Buckling	373	54,122

ISOSTATIC FAILURE OF ALUMINA SPHERES

Figure 3.3.3

Isostatic Failure of Alumina Hollow Spheres as a Function of Density for Buckling and Crushing Compared to Experimental Values

4.0 THERMAL CONDUCTIVITY OF HOLLOW SPHERES

Thin-walled, hollow ceramic spheres from conventional powder slurries which have been developed in this program are being targeted for use as high temperature, refractory insulation. Previous research has demonstrated that radiation transfer is the most significant contribution to the high temperature thermal conductivity of hollow spheres. A primary concern for this insulation is reducing the thermal conductivity, especially the contribution due to radiation transfer which is prominent at high temperatures. Available literature suggests that the degree of radiation transfer through a ceramic or glass is highly dependent on the microstructure of the material, and that materials with high infrared reflectance values show lower thermal conductivities. Infrared reflectance may be increased by adding second phase particles of a different refractive index to the microstructures of materials. This section explores the relationship between the microstructure, thermal conductivity, and infrared reflectance of thin-walled, hollow glass spheres containing second phase zirconia particles. The effects of zirconia content and particle size were studied.

Additions of zirconia particles significantly lowered the high-temperature thermal conductivity of glass spheres. The most effective composition lowered the thermal conductivity by slightly more than a factor of two. This reduction in thermal conductivity was a strong function of zirconia volume fraction. There existed a limit to the volume fraction of zirconia which was useful in lowering the thermal conductivity; exceeding this limit did little to reduce the thermal conductivity and may have even caused it to increase. This saturation limit occurred at approximately ten volume percent. The effect of particle size was less pronounced and inconclusive.

Infrared reflectance measurements were produced from glass pellets fabricated to duplicate the microstructure of the spheres. Zirconia scattering particles were found to significantly increase the infrared reflectance of these glass pellets. Like thermal conductivity, infrared reflectance was found to be a strong function of zirconia content, and also displayed saturation at approximately ten volume percent zirconia. The effect of particle size was again inconclusive.

Graphs of thermal conductivity vs. infrared reflectance demonstrated a nearly linear inverse relationship. In the future, infrared reflectance measurements may allow the accurate, rapid prediction of the thermal conductivity of hollow spheres while avoiding the time intensive process of fabricating spheres and measuring conductivity.

4.1 RADIATION TRANSFER IN CERAMICS

This work advances the hypothesis that infrared radiation transfer is a significant contribution to the total thermal conductivity of hollow spheres at elevated temperatures. To try and lessen this component, an understanding of a ceramic material's ability to transfer radiation is essential.

Dielectric materials emit radiation at all temperatures above absolute zero. The intensity and wavelength distribution of the emitted radiation change with temperature. With increasing temperature, the maximum in the wavelength distribution decreases, while the intensity of the radiation increases dramatically. The maximum in the radiation distribution, λ_m , is approximated by Wien's law:

$$\lambda_m T = 2897.8 \text{ } \mu\text{m}\cdot\text{K} \quad (2.6)$$

where T is the absolute temperature.

A material's complex coefficient of refraction, n^* , dictates much of its optical behavior, and is related to n, the index of refraction, and k, the index of absorption:⁷

$$n^* = n - ik \quad (2.7)$$

Both n and k are functions of wavelength and temperature. For most dielectric materials, the index of refraction, n, varies little with wavelength in the range with which this study is concerned.⁷ The index of refraction may increase or decrease slightly with temperature. The index of refraction is related to density, with more dense materials tending to possess higher values. For dielectric materials, the index of absorption is more a function of wavelength than temperature. In the visible and near infrared regions, absorption is relatively low. Higher absorption at wavelengths smaller than that of the visible spectrum is due to electronic transitions in atoms, while resonant lattice vibrations cause absorption in the far infrared region.

The indices of refraction and absorption will dictate how radiation behaves when passing through a dielectric material. When electromagnetic radiation impinges on a dielectric layer, such as a hollow sphere wall, the radiation may be transmitted or inhibited due to three factors. Surface reflection may take place at air/ceramic interfaces, while absorption or scattering may take place within the bulk of the solid.

Surface reflection is the result of a difference in complex coefficient of refraction between the gas and solid, and may have both a specular and diffuse component. A specularly reflected ray is reflected from the surface at an angle equal to the incident angle. Diffusely reflected rays leave the surface at all angles and diffuse reflectance increases with surface roughness. For radiation normal to a smooth surface having a low index of absorption, the surface reflectivity R is approximated by:

$$R = \left(\frac{n-1}{n+1} \right)^2 \quad (2.8)$$

where R is the fraction of radiation reflected at a surface.

Within the solid, radiation may be inhibited by absorption and/or scattering. The sum of the effect of absorption and scattering is called extinction. This relationship is given as:⁸

$$C_{ext} = C_{abs} + C_{sca} \approx C_{sca} \quad (2.9)$$

where C_{ext} , C_{abs} , and C_{sca} are the extinction, absorption, and scattering cross sections, respectively. Cross sections are functions of wavelength. If absorption is low at the wavelength of interest, then any extinction is due mainly to scattering as suggested in Equation 2.9.

Accounting for surface reflection, absorption, and scattering, the fractional in-line transmission, τ , through a material is expressed as:⁸

$$\tau = (1-R)^2 \exp(-C_{ext} \times t) \approx (1-R)^2 \exp(-C_{sca} \times t) \quad (2.10)$$

where t is the thickness of the material. The in-line transmission is the fraction of radiation beam energy that traverses the medium without being scattered, reflected, or absorbed. Increasing the scattering cross section results in a decreased in-line transmission.

