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SPINEL POWDER: PREPARATION BY USE OF FREEZE DRYING, CHARACTERIZATION AND CORRELATION WITH MICROSTRUCTURE

Chi-Shine Tao
(Ph. D. thesis)

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SPINEL POWDER: PREPARATION BY USE OF FREEZE DRYING, CHARACTERIZATION AND CORRELATION WITH MICROSTRUCTURE

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ABSTRACT

Reactive magnesium aluminate spinel (MgAl$_2$O$_4$) powders were prepared by calcining freeze dried aqueous solutions of magnesium sulfate and aluminum sulfate hydrates.

The freeze dried powders were characterized in terms of their structure, dehydration kinetics, thermal reactions, particle size distribution and particle aggregation. As a result of the understanding gained by the correlation of the freeze dried powders with the calcined spinel powders, the freeze drying process was modified in order to prepare freeze dried powders with the least amount of chemical segregation and calcined spinel powders nearly aggregate-free. On modifying the freeze drying process by narrowing down the freeze dried particle size distribution by avoiding particle aggregation at the quick freezing and sublimation stages, homogeneous ultrafine spinel powders were obtained after calcination. The calcined powders were characterized in terms of their crystalline phases, residue sulfate content, crystallite growth during calcination and spectrographic analysis.

The spinel powder characterizations were correlated with their sinterability and sintered microstructures. Using the hot stage scanning electron microscope, it was found that spinel powders of
nearly single crystalline phase and the finest crystallite size have
the fastest sintering rate. Increase of the packing homogeneity
also increases the sintering rate of powders that have the same
crystallite size.

The presence of strong spinel powder aggregates results in
heterogeneous sintered microstructures which have large pores
scattered in the dense matrix. Improvement of the freeze drying
process as described above effectively eliminated this microstructural
inhomogeneity. Powder packing homogeneity increases with increasing
green body density for powders with the same characteristics. Low
green density powder compacts (less than 50% theoretical density)
are less homogeneous and show exaggerated grain growth. Excess
residue sulfate results in a grain boundary second phase for short
time sinterings. This second phase was removed by annealing in air at
1500°C, leaving pores along grain boundaries. Small amounts of
residue sulfate form entrapped pores inside the grains during grain
growth. It was found that long time vacuum calcination of the powder
and secondary calcination in hydrogen remove the residue sulfate
and thus reduce the entrapped pores. Different crystallite sizes
generally affect the sintering kinetics.

Dry ball milling for a short period of time further reduces the
aggregate size and increases the packing uniformity of the freeze
dried powders in a desiccated condition. This procedure was found to
be a more effective way to produce uniform calcined powders free of
aggregates than ball milling the calcined spinel powders.
I. INTRODUCTION

Important technical properties of ceramic products such as mechanical, electrical, thermal, optical and magnetic are determined by their microstructures. The variation of microstructure is controlled by the history of its fabrication process including treatment of raw material. Dense, homogeneous sintered polycrystalline ceramics with controlled grain size generally had improved properties. Reproducible and controllable microstructures rely on the understanding of the fabrication process, especially the characterization of the raw material and its correlation with the heat treatment and the microstructure.

Dense polycrystalline ceramic bodies are mainly prepared by sintering powders in a finely divided form. Sintering is a thermally activated process, and the thermodynamic driving force is the reduction of the free energy of the system based on the difference of the reduced total solid/vapor free energy and the increased total solid/solid interfacial energy. Powders which have a fine crystallite size (high surface area and high total solid/vapor free energy), uniformity of desired chemical composition and uniform physical size often are readily sintered to desired dense homogeneous microstructure and are called reactive powders.

Various ways of preparing reactive ceramic powders can be used: coprecipitation, organo-metallic decomposition, decomposition of metal salts, solid-solid calcination, spray drying, and freeze drying. Each specific powder preparation method has problems associated with the processing steps to achieve the desired reactive
powders. Problems commonly encountered are realization of intimate mixing, removal of impurities, and powder aggregation. Also, the correlations of the powder characteristics with their sintering kinetics and sintered microstructure are not generally known for each special process.

Spinel \((\text{MgAl}_2\text{O}_4)\) is a technically important ceramic because of its high melting point, high resistance to chemical attack, and relatively high strength at elevated temperatures. There are numerous ways in which reactive spinel powders have been prepared; these will be discussed later. The freeze drying method was chosen for the preparation of spinel powder because of its potential of producing reactive spinel powders and because of an objective of studying the characteristics of the process itself. This research is a continuation of the author's masters thesis research,\(^1\) in which a freeze drying technique was developed for the preparation of magnesium aluminate spinel powders. Studies were made of the thermal reactions occurring during calcination of the freeze dried powders, and some preliminary work was done on the characterization of the freeze dried and calcined powders. In this research, the physical and chemical nature of the freeze dried and calcined powder were further characterized, powder aggregation was studied and reduced by improving the freeze drying process and the powder characteristics were more extensively correlated to their sintering kinetics and sintered microstructures.
A. Freeze Drying Technique

Freeze drying is the process which removes water from the system while the water is in the frozen state. Besides its extensive application to food and biological technology, in the past few years freeze drying has been utilized to prepare reactive ceramic powders. The three major steps included in this technique are solution mixing, quick freezing and sublimation drying. Oxide powders are then produced upon calcination of the freeze dried powders. This technique provides an intimate molecular mixing of the component materials, maintains the chemical and physical integrity of the frozen mixed solution throughout drying, and decomposes upon calcination to yield finely divided oxide powder of desired composition and controllable crystallite size.

