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Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Russell Bernard Bennett, B.Cer.E., M.Sc.

The Ohio State University
1970

Approved by
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INTRODUCTION

The general lack of reproducibility and reliability of ceramic materials prevents or limits their use in critical applications. The most notable example is in structural applications. Here the inability to assign a strength minimum to the materials as a result of the statistical nature of its strength poses a serious limitation. This situation arises because of the inability of ceramic materials to relieve stress concentrations associated with microcracks, pores, or other local inhomogeneities in the microstructure by local plastic flow. Thus, the material is flaw sensitive and tends to exhibit catastrophic failure over a wide range of strengths depending on the severity of the most critical flaw in the particular sample being evaluated.

That this variability is not necessarily an inherent characteristic of ceramic materials has been demonstrated for chemically strengthened and devitrified glass.¹ The high, reproducible strength exhibited by this material resulted from the control of microstructural and surface flaws. For ceramic materials processed by
conventional ceramic powder technology, however, such flaw control has not been achieved due to processing limitations. Thus, for these materials flaw-sensitive properties such as mechanical strength show a general lack of reproducibility and reliability.

In order to minimize powder processing limitations that lead to microstructural flaws and thus property variability, quantitative description and control of each step in the fabrication process from powder preparation and characterization to the final product must be achieved. The first step toward developing such a controlled process is to develop the techniques necessary for quantitatively characterizing those powder characteristics which are significant in determining the character development and variability in the finished ceramic body.

The primary objective of this investigation is to improve the ability to quantitatively evaluate those powder characteristics and processing parameters which affect microstructural development and variability, and consequently control property values and property variability.

The three principal problems associated with realization of the primary objective of this study are:

1. Identification of the powder characteristics which are significant in terms of character
development and variability of the finished ceramic body,

2. Quantitative characterization of the significant powder characteristics, including development of new or improved techniques where necessary, and

3. Quantitative analysis of the effects of significant powder characteristics on the character development and variability in the finished ceramic body.

For convenience, powder characteristics are classified in four categories, namely, (1) physical, (2) chemical, (3) surface chemical and rheological, and (4) structural. Although these categories may be interdependent, their separation is convenient for the purpose of discussion.
MODE OF INVESTIGATION

The experimental approach was based on the application of materials science principles to identify and quantitatively characterize those powder characteristics which are significant in terms of character development during subsequent processing and in terms of variability of the finished ceramic body. Similar principles were used in tracing the effect of variation of the significant powder characteristics on microstructural development during subsequent processing and in evaluating their effect on the microstructure and variability in the finished body. The scientific rationale for this approach was that variability in the finished body results from inhomogeneities in the microstructure which originate from variation of the original powder or from variations that occur during processing and are attributable to characteristics of the fine powder employed. Thus, quantitative characterization of ceramic powders, analysis of the effects of significant characteristics on microstructural development, and analysis of the effect of microstructural inhomogeneities on the variability of the properties of the
finished ceramic body were expected to lead to a better definition of the variations to be expected in the final body if a given starting powder and fabrication process were used.

In some cases incremental variations in powder characteristics were induced by special processing to provide the basis for evaluating hypotheses arrived at from observation of as-received commercial alumina powders. Emphasis was placed on identifying and eliminating the critical flaw responsible for product variability.
LITERATURE REVIEW

The term "characterization" has been increasingly used in technical literature during the past several years. However, the construed meaning of the term "characterization" is variant, depending on the interpretation by the particular author who uses the term in the title of his publication. Within this dissertation, and throughout the associated research program, the definition adopted by the Materials Advisory Board\(^2\) is accepted. The Committee on Characterization of Materials evolved the following working definition:

Characterization describes those features of the composition and structure (including defects) of a material that are significant for a particular preparation, study of properties, or use, and suffice for the reproduction of the material.

The Materials Advisory Board report goes on to say that although "... every characterization method uses some property of the atoms, ions, or molecules to determine the compositions, structures, and defects in materials ..." it must nevertheless be proven "... that the property measurement reflects directly and unambiguously the relevant compositional or structural features of a material before it can be accepted as a
valid characterization." Most property measurements do not do so and must, therefore, be supported by independent methods of characterizing the structure or composition of the material.

Similarly, the history or description of the preparation of a material has often been substituted for characterization, or at least has been considered necessary for characterization of a material. However, true characterization should be in terms that are independent of descriptions of past history.

Among the general recommendations of the MAB report is one which bears repeating.

Editors, referees, and policymakers of technical societies should insist on characterization of materials whose measured properties are submitted for publication.

The need for characterization during process and product improvement was pointed out by Bersch, who said that character was the link joining processing and properties. He defined a concept of "description (D) as " . . . the sum of the total characterization available (C_t) plus data on the properties (P) of the body plus the sample history (H) including raw material background and processing data." Thus, the equation:

\[ D = C_t + P + H \]
The importance of microstructural analysis in characterization was emphasized by Owens, who pointed out that understanding the effect of specific microstructural characteristics on a property(s) of a ceramic (material) is often an inducement to endeavor to change these characteristics; e.g. the achievement of translucency in Lucalox by Coble.

The pertinence of characterization to engineering design was discussed by Schlabach, who took the relationship between ingredients, the characterized material, and properties of the material as presented by the MAB report, and then showed an analogous relationship between materials of construction and their fabrication with the part or structure produced, its behavior or response, and the achievement of its intended use. He stated that "... the materials scientist and the designer come together in their common concern with materials and their properties but proceed from this meeting point to opposite ends of the materials spectrum; one atomistic and microstructural and the other, mechanistic and macrostructural." He concluded that more meaningful correlations between structure and properties must be established across this entire spectrum.
In another discussion of brittle ceramic materials from the designers' standpoint, the problem of material variability, particularly from the standpoint of flaws or defects in the material itself and surface defects on the specimen, was pointed out by Boland and Walton. This variability or lack of reliability of ceramics was more accurately designated by Bersch as being "poor predictability", since controlled or bounded variability might be endured. He stated that variability and unpredictability applied primarily to strength properties of ceramics. He also said that thermal, electrical, elastic and other properties which are influenced by compositional and microstructural variations are usually less variable than the strength properties. He attributed the strength variability to testing conditions, surface finish variations, and character of the ceramic specimen. He felt that the size, shape, location and distribution of defects were more critical influences on variability than pores, microcracks and cracks, but that variabilities in grain size, grain shape, and orientation are also factors. He considered that, except for cracks, body character would probably only be important to variability after test and surface deficiencies were under control.
The link between the processed ceramic body whose characterization and variability have just been discussed and particulate ceramic raw materials is "forming". The essential considerations of "forming" which follow characterization of the particulate material used and precede product realization were categorized by Pincus and Pask\textsuperscript{8} as follows:

1. Characterization of the process as a controlled engineering system
2. Rheological response of materials to forming energy
3. Topological aspects of the packing of matter (space filling)
4. Bonding and phase interaction
5. Forming - stress interpretation

Characterization of material used in cold forming processes was discussed by Allen.\textsuperscript{9} He referred to the mechanism of the compaction process which starts with a particulate system and ends with a shaped piece as "compaction response". Allen considered the use of characterized particulate raw materials with known physical and chemical properties to be a requisite to successful forming operation. Thus, characterization of the particulate raw material is the first step to reproduction in fabrication, and elimination of resultant microstructural and property variability.
Allen listed the properties considered important as:

1. Size distribution and shape
2. Surface area per unit weight and density
3. Crystal modifications, stoichiometry, and defect structure
4. Chemical activity (e.g. hydration behavior, iodine number, anion impurities)
5. Degree of chemical purity or controlled impurity

A comprehensive review of particulate characterization by Stover presented a set of definitions which are relevant to particulate characterization and processing as follows:

A particle is a solid, discrete grouping of atoms which are free to move as an entity. A grain is a part rigidly attached to other parts but which is surrounded by a discrete interface and which can be identified by distinctive characteristics. Particulate material is an assembly of particles, and if surface forces influence the behavior of the material, it is referred to as a powder. Colloidal material is particulate material in which inertial forces are insignificant. A particulate system is particulate material together with its fluid environment. In ceramic technology, an agglomerate is a particle composed of smaller particles which can be separated intact because of the relatively weak attractive forces acting between the smaller particles. An aggregate is a particle composed of grains which cannot usually be separated intact without some grains being fractured because of the strong connective bands.

He presented a classification of particulate systems in terms of characteristics, properties and
performance. He also pointed out that "By themselves, evaluation of none of these characteristics, properties or performance traits is of any value to the ceramic engineer unless he knows their relation and significance to steps in the ceramic processing operation."

He then presented a comprehensive literature review of the techniques of particulate material characterization. Some characterization techniques will be described in the appropriate procedural sections of this presentation.

Fuerstenau and Mular summarized properties of particles which serve to determine their behavior in fluid environments, considering that "the basic idea behind the term particle characterization is that the engineer must accumulate a sufficient amount of data on the properties of the powder or particles which comprise a batch so as to be able to predict its behavior during and after a forming treatment."

Thus far, the characterization of the finished ceramic material, the processing link between the material and the starting particulate system, and the characterization of the starting particulate system have been considered. One additional aspect of the materials fabrication spectrum, powder preparation, should also be mentioned.
The preparation of particles was categorized by Fuerstenau and Mular according to the method of production including: (1) comminution, (2) precipitation, (3) atomization, (4) thermal decomposition, (5) vapor deposition and (6) thermal quenching. XA-16 alumina produced by The Aluminum Company of America seems to be a representative powder for preparation of high-purity alumina materials for electrical and structural property applications. This particulate material is essentially a Bayer-process alumina which has been purified, calcined and then dry ball milled. In the Bayer process, finely divided bauxite is dissolved under pressure in hot concentrated caustic soda solution, forming soluble sodium aluminate and an insoluble siliceous residue often referred to as red mud. The undissolved residue is separated from the alumina solution by filtration and washing. The sodium aluminate is hydrolyzed to aluminum hydroxide by cooling, seeding and dilution with wash waters. This aluminum hydroxide is then crystallized, the precipitate is separated and washed, and then calcined to form alpha alumina. By-products are reworked to make other grades of alumina. During dry ball milling of XA-16 alumina, a grinding additive such as naphthenic acid.
is used to inhibit packing of powder in the mill.

Linde A alumina appears to be a representative powder for transparent alumina product fabrication powder. This particulate material is prepared by a proprietary process, thought to consist of calcination of ammonium alum \([(\text{NN}_4)_2 \text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3]\). The calcination is performed under conditions thought sufficient\(^{15}\) to transform the alumina decomposition product into alpha alumina, the most stable phase. Ceramic-grade Linde A powder consists of special lots that are selected on the basis of purity and surface area.

It should be noted that a researcher having the capability to prepare his own starting powder material realizes several obvious advantages when one considers the ability to control powder handling and exposure history, purity (or additives), and pre-processing treatment. For example, sintering aids can be added as co-precipitates for uniform distribution, particle size and size distribution can be controlled by calcination and comminution procedures, and exposure to contamination can be limited. One relatively simple procedure requiring relatively modest facilities is vapor deposition, as commonly used in preparation of titania pigments.\(^{16}\) Starting with high-purity aluminum metal ingots, the aluminum is first chlorinated, the
chloride is then oxidized, and finally the oxide is precipitated. The alumina phase assemblage which is precipitated seems to depend on the precipitation temperature. Thus far, solely alpha alumina has not been precipitated. Therefore, a calcination and comminution sequence would probably be required. The precipitation chamber material also places a restriction on chemical purity of the particulate powder product. Thus, high-purity fused alumina would make an outstanding chamber material.

The characteristics of a powder can be categorized as (1) physical, (2) chemical, (3) surface chemical or rheological, and (4) structural. The physical characteristics are expected to play a major role in both pressure compaction and sintering fabrication, microstructural development, and resulting properties. The chemical characteristics as a function of the impurities are expected to affect all the foregoing except the pressure compaction.

The rheological characteristics should affect pressure-compaction features directly, but other aspects only indirectly.

The structural characteristics should primarily affect sintering, microstructural development and, indirectly, properties. However, because the disruptive
influence of the transition of less stable alumina phases to alpha alumina at approximately 1150 C is well known, only alpha alumina is commonly sintered. Non-alpha-alumina powders would be calcined prior to use, and then perhaps ball milled to reduce the resultant aggregated material to a more usable powder form. Whatever the preliminary treatment of the powder, it is only the character of the resultant particulate product with which fabrication is undertaken that will affect the fabrication, microstructure, and properties of the finished ceramic body. Thus, structural character of powder raw materials can be considered non-variable, and only the effects of physical, chemical, and rheological characteristics will be reviewed. In this review, the fabrication and properties of the ceramic product as related to these particulate characteristics will be considered.

Powder processing such as calcination, ball milling, and pelletization will not be reviewed here, but will be discussed in the appropriate procedural sections.

**Chemical Characteristics**

The chemical characteristics of high-purity alumina powder would tend to be a function of the impurities present in the material. The following
discussion will refer to some of the reported effects of impurities in (or additions to) alumina on its fabrication and property development, including physical, electrical, mechanical, optical, and chemical properties. In some other ceramic systems magnetic characteristics would of course also be included.

Effect on Fabrication Processes

The effect of impurities on the sintering of alumina has received considerable attention in recent years, since impurities can either enhance or retard the densification process. For solid state sintering, material transport occurs by bulk or lattice diffusion of vacancies and/or by grain boundary diffusion. Impurities can affect both processes at various stages of the sintering process.

In reviewing work by Johnson, Cutler related that MgO additions as low as 100 ppm have been shown to retard the initial sintering of Al₂O₃. Cahoon and Christensen reported that amounts over 0.023 percent prevented discontinuous grain growth, allowing complete densification to occur. An increase in sintering rate during the final stages of sintering has been observed by Ringel for alumina with as much as 2.0 percent MgO. Limited solid solution of MgO in Al₂O₃ has been proposed as the mechanism which
increases the final sintering rate, while spinel formation at the grain boundaries is believed to inhibit initial sintering rates. Recent studies by Warman and Budworth have indicated that MgO transported in the vapor phase can enhance the sintering rate of "pure" alumina compacts. This phenomena may be responsible for discrepancies between investigators using apparently similar materials and techniques. At any rate, complete densification of alumina with MgO additives has permitted strong, fine-grained alumina ceramics to be fabricated commercially using the relatively inexpensive sintering fabrication technique.

Transparent alumina commercially prepared with 0.25 percent MgO by The General Electric Company indicates the significant effect that additives can have on a fabrication process. Additives other than magnesia have also been studied in a continuing attempt to isolate the effects of specific impurities on sintering. Keski and Cutler found that 0.2 to 0.4 percent MnO in Al₂O₃ gave a maximum initial sintering rate. Warman and Budworth reported that as little as 0.25 percent of either MgO, NiO, ZnO, or SnO₂ could be used to sinter Linde A to theoretical density in oxygen. Jorgensen and Westbrook found that NiO segregated at the grain boundaries of alumina sintered
to theoretical density with only 0.1 percent of the additive. Baggaley\textsuperscript{24} reported that 10 to 10,000 ppm of Na\textsubscript{2}O promoted exaggerated grain growth in Linde A and that even an atmosphere of Na\textsubscript{2}O had the same effect. He proposed that Na\textsubscript{2}O impurities form a second phase which stimulates the exaggerated grain growth. The formation of an impurity-rich second phase in 99.99 percent Al\textsubscript{2}O\textsubscript{3} implied by Patrick and Cutler\textsuperscript{25} and established by Mistler and Coble\textsuperscript{26} represents the current state-of-the-art of the effects of cation impurities on sintering of alumina.

More recently, attention has been directed to the effect of anion or gaseous impurities on the densification processes of oxide bodies. Warman and Budworth\textsuperscript{27} noted that alumina doped with 0.25 percent MgO was susceptible to bloating when rapidly heated to sintering temperatures in low vacuum atmospheres. Earlier, Paladino and Coble\textsuperscript{28} concluded that kinetic processes in alumina above a certain grain size would be controlled by oxygen anion diffusion. Prior to that Coble\textsuperscript{29} reported that alumina with 0.25 percent MgO would sinter to theoretical density in hydrogen or oxygen but not in air, nitrogen, helium or argon, and attributed the difference to varying solubilities of the gases in alumina. Bauer, et al.\textsuperscript{30} found that the volatization of Na\textsubscript{2}O from commercial alumina (0.08 percent Na\textsubscript{2}O) during fusion
casting produced porous, impact resistant, castings. Work at AVCO\textsuperscript{31} has indicated that vacuum hot pressing of Linde A alumina (VHP) promotes intercrystalline bonding by the removal of absorbed and otherwise trapped gases. Additional hot pressing studies\textsuperscript{32} revealed that ultra-high-purity alumina could also be vacuum hot-pressed to near theoretical density. Impurities, predominately C, Y, Cl, and H, in the fabricated samples were found to be inhomogeneously distributed. Continuing work in this area\textsuperscript{33} has recently shown that translucent specimens can be prepared by vacuum hot pressing ultra-high-purity alumina at 15,000 psi and 1350 C. Mass spectrographic analyses indicated that Cl was a predominant impurity in the "as-received" powders as well as in a sapphire single-crystal. In addition to the vacuum hot pressing fabrication method, AVCO\textsuperscript{32} has reported that hot-forging can be used to fabricate theoretically dense Linde A with 0.25 percent MgO. Translucent alumina was reported by hot forging\textsuperscript{34} when no MgO addition was incorporated.

Effect on Mechanical Properties

The effect of impurities on the intrinsic mechanical strength of alumina is difficult to determine because of the complicating effects of grain size and porosity. These will be discussed in a later section.
The most extensive study of the effect impurities have on the strength (modulus of rupture) of alumina was conducted by Rasmussen et al.\textsuperscript{35} using alumina prepared by the calcination of aluminum chloride. TiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, and Cr\textsubscript{2}O\textsubscript{3} impurities in amounts from 10 to \(10^4\) ppm were added to the base material containing about 10 ppm impurities. Modulus-of-rupture values obtained at room temperature under four-point-bending were normalized to an arbitrary grain size and porosity to eliminate extrinsic variables in the analysis of the data. Conclusions from this program were that Fe\textsubscript{2}O\textsubscript{3} and Cr\textsubscript{2}O\textsubscript{3} did not affect the intrinsic strength of the alumina, even when Fe\textsubscript{2}O\textsubscript{3} was present as a second phase. TiO\textsubscript{2} additions did not affect the strength when in solid solution, but drastically reduced the strength if a titanate phase formed. Earlier studies by Cutler\textsuperscript{18} of the effect of Na\textsubscript{2}O and MgO additives on the modulus of rupture of alumina at 1050°C indicated that these oxides also had little intrinsic effect, although the results were somewhat unreliable because of conflicting porosity and grain size effects.

Impurities which form precipitates or solid solutions with alumina have been found to affect its microhardness. Hsu, et al.\textsuperscript{36} found that 0.5 percent titanium increased the microhardness of
sapphire crystals. Brandt\textsuperscript{37} found the microhardness of dense polycrystalline alumina (containing 0.5 percent MgO as a sintering aid) increased linearly with Cr\textsubscript{2}O\textsubscript{3} content up to 12.5 percent. Jorgensen and Westbrook\textsuperscript{23} found that 0.05 to 0.25 percent MgO had little effect on the bulk hardness of sintered Linde A, but increased the grain boundary hardness over 35 percent. They noted that the theoretical density achieved during sintering of alumina with 0.1 percent of MgO, NiO, CoO, Fe\textsubscript{2}O\textsubscript{3}, and CaO was related to the relative increase in grain boundary hardness. By comparison, Westbrook\textsuperscript{38} reported that Aust et al.\textsuperscript{39} found that 0.5 percent Cr\textsubscript{2}O\textsubscript{3} softened the grain boundaries relative to the bulk material.

Alumina bodies have been strengthened by the formation of compressive surface layers of low-expansion solid-solutions or compounds, but the technique has only been partially successful. Kirchner et al.\textsuperscript{40} reported that ninety-six percent alumina was strengthened by refiring the material packed in Cr\textsubscript{2}O\textsubscript{3} to form Al\textsubscript{2}O\textsubscript{3}-Cr\textsubscript{2}O\textsubscript{3} solid solution layers, although the same technique was not successful with Linde A alumina. However, Kirchner and Walker\textsuperscript{41} found that single crystal alumina was strengthened by treating the material packed in CaCO\textsubscript{3} to form
low-expansion calcium aluminate surface layers. Measured strength improvements indicate that this technique might be most effective with high purity materials.

The high temperature creep of alumina is a mechanical property found to be significantly affected by even small amounts of impurities. Hewson and Kingery\textsuperscript{42} stated that 750 to 1500 ppm $MgO$ decreased the normalized creep rate of Linde A by an order of magnitude. However, 500 ppm $MgTiO_3$ did not affect the creep rate significantly because of the compensating effect resulting from equal substitution of $Mg$ and $Ti$ in the alumina lattice. Stuart\textsuperscript{43} compared the creep rates of Lucalox with that of commercial 99.5 percent alumina and found an order of magnitude difference in the creep rate. Creep was attributed to grain boundary sliding in the spinel layer at the grain boundaries of both materials, with a vitreous silica phase enhancing the creep rate of the commercial alumina.

For high temperature applications where creep resistance is important, $MgO$ is actually detrimental to creep resistance because it retards grain growth. The normalized data of Hewson and Kingery\textsuperscript{42} showed that $MgO$ reduced the creep rates by an order of magnitude, although the actual creep rate was increased 2 to 6
fold by differences in the grain size. This effect is common and indicates the importance of microstructural characterization for structural applications of ceramics.