Scattering Theory - An understanding of scattering, and how its effect can be increased to maximize infrared reflectance and, hopefully, reduce radiant thermal conductivity, is necessary to this effort. Scattering simply refers to the redirection of electromagnetic radiation. A beam of radiation striking a scattering medium will be redirected, or scattered, in all directions. Thus, a scattering ceramic will diffusely reflect and transmit radiation. In a ceramic, scattering may be caused by a second phase with an index of refraction different from the primary phase. For example, pores, having an index of refraction of approximately 1, in a matrix of alumina, with an index of 1.76, will scatter radiation. Deliberately adding a second phase to a ceramic to increase reflectance is termed "opacification".

Assuming spherical particles, the scattering cross section is equal to:

$$C_{sca} = \frac{3V_p K}{4r} \quad (2.11)$$

where V_p is the volume fraction of scattering phase, K is the scattering factor, and r is the radius of scattering particles.⁸ The scattering factor, K , is related to the radius of scattering particles, r , the wavelength of radiation, λ , and the relative refractive index, m . The relative refractive index is equal to the refractive index of the scattering phase divided by that of the surrounding matrix, and may be less than or greater than one, but always positive. More positive values give higher scattering factors, and hence stronger scattering. Figure 4.1.1 shows the relationship between these factors. The horizontal axis of this graph is the phase function, P , given as:⁴

$$P = \frac{4\pi r(m-1)}{\lambda} \quad (2.12)$$

The scattering factor, and hence scattering cross section, is very dependent on particle size. Figure 4.1.2 shows the scattering cross section as a function of particle size for a system of 1.0 V/O titania particles in glass, at a wavelength of 0.589 μm .⁷ Only a very narrow range of particles produces a maximum scattering cross section. Since all of the curves in Figure 2.9 show maximums at a phase function of 4.1, Equation 2.12 can be rewritten as:

$$d_{\max} = \frac{4.1\lambda}{2\pi(m-1)} \quad (2.13)$$

where $d_{\max}$ is the particle diameter producing a maximum in the scattering factor. This equation assumes spherical particles of a uniform size, and is a good estimate of the size of particles required to produce a maximum in the scattering cross section for a given volume fraction (the estimate is not exact, since the size of particles giving a maximum in the ratio K/r may be slightly smaller than those giving a maximum in K alone). For most systems, the diameter of particles producing a maximum in the scattering cross section is on the order of the wavelength of radiation.

In practice, producing a scattering system of monosized particles is difficult. Most particles, unless specially produced, will have a particle size distribution. For the scattering of thermal radiation, however, a distribution of particle diameters is desired, because there is a distribution of wavelengths to be scattered.

Dependent Scattering - A limit exists to the amount of scattering phase that is beneficial. Above a certain volume fraction, the electromagnetic fields surrounding

Figure 4.1.1

Scattering Factor, K, as a Function of Wavelength, Radius of Scattering Center, and Relative Refractive Index.

Figure 4.1.2

Effect of Particle Size on the Scattering Cross Section of a Fixed Volume of Particles (1.0 vol%) for a Relative Refractive Index of 1.8 (TiO₂ in Glass).

individual scattering particles will begin to interfere because of their proximity, and the overall scattering factor will decrease. This interference is known as dependent, or multiple, scattering. The interparticle distance, c , at which individual particles cease to scatter independently is given by:¹¹

$$\frac{c}{\lambda} = 0.3 \quad (2.16)$$

For a given wavelength, finer particles will encroach upon this limit at a lower volume fraction than coarse particles due to their greater number of particles per unit volume. This behavior is demonstrated in Figure 4.1.3¹¹, where X is a measure of particle size called the size parameter, equal to:

$$x = \frac{2\pi r}{\lambda} \quad (2.17)$$

The area to the left of the curve represents particles far enough apart to scatter independently. Those particles close enough together to fall to the right of the curve will scatter dependently, and their scattering factors will be lower than if they had been sufficiently spaced apart. Equation 2.13 assumes independent scattering, a condition that limits its applicability to systems containing small amounts of scattering phases.

Thermal Conductivity of Non-Opacified Hollow Spheres - The thermal conductivity curves for two samples of thin-walled, hollow ceramic spheres made of alumina are compared in Figure 4.1.4.¹⁵ Both sets of spheres were created in a like manner, the only difference being their bulk density. The general shape of these curves is typical of all hollow spheres, and the dramatic increase of thermal conductivity with temperature sharply contrasts with the behavior of solid (dense) polycrystalline aluminas. To understand this difference in thermal conductivity behavior, several factors must be recognized.

Hollow spheres, unlike bulk solids, possess a large volume of air both inside the spheres and in the interstices between spheres. Gas conductivity, therefore, contributes to the thermal conductivity of hollow spheres. However, the magnitude of the thermal conductivity due to air is in the range of 0.05 to 0.09 W/mK and is relatively low compared to the overall conductivity for hollow spheres. Although gas conductivity increases with temperature, the effect is minor and fails to explain the dramatic increase of thermal conductivity with temperature characteristic of hollow spheres.