Details of the freeze drying process were discussed previously. The three major steps are to be briefly described here.

1. Solution Mixing

Homogeneous mixing on an atomic scale of several chemical species can be achieved when they are mutually dissolved in a solution. A desired composition can be obtained by mixing the right proportion of each individual chemically analyzed solution. A mixed solution of relatively low solute concentration would yield an oxide powder of finer crystallite size than a higher concentration solution. High solution concentrations will increase the yield of particulate material, but, in most cases, the increase of concentration tends to depress the pH and the freezing point of the solutions which enhances the possibility of remelting of the frozen material during
Furthermore, some salt solutions with a high solute concentration have a tendency to supercool resulting in a glass-like phase from which it is difficult to remove the solvent by sublimation. 3

2. **Quick Freezing**

In general, hydrated salts segregate from an aqueous solution of mixed salts upon drying. Also, mixed salt solutions upon freezing under equilibrium conditions form hydrates which are immiscible with ice. In order to maintain the chemical integrity of the mixed salt solution and to form the desired physical morphology of the freeze dried powder (to be discussed in Chapter III), the mixed salt solution can be frozen at a fast rate under nonequilibrium conditions. This procedure minimizes the salt segregation and forms a physical structure of small ice crystals and islands of solid solution of mixed salts.

3. **Sublimation**

The purpose of sublimation drying is to remove the ice by vaporization. In by-passing the liquid state during drying, it is possible to maintain the integrity of the chemical and physical structure achieved by quick freezing. As long as the pressure remains below the critical pressure at the drying boundary, 4 the frozen mixed solution does not melt. In actual sublimation drying, melting would easily take place at the drying boundary on the surface or inside the frozen particle if the pressure in between or inside the particles rose above the critical pressure because of an unbalance between the sublimation rate and the water vapor diffusion rate. The melting of frozen particles during drying causes the system to pass through a liquid state which ruins the advantages gained by quick freezing.
There are several limitations of the freeze drying process. The starting salts are limited to those that are mutually soluble and to those that decompose upon calcination without melting. It is favorable if the decomposition temperatures of the starting salts are not too high and too different from each other. The sublimation drying step has to be handled carefully to avoid the occurrence of any melting. The freeze dried powders are hygroscopic and thus have to be stored in a desiccated condition.

B. Some Important Characteristics of Reactive Powders

There are many measurable properties of ceramic powders Technical papers on the subject of powder preparation and sintering cover some qualitative and quantitative properties. In some papers, the measured powder properties are correlated to their sintering kinetics and sintered microstructures but the correlation seems only applicable to that specially prepared powder. For powders with the same composition the difficulty of formulating a general correlation between powder characteristics and their sintering behavior is due to the numerous processing parameters of powder preparation and sintering. Because the number of processing parameters involved and the knowledge for controlling them are not fully known to the processor, it is difficult to obtain fully reproducible powders from laboratory to laboratory. Furthermore, for powders of different composition or derived by a different process, the correlation of powder characteristics to their sintering behavior is even more difficult. In this research the powder characteristics which were measured and their significances are discussed.
1. **Composition and Crystallinity**

The homogeneous single phase powder of desired composition is one of the essential requirements for a reactive powder. If additives are needed as a grain boundary motion inhibitor or for the formation of a liquid phase during sintering, they should be uniformly distributed. Due to the fact that most reactive powders are derived from the thermal reaction of mixed salts, an intimate mixing is essential to realize short atomic diffusion distances and a homogeneously reacted material. Because of polymorphic nature of some ceramic materials, phase transformations result in volume changes during sintering which are not desirable. A certain calcination temperature and time is needed for salt-derived ceramic powder to achieve a fully crystalline phase, free from undecomposed anion impurities. Because of the diffusional nature of mass transport during sintering, the vacancy concentration of the powder is important. Therefore, it is desirable not to overcalcine or undercalcine the powder so that the decomposition reaction is completed but the powder still has a high vacancy concentration.

2. **Crystallites, Particles, Agglomerates and Aggregates**

Crystallite size is defined as the size of individual crystals usually less than about 1000Å. The average crystallite size in the range between 40-1000Å can be measured by an X-ray line broadening technique. The fine crystallites do not physically exist as individual separated particles; rather, they adhere strongly to each other. The physically separable individual agglomerate which consists of a number of crystallites is considered as a powder particle. Ultrafine
particles usually refer to the powder particles in the size range from 0.01 to 10 μm. The definition of agglomerate refers to a group of particles which can be separated relative easily because of weak interparticle forces. An aggregate is defined as a group of particles which are strongly bonded and which can be reduced in size by fracture. Since there is probably a nearly continuous spectrum of interparticle bonding strengths, alternative terms such as "soft" or "hard" agglomerate have been used for loose agglomerate and aggregate, respectively.  