Effect on Electrical Properties

Little information is available on the electrical properties of high purity (99.9 percent) polycrystalline alumina because dense bodies have only recently been prepared commercially. Reviews of the electrical properties of alumina were published in 1966 by Perry\textsuperscript{44} and Gitzen.\textsuperscript{45} Compilations by Milek\textsuperscript{46} and Gitzen\textsuperscript{45} include data on high purity alumina but only a few references pertaining to dense bodies. The most notable work with high purity alumina was done by Atlas et al.\textsuperscript{47} from 1959 to 1962. This work, reviewed by Perry,\textsuperscript{44} was conducted with alumina sintered to a maximum of 92 percent of theoretical density. Si, Ti, Ca, Mg, Fe, and Cr impurities were studied by doping the original material which contained about 100 ppm total impurities.

Since the electrical property values of ceramics are affected by the measurement frequency and temperature as well as by the density and purity of the materials, the following discussion of impurity effects is intended to give only a general idea as to which electrical
properties are most affected by impurities. The dielectric constant is relatively unaffected by impurities at temperatures up to 500 C and frequencies above $10^6$ cps. However, at frequencies below $10^3$ cps, a 99.9 percent pure material had a K value as high as 200 at 500 C, about an order of magnitude higher than that of sapphire - most likely due to impurities. The dielectric strengths of polycrystalline aluminas range from average values of 200 to 600 volts per mil for commercial multi-phase aluminas to over 1700 volts per mil for special sintered aluminas. Such results are strongly influenced by the density and microstructure of the material.

The dielectric loss factor, defined as the product of the dielectric constant and loss tangent, is another electrical property of alumina with high sensitivity to the effect of impurities. Alkali impurities and Si tend to increase the loss factor by their adverse effect on the loss tangent. The loss tangent, or dissipation factor, is strongly affected by secondary phases in 92 to 96 percent alumina bodies, especially with SiO$_2$/CaO ratios favoring the formation of anorthite, where as much as a 100-fold increase in loss tangent has been observed. The effect is attributed to thermal expansion difference of the second phase compared to that of alumina. Similar effects were
observed for second phase titanate additions to high purity alumina by Atlas et al. Data compiled by Milek and Gitzen indicate that the loss tangent varies considerably with both temperature and frequency. The trend is toward lower losses with the denser, high purity materials. The high losses at elevated temperatures may be due to the effect of physically adsorbed water on sample chamber atmosphere as proposed by Snow and Cutler. Typical values at room temperature and 10^6 cps are 10^{-3} and 10^{-4}, although that of Lucalox is 3 \times 10^{-5}.

Electrical resistivity is another electrical property of alumina extremely sensitive to the effects of impurities. Data compiled by Gitzen and Milek indicate 100-fold differences in resistivity are common for similar materials at room temperature. A consolidated plot of resistivity-versus-temperature data from the above references and from Vournetti and Cook revealed that even higher scatter occurred at elevated temperatures. Resistivities of high purity aluminas ranging from 10^8 to 10^{13} ohm-cm at 500 C must be attributed to testing and atmosphere variables as well as to material variables, but impurities account for at least 10-fold differences in data obtained by the same investigator.
In addition to the properties of the bulk material, the physical and electrical properties of the surfaces of alumina ceramics are also important. For high frequency insulations the surface is glazed to prevent moisture or dust from forming a conductive path across the surface. In the microelectronic field, alumina used as a substrate for the deposition of microcircuitry must be free of surface alkalinity and have a smooth texture. Techniques for detecting and analyzing surface impurities such as submicron silica grains have been reported. Future development of high purity alumina for microelectronic substrates and possibly other applications will require a homogeneous distribution of impurities or at least the elimination of impurity segregation at surface or grain boundaries as has been reported.

**Effect on Optical Properties**

Translucent alumina has been prepared by a variety of fabrication techniques in recent years. In addition to having an esthetic appeal, translucent and/or transparent aluminas have practical applications for high-intensity lamps, high-power windows, and transparent armour. Translucent alumina is prepared commercially by sintering alumina containing 0.25 percent MgO. The final product transmits 90 percent
of incident light in the visible region, but the specular or in-line transmission is only 30 percent in this range. Rhodes, et al. at AVCO reported that Linde A hot-forged without MgO additions had an in-line transmission of 40 to 50 percent compared to less than 16 percent for Lucalox, making the hot-forged material more transparent.

Transparent specimens of 99.99 percent alumina have also been fabricated by vacuum hot-pressing, but this technique was not successful with Linde A. Translucency or transparency are a general guide to the physical and mechanical quality of a specimen since these qualities require a pore-free microstructure. Very high purity, fine-grained powders are necessary starting materials, but fabrication parameters are equally important for the production of theoretically dense materials.

Impurities affect the light transmission of polycrystalline alumina by their influence on the fabrication process and resulting microstructure, but have little intrinsic effect on transmission. Other optical properties of alumina such as color are more sensitive to impurities per se. Gitzen's review of alumina includes a discussion of color, thermoluminescence, optical spectrum, phosphorescence,
fluorescence and emissivity of alumina, but with the exception of the first three properties, the effects of impurities are not well known.

Effect on Chemical Properties

In general, alumina is considered inert to most corrosive solutions at room and elevated temperatures. An exception, however, is its poor resistance to phosphoric acid. Higher purity materials generally have a higher corrosion resistance because impurities are selectively attacked and removed. Recent emphasis on the use of alumina in contact with alkali metals, metal salts, and metal vapors has resulted in a few references to high purity materials. MacRae, et al.\textsuperscript{50} found that silica impurities above 500 ppm were extremely detrimental to the strength of polycrystalline alumina exposed to potassium vapor at 870°C. Higgins\textsuperscript{51} noted that \( \text{Cr}_2\text{O}_3 \) and \( \text{SiO}_2 \) impurities increased the weight loss of alumina exposed to cesium vapor at 600°C. Pitting observed in sapphire crystals under these conditions was attributed to \( \text{SiO}_2 \) and \( \text{BaO} \) impurities. Dawihl and Klingler\textsuperscript{52} studied the resistance of alumina to boiling inorganic acids and noted that \( \text{SiO}_2 \) impurities were even more detrimental than \( \text{Na}_2\text{O} \). As higher purity materials become available, the corrosion resistance of polycrystalline alumina may be expected
to approach that of sapphire.

**Rheological Characteristics**

The free flow of powders and the response of powders under the influence of externally applied forces constitute the two aspects of powder rheology.

Free flow of powder depends of course on particulate shape and frictional coefficient. To some extent particle size has also been reported to affect flow. Roller reported that a critical diameter existed which he attributed to electrostatic repulsive forces. Although coarser particles appeared to flow independently of particle size, submicron powders flowed in inverse proportion to particle size, as indicated by powder porosity measurements.

The movement of powders under the influence of external forces, or pressure-compaction, includes tapping or vibratory compaction. The effectiveness or degree of compaction is usually reported in terms of the porosity or percent of theoretical density (relative density) resulting for a particular pressure level. Studies of ideal packing arrangements such as by Graton and Fraser have indicated that spheres of identical size pack in a hexagonal arrangement to about 74 percent relative density. The effect of size variation or distribution has been shown to increase packing density.
Horsfield for example showed theoretically that a relative density of 85.1 percent would result from use of 5 sphere sizes, each size being that calculated to fill the interstices of the next larger. Others such as McGeary who produced a relative density of 95 percent experimentally, investigated packing arrangements of spheres of selected size distributions.

In real practice, the relative density of compacted powders is usually considerably lower due to frictional forces, inter-particulate bonding, and electrostatic repulsive forces. In addition, powders are not always compacted uniformly because of non-uniform pressure application or transmission.

Seelig discussed the existence of inter-particle bridges which cause non-uniform compression. Elimination of bridge-forming processes by vibrating the container was reported by Duffield and Grootenhuis. Various authors have considered decreasing the coefficient of friction through the use of lubricants. Yarnton and Davies showed that die-wall lubrication in very limited amounts yielded optimum results, and that an admixture served only to increase green compact strength. In an excellent review, Vergnon recommended minimizing depth/length ratio of the compact, or the use of
isostatic compression. Kingery\textsuperscript{61} described the effect of non-uniform green density in producing warpage during subsequent sintering. The direct relationship of green density to sintering densification of a reactive alumina was shown by Bruch.\textsuperscript{62} In a later publication Bruch\textsuperscript{63} attributed measles or small porous microstructural areas to non-uniform compaction of powders caused by porous aggregates.

**Physical Characteristics**

The physical characteristics of a powder include particle, agglomerate, or aggregate size distribution, shape, topography and microstructure. Also included are the surface area, bulk density and true density. For a powder consisting solely of alpha alumina, true density will be variable only within the limits of crystal perfection. The other physical characteristics have been seen to have significant effects on fabrication, microstructural development and properties of materials produced from a powder.

**Effect on Fabrication Processes**

As contrasted with the chemical character of the powder which chiefly affects the sintering or thermal processing stages of compaction fabrication, physical character affects the cold compaction of powders as
well. Although only dry compaction, or pressing, is considered within the scope of this investigation, it should be remembered that other cold-forming methods such as extrusion, slip casting, jiggering, molding, etc. are also greatly dependent on physical characteristics of the powder raw material. The effects of size and size distribution on pressure-compaction have been mentioned as only becoming significant for particles of less than 0.12 micron diameter. Kostelnik, Kludt and Beddow agreed, finding particle shape to be more significant and also that the effect of particle size on pressure-compaction decreased as particles became less irregular in shape. Cooper and Eaton considered that compaction was controlled first by filling of spaces greater than the particle sizes by particles sliding over one another. The second mechanism they proposed was the filling of spaces smaller than the particles by fragmentation or plastic deformation. The amount of spaces larger than particles would be a direct function of the bulk or tap densities of the powder. The amount of small spaces would be affected by the degree of agglomeration and/or aggregation as well as by particle size distribution. Topography, or particle surface texture would be expected to have a direct effect on friction
effects. Train and Carrington\textsuperscript{66} concluded that calculations of container-particle friction should include allowances for inter-particle friction and deformation of particles.

Particle size was shown by Oudemans\textsuperscript{67} to affect frictional forces. This was probably due to surface area correspondence with particle size.

Sintering densification has been shown to be extensively affected by physical characteristics of the powder raw material. Johnson and Cutler\textsuperscript{68} concluded that initial sintering was slowed by non-ideality of particles due to clustering (agglomeration) of powders, and agreed with the many other investigators who universally have found that initial sintering rate is an inverse function of particle size. They also reported that increased compaction pressure enhanced sintering of a clustered powder, but not a non-clustered powder. They reported grain boundary bulk diffusion as the mechanism of initial sintering. On the other hand, Prochazka and Coble\textsuperscript{69} recently used surface area decreases during sintering of alumina compacts to conclude that initial sintering is dominated by surface diffusion. Vergnon\textsuperscript{60} had reported identical surface areas of specimens formed from microspheres
before and after compaction. Fracture of corners from less regularly shaped particles and aggregate necks would tend to slightly increase pressed compact surface areas, but compact surface area would approximate particulate surface area, even in the latter cases.

Microstructural development is also profoundly influenced by particulate physical characteristics. Burke reported that discontinuous grain growth during later sintering stages may result from a distribution of sizes, even when green compaction is improved. Bruch attributed the formation of porous regions or "measles" in sintered microstructures to aggregates in the initial powders. Similarly, Mistler and Coble suggested that duplex microstructures might result from monosized, high purity powders, if agglomerated before pressing.

Effect on Properties

Properties of a finished ceramic body are more closely related to its microstructure than to the physical characteristics of the particulate raw material. The effects of microstructure on electrical, chemical and optical properties were discussed previously. The effects of the microstructural characteristics of grain size and porosity on
mechanical strength at room temperature have not yet been reviewed herein, although creep relationships were mentioned earlier. Since grain size is a direct function of particulate raw material size, a brief discussion is in order. Knudsen developed an expression based on his literature review and correlated it with experimental data, as follows:

\[ S = kG^a e^{-bP} \]

where 
- \( S \) = strength
- \( G \) = grain size
- \( P \) = porosity
- \( k \) = proportionality constant

and \( a \) and \( b \) = rate constants.

The rate constants \( a \) and \( b \) are typically 0.5 and 5.0, respectively. Although other equations have been proposed, the relationship of decreasing strength with increasing grain size and/or porosity are widely accepted.
EXPERIMENTAL PROCEDURE

The organization of the overall program is illustrated by the schematic diagram shown in Figure 1. The first phase involved the selection and preparation of powders to be studied and included the development of a technique to prepare an alumina powder by flame-reactor synthesis. In terms of the powder processing sequence, powder pretreatment was the logical second phase of the program. Chronologically, powder pretreatment studies were performed after phases one, three, four and five were carried out for as-received study powders. Work with the as-received powders thus indicated the need for and the direction of powder pretreatment studies. Powder characterization comprised the third phase of the investigation and included determination of physical, chemical, surface chemical and rheological, and structural characteristics of the powders. The fourth phase was specimen fabrication. The final and most important phase of the program was an evaluation of microstructural development and strength in bodies prepared from the different powders.
Figure 1. Schematic diagram of experimental procedure
under study and a correlation of powder characteristics, as determined in phases one or two, three, and four with microstructural development. Special approaches were used to better understand and clarify some of the more significant variations in characteristics. Because the most significant variations in as-received powders involved physical characteristics, and particularly aggregate structure, special attempts were made to better understand the effect of aggregates on powder processing, microstructural development, and strength properties.

Some of the special studies involved techniques of ball milling to comminute aggregated powders while others involved pelletizing methods. Still other studies involved the effect of calcination procedures on the origin of aggregate structures in alumina powders. All such powder pretreatments will be discussed later. Another special study was concerned with characterization of aggregate strength using pressure-compaction data, and is discussed in the Appendix.

Phase I - Selection and Preparation of Raw Materials

Aluminum oxide was chosen as the reference material for the investigation. This selection was
based on several criteria, one of which was the availability of different types of alumina powders. Not only were numerous commercial powders available, but experimental powders could be prepared by several different techniques to obtain powders with a wide variety of characteristics. One such powder had already been developed by calcination of ammonium alum. Preparation of ceramic powders by flame reaction of halogen compounds in the vapor state and by vapor phase decomposition of organometallic compounds were undertaken in an effort to obtain ceramic powders with improved characteristics. Experimental powders could also have been prepared by hydrogenation and calcination of organometallic compounds, by freeze drying and calcining aluminum salt solutions, or by precipitation and calcination of aluminum salt solutions. Although powders prepared by all of these techniques were not planned for evaluation in this program, this flexibility provided a means of attaining powders with specific characteristics as dictated by the early results of the program.

Other reasons for selection of alumina were (1) its wide acceptance as a useful, high-quality ceramic material, (2) the extensive background information available on the material both as regards research results and commercial production technology,
and (3) the sensitivity of alumina to microstructural variations and inhomogeneities. This latter criterion was also the basis for selecting "pure" alumina rather than a composition in which additives would be used to change its character.

Preparation of Powder by Flame Reactor Synthesis

The objective of this phase was to prepare powders for subsequent analysis and for use in fabricating research samples. The primary powder developed was an alumina prepared by vapor-phase flame-reactor synthesis. By this technique, a high-purity submicron powder which is essentially monodispersed (very narrow range of particle sizes) can be produced in a relatively un-agglomerated form. The technique is analogous to the synthesis of rutile (TiO₂) for the paint pigment industry. For the synthesis reaction being studied

\[ \text{Al}_2\text{Cl}_6(g) + \frac{3}{2} \text{O}_2(g) = \text{Al}_2\text{O}_3(s) + 3\text{Cl}_2(g), \]

with the free-energy change calculated to be -57.3 kcal/mole at 1300 K. The free-energy change is less negative at higher temperatures. When the Al₂Cl₆(g) and O₂(g) are mixed in an effective manner, some control over the number of nuclei is possible. With the proper number of nuclei, growth of the particles is limited to a narrow particle-size range, providing the reactant concentrations are controlled and the
residence time is limited. During synthesis of the powder and in subsequent handling of the powder, the powder was exposed only to -50 C dew point air, O₂, or N₂ and to the coating atmosphere. This allowed an analysis of the effect of absorbed water and possible structural water on powder characteristics. For the initial phases of the program, the target purity level was 99.99 percent.

The use of monodispersed powder was expected to simplify interpretation of the initial studies by essentially eliminating the effect of particle size distribution from the list of variables. In order to evaluate the effect of particle size, it was planned that at least two particle sizes would be prepared for evaluation. Tentatively, these two sizes were 0.05 and 0.5 microns.

Details of this powder synthesis development work were discussed by Mezey, Bennett, and Niesz.¹⁶

Selection of Commercial Powders

In addition to the synthesized alumina powder derived from AlCl₃, two commercial powders were selected for characterization and evaluation with respect to microstructural development as affected by powder characteristics. These powders were selected on the basis of high purity, small particulate
size, and variability in method of preparation and in the starting materials from which they were generated.

XA-16 alumina powder was supplied by Alcoa (The Aluminum Company of America) with a median particle size reputed to be 0.6 micron and a narrow size distribution. Published data indicated a typical purity level of the XA-16 powder of 99.78 percent alumina. The material is a superground calcined product, prepared by the Bayer Process, which is dry ball milled with the addition of a surface active agent to break down the powder to its ultimate particle size. Available information indicates that an organic grinding aid of proprietary nature is present in this alumina powder as supplied. Ceramic grade XA-16 alumina powder consists of specially selected lots of powder which are said to meet the purity specification of 99.78 percent alumina.

Although information concerning the processing history and origin of Linde A alumina powder is considered proprietary, this powder is thought to be a calcined product derived from ammonium alum \( \left[ \text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O} \right] \). According to published data, the median particle size of the Linde A alumina powder is 0.3 microns and the purity level is 99.98 percent alumina. Ceramic grade powder consists of screened lots which have been checked for agreement with
property specifications. The Linde A alumina powder was obtained from the Electronics Division of Union Carbide Corporation.

**Phase II - Powder Pretreatment**

In terms of the powder processing sequence, powder pretreatment is logically Phase II of this program. Sequentially, however, powder pretreatment was undertaken after completion of Phases III, IV and V for the three as-received powders. This was done because the reference data obtained with these materials showed that their physical characteristics, and particularly aggregate structure, dominated powder processing behavior and microstructural development to the 95 percent densification level. The work with pretreated powders included only those portions of Phases III, IV, and V selected to provide useful information regarding variation in aggregate character and the effect of aggregate variability on subsequent powder processing behavior and microstructural development and variability.

**Dry Ball Milling**

Dry-ball-milling experiments were performed only on Linde A alumina powder, since XA-16 was supplied as a dry-ball-milled powder and thus provided an excellent basis of comparison. The objective of
these experiments was to reduce Linde A alumina to its ultimate particles. It was felt that the most significant correlation between the as-received powder characterization and the sintered body microstructures resulted with Linde A alumina which was seen to be comprised of two dissimilar aggregate types, one of which was composed of relatively fine particles and was also highly porous, which resulted in porous zones or pockets in the sintered microstructures. Thus, the ball milling of Linde A to eliminate these aggregates offered an excellent opportunity to study and correlate the effect of aggregates in alumina powders on powder processing, microstructural development, and strength properties. The addition of naphthenic acid, a hydrophobic grinding aid, was made to reduce mill packing during grinding. This addition was made to 25.4 gram batches in incremental amounts of 1/4 weight percent at times found in preliminary experiments to correspond with an increasing tendency toward mill compaction, following the example of Berry and Kamack.814 grams of 1/2-inch-diameter milling media composed of 99.5 percent alumina (Degussit) were used for all reported grinding experiments. This resulted in a 32:1 ratio of grinding media to alumina charge weight, as suggested
by Somers. Initial attempts to increase milling yield by using about 1500 grams of media and 100 grams of alumina (15:1 ratio) resulted in mill packing.

All milling experiments were performed using a 1-liter Degussit ball mill composed of 99.5 percent alumina. The mill speed of 75 rpm was 60 percent of critical for this size ball mill as per usual milling practice. Various means of making the naphthenic acid additions were tried on a preliminary basis. These varied from adding by eye dropper into the powder charge, to coating the balls and mill liner with a solution of the naphthenic acid in IPA (isopropyl alcohol) and then drying prior to adding the powder charge, to making a slurry by mixing the powder charge into a solution of naphthenic acid in IPA before evaporating the IPA. The simple eye dropper additions were found equivalent to other methods tried, and were used in all reported work.

Milling Procedure Evaluation

Approximately 1-gram samples were drawn at elapsed milling times of 0, 1, 2, 5, 8, 10, 15 and 20 hours during dry-milling trials. After each draw the mill lid edges, seal, and neck were scraped free of accumulated powder using a rubber spatula.
Draw samples were examined visually with a Hitachi transmission electron microscope, chiefly at 30,600 and 96,000 magnifications. Surface area of each sample was determined using a Strohlein areameter.

**Powder Preparation and Study**

Based on the evaluation of draw-trial samples, milling times of 5 and 20 hours were chosen for preparation of study powders. These dry-ball-milled powders were then characterized and fabricated into research samples. Finally, the microstructure and strength properties of the sintered samples were correlated with powder characteristics and processing behavior.

**Pelletization**

Investigations of pelletization effects were performed using pellets prepared by a technique consisting of spraying a 3 percent solution of distilled water and wetting agent (Solar S-2552) into a rolling polyethylene drum containing dry-ball-milled Linde A alumina. Approximately 0.75 cc of solution per gram of alumina powder were required to obtain a consistency that would pelletize. Using a one gallon drum rolling at about 100 rpm, about 50-gram batches of powder
resulted in the best pelletizing behavior.