Figure 4.1.3

Independent and Dependent Scattering Regimes: x vs. F_v

Figure 4.1.4

Thermal Conductivity of Alumina Hollow Spheres

The contribution of solid state conductivity to the total conductivity will be less for hollow spheres than for solid ceramics, since hollow spheres are less dense. The bulk densities of the alumina spheres in Figure 4.1.4 are 0.26 g/cc and 0.38 g/cc, while the density of solid alumina is 3.98 g/cc. As the amount of solid decreases, the solid state conductivity will decrease. The fact that the spheres are in contact with each other in a very limited fashion, at small, loose points of contact, also serves to limit the solid state conductivity. At high temperatures, the solid state conductivity of both crystals and glasses is relatively independent of temperature. Thus, like gas conductivity, solid state conductivity cannot explain the large increase of hollow sphere thermal conductivity with temperature.

The radiation conductivity for hollow spheres is much higher than for solid ceramics because of the lower amount of material present to scatter radiation. This radiation conductivity will increase dramatically with temperature, as predicted by the Rosseland approximation for radiant conductivity, k_r , which states the ability of a dielectric material to transmit radiation energy: ⁴

$$k_r = \frac{16}{3} \sigma n^2 T^3 l_r \quad (2.5)$$

where σ is the Stefan-Boltzmann constant, n is the refractive index, T is the absolute (Kelvin) temperature, and l_r is the photon mean free path. This approximation applies when the mean free path is smaller than the sample thickness. Based on this temperature dependence, and armed with the knowledge that neither gas nor solid state conductivity explains the sharp increase of thermal conductivity with temperature of Figure 4.1.4, a reasonable assumption is that radiation transfer dominates the thermal conductivity of hollow spheres at high temperatures. Radiation conductivity explains the dramatic increase of thermal conductivity with temperature of hollow spheres.

Examining the thermal conductivity behavior of ceramic fibers lends credence to this interpretation. An analogy can be made between hollow spheres and ceramic fibers with respect to the fact that both have a continuous gas phase, a low solid volume to total volume ratio, and few and loose solid contacts. Air conductivity increases slightly with temperature, but is unaffected by changes in bulk density. Solid state conductivity through fibers increases slightly with bulk density, but seems unchanged by temperature fluctuations. The most significant change, with respect to both temperature and bulk density, is in the radiation component. The thermal conductivity due to radiation increases significantly with temperature, as predicted by the Rossland approximation. As the bulk density increases, this component decreases due to a larger quantity per unit volume of scattering material. Radiation transfer explains the majority of the increase of thermal conductivity with temperature of ceramic fibers and hollow spheres.

Thermal Conductivity of Graphite Opacified Hollow Spheres - Previous hollow sphere thermal conductivity research has suffered because the systems investigated have lacked an "ideal" scattering microstructure, i.e. one with discrete, separated scattering particles surrounded by a homogeneous matrix. Alumina and mullite hollow spheres, the emphasis of previous studies, are known to possess up to 30V/O of continuous porosity.¹⁶ While this porosity certainly affects radiation transfer in some way, classical scattering theory is based on discrete particles and is useless for predicting this behavior.

Furlong¹⁵ added particles of a second phase to alumina and mullite hollow spheres to scatter thermal radiation and decrease thermal conductivity. These second phases included chromia, silicon carbide, and zirconia. Also, graphite was added to some compositions as a "burn-out" material that would hopefully create, after firing, pores of a size suitable for scattering. Addition of graphite as a fugitive pore opacifier did significantly reduce conductivity at high temperatures. However, the graphite was flake like and produced flat pores 2-5 microns in diameter and 0.2-0.5 microns thick. These geometries do not fit the classical spherical geometries of scattering phases modeled in theory. As a result systematic changes with pore size and pore volume were not obtained.

Many of the comparisons made between the thermal conductivity of spheres with and without a second phase were inconclusive because bulk densities were not comparable. Additionally, analysis of the microstructure was limited to the viewing of fracture surfaces, and information regarding the size and separation distance of second phases, and the spatial relationship of these phases to the continuous porosity, could not be provided due to the difficulty of obtaining a flat polished surface from a microstructure of such high porosity.

4.2 ZIRCONIA OPACIFICATION OF HOLLOW GLASS SPHERE WALLS

A system was desired that would allow a closer comparison to classical scattering theory, one that would have minimal porosity. A glassy system for the sphere walls, one in which the raw materials are a clay and a feldspar, was chosen for two reasons. First, such a system undergoes liquid phase sintering and results in a microstructure with only a few large, separated pores. Thus the effect of porosity on radiation scattering can be assumed negligible. Secondly, this glass composition vitrifies at temperatures below which many second phase materials will begin to coarsen. During sintering, in a system of dispersed second phase particles, smaller particles may dissolve while larger particles may grow in size. This process is driven by the reduction of interfacial free energy, and is termed Ostwald ripening.⁷ Thus, particles may coarsen and become too large to effectively scatter radiation. Such coarsening would also make unreliable any interpretation of results based on the measured particle size distributions of the zirconia powders, since these distributions

would change. Whether or not such coarsening was a problem in previous hollow sphere thermal conductivity research is unknown. Zirconia was chosen as the second phase to provide infrared scattering. This material has an index of refraction significantly higher than glass, and was readily available in the size ranges desired. Additionally, zirconia particles were expected to be stable at the sintering temperature of the glass system, a temperature of 1200°C.