Fine size crystallite powders are chemically reactive during sintering because of their excess surface free energy. The disadvantages of fine crystallite material are the tendency to aggregation, difficulty in achieving chemical purity and difficulty of preparation. Most fine crystallites of oxide are derived from the decomposition of precursor salts. It is commonly observed that most oxide powders have macroscopic structures which are replicas or pseudomorphs of the salts from which they have been prepared. Thus, there may be strong orientation relationships of the crystallites of the final product as pseudomorphs of the crystals of the starting material. A good example of the pseudomorphic orientation is shown by the decomposition of brucite to MgO crystallites. Therefore, the aggregation of crystallites on the coarse scale of the starting material is unavoidable, and aggregation of the oxide particles after calcination depends upon the state of particle aggregation of the salts before decomposition. A narrow size distribution of the powder particles is essential to achieve uniform high density powder compaction before sintering. High density uniform powder compacts have
a high particle coordination number and a uniform shrinkage during sintering which is necessary to achieve a dense and homogeneous sintered microstructure. Unfortunately, most chemically derived oxide powders quite commonly have an aggregation of particles. Most powder aggregates are usually much larger than individual particles and are strong enough to retain their structure during the cold pressing step. The presence of large aggregates in the green compact causes sintered microstructures with large porous regions in a continuous dense matrix if their density is less than that of the overall compact.

3. Chemical Impurities

The major chemical impurities of chemically-derived reactive powders come from the incomplete calcination of the starting salts. Also impurities come from the incomplete removal of other chemicals used during processing. For many salts, especially sulfates, because of the kinetics of the decomposition reaction, last traces of salt would remain in the structure unless high temperature and long time calcinations are employed. Generally, residue chemical constituents from the incomplete calcination form a second phase which becomes segregated at grain boundaries during sintering. The second phase may remain a condensed phase which wets the grain boundary or it may decompose to form a gas which remains inside the microstructure as pores. The presence of the second phase, as a condensed or gaseous phase, has undesirable effects on the optical, mechanical, and electrical properties.

Completion of the calcination reaction is the key to the elimination of the second phase formed during sintering because of
the residue salts. Achieving intimate mixing of the starting salts such that the salts can be completely consummated during reaction, optimizing the calcination time, temperature and atmosphere, and removing the residue salts chemically are the various ways of increasing the chemical purity of the reactive powder.

Other sources of impurities are environmental contaminants during powder processing, such as containers, crucibles for calcination and sintering, vapor species in the furnace atmosphere, and composition of the ball mill. Minimization of environmental contamination requires care in the selection of furnace construction material, crucible and ball milling material.

C. Sintering and Microstructure Synthesis

In this research investigation was concentrated on the sintering of a single phase spinel from powders of different characteristics under different fabrication conditions. Since sintering itself is a complicated phenomenon that has been discussed in detail in various technical papers and textbooks, the discussion will emphasize only the microstructure synthesis and related problems.

In the synthesis of microstructures, principal control measures include the selection of powder characteristics, inorganic additives, fabrication method, compacting pressure, sintering time, temperature and atmosphere, and post fabrication treatment. With regard to the microstructure itself, important features are bulk density, pore size and distribution, grain boundary structure and distribution of any second phase. In a certain range, bulk density and grain size are more controllable than other features.
1. Crystallite Size, Surface Area and Powder Reactivity

Most sintering equations that take grain growth into account predict that the time necessary to accomplish a given shrinkage is inversely proportional to the cube of the linear dimensions of the crystallite.\(^8\) In other words, sintering occurs at a lower temperature, or it occurs faster at the same temperature, the finer the crystallite size. The statement is true with common experimental results, but the order of magnitude of the time needed for a certain shrinkage may not differ in the cubic relationship as much as the starting crystallite size may differ for a non-ideal (real) system.

Surface area has been measured frequently as an indication of powder reactivity. As long as the powder particulates have similar surface roughness and the same crystalline phase, this measurement is meaningful.

Both crystallite size and surface area measurements are indications of the powder reactivity towards sintering. The important factor, however, is the realization that crystallites are aggregated, and as a result the real sintering process frequently does not follow the derived equations. Also, in a real powder system, the surface roughness may be different for crystalline phases. The surface area of different crystalline forms of alumina are very different.

2. Particles, Aggregates and Powder Packing

To obtain dense homogeneous microstructures on sintering, there are two requirements for the powder compact. First, the powder should be evenly distributed. Second, the density of the powder compact, green density, should be as high as possible. Two general
mechanisms were considered in dense compaction of powders. The first is the realization of dense packing by application of pressure to overcome the frictional forces between particles. The second is associated with the filling of voids that are substantially smaller than the size of the original particles which can be accomplished only by plastic flow or by fragmentation of the particulates.

For fine crystallite powders, it is difficult to achieve a homogeneous high density packing because of the tendency for particle aggregation and high frictional forces due to the high surface area of the powder. A powder system that consists of a narrow size distribution of particles is ideal for powder compaction, but in all chemical processed ceramic powders aggregates of particles are quite common. The aggregates may be strong or weak, dense or porous. Direct measurement of the strength of aggregates has not yet been done. Indirect approaches have been made such as disintegrating the aggregates by ultrasonic vibration and wet sieving or analyzing the pressure-compaction data so that a qualitative ranking of the strength of aggregates in various powders can be obtained.