In a preliminary study, sample lots were prepared with concentrations of 0, 1-1/2, 3, and 4-1/4 percent stearic acid binder. Perhaps because wet milling was used in the preliminary work, the stearic acid adversely affected milling efficiency. Pressure-compaction data for the preliminary sample lots did not differ significantly, either. Therefore, for this base study of pelletization effects, no binder was added to the dry-ball-milled powder. In the preliminary pelletization study, each sample lot was split so that one segment was rolled as the last step before overnight drying, and the other segment was last sieved through a 20-mesh sieve with no subsequent rolling. The portion rolled last contained smoother and rounder pellets, whereas the pellets sieved last were rougher, but more uniform in size. For this base study, the pellets were rolled after sieve sizing.

Pelletization Procedure Evaluation

The goal of this study was to increase the bulk density of the powder and to improve its rheological or flow characteristics so that more uniform green compacts could be obtained. Therefore, comparison of the various pelletization experiment samples was based
on pressure-compaction curves, tap densities, and flow rates through a 20-degree cone.

**Powder Preparation and Study**

Linde A alumina dry ball milled for five hours was chosen as the powder material for initial study of the effect of pelletization on subsequent powder processing and microstructural development. After preparation as described above (no binder-rolled last), the pelletized powder was dried overnight at 125°C before characterization and incorporation in sample compacts. The microstructure and strength of sintered compacts were correlated with powder characteristics and processing behavior.

**Calcination Studies**

Another approach to linking microstructural defects to particulate physical properties, and especially aggregates, is to eliminate the aggregates present in Linde A alumina. For this study a sample lot of gamma-alumina powder representative of the Linde A precalcination material was obtained. The time-temperature calcination combinations for complete gamma-to alpha-alumina transition in room air accompanied by minimum interparticle sintering, were first obtained by experimentation.
The next phase of this calcination study was to calcine samples of the gamma alumina over selected temperature ranges for 2 hours under each of the following conditions:

1. Powder stationary in room air
2. Powder stationary in flowing dry air
3. Powder tumbling in flowing dry air
4. Powder stationary in vacuum
5. Powder tumbling in vacuum

Preparation of lots (2) and (3) were preceded by brief experiments to determine the dry air flow/powder mass ratio necessary for a minimal dew point or for maximum retained surface area, which ought to coincide. The first five methods above were selected on the basis of evidence indicating that moisture in the furnace atmosphere will promote sintering of alumina by surface diffusion, that tumbling of the powder will limit static particle contacts and thus inhibit sintering, and that surface diffusion in vacuum is slower than in air. The tube furnace used for these experiments was operated vertically in preparing lot (2) to force air to go up through the powder rather than over it and also to try for a
fluidized bed effect. The sixth method was added when initial results indicated that promotion of sintering effects might be desirable under certain conditions.

After comparative evaluation of the calcined alumina samples as described, preparation of research samples incorporating these powder samples and characterization of microstructural and property development were to follow if improved particulate structure were obtained. Such follow-up is not considered to be within the scope of this presentation. However, the results of calcination experiments are expected to be of considerable value in understanding aggregate behavior and character and will be included.

Calcination Procedure Evaluation

Evaluation of samples calcined by various procedures involved X-ray analysis, surface area determination, and examination by transmission electron microscopy. Higher measured surface area was taken to be an indication of less sintering for the calcined powders. X-ray analyses were performed using diffraction patterns run over the limited 2θ range of 42- to 46- degrees, which includes major alpha- and gamma-alumina peaks as determined using the 100 percent gamma-alumina precalcination material
and the 100 percent alpha-alumina Linde A. Relative amounts of the 2 alumina phases were determined as follows. For each sample, the ratio of the gamma peak intensity to that of the pure gamma alumina under identical testing conditions was calculated. The same was done for the alpha peak. The two amounts were then adjusted to total 100 percent, keeping their proportions constant.

Phase III - Powder Characterization

The objective of this phase was to provide a complete analysis of the powders being studied. Three powders were completely evaluated and used to study subsequent microstructural development. This established reference data and facilitated the choice of the most meaningful characterization methods for subsequent work. Other powders were partially evaluated in developing the techniques for producing any pretreated powders desired for subsequent study. Such partial evaluations are referred to as procedure evaluations. Characterization of pretreated powders was not as complete as was the case for non-pretreated powders. Instead, the pretreated powders received only that characterization deemed most meaningful for interpreting subsequent powder processing and
Microstructural development.

A combination of techniques was utilized to quantitatively determine the various particle characteristics thought to be significant in determining the microstructure developed during processing. In all cases, the measured characteristics were analyzed in terms of their effect on microstructure development. Measurement of those characteristics found insignificant was discontinued, whereas possibly new methods will eventually need development to characterize other properties not initially identifiable.

Chemical

Ceramic grade XA-16 powder from lot number D-9545-20 was obtained from Alcoa and is referred to as XA-16(2). Linde A alumina powder, ceramic grade, was obtained from the same lot, number 1400, used in a program at IIT Research Institute and is referred to as LA(2). Additional Linde A alumina referred to as LA(3) and LA(4) from lots 1547 and 1567, respectively, was obtained when the original supply was unexpectedly exhausted. Extreme care was taken to insure that lot-to-lot variability would not affect subsequent results. These powders were analyzed chemically by emission spectrography and by spark
source mass spectrography to determine their contaminating impurities. In addition, combustion techniques were utilized to determine carbon contents. All powder handling was performed on a laminar-flow clean bench. Plastic utensils were used to avoid introduction of metallic contaminants and handlers were required to wear lint-free smocks and caps. Before initial use and between samplings, powders were stored in a constant temperature, constant humidity clean room.

The reactor-synthesized powder identified as BMI-10 was also analyzed chemically by emission spectrography and by spark source mass spectrography to determine impurity content. Powder handling techniques were modified to include handling of BMI-10 powder in a nitrogen atmosphere during all sampling and handling procedures, through use of a polyethylene glove bag (Instruments for Research and Industry, Inc., Cheltenham, Pennsylvania).

In order to determine the location of impurities and their variation from particle to particle, electron microprobe analyses of selected particles were planned, and were to be related to other features of the particles such as size, shape, etc. This work has been deferred until the initiation of effort involving
higher sintered densities. Thus, the location of sintering aids will be traced as a function of processing methodology, using the electron microprobe.

Structural

Structural characterization involved phase analysis by X-ray diffraction for major phases and by electron diffraction on isolated particles to identify minor phases.

Differential thermal analyses were utilized to determine the temperatures at which conversion of alumina phases occurred in powders containing polymorphic phases other than the high temperature stable phase, alpha alumina. Alcoa XA-16 was run against Alcoa Tabular Alumina T-61, which is known to be solely alpha alumina. Linde A and BMI-10 alumina were then run against XA-16 alumina to minimize particle size variation effects. All determinations were made to 1200°C in air.

Physical

Physical measurements were made to determine surface area, particle size distribution, particle shape, particulate microstructure, and surface topography. In addition, the agglomerate size distribution, shapes and
microstructural, and the bulk and true densities of the powders were measured.

Surface area was measured by standard BET techniques, and by Strohlein areameter.

Particle and agglomerate size distribution and shape were studied by electron microscopy methods, because of the small particle size of the powders. Standard Coulter Counter measurements of particle size were also made. Since this technique does not distinguish between particles and agglomerates, it provided a convenient check on the degree of dispersion of a powder. The size distribution of pellets formed in pelletization pretreatment of Linde A was determined using conventional sieve analysis techniques with U. S. Standard Sieves.

The microstructure of particles and aggregates were determined by direct examination of particles on a very fine carbon grid, using a Hitachi transmission electron microscope with magnifications of 30,600 and 96,000X.

Surface topography studies of individual particles were also conducted to determine the significance of this particle characteristic on microstructure development. This characteristic of particles would be expected to have a decided effect on the structure
and properties of a consolidated body. If the particles are of a size that can be resolved (approximately 5 microns), their surfaces can be studied using optical microscopy with reflected or oblique illumination. However, only limited attempts have been made to study the surfaces of particles which approach the limits of resolution of optical microscopy or which require electron microscopy. Normally, when particles are examined by electron microscopy, they are dispersed on a substrate and placed directly in the microscope. Using this method, only the surface contours of the particles are seen, and, as a result, the true surface features cannot be determined.

The use of a Cambridge scanning electron microscope was chosen to provide useful knowledge regarding particle topography, by virtue of the greater depth of field available with this instrument, and also the universal stage feature which allows the viewing of a particle from various directions. Stereo pairs of photographs were obtained and viewed with accessory equipment, allowing still better insight into the topographic character of the powder samples. Because of limitations due to electrical charge build-ups on the non-conducting alumina particle surface, useful magnifications were limited to maximum of about 10,000X.
A thin gold film (few angstroms thick) was applied to particles dispersed on the electron-microscope stools by first dispersing the alumina particles with pH 3 water (adjusted with HCl), and then spraying the stool surface using a small atomizing bottle.

The bulk or tap density of powders was determined by volumetric analysis, and the true density by helium displacement. This latter technique involved use of a Beckman Model 930 air comparison pycnometer.

Rheological

Two techniques were employed to characterize the rheology of particulate systems. The flow rate through a 20-degree cone with a 3/16-inch diameter orifice was used to characterize the flow of the particulate system. The compaction behavior of particles during pressing were also analyzed quantitatively. A pressure-compaction curve was determined for the sample powders by determining the green densities of samples pressed uniaxially and/or isostatically at pressures ranging from 1.5 up to 100,000 psi. Comparison with the tap density of the powders prior to pressure application yielded compaction ratio information for the powders. The significance of these measurements in microstructural development was studied as a function of aggregate breakdown and particulate fracture, as well as compaction.
Two methods for obtaining compaction data at very low pressures (less than 1000 psi) were explored. The first involved use of an apparatus for examining intrinsic powder strength. The second involved pressing in a steel die. In the latter work, sample thickness/diameter ratio was minimized to reduce frictional effects. Both methods yielded essentially the same results on representative samples, so the easier die method was selected for subsequent work as reported.

Data from 1.5 to 20,000 psi were obtained using a double-acting steel die. The die was lubricated with a thin film of zinc stearate prior to initial loading of the powder using 60-cps vibratory compaction. Only a small powder charge was used to minimize frictional effects, resulting in a thin pressed disk. The density of the vibratory-compacted powder, referred to as the tap density, was determined using the fill volume and the weight of the resulting disk after compaction, according to the following relationship:

\[
\text{Tap Density} = \frac{\text{weight}}{\pi (\text{radius})^2 (\text{fill depth})}
\]

The compacted density corresponding to any pressure was determined from the sample height, the die diameter, and sample weight by use of the expression:

\[
\text{Density} = \frac{\text{weight}}{\pi (\text{radius})^2 (\text{sample height})}
\]
Sample height corresponding to a given pressure was obtained by punch travel measurements, made after pressure release.

Compaction data were determined over the range 1000 psi to 100,000 psi using isostatically pressed pellets. Powder was loaded into a thin rubber bag lining a 3/4-inch diameter by 1-inch deep mold with a hemispherical bottom, using 60 cps vibratory compaction. Air was evacuated from the packed powder by inserting a hypodermic needle connected to a vacuum manifold through a rubber cork fitted with a cotton insert, prior to sealing the rubber bag. Pressures in the range 1000 psi to 2700 psi were applied isostatically by introducing nitrogen gas into a steel bomb containing the pellet samples. Pressures in the range 3000 to 100,000 were applied to pellet samples in an isostatic pressing chamber utilizing a liquid pressure medium.

Densities of the irregularly shaped pressed sample pellets were determined by immersion methods, after applying a thin parawax coating to the samples to prevent slaking down of the samples during immersion. Allowance for the wax coating was made in the density calculations, by use of the following formula:
Density = \[ \frac{W}{T} \]

\[ \frac{W - W}{C} \frac{I - W}{D} - \frac{C - T}{D} \]

where

- \( W \) = true sample weight, in gms.
- \( T \) = coated sample weight, in gms.
- \( C \) = immersed weight of coated sample, in gms.
- \( I \) = density of water, in gms/cc.
- \( W \) = density of coating (determined from coating applied to impervious material of predetermined density, by manipulating the above formula), in gms./cc.

To provide a comparison of tap densities obtained during steel die charging, as previously described, data were taken for tap densities resulting from pellet mold loading procedures.

Tap density was taken to be the density of alumina powder charged into the pellet mold before application of isostatic pressure. This value was determined by weighing the powder required to pack the mold full and by pipetting a known volume of water to fill the mold to the same level and applying the formula:

\[ \text{Density} = \frac{W}{V} \]

\[ \frac{V}{W} \]
where $W$ = powder weight, in gms.

and $V_w$ = water volume, in cc.

Thus, tap density provided a zero pressure point on the isostatic pressure vs. density curves.

Examination of pressure-compaction data for the three as-received alumina powders revealed widely varied behavior. Attempts to correlate this data with observed differences in microstructural development in compacts fabricated from the powders indicated that the strength of aggregates in powders was important and that a better understanding of powder compaction behavior as reflected in pressure-compaction data might lead to an ability to predict the strength of aggregates in powders. If so, an important tool for correlating particulate character to powder processing and microstructural development would be the result. The Appendix describes special studies undertaken with regard to this attempted strength characterization of powder aggregates.

**Phase IV - Specimen Fabrication**

The objective of this phase of the investigation was to prepare research samples for evaluating the effects of various powder characteristics on microstructure development. The primary fabrication technique used was isostatic pressing and sintering. In the initial phases
of the program, an effort was made to fabricate specimens without the aid of binders or lubricants and without a preliminary powder treatment such as spray drying or pelletization to improve the flow characteristics of the powder. Sintering was conducted in a dry air atmosphere with a constant dew point.

Isostatic pressing was chosen for the preliminary consolidation technique because of the proven ability of this technique to minimize density gradations and inhomogeneities in green compacts. It also represents a forming technique utilized widely in the manufacture of high quality alumina shapes.

Sintering was chosen as the final densification technique since it represents the approach conventionally used to obtain dense fired ceramic bodies. Bodies densified by sintering are also more sensitive to variations in most powder characteristics than are those densified by other techniques such as hot pressing. Thus, the effects of powder characteristics can be more easily isolated. Initially, sintering was conducted at conventional heating rates in dry air (−48°F entering dew point) and modifications in this technique were not found necessary since measurements of dew point at the furnace tube exit did not show excessive variations.
Compacts from As-Received Powders

Approximately 1/2-inch diameter cylindrical bar samples were produced from each of the three as-received powders at 54.2, 55, 75, 90 and 95 percent of theoretical density by isostatic pressing and sintering. The 54.2 percent density samples were the green compacts, and the 55 percent density level was selected to examine the microstructures after sintering to a temperature where shrinkage was initiated.

The isostatic pressures used to obtain 54.2 percent relative densities for the green compacts were 5000 psi for Alcoa XA-16, 100,000 psi for Linde A alumina, and 85,000 psi for BMI-10 powder. The latter was calculated by allowing for conversion of the conglomerate alumina phases to alpha alumina during sintering, using as a basis the ratio of the measured true densities. The isostatic pressures noted above were used in order to eliminate green density as a variable, whereas significantly different results would have been obtained if pressing pressure has been held constant.

Processing data for fabricated samples are shown in Table 1. Powder compacts were sintered in a tube furnace with a proportional controller, with all
<table>
<thead>
<tr>
<th>Type of Alumina</th>
<th>Isostatic Compaction Pressure, psi</th>
<th>Sintering Temperature, °F</th>
<th>Furnace Air Exit Dew Point, °F</th>
<th>Apparent Density, g/cc</th>
<th>Relative Density, %</th>
<th>Percent Porosity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linde A</td>
<td>100,000</td>
<td>2735</td>
<td>-36</td>
<td>3.800</td>
<td>95.3</td>
<td>4.7</td>
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<td>&quot;</td>
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<td>-40</td>
<td>2.360</td>
<td>59.2</td>
<td>40.8</td>
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<tr>
<td>Alcoa XA-16</td>
<td>5,000</td>
<td>2730</td>
<td>-41</td>
<td>3.800</td>
<td>95.3</td>
<td>4.7</td>
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<tr>
<td>&quot;</td>
<td>2567</td>
<td>-37</td>
<td>3.595</td>
<td>90.2</td>
<td>9.8</td>
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<td>2417</td>
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<td>3.080</td>
<td>77.5</td>
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<td></td>
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<td>2.305</td>
<td>57.8</td>
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<td>EMI-10</td>
<td>85,000</td>
<td>2877</td>
<td>-40</td>
<td>3.771</td>
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<td>-30</td>
<td>3.553</td>
<td>89.1</td>
<td>10.9</td>
<td></td>
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<tr>
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<td>76.8</td>
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<td>-43</td>
<td>2.310</td>
<td>57.9</td>
<td>42.1</td>
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</table>

*All sinterings incorporated one hour soak periods.*

*Apparent densities were determined by xylene displacement method.*

*Relative density data are based on 3.987 g/cc theoretical density for alpha alumina.*

*Percent porosity data were obtained as difference between relative density and 100 percent.*
samples being heated to the normal sintering temperature at a rate of 360 F per hour and soaked one hour at maximum temperature. When the furnace power was turned off at the end of the hour, the temperature drop-off was quite fast. All furnace fixtures were 99.5 to 99.7 percent alumina, excepting a platinum tray holding T-61 alumina grain to support the samples.

The atmosphere used in sintering the samples was bottled air (-48 F dew point), flowing at 6 cubic feet per hour. Exit dew point measurements ranged from -32 to -43 F, as determined during the soaking portion of the sintering runs, using an Alnor dew pointer.

Relative densities determined by xylene displacement were used as a guide to determine the sintering temperatures resulting in the desired densification levels for sample compacts.

Successfully fabricated bars were finally machined into test samples, using diamond grinding techniques.

Compacts from Pretreated Linde A Alumina

Approximately 1/2-inch diameter cylindrical bar samples were prepared from each of the three pretreated study powders by isostatically pressing to 54.2 percent density, followed by sintering to 90 and 95 percent
theoretical density. The 54.2 percent green density was the same as that for previous samples fabricated from as-received Linde A for which reference data was obtained.

The isostatic pressures used to obtain 54.2 percent of theoretical density for the green compacts were 12,000 psi for Linde A dry ball milled 5 hours, 3000 psi for Linde A dry ball milled 12 hours, and 5000 psi for pelletized Linde A that had been dry ball milled for 5 hours. Thus, green density was eliminated as a variable.

Processing data are shown in Table 2 for samples sintered to densities that were nominally 90 to 95 percent of theoretical density. Powder compacts were sintered under the same conditions as previously described.

Phase V - Evaluation of Microstructural Development

The objective was to determine the significance of various powder characteristics on microstructural development and, consequently, on the property variability of the dense body. Evaluations included metallographic examinations, strength measurements, fractographic analyses, and a combination of techniques to trace the change in pore structure and free surface area of the compact. All of the measurements were made at several density levels in order to follow microstructure
<table>
<thead>
<tr>
<th>Powder Pretreatment Description</th>
<th>Isostatic Compaction Pressure, psi</th>
<th>Sintering Temperature, °F</th>
<th>Apparent Density, g/cc</th>
<th>Relative Density, percent</th>
<th>Percent Porosity</th>
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</thead>
<tbody>
<tr>
<td>As-received</td>
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<td>2751</td>
<td>3.775</td>
<td>94.68</td>
<td>5.32</td>
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<td>2760</td>
<td>3.813</td>
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<td>4.37</td>
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<td>&quot;</td>
<td>&quot;</td>
<td>2613</td>
<td>3.581</td>
<td>89.83</td>
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<tr>
<td>5 Hours Dry Ball Milling Plus Pelletization</td>
<td>5,000</td>
<td>2760</td>
<td>3.810</td>
<td>95.56</td>
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<td>2505</td>
<td>3.521</td>
<td>88.31</td>
<td>11.69</td>
</tr>
</tbody>
</table>

a All sinterings incorporated one hour soak periods.
b Apparent densities were determined by xylene displacement method.
c Relative density data are based on 3.987 g/cc theoretical density for alpha alumina.
d Percent porosity data were obtained as difference between relative density and 100 percent.
Chemical analyses were also performed at selected points during fabrication to note any impurity pickup. In addition, the sintering kinetics of various powders were examined.

**Evaluation of Sintering Kinetics**

The objective of this task was to define the initial sintering kinetics of the powder compacts. These data can be obtained by determining isothermal shrinkage as a function of time, at several temperatures. Because of the dependence of the rate of initial stage sintering on the activity of a powder, this technique can serve as a check on whether powder characterization has been complete enough to fully define the activity of the powder.

In the absence of isothermal measurements, useful qualitative comparisons of the relative sintering kinetics of powders can be made by examining data showing densification as a function of the sintering temperature, for samples sintered at constant soaking times. Thus, processing data generated in fabricating research powder compacts at various densification levels by sintering was used, in this program, to compare sintering kinetics of alumina powders.
Selected Chemical Analyses

Selected samples were analyzed chemically to determine the contaminative effects of powder handling and compact sintering procedures. Chips from the compacts were ground in a tungsten carbide mortar for emission spectrographic analysis, in a boron carbide mortar for spark source mass spectographic analysis, and in an alumina mortar for carbon analysis by the combustion technique.

Metallographic Analysis

The objective of this task was to quantitatively analyze the microstructures of samples at various density levels, including green compacts, dense bodies, and several intermediate density stages. Electron microscopy of polished sections was used for this work. To facilitate metallographic preparation, the methods used for these studies involved impregnating the porous green compacts with an epoxy material and then preparing polished cross sections through the impregnated compacts by normal metallographic methods. The prepared sections were then examined microscopically and evaluated for such features as contact area between the individual particles, volume fraction of porosity, distribution of porosity, grain size, and for the general microstructure
of the individual particles.