To demonstrate the relationship between diffuse infrared reflectance and thermal conductivity, a model system based on zirconia particles dispersed in a glass matrix was developed. To initiate the system, the approximate zirconia size required for optimal infrared scattering was calculated. This calculation is presented first in this section. Then, specifications of the raw materials used to fabricate this system are followed by physical properties of the fabricated spheres. Next, the instruments and procedures used for measuring thermal conductivity and infrared reflectance are described. Finally, microstructural and phase analysis techniques are specified.

Scattering Calculations - Selection of zirconia powders for infrared opacification was based on a calculation of the approximate particle size required to produce maximum scattering in a glass matrix. The particle size calculation required specification of an exact radiation wavelength. This was based on a maximum thermal conductivity measurement temperature of approximately 1000°C for the glass spheres. Above this temperature, the spheres stick together and their removal from the thermal conductivity apparatus becomes difficult. Thus, a reasonable approach was to reduce radiation conductivity where it was most significant, and since radiation conductivity increases with temperature, the upper limit of 1000°C was chosen as the temperature where a maximum in thermal radiation scattering was to be produced.

Wavelength maximums were calculated for both a vacuum and glass as a function of temperature using Wein's Law, Equation 2.6. These calculations recognize that the wavelength of radiation entering the glass will be divided by a number equal to the index of refraction of the glass. The index of refraction of the glass was assumed to be 1.54.¹⁶ At 1000°C, the maximum in the wavelength distribution of thermal radiation in the glass occurs at a wavelength of 1.48 μm . Assuming that the index of refraction for zirconia is 2.17¹⁸, then the relative refractive index, m , is 1.41. From Equation 2.13, the zirconia particle size producing the largest scattering factor for these parameters has a diameter of 2.36 μm .

There is some uncertainty in the values of refractive index. The indices for glass and zirconia are for visible wavelengths at room temperature. These values will certainly change somewhat at higher temperatures and longer wavelengths. Additionally, the value for zirconia is based on the monoclinic, or room temperature, form, and is the average of the index of refraction in the three crystalline directions. One of the zirconia powders was yttria stabilized, and likely possessed a different crystalline form (and somewhat different index of refraction) than the monoclinic phase. However, given the uncertainty of Equation 2.13 in accurately predicting the particle size

suitable for maximum reflectance, little purpose was seen in pursuing highly accurate refractive index values.

Raw Materials and Sphere Fabrication - Three different zirconia powders were used to gauge the effect of particle size on thermal conductivity and reflectance. These powders will be referred to as DK1, DK3CL, and RDF 371, and their particle size distributions are compared in Figure 4.2.1. DK3CL is the coarsest distribution, and RDF 371 is the finest. These powders were chosen because the particle size calculated in Section 3.1, $2.36\mu\text{m}$, lies within their distributions. Particle size analysis was performed with a Microtrac II Model 7997-20 SPA.

Feldspar (nepheline syenite) and clay (Georgia kaolin) were combined to provide the glass matrix in all sphere compositions, in a weight ratio of three to one. Varying amounts of the three zirconia powders were added to this standard feldspar/clay composition. Because thermal conductivity measurements were taken concurrently with sphere fabrication, the creation of spheres with increasing zirconia contents was halted when little additional effect was expected. This upper limit occurred at 20V/O zirconia.

All compositions were ball milled for approximately eighteen hours prior to hollow sphere fabrication. An attempt was made to fabricate all spheres with the same bulk density, to avoid the density effect on thermal conductivity. All compositions were fired to 1200°C for three hours in large alumina saggers. Spheres were packed in - 100 mesh tabular alumina to prevent sphere to sphere sticking. After cooling, the spheres were separated from the tabular alumina by screening.

The bulk densities and diameters of the spheres are recorded in Table 4.2.1. Bulk densities were based on three measurements with a one liter graduated cylinder. Spheres were poured into the cylinder without tapping, and their weight was divided by the volume. The diameter values were the average of six micrometer measurements. The bulk density and sphere diameter measurements are considered accurate to within $.02\text{ g/cm}^3$ and $.15\text{mm}$, respectively ($\pm$ two standard deviations).

Thermal Conductivity Measurements - Thermal conductivities were measured with a Unitherm Radial Thermal Conductivity Apparatus, Model 4141, manufactured by Anter Laboratories, Inc., of Pittsburgh, Pennsylvania. This device consists of a hollow ceramic cylinder (10cm inner diameter $\times$ 40cm length) surrounding a central axis heater. Three pairs of thermocouples lie in the gap between heater and cylinder at 120° intervals, and measure the temperature difference over a 3.0cm gap spanning the radius of the cylinder. Loose packed beds of spheres were introduced into the cylindrical cavity, without tapping, and thermal conductivities were calculated from heater power and the resulting temperature gradients. The theory of operation governing this apparatus has been discussed extensively elsewhere.^{15,17}

Figure 4.2.1

Combined Particle Size Distributions of RDF 371, DK1, and DK3CL Zirconia Powders.

Table 4.2.1

Diameters and Bulk Densities of Hollow Spheres.