Strong, porous aggregates lead to inhomogeneities in the powder compacts which result in microstructural inhomogeneities in the sintered or hot pressed product. These effects are more pronounced when lower pressing pressures are used. The microstructure is characterized by local regions of lower density which have a smaller grain size and complete intergranular fracture. This microstructural inhomogeneity caused by aggregates has been reported as non-uniform shrinkage in sintering or non-ideal sintering.
Ball milling is commonly used for the size reduction of strong aggregates. Depending on the fraction of fine powders, however, ball milling often compacts the fine powders. Since aggregates are formed from the pseudomorphs of the starting salts, it is reasonable to suggest the ball milling of the starting salts before calcination.

3. Grain Growth and Entrapped Gas

The grain boundary is a region of disorder between two grains or crystalline domains. Because of the curvature of the grain boundary, the vacancy concentration across the grain boundary is different. The difference in the chemical potential of vacancies across the grain boundary causes the movement of atoms across the grain boundary in the direction opposite to the center of curvature of that boundary. Consequently, the grain on the concave side of the boundary will grow at the expense of the other grain. When all the grains have similar grain boundary curvature, the grain growth is called normal grain growth. If a few larger grains exist, they will grow at the expense of the smaller ones. Thermodynamic analyses of grain boundary motion indicate that pores along the grain boundaries will pin the movement of planar grain boundaries and that a critical grain boundary curvature is necessary for grain boundaries to sweep past pores leaving them isolated inside the grain. For normal grain growth, most of the grain boundary curvatures do not exceed the critical value and thus pores will pin down the grain boundary movement. Pores
pinned on the grain boundary are normally annihilated through vacancy diffusion mechanism along the grain boundary. Whereas in exaggerated grain growth, the curved boundaries are able to migrate past pores which become trapped inside the grains. For all practical purposes, these pores are not annihilated and become the residual porosity.

In a nonuniformly packed powder compact due to the presence of aggregates, the more densely packed regions will sinter faster than the loosely packed regions and form larger grains leading to exaggerated grain growth.

At the onset of sintering, all pores connect to the surface of the specimen and are filled with the gas present in the furnace atmosphere. Eventually, as the sintering progresses, the pores become discontinuous and entrap the existing gas. In vacuum sintering, some entrapped gas may come from the decomposition of one of the solid phases at high temperature. For both cases, if the gas is insoluble, the pore will shrink until the gas pressure is equal to $2\gamma_{sv}/r$, where $r$ is the pore radius and $\gamma_{sv}$ is the surface energy, at which time the concentration of vacancies at its surface becomes the same as the concentration at grain boundaries and no further shrinkage occurs.

4. Factors Affecting Grain Growth

High green density powder compacts are usually more uniformly packed than the low green density ones. Therefore, exaggerated grain growth is less likely to occur, and the microstructure will have a more uniform grain size. Bruch investigated the sintering in hydrogen of Linde A alumina with 0.25 wt% MgO and found that, for
a fixed green density and initial crystallite size, sintered grain size depended only on the final porosity or bulk density and not on the sintering conditions used to achieve that density. In a study of a group of high purity sulfate-derived BeO powders whose mean crystallite size varied from 0.25 to 0.08 μm, Bannister found that the following empirical relationship held for each powder up to the commencement of exaggerated grain growth:

\[ P^{1.25} G = P_0^{1.25} G_0 \]

where \( P_0 \) = initial porosity,
\( P \) = final porosity,
\( G_0 \) = initial crystallite size,
and
\( G \) = final grain size.

This relationship has not yet been verified for other powders.

Grain growth during sintering can be controlled by the addition of a small amount of a second phase. The addition of MgO to \( \text{Al}_2\text{O}_3 \), \( \text{ThO}_2 \) to \( \text{Y}_2\text{O}_3 \) are examples. The control of grain growth by the addition of a second phase is generally explained on the basis of a decrease in the mobility of the grain boundary due to the segregation of the second phase at the grain boundaries which increases the activation energy for grain boundary movement.

5. Sintering Atmosphere

Many reported effects of sintering atmosphere on powder densification and grain growth are empirical. Coble found that \( \text{H}_2 \) and \( \text{O}_2 \) are able to diffuse out from closed pores during the
sintering of Al₂O₃. Vacuum firing reduces the gas pressure in
the powder compact. Atmospheric control is essential for the control
of the compositions of a number of non-stoichiometric oxides that
are sensitive to oxidizing or reducing conditions.

Lately, a theoretical development of the thermodynamics of
solid state sintering indicates that a critical ratio of \( \frac{\gamma_{SS}}{\gamma_{SV}} \),
where \( \gamma_{SS} \) is the grain boundary energy, could determine an end point
density for a given packing array of particles. The smaller
the ratio \( \frac{\gamma_{SS}}{\gamma_{SV}} \) is, the more favorable are the sintering conditions.
Both the addition of second phase and the furnace atmosphere can
affect this ratio.

D. Preparation and Sintering of Spinel Powders

In this section, a review will be made of some recent developments
on the preparation and sintering of spinel powder using different
starting materials and different methods.