The microstructural development of the alumina materials could not, in general, be satisfactorily followed by light microscopy due to the small grain size and to the roughness of the porous surfaces which, when polished, were not within the limits of resolution of the light microscope. In a few cases where the grains were large enough for examination with a light microscope at 1000X magnification, the resulting views were not clear, due to the limited depth of field at this magnification and to the slight roughness usually prevalent in a polished porous surface.

Samples were, therefore, examined using a Cambridge scanning electron microscope, after being coated by a thin layer of gold by vapor deposition to provide a conductive surface. The sintered samples had been etched in boiling $\mathrm{H}_3\mathrm{PO}_4$ and broken out of the epoxy polishing mounts prior to gold coating, to reduce the overall sample size sufficiently to fit on the stage of the scanning electron microscope.

Strength Evaluation

The objective of this task was to evaluate the strength of sintered compacts at several density levels. Five nominally identical samples were measured for each
density studied, but extra samples were included in cases where excessive variability was encountered. Because of the sensitivity of mechanical strength to microstructural variations, these measurements provided a meaningful evaluation of the quality of various microstructures.

The diametrical compression technique as adapted for studying dense, brittle materials at Battelle was used. The technique involves loading a solid, right-circular cylinder in compression in a direction perpendicular to the cylinder axis. Failure occurs along the diametral plane that passes through the lines where the load is applied, as a result of resolved tensile stresses. One of the principal advantages of this technique is convenience in the preparation of nominally identical samples, for determination of the variability of strength due to uncontrolled surface or microstructural variations.

Cylindrical samples were prepared from the approximately 1/2-inch diameter sintered bars by diamond grinding. These 0.4-inch diameter by 0.2-inch thick disks were tested using the 5,000-pound scale of a 20,000-pound capacity Instron tensile testing machine equipped with a chart-strip, load recorder with a head
travel speed of 0.1 inch/min. Small index card pieces were placed between the pressure plates of the loading fixture and the sample contact edges to better distribute the testing load, which was applied along the sample axis.

Strength calculations were made using the following expression:

$$\sigma = \frac{2P}{\pi D t}$$

$\sigma$ = maximum tensile strength, psi

$P$ = load at sample failure, pounds

$t$ = sample thickness, inches

$D$ = sample diameter, inches

Fractographic Studies

The objective of this phase was to analyze the fracture surfaces of sintered compacts at several density levels. Fractographic studies of materials is a rather recently developed method for evaluating materials and has been shown to be useful in providing information regarding the properties, behavior and characteristics of material. For example, a recent study has shown a direct correlation between the fracture mode and fracture temperature of alumina. These evaluations were made using a scanning electron microscope and were aimed at determining the fracture modes and the effect of such factors as impurities, porosity, and second-phases. Also,
particular attention was applied to determining the method of initiation of the fractures in the materials, and whether they were initiated by impurities or other microstructural features. However, the tendency of a fracture path to follow the path of least resistance caused the fracture path to pass through neck areas of partially sintered compacts. Thus, data concerning the variation of neck area from one contact point to the next provided considerable insight into microstructural development and the related effect of various particle characteristics. Also, fractography tended to point out the most severe flaws in the microstructure, which provided an effective means of evaluating these flaws, leading to their elimination.

In this program, fracture surfaces of alumina compacts were examined at various stages of densification using the Cambridge scanning electron microscope. Samples were the center segments of diametral compression strength test samples which broke near the average loading for a particular group. Gold coating techniques as described previously were utilized to prevent excessive charging during examination.

A practical limit of 10,000X magnification was established by the tendency toward charging, even in
the presence of the gold coating on the sample.

Evaluations of Porosity and Free Surface Elimination

The objective of this task was to trace the change in surface area and pore size distribution as density increased during the sintering process. BET techniques were used to measure surface area at several density levels. Since surface energy is the primary driving force in sintering, tracing the elimination of surface area was expected to prove helpful in analyzing microstructural development.

Surface area measurements were made on Linde A alumina by multiple point standard BET techniques. These data were used as a standard for all other data obtained, using a Strohlein areameter. Measurements were made for alumina compacts representing all densification stages studied.

The change in pore size distribution with density can be traced by mercury porosimetry. This measurement should be sensitive to inhomogeneities in the green compacts and, hopefully, should provide a means of tracing these inhomogeneities to defects in the final body. It was felt that this technique would be quite valuable as a quantitative technique for analyzing the way in which porosity is eliminated during sintering,
especially the larger pores introduced in the pressing operation as local inhomogeneities.

The bulk and true density changes and the permeability of the compacts were used to evaluate the interconnectivity of pores. These measurements were also expected to prove helpful in evaluating the microstructure development. Bulk density was determined by physical measurement methods, and apparent density was measured by the xylene displacement technique. Helium permeability was to have been measured using a technique widely employed for characterizing porous materials. However, these measurements were not made due to equipment difficulties.
DISCUSSION OF RESULTS

The schematic chart of program organization presented in Figure 1, will again be useful in discussing experimental results. The format will consist of discussing the results of program Phases II, III, IV and V in that sequential order. It should be pointed out that Phase II, which was concerned with powder pretreatment, chronologically followed the completion of Phases III, IV and V portions concerned with as-received alumina powders. Since one of the major program goals was the selection of the simplest set of powder characteristics that completely describe the powder in terms of its effects on powder processing, body fabrication, microstructural development and properties—and the results of Phases III, IV, and V for as-received powders permitted such a selection—this information was put to use during subsequent performance of Phase III, IV and V portions concerned with pretreated (ball milled and pelletized) powders. However, only selective characterization of the pretreated powders was carried out and the fabrication of compacts for study of microstructural development was
carried out at only some of the densification levels used for the as-received powder studies.

**Phase II - Powder Pretreatment**

The objective of every powder pretreatment method studied was to eliminate or simplify the agglomerate or aggregate structure of Linde A alumina. Thus, comparison of the effects of pretreated powders and as-received powders on powder processing, specimen fabrication, microstructural development and properties would provide information on the effect of aggregates on each of these events. The motivation for seeking this information on aggregate effects was that results of studies on as-received powders indicated that variations in the physical characteristics, and particularly aggregate structure, were most significant in terms of variability in microstructural development. Additional studies on characterization of the strength of agglomerates or aggregates are described in the Appendix.

**Dry Ball Milling**

Regardless of procedural variations, all attempts to dry ball mill 100-gram samples of Linde A proved unsuccessful due to packing of the powder charge on the mill walls. Such mill packing tendencies were reduced
when the powder charge was reduced to that amount sufficient to coat the milling media and the mill interior with a thin, not quite continuous powder layer. Powder charges of about 25-grams proved adequate to accomplish this effect. Milling of two such charges comprised Experiments 25A and 25A2. In Experiment 25A, 1/4-parts by weight of naphthenic acid were added initially and after 5 hours milling. Based on observations of mill packing tendencies during the surface area measurements from Experiment 25A, 1/4-part naphthenic acid additions were made initially and after 1, 8, and 15 hours milling in Experiments 25A2. As a result, less mill packing occurred during Experiment 25A2 at extended milling times.

Milling Procedure Evaluation

The effect of dry-ball-milling time on measured surface area of Linde A is shown in Figure 2, representing the two experiments with reduced alumina powder charges of 25.4-grams. The time dependent curves for the two dry-milling experiments showed similar patterns, each exhibiting an early peak followed by a subsequent partial drop and a later buildup and leveling off at about the early peak value. An overall increase
Figure 2. Effect of ball milling on surface area of Linde A alumina
of about 10 percent compared to the surface area of the as-received material is indicated, and might be attributed to fracture of inter-grain necks in aggregates.

Electron microscopy of dry-ball-milled Linde A alumina powder samples showed that dry milling was superior to any wet-milling technique attempted, and also indicated milling times useful to provide study powders for subsequent work. The results of the two dry-ball-milling experiments were similar, but it did seem that Sample 25A2, to which additional incremental naphthenic acid additions were made, was milled with slightly more efficiency at extended milling times.

Because initial electron microscopic observations of powders dry milled for 1, 5 and 20 hours showed extremely contrasting results, additional observations were made of samples milled for 2, 10 and 15 hours. However, the 1, 5 and 20 hour samples appeared to best represent discrete milling stages, whereas the others appeared to be somewhat intermediate.

After 1 hour, the powder aggregates were well dispersed but no significant breakdown of the two aggregate types present in as-received Linde A powder was observed (see Figure 3).
Figure 3. Electron micrographs showing the effect of dry-ball-milling time on particulate structure of Linde A alumina (30,600X magnification)
Because considerable repetition of terminology is anticipated, the chain-like aggregates composed of larger ultimate particles (≈0.1 to 0.3 microns) joined together by neck areas that in many cases approach the particle diameter in size will be referred to by an abbreviated form as LPAs for the remainder of this discussion. Likewise, the cluster-like aggregates composed of much smaller ultimate particles (≈0.01 to 0.02 microns) will be referred to as SPAs.

The SPAs were not fragmented and appeared to be present in about the same proportions as in as-received Linde A. Based on observation of many different sample fields, SPAs seemed to comprise about 10 volume percent of the total aggregate population. LPAs did not appear significantly affected after one hour of dry milling. By the end of five hours dry milling, no complete or significant fragments of SPAs were observable (see Figure 3). The small particles were observed to be attached in a very well distributed manner to the surfaces of the LPAs and the small particles are considered to be in their ultimate size condition. Only slight comminution of LPAs had been accomplished. After 20 hours dry milling, extensive breakdown of LPAs had taken place (see Figure 3). Almost all of the material appeared to be in the ultimate particle condition.
The small particles appeared to be well distributed over the surfaces of the larger particles.

**Preparation of Study Powders by Dry Ball Milling**

The Linde A powder dry ball milled for five hours comprised an interesting study powder because it was expected to isolate the effect of the LPAs since all SPAs were observed to be broken up after five hours milling. The Linde A dry milled for 20 hours also warranted further study, since this comprised a powder with essentially no aggregate structure, but otherwise like the as-received Linde A. Sufficient amounts of study powders representing both the 5 and 20 hour dry-milling periods were prepared so that characterization, specimen fabrication, and evaluation of microstructural development could proceed.

**Pelletization**

A third pretreatment study powder was prepared by pelletizing Linde A after five hours dry milling, because this provided an ideal way to study the effect of pelletizing, with no other variables. The Linde A that had been dry milled for 20 hours was not pelletized because of the time requirements for preparing enough powder for study by that technique, using the small high-purity alumina ball mill that was available, and
because it seemed that the goals of the pelletizing study could be met adequately by the Linde A dry milled for 5 hours.

The pelletization technique consisted of spraying a solution of distilled water with a wetting agent (Solar S-2552) into a revolving drum containing the dry-ball-milled Linde A. No binder was added because of the preliminary experiments which indicated that compaction data was unaffected by small amounts of stearic acid binder, and because of a desire to avoid any unnecessary compositional variables. The wetting agent was necessary because of the hydrophobic nature of the naphthenic acid grinding aid.

The pelletized material was sized between 20 and 100-mesh U. S. Standard Sieves to yield improved flow characteristics. Material outside this size range of approximately 149 to 841 microns was rejected.

Calcination

The results of calcination of stationary powder samples in room air using various time-temperature combinations are shown in Table 3. Calcination at 1225°C for 2 hours yielded the maximum surface area for a completely alpha alumina which was 20.8 m²/g. This compares with 16.03 m²/g for the lot of as-received
Linde A used in base studies.

**TABLE 3**

CHARACTERIZATION OF ALUMINA SAMPLES CALCINED WHILE STATIONARY IN ROOM AIR

<table>
<thead>
<tr>
<th>Calcination Temp, C</th>
<th>Time, hr</th>
<th>Surface Area, m²/g</th>
<th>Percent Indicated Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Gamma</td>
</tr>
<tr>
<td>1150</td>
<td>2</td>
<td>100.2</td>
<td>100</td>
</tr>
<tr>
<td>1150</td>
<td>10</td>
<td>78.0</td>
<td>80</td>
</tr>
<tr>
<td>1150</td>
<td>20</td>
<td>49.4</td>
<td>53</td>
</tr>
<tr>
<td>1175</td>
<td>2</td>
<td>93.2</td>
<td>96</td>
</tr>
<tr>
<td>1175</td>
<td>10</td>
<td>43.4</td>
<td>43</td>
</tr>
<tr>
<td>1175</td>
<td>20</td>
<td>10.32</td>
<td>--</td>
</tr>
<tr>
<td>1200</td>
<td>1</td>
<td>79.5</td>
<td>91</td>
</tr>
<tr>
<td>1200</td>
<td>2</td>
<td>79.6</td>
<td>86</td>
</tr>
<tr>
<td>1200</td>
<td>10</td>
<td>9.64</td>
<td>--</td>
</tr>
<tr>
<td>1200</td>
<td>20</td>
<td>5.93</td>
<td>--</td>
</tr>
<tr>
<td>1225</td>
<td>2</td>
<td>20.8</td>
<td>--</td>
</tr>
<tr>
<td>1225</td>
<td>10</td>
<td>5.37</td>
<td>--</td>
</tr>
<tr>
<td>1250</td>
<td>2</td>
<td>8.42</td>
<td>--</td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>116.5 to 121.0</td>
<td>100</td>
</tr>
</tbody>
</table>

Original experiment design called for preparation of samples by several methods chosen to inhibit sintering tendencies using the 1225 °C - 2 hour calcination condition to produce a series of alpha-alumina samples, and then to compare the characteristics, processing behavior, and microstructural development of these powders. However, limited angle x-ray examination of
those samples quickly showed that 1225 C - 2 hour calcination did not yield 100 percent alpha alumina for most experimental calcination methods. Therefore, a study was initiated to determine the relative temperature relationships for calcination to alpha alumina by each of the methods. Calcination in hydrogen was added to provide information under conditions definitely expected to promote sintering tendencies.

Brief preliminary experiments using 20-gram samples of gamma alumina in the particular experimental calciner, with flow rates ranging from 1 to 30 cfh, indicated that 10 cfh of dry air was necessary for a minimal dew point (-37 F), and maximum retained surface area. Two hours calcining time was held a constant because (1) time-temperature studies of calcination in room air indicated that 1225 C for 2 hours gave maximum surface area for a completely alpha-alumina calcined powder, and (2) overall experimental time could thus be held to a minimum.

Results of the x-ray measurements for the six experimental calcination methods are shown as a function of temperature in Figure 4. The temperature relationships differed for the various calcination methods. Conversion to all alpha alumina was most efficient in dry air, particularly when the dry air was forced
Figure 4. Comparison of alpha-alumina formation by various calcination methods.
through the powder with the tube furnace in a vertical position. Under the latter condition, 1200 C for 2 hours yielded 100 percent alpha alumina. Use of room air required a higher temperature of 1225 C, and hydrogen a still higher temperature, 1250 C, for complete alpha-alumina formation. Using vacuum, at least 1250 C was required for full conversion in 2 hours.

The relationships of surface area to calcination temperature for the various experimental methods are shown in Figure 5. Although this was a logical way to present the data, a much clearer understanding of the data resulted when surface area was plotted as a function of percent alpha alumina (Figure 6) for all the calcination methods. This plot strongly suggests surface area to be a direct function of the completeness of gamma-to alpha-alumina transformation, and to be independent of the calcination technique utilized. The plot also definitely indicates that a maximum surface area for alpha alumina obtained by calcining the Linde A precursor exists at about 20 m$^2$/g. A higher surface area for the same type powder would probably have to be obtained by some other means, such as ball milling, after calcination.
Figure 5. Comparison of surface area data corresponding to various calcination methods
Figure 6. Relationship between specific surface and percent alpha alumina in alumina powders prepared by various calcination methods.
Transmission electron microscope examination of calcined samples containing only alpha alumina yielded very interesting results. Some electron micrographs were selected to illustrate these results and are shown in Figures 7, 8, 9 and 10. The gamma-alumina starting material was composed entirely of large agglomerates or aggregates of very small ultimate particles, possibly 0.01 to 0.02 microns in size (see Figure 7).

Calcination in room air at 1225 C for 2 hours resulted in significant quantities of aggregates composed of the small 0.01-0.02 ultimate particles and comparable volume quantities of aggregates comprised of larger ultimate particles about 0.05 to 0.1 micron in size (Figure 8). Lower temperature calcination at 1200 C for 2 hours resulted in incomplete alpha-alumina formation. No aggregates composed of the smaller ultimate particles could be found in the sample calcined at 1250 C for 2 hours; however, some particulate portions had solidified into comparably large chunks of at least one micron size (see Figure 8).

Calcination of powder at 1200 C for 2 hours in a vertical stationary furnace using a high flow rate of dry air resulted in a mixture of aggregates composed of very small ultimate particles and aggregates composed of larger ultimate particles. The sample calcined
Figure 7. Electron micrograph of gamma alumina prior to calcination at 30,600X magnification.
Calcined at 1225°C for 2 hours

Calcined at 1250°C for 2 hours

Figure 8. Electron micrographs showing particulate structure of alpha alumina formed by stationary calcination in room air (30,000X magnification)
at 1225 C for 2 hours, however, contained only aggregates composed of the larger 0.05 to 0.1 micron ultimate particles (see Figure 9). While it contained no very large chunks, some of the larger ultimate particles were at least 0.2 micron in size. This less complex aggregate structure should make an ideal powder for comparison with as-received Linde A powder.

Rotation of the furnace tube containing the sample powder, while calcining in dry air at 1225 C for 2 hours, yielded a 100 percent alpha-alumina powder which contained a few aggregates composed of the 0.01 to 0.02 micron ultimate particles and mostly particles consisting of large sintered aggregates (see Figure 10).

Stationary calcination in partial vacuum at 1275 C for 2 hour resulted in a mixture of aggregates composed of smaller 0.01 to 0.02 micron particles and aggregates comprised of 0.1 to 0.2 micron ultimate particles. Similar results were obtained by calcination in hydrogen at 1250 C for 2 hours. Rotary calcination in partial vacuum gave similar results except that some aggregates had been sintered together into dense chunks of still larger ultimate particle size. Electron micrographs for these samples are not dissimilar from those present for other samples of the same description.
Figure 9. Electron micrograph showing particulate structure of alpha alumina formed by stationary calcination in dry air at 1225 C for 2 hours (30,600X magnification)

Figure 10. Electron micrograph showing predominant particulate structure of alpha alumina formed by rotary calcination in dry air at 1225 C for 2 hours (96,000X magnification)
It has not proven possible to obtain a calcined, 100 percent alpha-alumina powder with an agglomerate or aggregate structure consisting only of the small 0.01 to 0.02 micron ultimate particles. However, the aggregate structure obtained in an alpha alumina by calcination of powder at 1225 C for 2 hours in dry air in a vertical stationary furnace should provide a useful study powder. This aggregate structure is comprised of only 0.1 to 0.3 micron ultimate particles, resembling the larger aggregate type found in as-received Linde A. Thus, it would tend to isolate the effect of this type aggregate to gain further understanding of the effect of aggregates on processing behavior and microstructural development.

From a commercial viewpoint, the lower surface area of this calcined powder (10.03 m²/g) compared to as-received Linde A (16.03 m²/g) would indicate a less reactive alumina powder. However, the elimination of processing and microstructural development problems due to the porous aggregates might result in a superior product overall. Although ball milling is not really desirable since this would constitute an additional processing step, the difficulty and time required to properly comminute the aggregates would depend on aggregate strength.

This represents an unknown factor, but one which
could easily be determined by using the methods described in the Appendix to evaluate aggregate strength. If the aggregates proved to be weak and/or easily comminuted, a powder with uniformly sized particles of ultimate condition and with significant commercial potential, might easily result.

Phase III - Powder Characterization

Characterization of As-Received Powders

Chemical

Results of the analyses of the alumina powders by emission spectrography and spark source mass spectrography are shown in Tables 4 and 5, respectively.

Major contaminants in the Alcoa XA-16 are \( \text{SiO}_2 \) (0.064%), \( \text{MgO} \) (0.17%), \( \text{CaO} \) (0.028%), \( \text{Fe}_2\text{O}_3 \) (0.029%), and \( \text{Na}_2\text{O} \) (0.13%). The \( \text{SiO}_2 \) originates from bauxite, the mineral from which alumina is produced by the Bayer process and \( \text{Na}_2\text{O} \) is probably a residue of the caustic solution used to solubilize the bauxite. \( \text{MgO} \) is often added to aluminum oxide powder to inhibit grain growth during sintering, but it is uncertain whether the \( \text{MgO} \) analyzed represents such an addition. \( \text{Fe}_2\text{O}_3 \) impurities originate either in the bauxite raw material or from the crushing and grinding steps in processing.