Volume Percent Zirconia (%)	Bulk Density (g/cm ³)	Diameter (mm)
No Zirconia		
0.00	.46	2.4
RDF 371		
2.50	.47	3.0
5.00	.45	2.9
10.00	.44	2.4
15.00	.42	3.3
DK1		
2.50	.47	2.7
5.00	.50	3.3
7.50	.49	2.9
10.00	.51	2.8
15.00	.56	2.6
20.00	.54	2.5
DK3CL		
2.50	.46	3.0
5.00	.46	2.8
10.0	.51	2.7
15.0	.44	3.3
20.0	.45	3.3

The Unitherm apparatus at Georgia Tech yields data that is somewhat higher than values measured at other locales for the same materials. Figure 4.2.2 compares the manufacturer's specifications and thermal conductivity values measured with the Anter 4141 apparatus for K-23 and K-30 firebrick produced by Thermal Ceramics of Augusta, Georgia. The Anter 4141 readings were higher for both materials. Thermal conductivities measurements of the same sample of hollow alumina spheres from Georgia Tech and the University of Kentucky also indicate that the Anter 4141 values are higher, Figure 4.2.3. Additional materials are being compared to establish a calibration curve. Roughly, conductivities in the range of 0.2 W/mK appear to be approximately 20% high as measured by the Anter 4141 and actual values in the 1.0 to 1.2 W/mK range will measure 80% to 100% too high.

For the purpose of this work, reproducibility was more important than accuracy. Furlong¹⁵ twice measured the thermal conductivity of alumina hollow spheres with the Unitherm apparatus, emptying and reloading the machine between runs. He found the readings to agree within ± 0.01 W/mK. Ford¹⁷ followed the same procedure for a solid ceramic monolith, and the values agreed within ± 0.015 W/mK. The Georgia Tech Unitherm 4141 apparatus appears to provide thermal conductivity measurements that are high but reproducible. Therefore, specific thermal conductivity readings should be ignored in favor of relative values and trends.

Infrared Reflectance Measurements - Infrared reflectance measurements were made with a Perkin-Elmer diffuse reflectance (PEDR) accessory, housed in a Perkin-Elmer Series 1600 FTIR spectrometer. A diagram of the PEDR accessory is shown in Figure 3.5.¹⁹ The infrared beam enters the PEDR from the left and is reflected by five flat mirrors. The ellipsoidal reflector serves both to focus the beam onto the sample, and to collect the reflected radiation. The reflector collects radiation over a solid angle of π steradians.

Because of the small sample thickness, reflectance of hollow spheres could not be measured in the PEDR accessory. The sphere walls are thin enough to allow beam penetration and subsequent interaction with the sample holder. Additionally, since spheres have a curved surface, the direction of specular reflectance would change with sphere orientation and produce erroneous results. To avoid these problems, it was necessary to fabricate solid conical samples having the same microstructures as the hollow spheres. To this end, molds in the shape of the sample holder were manufactured. Slurries containing a 3 to 1 feldspar to clay weight ratio and varying zirconia content were wet milled to adequately mix the powders, and poured onto a flat piece of glass to facilitate rapid drying. The mixed powders were combined with a small amount of water to produce thick pastes, and pressed into the molds and allowed to dry. A thick paste was desired because zirconia is more dense than the feldspar or clay, and settling may have occurred if the original fluid slurry had been used. Five samples were fabricated of each composition.

Figure 4.2.2

Comparison Between Georgia Tech Thermal Conductivity Measurements and Manufacturer's Specifications for K-23 and K-30 Firebrick.

Figure 4.2.3

Thermal Conductivity of Alumina Hollow Spheres Measured at Georgia Tech and the University of Kentucky.

The solid spectrometer samples, like the spheres, were fired to 1200°C for 3 hours. The upper surfaces of the fired samples, those which would face the infrared beam, were uneven and rough. To prevent errors due to the surface texture variability, all upper surfaces were ground and polished with 180, 320, 600, and 1200 grit silicon carbide paper. The spectrometer samples had an upper surface diameter and thickness of approximately 9.3 and 2.7 mm, respectively, and filled a majority of the volume of the sample holder. One infrared scan was performed on each sample, producing five scans for each composition. The scans performed were ratio scans, meaning that they were taken relative to a standard. The standard was chosen as the glass/zirconia composition showing the highest infrared reflectance, so that all other compositions would be less than 100%. The sample containing 21.74V/O DK1 had the highest reflectance and was used as the standard. Infrared reflectance is shown for the three zirconias in Figure 4.2.4

Thermal Conductivity Results - All three zirconia powders significantly reduced the high temperature thermal conductivity of glass spheres, Figures 4.2.5-4.2.8. Conductivities at 1000°C plotted as a function of zirconia content show the dramatic effect at high temperatures, Figures 4.2.9-4.2.10. Small amounts of zirconia reduced thermal conductivity dramatically, but additions in excess of approximately ten volume percent caused little change. In fact, RDF 371 glass spheres showed an increase in thermal conductivity as the zirconia content was raised from ten to fifteen volume percent.

4.3 THERMAL CONDUCTIVITY AND INFRARED REFLECTANCE

The reflectance graphs, if turned upside down, are similar in shape to the graphs of thermal conductivity and α coefficient vs. volume percent zirconia. This resemblance is especially true for the DK1 and DK3CL curves, and implies that a relationship may exist. Figures 4.3.1 AND 4.3.2 show the thermal conductivity at 1000°C versus reflectance for the DK1, DK3CL, and RDF 371 glass/zirconia systems. Since many of the spectrometer samples did not possess a zirconia fraction that corresponded exactly to that of the spheres, the raw data could not be compared directly. The data points shown, therefore, are from the best fit curves at various zirconia contents. The best fit straight lines, obtained using linear regression, are plotted together in Figure 4.3.2. All three compositions show a reasonably linear relationship. The best fit lines for the DK1 and DK3CL compositions are closely positioned to each other. The RDF 371 data yields a best fit line positioned lower on the graph.