Different methods have been used for the preparation of reactive
spinel powder: coprecipitation of magnesium and aluminum hydroxides
followed by calcination, spray drying of an aqueous solution of
magnesium sulfate and aluminum sulfate followed by calcination,
reaction of aluminum trihydrate with magnesium hydroxide, boiling
off the solvent of a magnesium carbonate and aluminum sulfate solution
followed by calcination, boiling off the excess water from a
magnesium sulfate hydrate and ammonia-aluminum alum aqueous solution
followed by calcination, cocrystallization of a saturated aqueous
solution of hydrated magnesium sulfate and hydrated aluminum sulfate
followed by calcination, co-melting mixed aluminum and magnesium
hydrate nitrates and solidifying the molten mixture followed by
calcination, calcination of Linde A alumina and Baker reagent grade
magnesia, and freeze drying of the aqueous solution of magnesium
sulfate and aluminum sulfate followed by calcination. For the
development of high density spinel microstructures, powders prepared
by proprietary techniques by different companies, such as W. R. Grace
and Co., Adolph Meller Co., Dow Chemical, Franklin Institute Research
Laboratories, Coors Porcelain Co., and etc, were evaluated.

Spinel powders have been densified by sintering, hot pressing
and press forging. Single phase spinel has not yet been densified
to full density without a small amount of some additive material.
It may be due to a similar activation energy for grain growth and
sintering (by volume diffusion) resulting in grain growth and
entrapments of pores inside the grains during densification. Studies
of nonstoichiometric compositions, indicate that excess MgO enhances
sintering but excess Al$_2$O$_3$ does not. Nearly full dense sintered spinel
was obtained with powders having an MgO content at the solid solution
limit. Additives such as LiF, Li$_2$O, and combinations of SiO$_2$
and Li$_2$O have been used successfully in obtaining fully dense
microstructure by sintering, hot pressing and press forging. A
small CaO addition made it possible to obtain a translucent sintered
spinel microstructure.

As for different densification techniques, hot pressing is so
far the most effective method of producing fully dense fine grain
(10-20 µm) spinel. Sintering to full density requires higher
temperatures than hot pressing and results in a large grain size
(100-200 μm). Powders prepared by mixing and prereacting reactive alumina and magnesia, by mixing of magnesium sulfate hydrate and ammonia-aluminum alum aqueous solution and calcination of the mixed salts, and by some undisclosed technique were successfully densified to full density with proper doping and processing techniques. All of these powders had the same unique set of properties required for achieving fully densified microstructures: uniform particle size, small crystallite size and chemical purity.
II. EXPERIMENTAL PROCEDURES

A. Freeze Dried Powders

1. Preparation
   a. Solution mixing. Reagent grade magnesium sulfate hydrate (MgSO$_4$·7H$_2$O) and aluminum sulfate hydrate (Al$_2$(SO$_4$)$_3$·18H$_2$O) were used as starting materials. Aqueous solutions of each salt were prepared and the exact molarities of the solutions were determined by chemical analysis: 0.959M and 0.267M, respectively. The magnesium sulfate solution was determined titrimetrically with EDTA reagent and aluminum sulfate solution was determined gravimetrically by precipitation with 8-hydroxyquinoline. The pH of the aluminum sulfate solution was adjusted to ~1 by adding sulfuric acid to prevent the precipitation of aluminum complex ion after aging.

   b. Quick freezing. The mixed solution under an argon pressure of 40 psi was atomized through a pneumatic jet onto the surface of an organic media: liquid freon-12, mixed hexane or heptane.* Freon-12 has a boiling point of -28°C and the mixed hexane and heptane were chilled by dry ice and acetone to about -60°C. The small droplets of the mixed solution were frozen into small icy particles as soon as they hit the liquid surface and, depending on the difference of the density of the organic freezing media and the mixed aqueous solution, either floated or sank to the bottom of

* Appendix.
The mixed solution was heavier than the mixed hexane and heptane but lighter than freon-12. The freon-12 was contained in a 6 in. diameter glass jar and the pneumatic jet sprayed the mixed solution onto the same area of freon-12 while vigorous agitation was provided. Big aggregated particles of the frozen solution formed as the liquid droplets hit onto the already frozen particles floating on the freon-12 surface. Aggregates of frozen particles during the quick freezing step resulted in aggregated freeze dried powders. Droplets of the mixed solution frozen on the surface of the already frozen particles could also lower the freezing speed and thus cause possible compositional segregation.

The quick freezing process was then improved in order to minimize compositional segregation and aggregate formation. Mixed hexane or heptane was chilled in a 2-1/2 ft by 1 ft by 6 in. stainless steel tank jacketed by a dry ice and acetone mixture. The pneumatic jet sprayed over a large area while hand agitation was provided, Fig. 1. The frozen particles sank to the bottom of the tank because of the density difference and were collected by a fine mesh strainer.

c. Sublimation drying. A Virtis model 10-800 freezer, shown in Fig. 2, was used. This freeze drier was a vacuum chamber with a built-in condenser. An additional liquid nitrogen condenser was added between the vacuum pump and the chamber to collect the residue organic liquid in the early stage of the drying process. The sample plate could operate in the temperature range -40 to 120°C. The chamber pressure as measured by a Mcleod vacuum gauge operated below 20 micron Hg. A radiant heating plate at about 35°C was put over the frozen material
Fig. 1. Quick freezing device.
Fig. 2. Virtis model 10-800 freeze dryer.
to provide additional heat of sublimation. The sample plate in the freeze drier was precooled to -40°C before loading the frozen material. A stabilized chamber pressure under 20 μm Hg was appropriate before heating was employed to increase the drying rate. The shelf temperature was raised to the final drying temperature at 10 to 20°C intervals. The drying was considered to be complete when the powder temperature reached the shelf temperature.