The Linde A powder sample contained \( \text{SiO}_2 \) (0.021%)
### TABLE 4
**EMISSION SPECTROGRAPHIC ANALYSES OF AS-RECEIVED ALUMINA POWDERS**

<table>
<thead>
<tr>
<th>Oxide Constituent</th>
<th>Linde A</th>
<th>Alcoa XA-16</th>
<th>BMI-10</th>
<th>Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SiO}_2$</td>
<td>0.021</td>
<td>0.064</td>
<td>0.107</td>
<td>0.002</td>
</tr>
<tr>
<td>$\text{ZrO}_2$</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>0.002</td>
</tr>
<tr>
<td>$\text{TiO}_2$</td>
<td>N</td>
<td>T</td>
<td>N</td>
<td>0.002</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3$</td>
<td>0.001</td>
<td>0.029</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>$\text{Cr}_2\text{O}_3$</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>0.001</td>
</tr>
<tr>
<td>$\text{Ga}_2\text{O}_3$</td>
<td>0.004</td>
<td>0.004</td>
<td>N</td>
<td>0.001</td>
</tr>
<tr>
<td>$\text{B}_2\text{O}_3$</td>
<td>N</td>
<td>N</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>$\text{MgO}$</td>
<td>T</td>
<td>0.170</td>
<td>T</td>
<td>0.002</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>T</td>
<td>0.028</td>
<td>0.003</td>
<td>0.001</td>
</tr>
<tr>
<td>$\text{BaO}$</td>
<td>N</td>
<td>0.003</td>
<td>N</td>
<td>0.001</td>
</tr>
<tr>
<td>$\text{PbO}$</td>
<td>0.022</td>
<td>N</td>
<td>N</td>
<td>0.001</td>
</tr>
<tr>
<td>$\text{SnO}$</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>0.001</td>
</tr>
<tr>
<td>$\text{MnO}$</td>
<td>N</td>
<td>T</td>
<td>N</td>
<td>0.001</td>
</tr>
<tr>
<td>$\text{CuO}$</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>0.001</td>
</tr>
<tr>
<td>$\text{NiO}$</td>
<td>N</td>
<td>N</td>
<td>T</td>
<td>0.001</td>
</tr>
<tr>
<td>$\text{Na}_2\text{O}$</td>
<td>N</td>
<td>0.130</td>
<td>N</td>
<td>0.007</td>
</tr>
<tr>
<td>$\text{Ag}_2\text{O}$</td>
<td>N</td>
<td>N</td>
<td>T</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Symbols:  
N = Analyzed for, but not detected  
T = Trace, but less than detection limit
TABLE 5
SPARK SOURCE MASS SPECTROGRAPHIC ANALYSES AND COMBUSTION ANALYSES OF AS-RECEIVED ALUMINA POWDERS

<table>
<thead>
<tr>
<th>Oxide Constituent</th>
<th>Linde A (Weight Percent)</th>
<th>Alcoa XA-16 (Weight Percent)</th>
<th>EMI-10 (Weight Percent)</th>
<th>Analysis Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>0.0130</td>
<td>0.0640</td>
<td>0.0640</td>
<td>Emiss. Spec.</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.0029</td>
<td>0.0430</td>
<td>0.0009</td>
<td>&quot;</td>
</tr>
<tr>
<td>As₂O₃</td>
<td>&lt;0.0005</td>
<td>&lt;0.0001</td>
<td>N</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>T</td>
<td>0.0003</td>
<td>T</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ga₂O₃</td>
<td>0.0130</td>
<td>0.0130</td>
<td>N</td>
<td>&quot;</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>N</td>
<td>N</td>
<td>0.0003</td>
<td>&quot;</td>
</tr>
<tr>
<td>MgO</td>
<td>&lt;0.0050</td>
<td>0.1600</td>
<td>N</td>
<td>&quot;</td>
</tr>
<tr>
<td>CaO</td>
<td>0.0014</td>
<td>0.0280</td>
<td>0.0021</td>
<td>&quot;</td>
</tr>
<tr>
<td>BaO</td>
<td>&lt;0.0002</td>
<td>0.0056</td>
<td>N</td>
<td>&quot;</td>
</tr>
<tr>
<td>PbO</td>
<td>0.0160</td>
<td>&lt;0.0005</td>
<td>N</td>
<td>&quot;</td>
</tr>
<tr>
<td>SnO</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>&quot;</td>
</tr>
<tr>
<td>MnO</td>
<td>0.0003</td>
<td>0.0026</td>
<td>T</td>
<td>&quot;</td>
</tr>
<tr>
<td>CuO</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0005</td>
<td>&quot;</td>
</tr>
<tr>
<td>NiO</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0003</td>
<td>&quot;</td>
</tr>
<tr>
<td>CdO</td>
<td>&lt;0.0010</td>
<td>&lt;0.0004</td>
<td>N</td>
<td>&quot;</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.0034</td>
<td>0.0540</td>
<td>0.0013</td>
<td>&quot;</td>
</tr>
<tr>
<td>K₂O</td>
<td>&lt;0.0012</td>
<td>&lt;0.0012</td>
<td>0.0002</td>
<td>&quot;</td>
</tr>
<tr>
<td>Li₂O</td>
<td>N</td>
<td>N</td>
<td>T</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ag₂O</td>
<td>0.0007</td>
<td>&lt;0.0002</td>
<td>N</td>
<td>&quot;</td>
</tr>
<tr>
<td>P</td>
<td>0.0003</td>
<td>&lt;0.0003</td>
<td>T</td>
<td>&quot;</td>
</tr>
<tr>
<td>S</td>
<td>0.0040</td>
<td>0.0040</td>
<td>0.0030</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cl</td>
<td>0.0010</td>
<td>0.0010</td>
<td>0.1000</td>
<td>&quot;</td>
</tr>
<tr>
<td>C</td>
<td>0.013</td>
<td>0.143</td>
<td>0.011</td>
<td>Combustion</td>
</tr>
</tbody>
</table>

N = Analyzed for, but none found
T = Trace, less than the 1 ppm detection limit
< = Less than
and PbO (0.022%) as the most significant contaminants. The processing treatment of Linde A alumina is regarded as proprietary, so the origin of these impurities is uncertain. However, it was learned that Linde A lots that are especially low in Fe₂O₃ can be expected to be higher in PbO.

The BMI-10 powder was 99.89 percent alumina (by difference), as compared to 99.57 and 99.95 percent for XA-16 and Linde A alumina powders, respectively. The major contaminant in the BMI-10 powder was silica (0.107 percent). Since a 99.999 percent alumina metal ingot was used as a starter material for BMI-10, the silica was probably introduced by contamination from the fused silica reactor material. A 99.99 percent alumina powder might result from elimination of the silica contamination in BMI-10 either by substitution of an alumina reactor tube or by lowering of the operating temperatures for fused-silica reactors. The latter course is considered feasible because it appears necessary to calcine the reaction product to produce the alpha phase. Preliminary development work showed that gamma-alumina formation can be effected at considerably lower precipitator temperatures than the 1300 C used for BMI-10 powder.

Combustion analysis data were added to Table 5 and showed 0.011 percent carbon in BMI-10 compared to 0.143
percent in Alcoa XA-16 and 0.013 percent in Linde A, as reported previously. The relatively high carbon content in Alcoa XA-16 is probably attributable to the addition of a hydrophobic grinding aid to this powder, whereas the slightly lower carbon in BMI-10 compared to Linde A may be due to the additional cleanliness of the nitrogen-filled glove bag in which BMI-10 was handled.

In any event, it would be expected that the carbon would be burned out of the alumina powders during heating at sintering temperatures. This uncertainty regarding the origin of powder variables does, however, point out the need for a powder that is produced under conditions where the investigators have complete control over all steps involved in the history of the powder. Such knowledge of the history would aid in pinpointing the origin of variables which affect powder characteristics and, thus, the microstructures of sintered bodies made from the powders.

Although the spark source mass spectrometer method of analysis is usually preferred for quantities of impurities in the order of 10 or less ppmw, it is interesting to compare the metal ion values obtained with those from the emission spectrographic analysis. Doing so results in no major disagreements that cannot be explained by the difference in intended usage for the
two analytical methods.

The high chlorine content (0.10 percent) found in BMI-10 by the spark source mass spectrometer analysis would not be expected to adversely affect microstructure development and properties and might well be eliminated during the sintering process. This chlorine content probably reflects efficiency in oxidizing the $\text{Al}_2\text{Cl}_6$ during production of the BMI-10 powder.

Simultaneous thermogravimetric analysis mass-spectrometry (TGA-MS) was used to examine Linde A, Alcoa XA-16 and BMI-10 from room temperature to 950°C. The TGA-MS equipment consisted of a Cahn recording microbalance coupled to an AEI-MS10 low resolution mass spectrometer. Samples were heated at 4°C per minute from room temperature to 950°C, and the samples were subjected to the high vacuum system used for the spectrometer (less than $10^{-5}$ torr). Weight loss thermograms are shown in Figure 11 for the three alumina powders.

The Linde A alumina powder sample exhibited an abrupt weight loss upon heating, undoubtedly due to loss of surface or free moisture. The rate of weight loss decreases up to 750°C, and no further weight loss was observed from 750 to 950°C. The mass spectral scans exhibited essentially air background with water the only
Figure 11. TGA thermograms for alumina powders
other major peak at m/e 18. The lead impurity in Linde A is evidently tied up in a fairly stable compound.

The greatest weight loss of the three was exhibited by the Alcoa XA-16 alumina powder sample. Mass spectral scans at 100 C showed a variety of peaks above background, e.g. 14, 16, 28, 32 and 44. These could arise from nitrogen, oxygen, and carbon dioxide. Water was also large. By 900 C, mass spectral scan exhibited peaks, above background, at m/e 14, 15, 26, 27, 28, 29, 32, 40, and 41. Undoubtedly the 0.143 percent carbon present in the grinding aid resulted in this complex spectra.

Upon evacuation, but prior to heating, the BMI-10 alumina sample lost 0.17 weight percent. A mass spectral scan of the evolved volatiles indicated normal background plus m/e 18 and 35 suggesting weight loss primarily due to loss of water and chlorine. The relative intensity of the 35 peak increased upon heating up to 250 C and then decreased.

**Structural**

Phase analysis was performed by x-ray techniques for major phases and by electron diffraction on isolated particles to identify minor phases. X-ray analyses were made using high sensitivity diffractometer techniques. As shown in Table 6 only alpha alumina was found in Linde A
and Alcoa XA-16 alumina powders. However, gamma alumina in amounts less than 5 percent could have been present, but undetectable in the samples due to sensitivity limits of the techniques. The BMI-10 flame-reactor-synthesized alumina powder was found to contain less than 20 percent alpha alumina, more than 70 percent theta alumina and equivalently small (less than 8 percent) amounts of kappa alumina and delta alumina. Analysis of electron diffraction data obtained for each of the three aluminas is, thus far, inconclusive with respect to the presence or absence of minor phases.

TABLE 6

<table>
<thead>
<tr>
<th>Phases Observed</th>
<th>Estimated Percent of Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Linde A</td>
</tr>
<tr>
<td>Alpha Alumina</td>
<td>95</td>
</tr>
<tr>
<td>Theta Alumina</td>
<td></td>
</tr>
<tr>
<td>Kappa Alumina</td>
<td></td>
</tr>
<tr>
<td>Delta Alumina</td>
<td></td>
</tr>
</tbody>
</table>

Differential thermal analyses were made for each of the three alumina powders, and the results are presented in Figure 12. Alcoa XA-16 alumina was run against Alcoa
Figure 12. DTA curves for alumina powders
Tabular Alumina T-61, which is known to be solely alpha-alumina. A broad endothermic peak was observed at 360 °C (165 to 525 °C), probably due to a high rate of water loss over this range. No other peaks were observed for XA-16 powder, indicating that no alumina inversions took place. This is evidence that XA-16 is comprised of only alpha alumina. The exothermic change in direction of the background curve at about 1170 °C might be due to the initiation of sintering.

Linde A alumina was run twice against XA-16 alumina as a standard because of the rather complex behavior observed. The plot shown was obtained by subtracting the XA-16 background curve from the DTA trace curve.

Only a small endothermic peak is noted at 375 °C where surface absorbed water was expected to come off. Another small endothermic peak is seen at 750 °C, but its origin has not been explained. Although the Linde A alumina curve is considerably less smooth than the XA-16 trace, no positive evidence of alumina inversion was observed. This indicates that Linde A is essentially alpha alumina.

BMI-10 alumina was also run against XA-16 alumina as a standard. An endothermic peak at 375 °C is probably due to dissipation of water. A broad endothermic peak extends from 900 to 1135 °C and a very sharp, large peak
is centered at 1150 C where inversion to alpha alumina was expected to occur. Delta alumina is expected to invert to theta alumina at 1060 and theta inverts to alpha at 1150, as does kappa alumina.

Physical

Wherever possible, physical measurements were made to determine particle size distribution, particle shape, particulate microstructure, surface topography, agglomerate size distribution and surface area. Meaningful particle size distribution data were not obtainable for Linde A alumina and Alcoa XA-16 alumina because of the physical characteristics of the powder, observable in the photomicrographs of Figures 13, 14, 15, and 16 and in Table 7. Linde A alumina, shown in Figure 13, consisted of particles falling into two separate size groups with average particle sizes of 0.3 and 0.02 microns. The larger particles were sintered into strong aggregates; the finer ones also appeared to be aggregates. Figure 16 illustrates the degree of aggregation of the Linde A powder sample. The average aggregate size was determined to be 2.54 microns.

Particles of Alcoa XA-16 were quite irregular in shape as shown in Figure 14, with an average particle size of 0.25 micron. The agglomerates observed in Figure 16
Figure 13. Electron micrograph showing particulate structure of as-received Linde A alumina (124,000X magnification)
Figure 14. Electron micrograph showing particulate structure of as-received Alcoa XA-16 alumina (20,000X magnification)
Figure 15. Electron micrograph showing particulate structure of as-received BMI-10 alumina (80,000X magnification)
Figure 16. Electron micrographs of as-received alumina powders (10,000X magnification)
are apparently very loosely bound clusters as evidenced by comparison with Figure 14, which shows no neck areas between particles.

TABLE 7

ELECTRON MICROSCOPE EVALUATION OF PARTICULATE ALUMINAS

<table>
<thead>
<tr>
<th>Type Alumina Powder</th>
<th>Average Particle Size, microns</th>
<th>Average Agglomerate Aggregate Size, microns</th>
<th>Comments on Particulate Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linde A</td>
<td>0.30</td>
<td>2.54</td>
<td>Two separate size particle groups. Larger particles sintered into aggregates. Finer particles also appear to be aggregated.</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcoa XA-16</td>
<td>0.25</td>
<td></td>
<td>Particles quite irregular in shape.</td>
</tr>
<tr>
<td>BMI-10</td>
<td>0.13</td>
<td>0.64</td>
<td>Particles generally aggregated into chains with each particle being roughly spherical in shape.</td>
</tr>
</tbody>
</table>

The flame-reactor-synthesized BMI-10 particles shown in Figure 15 generally occurred as chains of weakly aggregated particles, with each particle being roughly spherical in shape. Average aggregate size of BMI-10 powder was 0.64 microns. The particulate roundness
was especially evident by observation of a stereo pair of the scanning electron micrograph shown in Figure 16. Observations of stereo pair electron micrographs though not usable in these figures, have been used throughout this program in evaluating particulate and grain shape and topography. Because of the spherical nature of the BMI-10 particles, size distribution data as shown in Figure 17 were obtainable. The electron micrographs taken at 10,000X magnification with the Cambridge scanning electron microscope were used to determine the particle size distribution of BMI-10 by a direct measurement method. The size distribution of BMI-10 powder was narrow with average particle size of 0.1 microns for the roughly spherical grains. Because of difficulties encountered during the extended BMI-10 production time necessary to get sufficient powder for characterization, this powder did not have uniformity of size and spheroidicity achieved in experimental powder BMI-9, as shown in Figure 18. The powder produced in the small BMI-9 run indicates the potential of the flame-reactor synthesis for producing monodispersed powder. Further work is needed, however, to reduce powder production difficulties.

Coulter Counter results are presented in Figure 19, and show that the agglomerate or aggregate size
Figure 17. Particle size distribution analysis of BMI-10 alumina.
Figure 18. Electron micrograph of BMI-9 flame-reactor synthesized alumina powder (10,000X magnification)
Figure 19. Agglomerate or aggregate size distribution of alumina powders from Coulter Counter measurements.
distributions of Linde A alumina powder and XA-16 alumina powder were similar, with median size of 20 to 25 microns. The considerably lower size distribution observed for BMI-10 powder indicates a considerably lower degree of agglomeration or aggregation. Linde A alumina was dispersed readily with a 1 percent sodium chloride solution. Alcoa XA-16 did not disperse easily, but did disperse better in isopropyl alcohol than in the sodium chloride solution. The BMI-10 powder dispersed very well in isopropyl alcohol. The disparity between these measurements and electron microscopic measurements is indicative of the relatively low accuracy of Coulter Counter measurements on very fine particles. However, preliminary work with methods of dispersing these five alumina powders had shown that a better dispersal resulted from the use of pH 3 solutions of hydrochloric acid, so the disparity between size measurements may be due to insufficient dispersal of particles in the Coulter Counter solution. The pH 3 solution was not used in Coulter Counter work in order to protect the small and delicate internal orifices of the equipment.

Surface area determinations for the alumina powders are listed in Table 8. Linde A powder surface area was determined by multipoint BET techniques to be 16.03 m²/g on the basis of 3 separate sets of
measurements. All other data were obtained using a Strohlein areameter, and the small inherent error of this single-point measurement was corrected on the basis of Linde A powder standard determinations. The lower specific surface of 13.60 m²/g determined for Alcoa XA-16 powder is probably due to the smaller ultimate size observed for one group of Linde A particles. The still smaller 11.25 m²/g specific surface measured for BMI-10 must be attributable to the roundness of the particles, since the average particle size is smaller than that of Alcoa XA-16 powder.

It is interesting to note that the reproducibility of measurements with the Strohlein areameter was much better than those with the multipoint BET technique. The respective data spreads are 0.72 m²/g for four determinations by Strohlein areameter and 1.80 m²/g for three determinations by the multipoint method.

True density determinations were made with a Beckman Model 930 air comparison pycnometer using helium gas, and the results are listed in Table 8. Both Linde A (3.972 g/cc) and Alcoa XA-16 (3.962 g/cc) powders were close to the 3.987 theoretical density of alpha alumina. The BMI-10 alumina powder (3.691 g/cc) was lower, as expected from the x-ray phase analysis.
Assuming complete accuracy of that analysis, the calculated true density would be about 3.595 g/cc.

TABLE 8
SURFACE AREA AND DENSITY MEASUREMENTS FOR ALUMINA POWDERS

<table>
<thead>
<tr>
<th>Type Powder</th>
<th>Specific Surface m²/g</th>
<th>True Density in Helium g/cc</th>
<th>Tap Density (Vibrated) g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linde A</td>
<td>16.03</td>
<td>3.972</td>
<td>0.523</td>
</tr>
<tr>
<td>Alcoa XA-16</td>
<td>13.60</td>
<td>3.962</td>
<td>1.332</td>
</tr>
<tr>
<td>BMI-10</td>
<td>11.25</td>
<td>3.691</td>
<td>1.114</td>
</tr>
</tbody>
</table>

Rheological

Rheological analysis by measurement of flow rate through a 20-degree cone was deferred until characterization work involving pretreatment of powders was in progress, because it was felt that untreated powders would not flow readily and also because direct comparison should provide more meaningful results. These predictions proved to be correct. None of the three as-received alumina powders would flow from the cone unless external force was applied.

Powder compaction data was originally obtained for Linde A, XA-16, and BMI-10 alumina powders, pressed
isostatically at 5000, 10,000, 25,000, 50,000, 75,000 and 100,000 psi, with a minimum of 3 determinations for each datum point. Results are presented in Figure 20 as relative density vs isostatic pressure. BMI-10 compaction data are plotted twice, using measured true density as one basis and the theoretical density of alpha alumina as a second basis. The former curve is useful for comparing powder behavior, the latter for discussing sintering behavior as a function of powder compaction.

It is noticeable that BMI-10 powder is somewhat intermediate to Linde A alumina and Alcoa XA-16 powder in compaction behavior as judged by the pressure at which linear dependency of density on pressure is achieved (about 30,000, about 50,000, and about 10,000 psi, respectively). To more clearly illustrate the comparative behavior of the three alumina powders, Figure 21 is a plot of the same data using a log scale for isostatic pressure.

The slopes of the curves for XA-16 and BMI-10 powders were noticeably shallower than that for Linde A powder. In addition, observed deviations of the data from linearity in the cases of XA-16 and BMI-10 were initially interpreted as possible curve breaks, although it was realized that such an interpretation was based on minimal data. Because it was felt that such varied
Figure 20. Effect of isostatic compaction pressure on relative density of green alumina compacts
Figure 21. Effect of isostatic compaction pressure on relative density of green alumina compacts
compaction behavior could be indicative of important effects of the powder physical characteristics on compaction mechanisms, and because of a lack of interpretive literature on the subject, further study of compaction characteristics using more extensive data seemed warranted. Such a study is described in the Appendix.

Characterization of Pretreated Linde A Alumina

Characterization of the ball-milled and pelletized powders was selective. Only those measurements which could reasonably be expected to vary with powder pretreatment were performed. Measurement techniques which were discussed in detail in previous sections will be referred to only briefly in this section.