The most interesting feature of the thermal conductivity vs. zirconia percent graphs is the upturn of the RDF 371 curve as the zirconia content is raised from 10V/O to 15V/O. Assuming that the thermal conductivity is related to reflectance, this upturn could be due to dependent scattering. This curve appears opposite in behavior to the curves in Figure 2.13, in which reflectance actually decreases above a certain volume

Figure 4.2.4

Combined Reflectance of DK1, DK3CL, and RDF371 Opacified Glass Spectrometer Samples Vs. Zirconia Volume Percent.

Figure 4.2.5 Thermal Conductivity of Unopacified Glass Spheres Vs. Temperature.

Figure 4.2.6 Thermal Conductivity of DK1 Opacified Glass Spheres Vs. Temperature.

Figure 4.2.7

Thermal Conductivity of DK3CL Opacified Glass Spheres Vs. Temperature.

Figure 4.2.8

Thermal Conductivity of RDF 371 Opacified Glass Spheres Vs. Temperature.

Figure 4.2.9

Thermal Conductivity of DK1 Opacified Glass Spheres Vs. Zirconia Volume Percent, at 1000°C.

Figure 4.2.10

Combined Thermal Conductivity of DK1, DK3CL, and RDF 371 Opacified Glass Spheres VS. Zirconia Volume Percent, at 1000°C.

Figure 4.3.1

Thermal Conductivity at 1000°C Vs. Reflectance for DK1 Opacified Glass.

Figure 4.3.2

Thermal Conductivity at 1000°C Vs. Reflectance for DK1, DK3CL, and RDF 371 Opacified Glass.

content. However, the reflectance curve for RDF 371 does not show a downturn at similar volume fractions of zirconia, raising doubts about this interpretation.

The effect of zirconia particle size on thermal conductivity was difficult to assess. The DK1 and DK3CL curves are nearly identical, and demonstrate no observable particle size effect. The finer RDF 371 distribution did show lower thermal conductivities. However, unlike reflectance, where a particle size effect seemed evident because the results matched so closely to theory and to a similar previous study, the variation in thermal conductivity is not as easily explained by a particle size difference. At low volume percentages, the RDF 371 curve does drop more quickly with zirconia content than either DK1 or DK3CL, similar to the large change associated with the RDF 371 reflectance curve. However, unlike the reflectance curve, the RDF 371 thermal conductivity curve does not cross back over the DK1 and DK3CL curves. The effect of particle size on thermal conductivity is inconclusive.

Model - There appears to be a linear relationship between the thermal conductivity, measured at 1000°C, and the reflectance at 2.28μm (also between the c coefficient and reflectance). Based on this observed behavior, the following model is proposed. If there is no absorption, then the energy, I_o , of a beam passing through a scattering solid is given by:

$$I_o = R_H + \tau_H \quad (5.1)$$

R_H is the hemispherical reflectance, composed of surface reflection and radiation scattered greater than 90°. τ_H is the hemispherical reflectance, composed of unscattered in-line transmission and radiation scattered less than 90°. This equation is rewritten as:

$$\tau_H = I_o - R_H \quad (5.2)$$

At this point, the amount of radiation passing through the solid, τ_H , is assumed to be proportional to the heat transfer per unit time, H , from Equation 2.1 (and, therefore, the thermal conductivity k):

$$\tau_H \propto H \propto k \quad (5.3)$$

Substituting k for τ_H :

$$k \propto I_o - R_H \quad (5.4)$$

and introducing the constants A and B:

$$k = A - BR_H \quad (5.5)$$

This equation is suitable for this data if one more assumption is made. The reflectance acquired with the PEDR accessory is assumed to be proportional to the hemispherical reflectance, R_H , even though it is taken over a smaller angular range:

$$k = A - BR_{PEDR} \quad (5.6)$$

Equation 5.6 is in the form of a straight line, and fits the graphs of thermal conductivity vs. reflectance well. The thermal conductivity term in Equation 5.6 may be replaced with the coefficient c . This equation assumes that the reflectance is read at a wavelength corresponding to the thermal conductivity temperature, as expressed by Equation 2.6.

The linear regression data fitting Equation 5.6, is plotted as the straight lines in Figure 4.3.2. All compositions agree well with the linear model. Based on its lack of similarity between hollow sphere and spectrometer sample microstructures, one may have expected the DK3CL system to show a significant deviation from this linear model, but this is not the case. The linear regression lines for DK1 and DK3CL are nearly identical in slope and position, while that of RDF 371 is lower on the graphs of both 1000°C thermal conductivity and c coefficient vs. reflectance. This variance in position may be explained by absorption, an effect that was assumed negligible. Some absorption will exist due to the presence of zirconia, and its magnitude will be a function the zirconia's exact chemical identity. DK1 and DK3CL are manufactured by the same company, and are unstabilized. RDF 371 is stabilized with yttria. Yttria may alter the overall absorption of the system, and change the exact relationship of thermal conductivity to reflectance.

The addition of zirconia significantly affects both the infrared reflectance and thermal conductivity of hollow glass spheres. Additions of zirconia increase the reflectance and decrease the thermal conductivity of glassy spheres by more than a factor of two. At low zirconia loading, the reflectance increases in a nearly linear fashion with zirconia content, as predicted by scattering theory. Reflectance levels off at higher zirconia volumes because of dependent scattering. Plots of thermal conductivity vs.

reflectance show a linear relationship, for which there is a theoretically reasonable, if somewhat simplified, model available.