The most critical factor in the drying step was the prevention of remelting of the frozen particles. Remelting of the frozen particles as discussed before was mainly caused by a local pressure build up inside the bed of the frozen particles. High points of the bottom of the sample plate were eliminated for uniform heat conduction by applying a film of laboratory vacuum grease, which has a fair heat conductivity, in between the sample plate and the sample shelf. Two different drying cycles were designed to create open channels inside the frozen particle bed to prevent remelting from taking place:

(1) The shelf temperature was kept at around -15°C while vacuum was applied for about 1 day in order to create open channels in the frozen particle bed. The system was then warmed up gradually to room temperature by the surroundings before heat was applied from the shelf and the radiant plate.

(2) After the chamber pressure was stabilized below 20 μm Hg, the shelf temperature was kept at around -15°C while turning on the radiant plate. When the temperature of the upper part of the frozen particles reached around 25°C, the shelf was then gradually raised to the final drying temperature.
Both methods were successful in avoiding remelting of the frozen material during drying, but the latter method was more efficient in terms of drying rate. The final drying temperature determines the residue water content of the freeze dried powder. Powders finally dried at 25, 65 and 120°C were used to study the relationship between powder aggregation (after calcination) and their residue water content. The dried powders were passed through a 208 µm sieve and stored in vacuum before calcination.

2. Characterization

a. Thermogravimetric analysis. To study the relationship between final drying temperature and residue water content, a vacuum thermogravimetric analysis was made of the powder freeze dried 25°C at an ambient pressure of about 20 µm Hg. The powders were placed in a platinum crucible which was suspended from an Ainsworth micro-galance that was also within the vacuum system. The powders were vacuumed at room temperature for 30 min to drive off physically adsorbed water. The temperature was quickly raised to 65°C and kept constant until the weight loss rate was less than 0.2 wt% per hour. The temperature was raised to 120, 210 and 450°C in the same manner for a total drying time of 20 hr. The cumulative percent weight loss vs temperature was plotted. From the weight loss data, the amount of average residue hydrate water in the freeze dried powders was calculated.
b. X-Ray analysis. X-ray diffraction patterns for the different freeze dried powders were obtained. The results and analysis will be covered in the section on results and discussion.

c. Size distribution analysis. The data for the size distribution were obtained by sieve analysis for the powders prepared by freezing in freon-12 and heptane. Sieves with openings of 37, 53, 74, 104, 208 and 295 μm were used. Cumulative wt% powder was plotted against particle sizes. The spray freezing conditions were kept the same for different batches of the same freezing media which resulted in a reproducible size distribution.

d. Scanning electron microscope analysis. A scanning electron microscope was used to examine the physical morphology of the freeze dried powders. The scanning electron microscope was the advantage of bringing up the topographical details of the freeze dried powders. Powders frozen in different media at different temperatures, powders dried at different temperatures, powder aggregation due to remelting during the drying stage, and the effect of the physical morphology of the freeze dried powders after long time exposure in air were examined. To prepare a specimen, a double adhesive tape was stuck on the surface of a brass sample holder and the freeze dried powders were then stuck onto the surface of the tape. A microduster was used to blow away excess powders on the tape and the powders were then coated with gold to form a conducting surface.
B. Calcination of the Freeze Dried Powders and Characterization of the Calcined Powders

1. Furnaces

The freeze dried powders were calcined in air, vacuum and flowing hydrogen. For air calcination, a MoSi$_2$ resistance heating vertical furnace was used. The specimen was calcined essentially isothermally by being pushed directly into the heating zone. For vacuum and hydrogen calcination, a horizontal tube furnace was built, Figs. 3 and 4. A mullite tube was fitted into a 3-3/4 in. I.D. alumina tube which was wound with Kanthal resistance heating wire and packed with refractory brick. The maximum operating temperature was 1200°C. This horizontal tube furnace can be operated in vacuum at around 10 μm Hg or flowing H$_2$ at a positive pressure up to 3 psi. For the purpose of this research, the calcined spinel powders were treated with flowing H$_2$ at 1/3 psi positive pressure at 750°C.

2. Characterization

a. X-ray analysis. A Norelco diffractometer was used for the X-ray diffraction study of the calcined spinel powders. X-ray diffraction was used for structure study, phase identification and crystallite size measurement.

A transmission pinhole photograph of the calcined spinel powders was taken in Laue camera to examine any possible preferred orientation of the calcined spinel powders.
Fig. 3. Schematic layout of the atmosphere calcination furnace.
Fig. 4. The atmosphere calcination furnace (furnace section).
b. **Spinel crystallite size growth analysis.** One gram portions of the freeze dried powders were calcined for 1 hr from 900 to 1400°C at each 50°C interval to study their crystallite growth. Crystallite growth was also obtained for powders calcined in air isothermally at 1000 and 1300°C for different periods of time. Freeze dried powders of different size fractions were also calcined isothermally at 1000°C to determine any differences in crystallite growth. Using the X-ray line broadening technique, the average spinel crystallite size was measured at \{220\} and \{511\} orientations. The Scherrer's method was used for measuring the X-ray line broadening. The calculated average crystallite sizes were plotted vs temperature and time.

c. **Chemical analysis.**

(i) **X-ray fluorescence and spectrographic analysis.** A qualitative X-ray fluorescence analysis of the freeze dried powders indicated that Mo, Zn, Cu, Pb, Fe and Ar are the major impurity elements. Using this information as a guide, semi-quantitative spectrographical analyses of the starting sulfates, freeze dried powders and the calcined spinel powders of the same batch were made, to check the possibility of picking up impurities during processing.