Chemical

Chemical analyses of the dry-ball-milled and pelletized study powders are shown in Table 9. An analysis for as-received Linde A from the same sample lot (1567) is shown for comparison. Cations were analyzed by emission spectrography and carbon by the combustion method. Slight amounts of CaO were picked up by the powders during processing. Noticeably missing is the PbO content which was analyzed at 0.022 weight
<table>
<thead>
<tr>
<th>Constituent</th>
<th>As-received Linde A</th>
<th>Linde A Dry Milled for 5 Hours</th>
<th>Linde A Dry Milled for 20 Hours</th>
<th>Linde A Dry Milled for 5 Hours; then Pelletized Analysis Technique</th>
<th>Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>0.004</td>
<td>0.004</td>
<td>0.004</td>
<td>0.004 Emiss. Spec.</td>
<td>0.002</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>&quot;</td>
</tr>
<tr>
<td>TiO₂</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>0.002</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>T</td>
<td>0.001</td>
<td>T</td>
<td>T</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>0.001</td>
</tr>
<tr>
<td>Ga₂O₃</td>
<td>0.004</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
<td>&quot;</td>
</tr>
<tr>
<td>BaO</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>&quot;</td>
</tr>
<tr>
<td>MgO</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>0.002</td>
</tr>
<tr>
<td>CaO</td>
<td>T</td>
<td>0.004</td>
<td>0.004</td>
<td>0.004</td>
<td>&quot;</td>
</tr>
<tr>
<td>BaO</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>&quot;</td>
</tr>
<tr>
<td>PbO</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>0.001</td>
</tr>
<tr>
<td>MnO</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>&quot;</td>
</tr>
<tr>
<td>CuO</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>0.001</td>
</tr>
<tr>
<td>NiO</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>&quot;</td>
</tr>
<tr>
<td>Na₂O</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ag₂O</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>0.001</td>
</tr>
<tr>
<td>C</td>
<td>0.055</td>
<td>0.590</td>
<td>0.930</td>
<td>0.690 Combustion</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Symbols:  
N = Analyzed for, but none detected  
T = Trace, but less than detection limit
percent in the as-received Linde A of Lot 1400. This was expected because discussions with the commercial suppliers had mentioned work to eliminate the PbO from ceramic grade Linde A. The increases in carbon content are directly attributable to naphthenic acid additions which totaled 1/2 and 1 percent, respectively, for the material dry ball milled for 5 and 20 hours. The pelletized material was slightly higher in carbon than the corresponding unpelletized material due probably to both the use of the Solar solution and to the extra handling of the pelletized material.

**Structural**

No structural analyses were made since room temperature physical processing of the Linde A powder would not be expected to alter this characteristic.

**Physical**

Physical analysis comprised evaluation of particle and aggregate size distribution, shape and microstructure with a transmission electron microscope. It also included determination of surface area and bulk or tap density. Since the Linde A powder used in this study was from a different lot than that used in the earlier ball-milling studies, and because it was realized that in draw-trial milling studies
results might vary slightly from milling an undiminishing sample, characterization will not include the data from the milling studies.

Transmission electron microscopy showed that the samples of Linde A dry ball milled for 5 hours and for 20 hours duplicated the results of the milling trials as shown in Figure 3. Linde A dry milled for 5 hours consisted entirely of strong aggregates made up of grains approximately 0.1 to 0.3 microns in size, to which small nonaggregated particles approximately 0.01 to 0.02 microns in size were attached with uniform distribution. Linde A dry milled for 20 hours was composed almost entirely of unaggregated particles, approximately 0.1 to 0.3 microns in size, to which smaller nonaggregated particles approximately 0.01 to 0.02 microns in size were attached with uniform distribution. The shape of the larger particles was somewhat masked by the attached smaller particles, but appeared to be irregular and to contain no internal porosity.

Measured surface areas were 16.50, 19.27 and 15.30 m²/g, respectively, for the Linde A milled for 5 and 20 hours and for as-received Linde A from the same lot (1567). These increases of 7.8 and 25.9 percent, respectively, compare well with those measured on draw
trial samples during the milling studies. Tap densities were 1.14, 1.18 and 0.43 g/cm³, respectively, for Linde A milled for 5 and 20 hours and for the as-received Linde A. The similar increases for the two milled powder samples are probably due to the agglomerating effect of the naphthenic acid milling aid additions.

The size distribution of the pellets containing Linde A dry ball milled for 5 hours was determined by sieve analysis using U. S. Standard sieves. The data, shown in Table 10, indicates a fairly uniform distribution of sizes between the target range of 20 to 100 mesh, but that some pellets have been broken resulting in -100 mesh material.

**TABLE 10**

SIZE DISTRIBUTION DATA FOR PELLETS MADE FROM LINDE A DRY BALL MILLED FOR 5 HOURS

<table>
<thead>
<tr>
<th>U. S. Standard Sieve Size (meshes/in)</th>
<th>Mesh Opening Size (microns)</th>
<th>Weight Percent Retained on Stated Sieve Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>841</td>
<td>None</td>
</tr>
<tr>
<td>40</td>
<td>421</td>
<td>29.4</td>
</tr>
<tr>
<td>60</td>
<td>250</td>
<td>32.4</td>
</tr>
<tr>
<td>80</td>
<td>177</td>
<td>20.7</td>
</tr>
<tr>
<td>100</td>
<td>149</td>
<td>10.9</td>
</tr>
<tr>
<td>---Amount Passed Through 100 Mesh----</td>
<td></td>
<td>6.6</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.0</td>
</tr>
</tbody>
</table>
Rheological analysis was based on pressure-compaction data over the pressure range 1.5 to 100,000 psi, and also on attempted measurements of flow rate through a 20 degree cone with a 3/16-inch orifice.

Pressure-compaction data is presented in Figure 22, using the method described in the Appendix. The curve shown for as-received Linde A from the new lot duplicated exactly the data on previous lots. The pressure-compaction curves for the dry-ball-milled Linde A powders differ strikingly from those for the as-received Linde A. The Linde A powder milled for 5 hours resembles the curve for as-received Alcoa XA-16 (see Figures 57 and 58 for Alumina-II curve) ball-milled commercial reactive alumina. A slight curve break was observed at 4.5 psi and indicated the presence of relatively low strength or weak agglomerates. The fact that no break was seen at a higher pressure is interpreted to mean that the strength of the aggregates composed of larger 0.1 to 0.3 micron ultimate particles, the only aggregates present after 5 hours dry milling, was comparable to that of individual grains due to the large neck areas joining grains. This result verifies previous interpretations (see the Appendix) that the observed break in the compaction curve for as-received
Figure 22. Compaction behavior of dry-ball-milled Linde A alumina
Linde A was due to the porous aggregates composed of smaller 0.01 to 0.02-micron ultimate particles.

The pressure-compaction curve for Linde A dry ball milled for 20 hours contained no noticeable break within the measuring range of pressures. This was interpreted to mean that any agglomerates present were weaker than those in the Linde A dry milled for 5 hours, perhaps due to a slight interloacking of the aggregates present in the latter case. This improved compaction behavior suggested that considerable improvement in microstructural development was possible.

A pressure-compaction curve was also determined for pelletized Linde A that had been dry ball milled for 5 hours. A slight increase was observed in the relative pellet strength over that of the agglomerates of non-pelletized, but otherwise similar, material. At higher pressures, a short range of accelerated compaction of the pelletized material was indicated, after which the slope of the compaction curve matched that of the non-pelletized, but otherwise similar, material.

The 20-degree cone flow measuring device has yielded little data, because most of the powders placed in the cone would not flow through the orifice unless external force was applied, e.g. by vibration. Thus, to date this characterization device has given only flow
versus no-flow type information. Therefore, suffice it to say that whereas as-received XA-16, Linde A and Linde A dry ball milled for 5 and for 20 hours did not flow, the pelletized material did flow. As with all other preliminary pelletized samples evaluated, a 5-gram sample flowed from the cone in approximately 1.2 seconds. These determinations on small samples are not considered representative of results on larger samples, where the gravitational force of overlying material would become a factor.

Phase IV - Specimen Fabrication

All sample compacts were fabricated by isostatic compaction to a predetermined green density level or at predetermined pressures, followed by sintering to a pre-selected densification level.

Compacts from As-Received Powders

Baseline studies were made using compacts which were isostatically pressed to a green density level of 54.2 percent of theoretical density (3.987 g/cc) followed by sintering to varying, predetermined final density levels. Relative density as a function of sintering soak temperature is shown in Figure 23. Sintering densification progressed significantly at slightly above 2000 °F for Linde A and Alcoa XA-16 aluminas. The densification
Figure 23. Effect of sintering soak temperature on relative density of alumina compacts

Figure 24. Sintering kinetics of alumina powders
of BMI-10 powder lagged behind, with compacts being less dense at similar sintering temperatures. This might have been due to energy diversion or to structural disruption, since another factor to be considered is that the various alumina subforms had inverted to alpha alumina before the lowest sintering temperature plotted on the curve for BMI-10. X-ray analysis of the BMI-10 material sintered at that lowest temperature (2094 F) substantiated the DTA data, indicating all alpha alumina in the sintered sample. The lower densification observed with respect to temperature increases above the 90 percent relative density level is probably due to significant grain growth or to the formation of significant amounts of closed porosity.

Since sintering is a thermally activated process, an equation of the type

$$P = P_0 \cdot e^{\frac{Q}{RT}}$$

or

$$\ln P = \ln P_0 + \frac{Q}{RT}$$

where $P$ = porosity

$P_0$ = initial porosity

$Q$ = activation energy

$T$ = absolute temperature

and $R$ = gas constant

should describe the sintering kinetics. The slopes of $\frac{1}{T}$ vs log porosity curves indicate the relative activation
energies of the three aluminas. Because the data are not isothermal, an error would certainly result in calculating activation energies from the curves shown in Figure 24. However, comparisons of the slopes for the three aluminas provides a valid basis for comparing the sintering kinetics of the three alumina powders. Linde A and Alcoa XA-16 aluminas appeared quite similar in initial stage sintering kinetics, with Linde A having a slightly lower activation energy. BMI-10 had a somewhat lower activation energy than either Linde A or Alcoa XA-16 alumina, as evidenced by its lower slope.

Very definite breaks occur at about the same temperature in all three curves, possibly indicating changes in activation energy. The curve slopes are linear from about 75 percent to about 93 percent relative density. At higher densities, the curves indicate less response to temperature increases, due to the influences of grain growth and closed porosity.

Compacts from Pretreated Linde A Alumina

Based on pressure-compaction data, isostatic compaction pressures were selected so that uniform green densities of 54.2 percent of theoretical would result for compacts fabricated from pretreated Linde A powders. This was done to allow direct correlation with results
for compacts fabricated from as-received Linde A alumina. Specimens representing these pretreatment methods were sintered to both 90 and 95 percent densification levels using sintering methods equivalent to those for the as-received material.

Although data representing two density levels was insufficient to plot sintering curves and permit evaluation of the kinetics, some interesting observations can be made when the sintering data for the three pretreated powders and the as-received alumina powders are compared (see Figure 25). Firstly, the new lot of as-received Linde A seemed somewhat less sinterable than the previously used original lot. Secondly, the pelletized Linde A dry milled for 5 hours seemed slightly more sinterable and the Linde A dry milled for 20 hours was significantly more sinterable than the as-received Linde A from the same lot. The data for the Linde A milled for 5 hours and not pelletized seems inconsistent.

**Phase V - Evaluation of Microstructural Development**

**Compacts from As-Received Powders**

**Selected Chemical Analyses**

Emission spectrographic and carbon analyses were obtained for selected samples to determine the amount of contamination introduced by different processing steps.
Figure 25. Effect of sintering soak temperature on relative density of compacts from pretreated Linde A alumina
The results listed in Table 11 for green-pressed and for sintered compacts may be compared to the powder analyses listed in Tables 4 and 5.

Comparison of the analysis for green-pressed Linde A alumina to that for Linde A powder indicates no significant differences; the discrepancy in reported PbO values is within the limits of accuracy of the emission spectrographic method. The close agreement noted indicates that the powder handling techniques used precluded contamination of the alumina powders. Comparison of cation contents shows a general trend for increase in SiO₂, TiO₂, Fe₂O₃, MgO, and CaO content as a result of sintering, and to a greater extent with higher temperature sintering. In an attempt to determine the source of contamination, the porous alumina refractory used for baffles within the sintering tube was analyzed in the as-received condition and after being used in the furnace atmosphere entry end of the sintering tube throughout the sintering work of the base studies. The analyses shown in Table 12 indicate the presence of significant quantities of SiO₂, Fe₂O₃, MgO, ZrO₂, and CaO in the baffle material and also that MgO had been depleted in the refractory at the entry end of the furnace tube. This contamination might well affect grain growth during sintering to higher densities. It
<table>
<thead>
<tr>
<th>Component</th>
<th>Linde A</th>
<th>XA-16</th>
<th>BMI-10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Green Compact</td>
<td>55 PSD</td>
<td>95 PSD</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.021</td>
<td>0.064</td>
<td>0.064</td>
</tr>
<tr>
<td>TiO₂</td>
<td>N</td>
<td>N</td>
<td>T</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>T</td>
<td>0.001</td>
<td>0.004</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Ga₂O₃</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>MgO</td>
<td>T</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td>CaO</td>
<td>T</td>
<td>T</td>
<td>0.001</td>
</tr>
<tr>
<td>BaO</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>PbO</td>
<td>0.011</td>
<td>0.022</td>
<td>0.022</td>
</tr>
<tr>
<td>MnO</td>
<td>N</td>
<td>N</td>
<td>T</td>
</tr>
<tr>
<td>CuO</td>
<td>T</td>
<td>T</td>
<td>T</td>
</tr>
<tr>
<td>NiO</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Na₂O</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Ag₂O</td>
<td>T</td>
<td>T</td>
<td>T</td>
</tr>
<tr>
<td>S</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Cl</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>C</td>
<td>0.015</td>
<td>0.011</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Symbols: PSD = Percent densification of sintered compact
T = Trace, but less than detection limit
N = Analyzed for, but none detected
NA = Not analyzed for this constituent
TABLE 12
EMISSION SPECTROGRAPHIC ANALYSES OF POROUS ALUMINA REFRACTORY FROM SINTERING FURNACE

<table>
<thead>
<tr>
<th>Oxide Constituent</th>
<th>Weight Percent in As-received Brick</th>
<th>Weight Percent in Baffle from Furnace</th>
<th>Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>0.214</td>
<td>0.214</td>
<td>0.002</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.5-2.0</td>
<td>0.5-2.0</td>
<td>0.002</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.003</td>
<td>0.003</td>
<td>0.002</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.071</td>
<td>0.071</td>
<td>0.001</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>N</td>
<td>N</td>
<td>0.001</td>
</tr>
<tr>
<td>Ga₂O₃</td>
<td>0.067</td>
<td>0.067</td>
<td>0.001</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>N</td>
<td>N</td>
<td>0.003</td>
</tr>
<tr>
<td>MgO</td>
<td>0.332</td>
<td>0.166</td>
<td>0.002</td>
</tr>
<tr>
<td>CaO</td>
<td>0.090</td>
<td>0.090</td>
<td>0.001</td>
</tr>
<tr>
<td>BaO</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>PbO</td>
<td>T</td>
<td>N</td>
<td>0.001</td>
</tr>
<tr>
<td>MnO</td>
<td>T</td>
<td>T</td>
<td>0.001</td>
</tr>
<tr>
<td>CuO</td>
<td>N</td>
<td>N</td>
<td>0.001</td>
</tr>
<tr>
<td>NiO</td>
<td>N</td>
<td>N</td>
<td>0.001</td>
</tr>
<tr>
<td>Na₂O</td>
<td>N</td>
<td>N</td>
<td>0.007</td>
</tr>
<tr>
<td>Ag₂O</td>
<td>T</td>
<td>T</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Symbols:  
N = Analyzed for, but none detected  
T = Trace, but less than detection limit
is also possible that a second minor phase such as spinel could be generated in sintering to higher density levels. However, no such phases were observed in samples densified to the 95 percent level.

**Metallographic Analyses**

Examination of the polished samples indicated that samples in the green pressed condition and those sintered to the 45 and 25 percent porosity levels had not been truly polished, but that grains had been pulled out to keep the sample surface level. Real polishing was accomplished only for the 10 and 5 percent sintered porosity levels. Figures 26, 27, 28 and 29 are electron micrographs of these polished samples subjected to a boiling phosphoric acid etch treatment and gold coating by vapor deposition. The distribution of porosity, the volume fraction of porosity, and grain size distribution can best be evaluated from the 2000X photographs shown in Figures 26 and 28. Grain size, shape, and contact area may best be observed in the 10,000X photographs of Figures 27 and 29.

Linde A alumina microstructures at the 90 and 95 percent density levels consist of zones of two distinctly different types. One type has larger grains, less porosity and smaller pores. These denser areas
Figure 26. Electron micrographs of \( \sim 10 \) percent porosity sintered alumina compacts from as-received powders (polished and etched, 2000X magnification)
Figure 27. Electron micrographs of ~10 percent porosity sintered alumina compacts from as-received powders (polished and etched, 10,000X magnification)
Figure 28. Electron micrographs of ~5 percent porosity sintered alumina compacts from as-received powders (polished and etched, 2000X magnification)
Figure 29. Electron micrographs of ~5 percent porosity sintered alumina compacts from as-received powders (polished and etched, 10,000X magnification)
probably had a head start in the densification process, perhaps as a result of agglomeration or aggregation effects on packing of the Linde A powder. In Figure 29 it is quite noticeable that the porosity in these denser areas of the Linde A compact was reduced well below the average. The pores in the less dense areas appear larger and exhibit the angularity and connectivity usually attributed to less advanced sintering, whereas the pores in the denser areas appear smaller and more rounded as has usually been observed for more advanced sintering.

The material appearing to have been exuded at many Linde A grain boundaries at the 5 percent porosity level appears to be above the grain surface, and therefore is not thought to be a grain boundary phase but rather the result of etchant, cleaning or gold coating procedure. The irregular shape of the grains at these stages of development and the incompleteness of the etching process preclude quantitative data on grain size from these pictures.

The pore distribution in Alcoa XA-16 at 90 percent density appears quite uniform in Figure 26. Figure 27 shows the pores to consist of smaller, rounder trapped pores and larger less regular shaped pores. Grain size,
while not uniform appears more so for XA-16 than for Linde A.

Average grain size of Alcoa XA-16 was considerably increased at the 95 percent density level as noted in Figures 28 and 29. Distribution of porosity appears less uniform and the portion of smaller, rounded trapped pores appears increased. Grain corners have become decidedly angular and appear to be resolving toward the 120-degree equilibrium shape for sintered grains. There is some appearance as though either a few alumina grains were dug out during polishing, or that a second more soluble phase might have been dissolved during the boiling phosphoric acid etch. However, the similarity of Figure 30 (unetched) indicates multiple grain pullout is probably responsible.

Like Alcoa XA-16, BMI-10 alumina at the 90 percent density level had a very uniformly distributed porosity as observed in Figure 26. Average pore size seemed significantly smaller for the BMI-10 sample, and grain size appeared to be fairly uniform. Again the presence of smaller, rounded pores trapped during grain growth can be contrasted to larger, irregular porosity between the enlarged grains.

At 95 percent density, the remaining porosity in BMI-10 alumina is less uniformly distributed than at
Figure 30. Photomicrograph of \(~5\) percent porosity sintered alumina compact from as-received XA-16 powder (not etched, 1000X magnification)
90 percent as judged by Figure 28, but certainly more uniformly distributed than for the Linde A sample. Grain size increased and appeared less uniform than at the 90 percent density level. Grain shape in the BMI-10 sample had not become as well defined as for either the Alcoa XA-16 or the Linde A aluminas at this level of densification.

**Strength Evaluation**

The maximum tensile strength values listed in Table 13 generally represent the average of five values. Any value deviating excessively from the average was omitted in calculating the averages.

Log strength is plotted as a function of porosity (Figure 31) in order to compare the results with the conventional strength-porosity relationship which can be written as

\[
\sigma = \sigma_0 \cdot e^{-AP}
\]

or

\[
\ln \sigma = \ln \sigma_0 - AP
\]

where \( \sigma \) = strength in psi
\( \sigma_0 \) = strength at zero porosity
\( A \) = constant
\( P \) = porosity expressed as a percent.
TABLE 13
STRENGTH OF COMPACTS FROM AS-RECEIVED POWDERS

<table>
<thead>
<tr>
<th>Type of Alumina</th>
<th>Compact Condition</th>
<th>Relative Density,$^a,b$ percent</th>
<th>Maximum Tensile Strength, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linde A</td>
<td>Green</td>
<td>54.4</td>
<td>165</td>
</tr>
<tr>
<td>&quot;</td>
<td>Sintered</td>
<td>59.2</td>
<td>5,960</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>77.1</td>
<td>20,800</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>90.6</td>
<td>25,600</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>95.3</td>
<td>27,800</td>
</tr>
<tr>
<td>XA-16</td>
<td>Green</td>
<td>54.2</td>
<td>56</td>
</tr>
<tr>
<td>&quot;</td>
<td>Sintered</td>
<td>57.8</td>
<td>3,000</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>77.5</td>
<td>14,000</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>90.2</td>
<td>23,100</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>95.3</td>
<td>29,600</td>
</tr>
<tr>
<td>BMI-10</td>
<td>Green</td>
<td>54.2$^c$</td>
<td>---</td>
</tr>
<tr>
<td>&quot;</td>
<td>Sintered</td>
<td>57.9</td>
<td>4,720</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>76.8</td>
<td>11,400</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>89.1</td>
<td>15,000</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>94.6</td>
<td>16,700</td>
</tr>
</tbody>
</table>

$^a$Apparent densities determined by xylene displacement method were used to calculate relative density data.

$^b$Relative density data are based on 3.987 g/cc theoretical density for alpha alumina.

$^c$Relative density was calculated on alpha-alumina basis for this sample.
Figure 31. Relation between strength and porosity of alumina compacts
Thus, the log strength would be expected to be a linear function of porosity with a negative slope. The intercept of log strength at zero porosity indicates the strength at theoretical density. Data plots for the three aluminas are fairly linear at relative densities greater than 75 percent. The zero porosity intercepts are 30,000, 37,000 and 18,500 psi for Linde A, Alcoa XA-16, and BMI-10 samples, respectively. The value 37,000 psi obtained for Alcoa XA-16 by this method agrees very well with published values of 37,500 psi for fully dense alpha alumina. The lower strength value of 30,000 psi obtained for Linde A alumina may be due to the nonuniformity of microstructure observed at the 10 percent and 5 percent porosity levels. The lower strength value of 18,500 psi obtained for BMI-10 powder may partially be explainable by microstructural development, which appears less uniform than that of the Alcoa XA-16. It may also be partially attributable to the inversion of other alumina phases to alpha alumina at 1150 C, which is certainly above the temperature at which sintering begins for these reactive alumina powders. The corresponding disruption of structure may have caused internal flaws responsible for the low strength values obtained for BMI-10.
Fractographic Studies

Electron micrographs of the fracture surfaces are shown at both 2000 and 10,000X magnification for Linde A, Alcoa XA-16, and BMI-10 alumina compacts at five densification stages in Figures 32 through 38. Discussions take into account observations of stereo pairs of the 10,000X electron micrographs, which aided considerably in interpretation. Sets of pictures at two magnifications were necessary because grain growth of an order of magnitude was involved, and pictures showing grain detail often did not contain sufficient numbers of the enlarged grains to provide a representative sample. Pictures at 10,000X with 25 times as much field as those included in this report were obtained by enlargement of the 2000X electron micrographs. Examination of the enlargements gave additional insight on distributional effects.