The zirconia size affects infrared reflectance, but to a small degree. A significant difference in thermal conductivity present between one size distribution and two others may or may not be due to a particle size effect. In retrospect, although three different sized distributions were tested, they all shared the same range of particles. Based on these conclusions, the following recommendations are made:

1. In order to see any effects of particle size on reflectance and thermal conductivity, the zirconia size distributions should be narrower and more widely separated from each other.
2. The PEDR accessory should be used to examine the reflectance of compositions, such as mullite and alumina, that are more viable high temperature insulators. The size, volume percent, and distribution of pores in these two materials may significantly affect infrared reflectance, and much can be done to alter these parameters.

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5.0 TECHNOLOGY TRANSFER

5.1 ADVISORY MEETING AND INDUSTRIAL VISITS

A major task of this program was to provide transfer of hollow sphere technology covering fabrication, properties of spheres and foams, and potential applications. To facilitate this process, Dr. Carl Vander Linden, Littleton, CO, agreed to serve as a "Technology Transfer Coordinator" and as a result of his efforts, an extensive number of visits and subsequent interactions resulted, many of which are continuing to this date. Technology transfer was initiated by organizing a planning committee meeting in Atlanta, GA. In the fall of 1989, personnel from industry, universities, and government met to review the hollow-sphere technology with the goal of commercializing this technology. In general, this group identified potential application areas and thought it appropriate to inform industry about the spheres at trade shows and through individual visits, rather than by trying to attract a large audience through a formal technology transfer conference. It was thought that by meeting with individual companies, the exchanges would be much more open and applications would be discussed more freely compared to an open conference where competitors at the same table would not want to exchange their application ideas.

The dissemination of sphere technology and property information to the industrial community was initiated in January 1990. Dr. Carl Vander Linden arranged most of the visits and Drs. Cochran and Vander Linden made 45 presentations to the 39 organizations listed below. These visits covered the time period 1991 and 1992. Multiple visits were made to Alcoa, Carborundum, and Thermal Ceramics. Extensive trip reports have been prepared by Dr. Vander Linden and an example of one to Rohr Industries is provided below for information. A typical visit would consist of a background presentation by Dr. Vander Linden for 10-15 minutes followed by a technical presentation by Dr. Cochran of 1-1.5 hours which included examples of many sphere compositions and point contact bonded foams.

As a result of these visits, many new applications have been uncovered where a unique property of the spheres provides a refractory product not previously available. Three examples follow: (a) the interest in the basic magnesia or spinal sphere is continually expressed and spheres of these compositions have been prepared at Georgia Tech, (b) during a visit to a major oil company, the need for a refractory to withstand the very corrosive atmospheres (containing fluorine and chlorine gases) present in hazardous waste incinerators used in most petrochemical plants was identified, and samples have been provided for testing by the interested company, and (c) the industry sponsored, Gas Research Institute, stated the need for a flat burner plate to spread heat uniformly over wide areas for drying. The capability to produce low expansion refractory ceramic spheres along with the uniform channels between

the monosized spheres suggested bonded-sphere plates may provide a superior product for this application, and samples have been fabricated for testing. These samples were provided to a GRI sponsored company and they performed well as radiant gas burner plates. This is an extreme thermal shock condition and suggests that bonded aerosphere monoliths have excellent thermal shock resistance.

Technology transfer trips continued into a second year under the direction of Dr. Carl Vander Linden and these visits created many subsequent interactions particularly with Rohr Industries and Hi Temp Corporation. In addition, a trade show booth at the American Ceramic Society Exposition in Cincinnati in May, 1991 and May, 1992 sponsored by Ceramic Fillers Inc. demonstrated Aerosphere™ (trade name for hollow spheres manufactured by the coaxial nozzle process) technology and generated considerable industrial interest.

As a result of these technology transfer contacts and the success that mullite radiant burner tiles have demonstrated under severe thermal shock conditions, the Gas Research Institute has funded two projects (one for one year and one for two years) to develop high emissivity radiant burner tiles based on the mullite point contact bonded hollow sphere foams as diffuser base flame arrestors. Another aerosphere monolithic insulation application is induction furnace insulation at the Y-12 plant where two design iterations have resulted in fabrication of a mullite tube 70 inches tall, 27 inches in diameter and a wall thickness of 1.5 inches, Figure 5.1.1. This tube was fabricated in four nesting parts with each section being 18 inches tall. Tolerances of 0.4 % were met in these near net shapes. In addition, insulation plates at Hi Temp Corporation and alumina aerosphere boards at Lawrence Livermore Laboratory have been supplied. The continued, growing interest in this technology by American industry is the best measure available for the success of the overall program. It should be noted that as a result of this program, 300,000 pounds of spheres are being manufactured annually for incorporation into syntactic foams where the polymer matrix is also foamed. These foams are being used as energy absorbing components for passenger protection in 6-8 different automobiles.

5.2 TECHNOLOGY TRANSFER TRIP REPORT

Hollow Sphere Technology Transfer with Rohr Industries in Chula Vista, CA (Prepared by Dr. Carl Vander Linden)

Joe Cochran and I met with the following people from Rohr Industries at their Chula Vista headquarters on April 8, 1991. Their address is:

Rohr Industries, Inc.