*American Spectrographic Laboratories.*
(ii) Residue sulfate analysis. In the final stage of sintering, residue sulfate is detrimental because either forming a second phase segregated at grain boundaries or decomposing to form trapped gas in the sintered body. High temperature vacuum calcination is one way to minimize the residue sulfate content in the calcined sintered powders. High temperature calcination, however, increased the strength of the already present powder aggregates and coarsened the spinel crystallite size. Another way of removing residue sulfate is to reduce the sulfate in the powder by hydrogen at low temperatures.

The residue sulfate content of the powders calcined for the crystallite growth study was chemically determined as residue sulfur.* Analyses were also made of freeze-dried powders calcined in vacuum at 650°C for 2-1/2 and 22 hr, at 750°C for 14 hr, and 1000° and 1160°C for 1 hr. A portion of the latter three calcines were treated in flowing H₂ at 750°C with a positive pressure of 1/3 psi.

(iii) Kinetics of reduction reaction of MgSO₄ and Al₂(SO₄)₃ in hydrogen. Thermogravimetric analyses were made of the freeze dried anhydrous Al₂(SO₄)₃ and MgSO₄ powders in a flowing hydrogen atmosphere to study their reaction kinetics. The powders were placed in a platinum crucible which was suspended from an Ainsworth microbalance which was also within a positive pressure leak proof system. The system was first purged with N₂ and then H₂ was introduced and regulated to a positive pressure of 1/3 psi. An approximate constant heating rate of 8 to 10°C per minute

* Coors Chemical Laboratory, Golden, CO.
was followed. Comparison of the calculated weight loss assuming complete reduction and the experimental weight loss indicated a ±1% experimental error.

d. **Scanning electron microscopy analysis.** Scanning electron microscopy is a powerful tool to characterize powders by their morphology. The morphology of the calcined spinel powders was pseudomorphic to the freeze dried powders. To prepare a specimen, a dilute isopropyl alcohol dispersion of the spinel powders with an additional drop of photo flow agent was dropped onto a well polished brass sample holder, the isoprophy alcohol was evaporated, and the powders were then coated with a thin layer of Au to form a conducting surface.

e. **Powder aggegration analysis.** Efforts were directed toward the understanding of the possible aggregation mechanisms in this freeze drying process. Collision of solution droplets with frozen particles during quick freezing, remelting during the drying stage, and melting of the hydrated freeze dried powders during calcination were postulated as causes. Four small batches of powder were prepared in an effort to eliminate these causes progressively. Details of the four batches are tabulated in Table I. The calcined powders and sintered microstructures were examined by SEM which indicated that hard aggregates were eliminated progressively. The fourth batch thus resulted in an aggregate-free uniform ultra-fine spinel powder which sintered to high density at a low temperature. Efforts to reproduce this ultrafine powder in a larger batch of approximately 25 gms was not as successful. But, the number of hard aggregates was
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greatly reduced by carefully bypassing the aggregate forming steps. The reason why the uniform ultrafine powders were produced and the difficulties of reproducing them are to be discussed in Chapter III.

During the calcination step, new aggregates were formed by partial sintering of the fine crystallites on the coarsest scale within pseudomorphs of the freeze dried powders. Strengthening of the aggregates also occurred after a long time and high temperature calcinations.

Failure to reproduce aggregate-free uniform ultrafine spinel powders required milling to be used to break down the aggregate structures. A high speed planetary sintered sapphire ball mill was used.* This ball mill has a volume of 300 cc and useful capacity of 200 cc. The principal operation of this ball mill is having three or four grinding vessels overhang the periphery of a heavy carrier plate. Rotating with the carrier plate they impart a centrifugal force to the material being ground. At the same time, the grinding vessels rotate on their own axis in the opposite direction, Fig. 5a. The ratio of the two steps can be synchronized in such a way that the contents of the grinding vessels are given a cascading action similar to that of the heavy horizontal mills, Figs. 5b and 5c.

In order to break up the aggregate structure of the freeze dried powders that remained as a pseudomorph structure in the calcined

*Laboratory planetary ball mill, Pulberit 6, Cat. No. 022, sintered alumina (99.7% alumina). Geoscience Instruments Corporation, Mount Vernon, NY.
Fig. 5. Schematic drawing of the movements of grinding balls and powder particles in a planetary ball mill.
powders, the freeze dried powders were cry milled in this ball mill for 7 to 15 min and redried in vacuum at 120°C prior to calcination. The milled and calcined powders were examined by SEM.

Spinel powders directly calcined from unmilled freeze dried powders were dry milled in this planetary ball mill for 1 hr and were examined by SEM prior to sintering.