Little grain growth was observed in Linde A, Alcoa XA-16, or BMI-10 aluminas at the 75 percent density level. Fracture was entirely intergranular, and on a macroscopic scale fracture surfaces were observed to be fairly smooth and flat. As the density increased, fracture surfaces became less smooth and regular, perhaps due to increasing irregularity of the path of least resistance.
Figure 32. Fractographs of green pressed alumina compacts from as-received powders (10,000X magnification)
Figure 33. Fractographs of ~45 percent porosity sintered alumina compacts from as-received powders (10,000X magnification)
Figure 34. Fractographs of ~25 percent porosity sintered alumina compacts from as-received powders (10,000X magnification)
Figure 35. Fractographs of ~10 percent porosity sintered alumina compacts from as-received powders (2000X magnification)
Figure 36. Fractographs of ~10 percent porosity sintered alumina compacts from as-received powders (10,000X magnification)
Figure 37. Fractographs of ~5 percent porosity sintered alumina compacts from as-received powders (2000X magnification)
Figure 38. Fractographs of ~5 percent porosity sintered alumina compacts from as-received powders (10,000X magnification)
Considerable grain growth, resembling secondary recrystallization, was observed in the samples representing 10 percent porosity. Linde A was typified by scattered, very large grains of 3-6 microns size, areas of 1-2 microns grain size, and pockets of material where grains were 0.3 to 0.5 microns. A possible flaw is observed to be about 2-8 microns in length, bordering one of the large recrystallized grains (see Figure 36). XA-16 also had undergone considerable grain growth at the 10 percent porosity level but retained an overall appearance of size uniformity. Grains up to 5.5 microns in size were observed, but the smaller size grains were intermixed in a rather random manner and very few grains remained at less than the 1-2 micron size.

Less grain growth had taken place in the 10 percent porosity, BMI-10 sample, and fewer large recrystallized grains were observed. The majority of grains appeared to be 0.5 to 1 micron in size but were uniformly dispersed in similar fashion to XA-16 rather than like the Linde A sample.

The dual nature of the Linde A microstructure is observed again in the 5 percent porosity sample. Large well-defined zones of large grains are interspersed with zones of smaller grains 0.5 to 1 micron in size.
The cause of this phenomena may be the relatively poor packing of the Linde A powder prior to isostatic compaction. Two types of porosity are noted in the microstructure—the more rounded, trapped pores in the large grains and the more irregular porosity between grains. Some transgranular fracture was observed in the enlarged grains at both the 10 percent and 5 percent levels, in proportion to the amount of enlarged grains.

Although grain growth has proceeded to the point that enlarged grains 6-8 microns in size make up a large portion of the microstructure of the XA-16 sample, their overall distribution is fairly uniform in the 5 percent porosity sample. As in the Linde A samples, porosity trapped within grains is noticeably more rounded than that between grains. Considerably less transgranular fracture was observed for the XA-16 samples than for the Linde A samples.

The fractograph of BMI-10 at 5 percent porosity exhibits the same dual zone grain size as the comparable Linde A sample. Porosity trapped within grains is of a more rounded nature than that between grains. A considerably greater amount of transgranular fracture of enlarged grains was observed in the BMI sample than for Linde A. Possibly, grains were weakened by stresses imposed during
the alpha-alumina inversion during the sintering cycle.

A further observation on the dual zone grain size observed in Linde A and BMI-10 samples seems in order. The volume proportion of large recrystallized grains was few or nil at the 10 percent porosity level, but increased to half or more at the 5 percent porosity level. It is likely that at even higher densities an entirely recrystallized structure would result. In fact if only dense samples had been examined, this phenomena might not have been observed. It appears very possible that the accompanying nonuniform shrinkage on a microscale would induce microstress conditions and weaken the resultant microstructure. In fact, the low incidence of transgranular fracture in the stronger XA-16 samples seems to indicate that flaws, microstresses, or grain weakening had been induced in the Linde A and BMI-10 samples. This might explain why the estimated strength at theoretical density was lower for Linde A than for XA-16 alumina. As mentioned previously, a possible additional weakening factor for BMI-10 samples would be the alpha-alumina inversion.

**Evaluation of Porosity and Free Surface Elimination**

Surface area measurements were made for alumina compacts representing five densification stages, using the
Strohlein areameter, with Linde A powder as a standard. Specific surface data are listed in Table 14, and the temperature relationship of surface area is shown in Figure 39. Linde A alumina and XA-16 alumina show an almost linear relationship of surface area to sintering temperature, whereas BMI-10 alumina exhibited less surface reduction for equivalent temperature increases at the higher density levels. This apparent inconsistency might be related to the creation of internal flaws during sintering at higher temperatures, which would tend to decrease the net measured surface area reduction and could also explain the relative weakness of BMI-10 alumina at higher sintered densities. The small deviation of the Linde A curve from linearity at the 10 percent porosity level may have resulted from creation of a small portion of flaws due to differential sintering rates in the dual grain size regions of the Linde A alumina microstructure.

The porosity vs surface area relationship for sintered alumina compacts have been plotted in Figure 40. Although a definite pattern is observed, the most significant relation is not apparent. Surface area reduction potentially corresponds to creation and growth of neck areas during sintering, so a plot of log surface area reduction vs porosity as shown in Figure 41 should correspond to the Knudsen plots of log calculated contact
TABLE 14
SURFACE AREA MEASUREMENTS OF COMPACTS
FROM AS-RECEIVED POWDERS

<table>
<thead>
<tr>
<th>Type of Alumina</th>
<th>Sample Description</th>
<th>Nominal Percent Porosity</th>
<th>Specific Surface, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linde A Powder</td>
<td>---</td>
<td>16.03*</td>
<td></td>
</tr>
<tr>
<td>&quot; Green Compact</td>
<td>45.8</td>
<td>17.54</td>
<td></td>
</tr>
<tr>
<td>&quot; Sintered Compact</td>
<td>45</td>
<td>8.01</td>
<td></td>
</tr>
<tr>
<td>&quot; &quot; &quot;</td>
<td>25</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>&quot; &quot; &quot;</td>
<td>10</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>&quot; &quot; &quot;</td>
<td>5</td>
<td>0.097</td>
<td></td>
</tr>
<tr>
<td>XA-16 Powder</td>
<td>---</td>
<td>13.60</td>
<td></td>
</tr>
<tr>
<td>&quot; Green Compact</td>
<td>45.8</td>
<td>13.55</td>
<td></td>
</tr>
<tr>
<td>&quot; Sintered Compact</td>
<td>45</td>
<td>7.65</td>
<td></td>
</tr>
<tr>
<td>&quot; &quot; &quot;</td>
<td>25</td>
<td>2.65</td>
<td></td>
</tr>
<tr>
<td>&quot; &quot; &quot;</td>
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<td>BMI-10 Powder</td>
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<td></td>
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<tr>
<td>&quot; Green Compact</td>
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<td>11.51</td>
<td></td>
</tr>
<tr>
<td>&quot; Sintered Compact</td>
<td>45</td>
<td>7.16</td>
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<td>2.16</td>
<td></td>
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<tr>
<td>&quot; &quot; &quot;</td>
<td>10</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>&quot; &quot; &quot;</td>
<td>5</td>
<td>0.062</td>
<td></td>
</tr>
</tbody>
</table>

*This value was obtained by multiple point BET measurements (3 determinations).
Figure 39. Effect of sintering soak temperature on surface area of alumina compacts
Figure 40. Relation between surface area and porosity of alumina compacts
Figure 41. Relation between surface area reduction and porosity of alumina compacts
area vs porosity. As was pointed out by Knudsen,\textsuperscript{72} the resemblance of the surface area to porosity relationships (Figure 41) to the strength vs porosity relationships (Figure 31) is unmistakable. A linear relation of log strength to log surface area reduction during sintering is indicated in Figure 42. Linearity is observed for samples of XA-16 and Linde A at all sintered density levels. It may be recalled that the strength vs porosity relationships (Figure 31) showed linearity only at density levels above about 75 percent. Lack of linearity for the BMI-10 curve (Figure 41) might be due to structural disruption accompanying the alpha-alumina inversion. A high green strength for BMI-10 is indicated and was confirmed by qualitative observation, although powder shortage did not permit quantitative data to be obtained.

Data on pore size distribution were not obtained quantitatively by mercury porosimetry. Efforts to obtain such information by Quantimet analysis of polished microstructures were curtailed due to poor polishing behavior of the less dense sintered compacts. Qualitative observations based on examination of fractographs and electron micrographs of higher density polished sections were discussed earlier.
Figure 42. Relation between surface area reduction and strength of alumina compacts
Bulk and apparent density measurements for the various densification levels of the alumina compacts are listed in Table 15. Helium density measurements were made using an air pycnometer but were not considered very accurate due to the small sample sizes. Percent porosity data obtained from the bulk measurements include both open and closed porosity, whereas the porosity obtained from the apparent density measurements, made by xylene impregnation techniques, is essentially open porosity. The difference between the two values can be taken as an indication of closed porosity. The percent of total porosity represented by closed pores can be correlated with observations of microstructure. These percentages increased as sintering progressed and became quite high for all three aluminas at the 95 percent theoretical density level.

Compacts from Pretreated Linde A Alumina Metallographic Analyses

Microstructures of the sintered alumina compacts were examined with a Cambridge scanning electron microscope, using techniques for polishing, etching, gold deposition, and examination as described previously. Figures 43, 44, 45, and 46 show electron micrographs of the polished compact cross-sections for pretreated
<table>
<thead>
<tr>
<th>Type of Alumina</th>
<th>Compact Condition</th>
<th>Bulk Density, g/cc</th>
<th>Percent Total Porosity</th>
<th>Apparent Density, g/cc</th>
<th>Percent Open Porosity</th>
<th>Percent of Closed Porosity in Total Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linde A Green</td>
<td>Sintered</td>
<td>2.153</td>
<td>46.00</td>
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<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>2.334</td>
<td>41.46</td>
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<td>40.81</td>
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<td>&quot;</td>
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<td>3.508</td>
<td>10.51</td>
<td>3.615</td>
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<td>&quot;</td>
<td>&quot;</td>
<td>3.761</td>
<td>5.47</td>
<td>3.800</td>
<td>4.69</td>
<td>14.25</td>
</tr>
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<td>XA-16 Green</td>
<td>Sintered</td>
<td>2.075</td>
<td>47.96</td>
<td>---</td>
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<td>---</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
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<td>2.305</td>
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<td>3.021</td>
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<td>3.595</td>
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<td>7.53</td>
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<tr>
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<td>&quot;</td>
<td>3.744</td>
<td>6.09</td>
<td>3.800</td>
<td>4.69</td>
<td>23.00</td>
</tr>
<tr>
<td>BMI-10 Green</td>
<td>Sintered</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>2.282</td>
<td>42.76</td>
<td>2.310</td>
<td>42.06</td>
<td>1.64</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>3.066</td>
<td>23.10</td>
<td>3.064</td>
<td>23.15</td>
<td>0</td>
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<td>13.09</td>
<td>3.553</td>
<td>10.89</td>
<td>16.80</td>
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<tr>
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<td>&quot;</td>
<td>3.723</td>
<td>6.62</td>
<td>3.771</td>
<td>5.42</td>
<td>18.13</td>
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</table>

*Bulk densities were obtained by linear measurement-weight method.

*bPercent porosity data are based on 3.987 g/cc theoretical density for alpha alumina.

cApparent densities were determined by xylene displacement method.
Figure 43. Electron micrographs of ~10 percent porosity sintered alumina compacts from pretreated Linde A alumina (polished and etched, 2000X magnification)
Figure 44. Electron micrographs of ~10 percent porosity sintered alumina compacts from pretreated Linde A alumina (polished and etched, 10,000 magnification)
Figure 45. Electron micrographs of ~5 percent porosity sintered alumina compacts from pretreated Linde A alumina (polished and etched, 2000X magnification)
Figure 46. Electron micrographs of ~5 percent porosity sintered alumina compacts from pretreated Linde A alumina (polished and etched, 10,000X magnification)
Linde A powders and for as-received Linde A. In some cases grain relief was not obtainable without causing grain pullout during the boiling phosphoric acid etch treatment. The wrinkled appearance noticeable on some grain representations is an artifact caused by excessive gold deposition.

Alumina microstructures for as-received Linde A at the 90 and 95 percent density levels consisted of zones of two distinctly different types. One zone had larger grains, less porosity and smaller pores. As has already been suggested, the porous areas where sintering was retarded resulted from inefficient compaction characteristics of the porous aggregates in Linde A. The pores in these less dense areas were larger and exhibited the angularity and connectivity usually attributed to less advanced sintering, whereas the pores in the denser areas were smaller and more rounded as usually associated with more advanced sintering.

The pore distribution both with respect to size and location appeared much more uniform at both the 90 and 95 percent densification levels for compacts sintered from Linde A dry ball milled for 5 hours. Grain size also appeared much more uniform at both the 90 and 95 percent densification levels.
The microstructures at the 90 and 95 percent densification levels in compacts sintered from pelletized Linde A that had been dry milled for 5 hours seemed considerably less uniform than for similar non-pelletized material. Considerable resemblance to the microstructures of compacts fabricated from as-received Linde A resulted with use of the pelletization process. The location and size distribution of porosity seemed less uniform than for the compacts fabricated from non-pelletized Linde A dry milled 5 hours, but was less variant than when as-received Linde A was used. The distribution of grain sizes resulting from use of the pelletized material also seemed intermediate.

The pore size and shape distributions appeared extremely uniform, especially at 95 percent densification, in microstructures of compacts sintered from Linde A dry ball milled for 20 hours. Both grain and pore sizes appeared smaller, though not necessarily more uniform, in microstructures resulting from 20 hours dry milling compared to those from 5 hours dry milling.

**Strength Evaluation**

The mechanical strengths of alumina compacts representing the various processing conditions and density levels were obtained by diametral compression measurements
as previously described. This data was obtained to allow comparisons for the various microstructures rather than as statistical strength data. The maximum tensile strength values listed in Table 16 consist of the average of five values in general. Comparison of average strength values for the three powders studied to those for as-received Linde A must be done on a normalized basis, because porosity of the various sample compacts at the nominally 90 and 95 percent densification levels was unavoidably somewhat variable. Figure 47 shows the strength data from Table 16 superimposed on data for compacts fabricated from as-received alumina powders.

The strength data for compacts fabricated from Linde A dry ball milled 5 hours and for those from the pelletized Linde A that had been dry milled for 5 hours were difficult to interpret, in that each appeared stronger than compacts from the as-received Linde A at one of the densification levels but not the other. Compacts fabricated from Linde A dry milled for 20 hours were consistently stronger than those from as-received powder. The compacts sintered from this new lot (1567) of as-received Linde A were also consistently weaker than those fabricated from the base lot (1400) as previously discussed.
### TABLE 16

**STRENGTH OF SINTERED COMPACTS FROM PRETREATED LINDE A ALUMINA**

<table>
<thead>
<tr>
<th>Powder Pretreatment Description</th>
<th>Relative Density,(^a,b) percent</th>
<th>Maximum Tensile Strength, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>94.68</td>
<td>23,300</td>
</tr>
<tr>
<td>&quot;</td>
<td>89.21</td>
<td>18,500</td>
</tr>
<tr>
<td>5 Hours Dry Ball Milling</td>
<td>95.63</td>
<td>23,000</td>
</tr>
<tr>
<td>&quot;</td>
<td>89.83</td>
<td>22,100</td>
</tr>
<tr>
<td>5 Hours Dry Ball Milling</td>
<td>95.56</td>
<td>26,900</td>
</tr>
<tr>
<td>Plus Pelletization</td>
<td>91.35</td>
<td>17,600</td>
</tr>
<tr>
<td>20 Hours Dry Ball Milling</td>
<td>95.77</td>
<td>25,600</td>
</tr>
<tr>
<td>&quot;</td>
<td>88.31</td>
<td>18,100</td>
</tr>
</tbody>
</table>

\(^a\)Apparent densities determined by xylene displacement method were used to calculate relative density data.

\(^b\)Relative density data are based on 3.987 g/cc theoretical density for alpha alumina.
Figure 47. Relation between strength and porosity of compacts from pretreated Linde A alumina
Fractographic Studies

Fracture surfaces of alumina compacts were examined with the Cambridge scanning electron microscope using techniques identical with those previously described. Figures 48, 49, 50, and 51 show electron micrographs of fracture surfaces of specimens from strength tests.

Comparison of the fractographs for samples fabricated from dry-ball-milled and pelletized Linde A at the 90 percent densification level revealed some apparent differences from those resulting from as-received Linde A. Each contained scattered large grains of 3 to 6 microns in size, among a majority of grains that were 1 to 2 microns in size. However, no pockets of smaller 0.3 to 0.5 micron grains were observed in the compacts from dry-milled and pelletized Linde A powders as had been seen in the compacts from as-received Linde A. The average grain size in the compact from Linde A dry milled 20 hours appeared smaller than for the other three samples.

The dual character of the microstructure at the 95 percent densification level resulting from as-received Linde A is clearly seen in Figures 50 and 51. Denser zones of large grains were interspersed with more porous zones of smaller grains 0.5 to 1 micron in size. Two types of porosity were noted in the microstructure—the
Figure 48. Fractographs of ~10 percent porosity sintered alumina compacts from pretreated Linde A alumina (2000X magnification)
Figure 49. Fractographs of ~10 percent porosity sintered alumina compacts from pretreated Linde A alumina (10,000X magnification)
Figure 50. Fractographs of ~5 percent porosity sintered alumina compacts from pretreated Linde A alumina (200X magnification)
Linde A milled 5 hours  

As-received Linde A (Field 1)  

Linde A milled 5 hours and pelletized  

As-received Linde A (Field 2)  

Figure 51. Fractographs of \( \pm 5 \) percent porosity sintered alumina compacts from pretreated Linde A alumina (10,000X magnification)
more rounded, trapped pores in the large grains and the more irregular porosity between grains. Some transgranular fracture was observed in the enlarged grains at both the 10 and 5 percent porosity levels, in proportion to the amount of enlarged grains.

The fractographs for the 95 percent dense compacts of the dry-ball-milled and pelletized Linde A powders were noticeably different from those for as-received Linde A. A wide distribution of grain sizes ranging from 0.1 to 5 or 10 microns was observed in the compacts fabricated from the Linde A dry milled 5 hours, whether pelletized or not. As usual, most enlarged grains contained small round trapped pores compared to irregular, larger pores elsewhere. These two samples differed from specimens made from as-received Linde A in that the locational distribution of varied grain sizes seemed considerably more random and the dual zoned aspect was not apparent for the compacts from dry-milled powders.

The fractograph for the 95 percent dense compact made from Linde A dry ball milled 20 hours appeared unique. This fractograph showed scattered large grains up to about 5 microns in size in a finer grained matrix. These enlarged grains, however, contained noticeably less trapped porosity than was the case for Linde A either
as-received or dry ball milled for 5 hours. This sample exhibited no tendency toward porous zones consisting of very fine grains. However, this sample did appear to contain flaws of a type usually associated with enlarged grains. It seems probable that the relatively low isostatic pressure (3000 psi) used to obtain the desired green density of 54.2 percent for this compact was responsible for this flaw condition. Additional work on samples pressed with higher isostatic pressures should be done to clarify this result, since the microstructures of compacts fabricated from Linde A dry ball milled for 20 hours seem very promising in all other respects.

**Evaluation of Porosity**

Bulk and apparent density results for the various samples at both the 90 and 95 percent densification levels are shown in Table 17. Percent porosity data obtained from the bulk measurements include both open and closed porosity, whereas the porosity obtained by liquid displacement essentially represents only open porosity. The percentage of total porosity represented by closed porosity tended to increase as densification increased from 90 to 95 percent. The indicated closed porosity was high for all compacts at the 95 percent densification
<table>
<thead>
<tr>
<th>Powder Pretreatment Description</th>
<th>Bulk Density(^a) g/cc</th>
<th>Percent Total Porosity, (^b)</th>
<th>Apparent Density, (^c) g/cc</th>
<th>Percent Open Porosity(^b)</th>
<th>Percent of Closed Porosity in Total Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>3.760</td>
<td>5.69</td>
<td>3.775</td>
<td>5.32</td>
<td>6.52</td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>3.551</td>
<td>10.94</td>
<td>3.557</td>
<td>10.79</td>
<td>1.37</td>
</tr>
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<td>5 Hours Dry Ball Milling</td>
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<td>4.82</td>
<td>3.813</td>
<td>4.37</td>
<td>9.35</td>
</tr>
<tr>
<td>&quot; &quot; &quot;</td>
<td>3.575</td>
<td>10.33</td>
<td>3.581</td>
<td>10.17</td>
<td>1.55</td>
</tr>
<tr>
<td>5 Hours Dry Ball Milling Plus Pelletization</td>
<td>3.807</td>
<td>4.51</td>
<td>3.810</td>
<td>4.44</td>
<td>1.55</td>
</tr>
<tr>
<td>&quot; &quot; &quot;</td>
<td>3.630</td>
<td>8.95</td>
<td>3.642</td>
<td>8.65</td>
<td>3.36</td>
</tr>
<tr>
<td>20 Hours Dry Ball Milling</td>
<td>3.804</td>
<td>4.59</td>
<td>3.818</td>
<td>4.23</td>
<td>7.85</td>
</tr>
<tr>
<td>&quot; &quot; &quot;</td>
<td>3.495</td>
<td>12.34</td>
<td>3.521</td>
<td>11.69</td>
<td>5.26</td>
</tr>
</tbody>
</table>

\(^a\)Bulk densities were obtained by linear measurement-weight method.