STRUCTURAL INSULATION from AEROSPHERE FOAMS

➤ Hollow Ceramic Spheres

➤ Furnace Insulation for Y-12 Plant

➤ Point Contact Bonded
Hollow Sphere Foams

Figure 5.1.1 Point-Contact-Bonded, Hollow-Sphere, Mullite, Structural Insulation for Induction Furnace at Y-12 Plant.

Foot of H Street
P.O. Box 878
Chula Vista, CA 92012-0878

Dr. Brian Morris had arranged the meeting.

Dr. Brian Morris	Eng. Staff Specialist R & D Metals	619-691-3646
Frank Gojny	Deputy Project Mgr. R & D Metals	619-691-6465
Uwe Bockenhauer	Director of R & D	619-691-2516
Bruce Spivack	Eng.. Specialist Refractory Composites Carbon-carbon & Ceramics	619-691-3771
Paul Leholm	Sr. Research Eng.. Metals	619-691-3952
Rafael Castrejon	Research Eng.. Metals & Metallic Composites	619-691-2743
Herb Nagler	Eng.. Specialist	619-691-2354
Woody Wongwiwat	Eng.. Specialist	619-691-4227
Paul Lu	Eng.. Specialist	619-691-3925

Brian took us on a short tour before the meeting. We learned that Rohr is the largest user of titanium metal in the US. We saw the manufacture of titanium honeycomb panels. They supply both commercial and military aircraft, space vehicles, missiles, NASA shuttles, etc.

Joe gave his 35 mm slide presentation of both hollow ceramic spheres and hollow metal spheres, and shapes formed from these spheres. The reception was excellent with many questions and comments. The presentation and questions covered a two hour time period.

Brian expressed an interest in use of fibers in the sphere formation. There was a question about the effect of thickness on the strength of the shapes formed from the spheres. There was major interest in metal spheres. Joe said the density of the nickel

spheres (which had been made by forming nickel oxide spheres and reducing in hydrogen) was 0.9 g/cc and that it may be possible to achieve 0.5 g/cc.

The discussion then turned to titanium spheres which appeared to be a major interest. Frank Gojny was the most vocal spokesman. There was a discussion about possible methods of making them including use of a hydride as a starting material and possible use of titanium powder. They expressed concern about possible contamination if the hydride is a starting material. This led to a suggestion by Frank of a sponsored proprietary research project on making titanium spheres. Joe responded to Frank's question of "about how much" with a guess of \$50,000. Frank asked for a ball park estimate of the cost of making metal spheres exclusive of the material cost. Joe came up with an off the top of his head estimate of about \$500 per cubic foot. Joe and Frank discussed a joint project seeking funding from another agency. This also appeared to be of interest.

Someone talked about "spheres" they have made from titanium foil by rolling the foil to a tube and then stamping out the sphere. They cost about \$1,000 per cubic foot.

It was not clear what density sphere they needed. Their titanium honeycomb is 5 pcf at the low end and 12 pcf at the high end. Spheres may be better than honeycomb for sound attenuation on commercial aircraft. They asked about carbon spheres. They told us that Clarkson College of Technology is making spheres from colloids. They suggest that we talk with Lockheed about ferrite spheres. They mentioned that Al Taylor at NASA Langley handled shuttle materials problems.

5.3 TECHNOLOGY TRANSFER PRESENTATIONS

1. Alcoa, Alcoa Center, PA
2. Allied Signal, Ceramic Components, Div., Torrance, CA
3. Amoco, Naperville, IL
4. Bethlehem Steel Corp, Bethlehem, PA
5. Babcock & Wilcox, Barberton, OH
6. Boeing Aerospace Corp. Seattle, WA
7. Carborundum Company, Keasbey, NJ
8. Chicago, Fire Brick, Chicago, IL
9. Coors Ceramics, Golden CO.
10. Dylon Ceramic Technologies, Berea, OH
11. Foseco, Inc. Cleveland, OH
12. Gas Research Institute, Chicago, IL
13. General Refractories Co., Warren, OH
14. Harbison-Walker, Refractory, Pittsburgh, PA
15. Hi Temp Insulation, Inc., Camarillo, CA

16. Institute of Gas Technology, Chicago, IL
17. Magneco/Metrel, Inc., Addison, IL
18. NASA Amer. Research Center, Moffett Field, CA
19. National Refractories, Livermore, CA
20. Naval Civil Engineering Laboratory, Port Hueneme, CA
21. Naval Research Laboratories, Washington, D.C.
22. North American, Refractories, Cleveland, OH
23. Pittsburgh Corning Corp, Plum, PA
24. Plibrico Co., Chicago, IL
25. Premier Refractories, King of Prussia, PA
26. Pryor-Giggey Company, Whittier, CA
27. Quigley Company, Easton, PA
28. Resco Products, Inc. Norristown, PA
29. Riverbank Acoustical Laboratory, Geneva, IL
30. Rohr Industries, Chula Vista, CA
31. Suppression Engineering, Walnut Creek, CA
32. The Refractories, Institute, Pittsburgh, PA
33. Thermal Ceramics, Augusta, GA
34. Timken Co, Canton, OH
35. UOP, Des Plaines, IL
36. USG Corp. Libertyville, IL
37. USX Corp, Monroeville, PA
38. W.R. Grace, Columbia, MD
39. Zedmak Refractories, Dover, OH