\(^b\)Percent porosity data are based on 3.987 g/cc theoretical density for alpha alumina.

\(^c\)Apparent densities were determined by xylene displacement method.
level, except for the pelletized samples. This indication of low closed porosity for the pelletized samples shows no correlation with electron micrographs for that sample.
SUMMARY

The objective of this investigation was to improve the ability to quantitatively evaluate those powder characteristics which affect microstructural development and variability, and consequently control property values and property variability of fired ceramics. The identification and quantitative measurement of significant powder characteristics followed by the analysis of the effects of those characteristics on character development and variability in the finished ceramic body were problems involved in realization of the primary objective of this investigation.

This type of study is considered important because, historically, flaw sensitivity of the strength of ceramic materials has limited their usefulness in structural applications. To eliminate the creation of such flaws, control over the entire process leading up to the finished ceramic body is necessary. The first stage of such control is preparation of a ceramic powder with proper character, and to do so requires the ability
to quantitatively evaluate those powder characteristics which have significant affects on powder processing, microstructural development, and final properties.

Reactive alumina powders were selected as study materials because of their usefulness and degree of variation. Two commercial powders extensively used for fabricating technical ceramics and a specially prepared laboratory powder were chosen for initial studies. These three reference powders were thoroughly analyzed for chemical, structural, physical, and rheological characteristics. Using isostatic compaction and sintering, bodies of controlled incremental densification levels were prepared from each reference powder. After examination of the microstructures and strengths of the sintered compacts, these features were correlated with powder characteristics and processing behavior.

The chemical characteristics of the reactive alumina powders did not appear to affect microstructural development or strength, but will certainly be expected to do so in densification of compacts above the 95 percent level which was maximum in this investigation. Structural character of the powder used was shown to be quite important in that the one powder which was not completely alpha alumina sintered less efficiently, and the resulting compacts were considerably weaker. Conversion of a
non-alpha alumina entails calcination and also probably some form of comminution of resulting powder aggregates. Rheological character was found to vary widely and to be controlled by agglomeration and/or aggregation of the powder. Physical character of the three reference alumina powders was seen to vary chiefly in the degree and mode of agglomeration and/or aggregation, and this characteristic was dependent on preparation history.

The most notable variation in microstructural development of compacts fabricated from the reference powders was the marked lack of homogeneity observed in samples fabricated from powders containing aggregates. Predictions that aggregates were responsible for differences in powder processing behavior and variability in microstructural development were substantiated by the results of subsequent ball-milling studies. Simplification or elimination of particulate aggregate structure by ball milling was accompanied by a corresponding increase in microstructural homogeneity in sintered compacts. Study of strength variability will require statistical treatment of strength data which is not within the scope of this present investigation.

Calcination studies showed that aggregation is probably unavoidable in preparing alpha alumina, but that the degree and type of aggregates formed might be
controllable under proper conditions.

The most significant finding of this investigation is that the physical characteristics of powders, including in particular the structure of aggregates, exert a marked effect on powder processing, microstructural development and its variability, and subsequent sintered properties.

The proposed method of detecting aggregate presence and measuring aggregate strength through analysis of pressure-compaction data is not yet quantitative; however, even the present qualitative method appears to have considerable value for predictions of powder processing behavior and microstructural development. The ability to control powder characteristics and subsequent powder processing behavior and variability in microstructural development by use of pretreatments such as calcination and/or comminution to control aggregate structure and strength has been shown. Thus, a substantial advance in the ability to eliminate microstructural flaws from finished ceramic bodies through reductions in the variability of the particulate raw materials is indicated.

The problem of variability in particulate raw materials is not exclusive to the reactive alumina powders chosen for this investigation. The results should also be of interest when processing methods other than the
Isostatic pressing and sintering of this investigation are utilized.

Complexity of aggregate structure is not unique to Linde A alumina. The preparation of alpha alumina, a necessity for successful sintering processes, invariably involves some form of calcination treatment. Since surface area reduction through interparticulate bonding appears inevitable during such calcination, some type of aggregate structure also appears unavoidable. A survey of other reactive alumina powders as they have appeared on the market has verified this conclusion. Thus, the ability to detect and measure aggregate strength, to select and evaluate calcination methods resulting in the most advantageous aggregate structure, or to select and evaluate comminution techniques yielding sufficient reduction or elimination of aggregate structure should be of real value to either the potential producer or user of ceramic alumina powders.

Although this investigation has utilized aluminas as study materials, it is expected that the findings will also be of interest to those concerned with other materials, (e.g. spinel, magnesia, zirconia) for which powder preparation and processing have significant roles in fabrication of the finished product, since many of the same principles will apply.
CONCLUSIONS

The results of this investigation of alumina particulate characterization and microstructural evaluation as herein reported seem to justify the following conclusions:

1. Regarding the events which determine the character of a finished alumina ceramic body - particulate character, powder pretreatment, powder processing (in this case vibratory compaction, isostatic compaction, and sintering) - each is dependent on every preceding event in the sequence of microstructural development.

2. Particulate character and variability are the initial, and thus the most important factor in determining the character and variability of the finished body.

3. Within the scope of this investigation the most variable, and thus the most critical particulate characteristics are the physical characteristics, especially the agglomerate and/or aggregate structure
and strength.

4. Pressure-compaction data can be utilized to detect the presence of and qualitatively measure the strength of agglomerates and/or aggregates in powders.

5. Microstructural flaws, which are an important aspect in the variability of ceramic bodies, can originate directly from aggregates in powders or indirectly from the influence of aggregates and/or agglomerates on rheological-compaction characteristics of powders.

6. The variability in important particulate characteristics may be traced directly to the history of powder preparation; pretreatment of the powders may be used to beneficiate the aggregate structure of the powders.

7. The complex aggregate structure of a reactive alumina powder can be simplified by comminution pretreatment to eliminate porous aggregates or to produce ultimate type particles, thus improving subsequent powder processing characteristics, and reducing variability in microstructural development.
8. Calcination pretreatment technique has an important effect on aggregate structure and strength; a simplified aggregate structure which might improve powder processing characteristics and reduce variability in microstructural development has been effected by modification in calcining methods.

9. The formation of aggregate structures during calcination to obtain alpha alumina appears to be unavoidable, since a relationship whereby considerable surface area reduction accompanied conversion to 100 percent alpha alumina was definitely indicated.

10. Listing a set of characterization techniques that will completely define the significant particulate characteristics and omit the insignificant ones will not be possible until research has been extended to include completely densified alumina compacts; nevertheless, techniques which have been proven indispensable to date are chemical analyses, x-ray or DTA structural analyses, visual examination by light or electron microscopic techniques, measurement of surface area, and pressure-compaction analysis.
APPENDIX

Strength Characterization of Powder Aggregates

Introduction

In powder processing, strong, porous aggregates lead to inhomogeneities in powder compacts which result in microstructural inhomogeneities in the sintered or hot-pressed product. Strong or hollow agglomerates formed by spray drying can produce similar inhomogeneities. Figure 52 shows the fracture surface of an alumina specimen fabricated by isostatic pressing at 100,000 psi and sintering to 95 percent of theoretical density. The apparent microstructural inhomogeneities, caused by strong aggregates in the reactive calcined alumina powder used to prepare this material, are more pronounced when lower pressing pressures are used. The microstructure is characterized by regions of different densities in which the low-density regions are characterized by a smaller grain size and complete intergranular fracture, and the dense areas by a larger grain size and appreciable transgranular fracture. The fracture surface exaggerates the
Figure 52. Fractograph of an alumina specimen isostatically pressed at 100,000 psi and sintered to 95 percent of theoretical density
percentage of porous areas, since the crack front tends to propagate through these areas of lower strength. A polished section of this material shows that the dense areas predominate, and the porous areas are fairly well isolated. These porous areas are the remnants of porous aggregates that were not broken down during pressing, thus producing inhomogeneities in a green compact. Mistler and Coble have reported similar observations for alumina pressed at lower pressures and sintered to lower density. The literature contains numerous other references to microstructural inhomogeneities that are attributable to inhomogeneities in green compacts caused by strong aggregates which were not broken down during processing.

Many powders used in fabricating ceramic bodies are prepared by precipitation or by blending, followed by calcination. Calcination almost always results in formation of porous aggregates whose strength depends on the material, as well as the time, temperature, and atmosphere used during calcination. The strength of these aggregates significantly affects subsequent processing parameters, microstructure development, and properties. Milling is normally employed in ceramic processing to break down porous aggregates, and the amount of milling required is quite dependent on the aggregate strength. In spite of the recognized importance of
aggregate strength and porosity, no quantitative techniques are available for measuring these powder characteristics.

Background

The crushing strength of large aggregates, such as those conventionally used for making refractory brick, can be evaluated qualitatively by crushing the aggregate with a pin point or similar sharp instrument under a microscope. Snyder, et al. developed a technique for evaluating the intrinsic strength of fly ash, which was based on the compaction or crushing behavior of a thin layer of material in a modified uniaxial die. They plotted their results on a linear-linear scale which gave typical pressure-compaction curves. Several investigators have noted that pressure-compaction data when plotted as log pressure versus density, porosity, or relative volume give a linear relationship over certain pressure ranges. However, the reason for this relationship has received little consideration. Early in this investigation, it was hypothesized that this behavior is related to the strength-porosity relationship of brittle materials and that the strength of a particulate should be determinable from the data.
In discussing Ryshkewitch's paper, Duckworth suggested that the strength-porosity relationship could be described by an equation of the form

$$\sigma' = \sigma_0 e^{-bp}$$  \hspace{1cm} (A-1)

where

- $\sigma'$ = strength of porous body
- $\sigma_0$ = strength of nonporous body of same material
- $e$ = the Napierian number, 2.71828
- $b$ = an empirical constant
- $p$ = porosity expressed as a fraction.

If the strength of the porous body is replaced by the pressing pressure ($P$), a similar relationship can be written as

$$P = P_0 e^{-bp}$$  \hspace{1cm} (A-2)

By taking the logarithm of both sides, it can be seen that

$$\ln P \propto p + \text{Constant}$$  \hspace{1cm} (A-3)

The logarithm of pressure is similarly related to porosity expressed as a percentage, and to density expressed as a fraction or as a percentage of theoretical density.

Materials

Two types of reactive alumina powders were studied. Alumina I (Linde A) was a calcined, but unmilled, reactive powder. This powder was used to fabricate the compact that
yielded the fracture section shown in Figure 52. This powder has a characteristic aggregate structure, as shown in Figure 53 in which two types of aggregates may be noted. The larger type appears to be in the form of chains of particles with large neck areas having approximately the same diameter as the particles. The smaller aggregates, which are made up to ultimate particles in the 100 to 200-angstrom range, also appear to have significant neck areas between individual particles. However, these aggregates appear to be rather porous.

Alumina II (Alcoa XA-16) was a dry-milled reactive alumina powder. The porous aggregates usually found in a calcined powder have been broken down during milling, and numerous dense agglomerates have been formed. In an electron micrograph of Alumina II (Figure 54), this powder appears to be broken down to its ultimate particle size. Although some particle-particle bonding can be seen, it is believed to be primarily due to the dry-milling agent.

To obtain a better understanding of the effect of aggregate strength, a series of powders was prepared by calcining Alumina II at different temperatures in an effort to achieve powders containing aggregates of different strengths. Material for this study was prepared by spreading 200-gram lots of powder in a loose, 1/2-inch-thick bed in alumina saggers, heating to the indicated
Figure 53. Electron micrograph of Alumina I particles

Figure 54. Electron micrograph of Alumina II particles
calcination temperature in air, holding for 1 hour, and then allowing the powder to cool with the furnace. The loosely bonded materials from the beds were passed through a 20-mesh U. S. Standard stainless steel sieve to reduce them to flowable powders. An exception to this was the material calcined at 2400 F, which was so strongly bonded that such screening would have either broken down aggregates or removed a significant portion of the calcined powder. Figure 55 shows Alumina II after calcination for 1 hour at 2200 F. There is little change in the crystallite size, although a considerable change in the neck area formed between particles is evident. Figure 56 shows Alumina II after calcination for 1 hour at 2400 F. The resulting aggregates are an order of magnitude larger in size, and they are almost completely dense.

The Madagascar graphite powder utilized for comparative purposes was a natural graphite composed of platelet particles and sized at -100 200 mesh. Copper and aluminum powders composed of -325 mesh particles were also used for comparison purposes.

Experimental Procedure

Pressure-compaction data was obtained over the range 1.5 psi to 100,000 psi by two compaction methods. Data from 1.5 to 20,000 psi were obtained using a
Figure 55. Alumina II aggregates after calcination at 2200 F for 1 hour in air

Figure 56. Alumina II aggregates after calcination at 2400 F for 1 hour in air
double-acting steel die. The die was lubricated with a thin film of zinc stearate prior to initial loading of the powder using 60-cps vibratory compaction. Only a small powder charge was used to minimize frictional effects, resulting in a thin pressed disk. The density of the vibratory-compacted powder, referred to as the tap density, was determined using the fill volume and the weight of the resulting disk after compaction. Disk thickness was determined as a function of applied pressure by measurements of ram travel which were made after pressure release. The density corresponding to the applied pressure was determined using the disk thickness, the disk diameter, and the disk weight.

Compaction data were determined over the range 1000 psi to 100,000 psi using isostatically pressed pellets. Powder was loaded in a thin rubber bag lining a 3/4-inch diameter by 1-inch deep mold with a hemispherical bottom, using 60 cps vibratory compaction. Air was evacuated from the packed powder by inserting a hypodermic needle connected to a vacuum manifold through a rubber cork fitted with a cotton insert, prior to sealing the rubber bag. Pressures in the range 1000 psi to 2700 psi were applied isostatically by introducing nitrogen gas into a steel bomb containing the pellet samples. Pressures in the range 3000 to 100,000 psi were
applied to pellet samples in an isostatic pressing chamber utilizing a liquid pressure medium.

Densities of the irregularly shaped pressed sample pellets were determined by immersion methods, after applying a thin wax coating to the samples. Allowance for the wax coating was made in the density calculations.

Results and Discussion

In order to gain a better understanding of the possible influence of particle strength on the compaction curves plotted as logarithm of pressure versus percentage of theoretical density, aluminum and copper powders were investigated. It was felt that the compaction of these powders would be controlled by their yield points over a large pressure range. As shown in Figure 57, the data for each material can be fitted to two linear portions when plotted as logarithm of pressure versus relative density. In the low-pressure region, compaction is believed to be due primarily to particle-particle rearrangement controlled by particle-particle friction. Above the break point in the curve, particle-contact pressures apparently exceed the yield point of the metal particles, and plastic deformation controls compaction.

By direct analysis with the strength-porosity relationship discussed earlier, extrapolation of the data
Figure 57. Compaction behavior of several materials.
to 100 percent relative density should indicate the yield strength of the powder particles. However, the data for aluminum are not linear to 100 percent of theoretical density. This is believed to be due to closing off and elimination of pores, leaving a compact with isolated pores. The stress developed around pores in this type of compact deviates from that which dominates at lower densities and causes the data to deviate from linearity. Extrapolation of the upper linear portions of the curves for copper and aluminum to 100 percent of theoretical density indicates that the particles in the copper powder have a higher yield point than those in aluminum powder, as would be expected from the conventional yield points of these metals. The high yield points indicated by these data are believed to be due to the stress state developed during isostatic compaction.

Extrapolation of the two linear portions of the curves for aluminum and copper in Figure 57 indicates that the break point of the curve for copper occurs at a higher pressure than that for aluminum, again indicating copper has the higher yield point. Because of the stress intensification at the particle-particle contacts, however, the pressure at the break point is not directly related to the yield point of the powder particles.
Figure 57 also shows compaction data for the two alumina powders and for natural-graphite powder. Alumina I has a low tap density which is believed to be caused by its fine particle size and the presence of porous aggregates. As that for the metal powders, the data for Alumina I can again be fitted to two linear regions. In the low-pressure region, compaction is believed to be primarily particle-particle rearrangement controlled by particle-particle friction. In the high-pressure region, compaction is believed to be primarily particle rearrangement controlled by strength of the porous aggregates.

Alumina II has a higher tap density than Alumina I, which is believed to result from presence of numerous dense agglomerates that were formed after the porous aggregates in the calcined powder broke down during milling. The major compaction mechanism for this powder is believed to be particle rearrangement controlled by particle-particle friction. Below the break in the curve at approximately 10 psi, compaction is believed to be controlled by crushing of agglomerates. Based on this interpretation of the data, another break would be expected somewhere above 100,000 psi where compaction becomes controlled by fracture of the alumina particles.
The compaction curve for graphite is rather unique. At low pressures, compaction is believed to be controlled by particle-particle friction inhibiting particle rearrangement. Above 30 psi the curve takes a sharp upward break indicating a change in compaction mechanism. In this range, compaction is believed to be primarily particle rearrangement, but the controlling mechanism is believed to be elastic bending of graphite platelets. Because of the thin-platelet character of the powder and its low coefficient of friction, high densities are obtainable with the natural-graphite powders. Above about 1000 to 2000 psi, the curve begins to take on a shallower slope. In this region, particle fracture is believed to control compaction. This essentially inhibits further densification, and little increase in density is noted between 3000 to 100,000 psi, although further increases would undoubtedly be noted if density were measured before releasing pressure.

In order to obtain a better understanding of the effect of aggregates strength on the shape of the pressure-compaction curve, a series of powders containing aggregates of different strengths was prepared by calcining Alumina II to different temperatures. Figure 58 shows the pressure-compaction data for Aluminas I and II, and for Alumina II after calcination at various
Figure 58. Compaction behavior of calcined aluminas
temperatures. After calcination at 1200 F, the curve is essentially identical to that of the as-received powder. There is a change in the tap density with increased calcination temperature which is believed to be a result of densification of the aggregates that originally made up the agglomerates in the dry-milled powder. The curves for the calcined powders have similar slopes in both the high-pressure and low-pressure regions. The curve for as-received powder is somewhat different.

In contrast to the data on metal powders, the pressure obtained by extrapolation of the data to 100 percent relative density was not useful in distinguishing among the calcined powders. The apparent lack of sensitivity to the strength of the aggregates in the powder resulted, at least in part, from the amount of extrapolation required. However, the primary reason for this lack of sensitivity is believed to be more fundamental.

The complication can best be explained on the basis of data on the strength of brittle materials as a function of porosity. In most cases, strength-porosity data obey Equation (A-1). However, data taken on a series of compacts sintered at different temperatures show that a certain amount of sintering must take place before this relation is obeyed. This apparent anomaly is believed
to result from the fact that a considerable strength increase results as surface diffusion increases the diameters of the neck areas between particles. Since this increase in strength occurs without a decrease in porosity, the relationship in Equation (A-1) is not obeyed until sintering progresses to the point where surface diffusion is negligible. This indicates that the fundamental relationship for a typical powder compact is between strength and neck diameter rather than strength and porosity. Knudsen arrived at a similar conclusion on the basis of analytical considerations. Aggregate strength is also a function of the neck areas between its ultimate particles. Therefore, the pressure obtained by extrapolation of pressure-compaction data from a region where aggregate strength controls compaction to 100 percent of theoretical density should not be related to the strength of the aggregate. Rather, it is related to the strength the aggregate would have if it were 100 percent dense.

On the other hand, the pressure at which aggregate strength begins to control compaction should be related to the strength of the aggregate. In Figure 58 the two linear portions of the curves have been extrapolated to show the intersections. These intersections occur at 60, 150, 875, and 2000 psi for powders calcined at 1800, 2000,
218, and 2400 F, respectively. Thus, the pressure at which these intersections occur is rather sensitive to the calcination temperature which is, in turn, related to the neck areas formed between particles within aggregates and, therefore, to their strength.

Proof of this was sought by further characterizing the series of calcined powders. Surface area was measured by a modified BET technique, aggregate size distribution was measured with a Coulter Counter, and the powders were examined directly with the scanning electron microscope and the transmission electron microscope as shown earlier. With increasing calcination temperature, the average aggregate size increased, the surface area decreased, and the neck areas between particles seemed to increase. The way in which the density of the aggregates should be factored into a quantitative evaluation of their strength is somewhat uncertain at this time, but further studies are under way in this area. It is believed that the strengths should be compared at the same relative density in a manner similar to that in which strength data for brittle materials are normalized. This normalization would account for the porosity within the aggregates and not the porosity between the aggregates of the powder.
Summary

It has been shown that pressure-compaction data for a wide variety of powders can be described by one or more linear regions on a plot of relative density versus logarithm of pressure. A different mechanism controls compaction in each region. For powders containing aggregates, one linear portion of the curve corresponds to control of compaction by aggregate strength. The pressure at which the extrapolation of this linear portion and the one for the next lower pressure region intersect correlates well with the strength of the aggregates in a powder. On the basis of present data, analysis of pressure-compaction data can show the presence or absence of aggregates in a powder and can qualitatively rank the strength of aggregates in various powders.
BIBLIOGRAPHY