C. Sinterability and Microstructure Development

1. Sinterability

The effect of crystallite size and packing homogeneity on the kinetics of nonisothermal sintering was studied. Freeze dried powders were dry milled for 7 min, redried at 120°C in vacuum, and calcinated at 750°C in vacuum for 2 hr, 900°C in vacuum for 1 hr and 1300°C in air for 1 hr. All the calcined powders were treated with flowing H₂ at 750°C with a positive pressure of 1/3 psi. The morphology and aggregate structure of the milled freeze dried powders and calcined spinel powders were examined by SEM. X-ray diffraction patterns were also taken of the calcined powders before and after H₂ treatment. Powder compacts of these three calcined powders were made by uniaxial pressing to 53.1% (specimen 1), 53.0% (specimen 2) and 52.8% (specimen 3) of their theoretical density, respectively. The powder calcined at 900°C but without H₂ treatment was also cold pressed to 53.5% of theoretical density (specimen 4). The powder calcined at 1300°C and treated with H₂ was ground with pestle and an agate mortar and cold pressed to 53.5% theoretical density (specimen 5). Similar green densities were obtained by weighing
a certain amount of powder and pressing to the same volume by using spacers. The green density was measured by dividing the pellet weight by its volume measured geometrically by micrometer. Fractured fragments of all five green compacts were examined by SEM.

These compacts were heated in the hot stage of the SEM to study their sintering kinetics.\(^{29}\) Temperature was raised manually to 1000°C and then increased by programmed heating rate of 9.4°C/min to different sintering temperatures. For specimens 2 and 3, the temperature was raised to 1500°C and held at this temperature for 30 min. The heater burned out for specimen 5 when the temperature had just reached 1500°C. For specimens 1 and 4, the heater burned out when temperatures of 1580 and 1440°C, respectively, were reached.

The horizontal linear shrinkage of the compacts was monitored by placing 10 to 20 μm tungsten sphere markers on the surface of the sample and recording the movement of the markers: at each 20°C interval on a 16 mm movie film. Data were collected by projecting the image at a fixed distance and measuring the distance between centers of the tungsten spheres. Each datum point was the average of 3 to 4 individual shrinkage measurements. The percent linear shrinkage of each specimen was plotted against temperature.

The above shrinkage measurements were based on the distances between tungsten markers at 1000°C. From the percent linear shrinkage vs plot, it is expected that specimens 2 and 4 should have some appreciable shrinkage before the temperature reached 1000°C. A complementary experiment was to sinter specimens 2 and 4 in vacuum from room temperature to 1000°C for 20 min and measuring their
dimensional-change by a micrometer.

2. Microstructure Development

The processing details for each specimen are listed in Table I.

Five heating schedules were used in the study: A, 1, 2, 3a and 3b. Heating schedule A was applied to specimens 1, 2, 3 and 4 which were heated in air at a rate of about 8°C per min to 1550°C, held for 3 hr and furnace cooled. A MoSi$_2$ resistance vertical furnace was used.

Specimens 5 to 8 were prepared to study the sintering of spinel powders with progressive elimination of aggregates by improving the freezing and drying techniques. The powders were cold pressed to a low green density to avoid extensive crushing of the aggregates by the compressive force. The cold pressed specimens were contained inside an alumina crucible and separated from each other with 20 mil thick Mo spacers. A tungsten resistance heating furnace * with a 2 in. in diameter by 3 in. heating zone and a manual power control was used. It operated in vacuum ranging from $10^{-5}$ to $10^{-6}$ mm Hg. During the sintering run, the temperature was progressively raised and held at increments to prevent the furnace pressure from increasing. The specimens were held at 1350°C for 4 hr and raised rapidly to 1650°C for another 4 hr. The details of this heating schedule (schedule No. 1) are shown in Fig. 6.

* Richard D. Brew and Co., Concord, NH
Fig. 6. Heating schedules for sintering.
For the rest of the microstructure synthesis, specimens A to T, a tantalum resistance heating furnace with a heating zone 10 cm in diameter by 20 cm was used. The temperature was monitored and controlled by a Leeds and Northrup Speedomax-H Recorder-Controller through a W5Re-W26Re thermocouple. The specimen temperature could also be measured by a Leeds and Northrup optical pyrometers. Two programmed heating schedules, schedules 2 and 3, were used, Fig. 6.

Freeze dried powders calcined in vacuum at 900°C with H\textsubscript{2} treatment that were used in the hot stage SEM sinterability study were cold pressed to 28.0%, 45.0%, 55.0% and 61.0% of theoretical density, specimens A, B, C and D, and sintered according to heating schedule 2. Their polished microstructures were etched and examined by SEM.

Freeze dried powders ball milled and calcined at 750, 900 and 1300°C, with and without H\textsubscript{2} treatment, that were used to study the crystallite size effect on sintering in the hot stage SEM, were cold pressed to give approximately 53% theoretical density, specimens E to K, and sintered according to heating schedule 2. Their polished microstructure were examined to study the effect of residue sulfate on the sintered microstructures.

Freeze dried powders that were calcined the same as the powders for the spinel crystallite size growth analysis at 950, 1150, 1250 and 1350°C with and without hydrogen treatment, were ball milled,

cold pressed and sintered following heating schedule 3, specimens M, N, O, O, M-1, N-1, O-1 and P-1. The sintered specimens were polished, etched and examined to study the relationship between the crystallite size of the spinel powders and their sintered microstructures.

Freeze dried powders were calcined at 650°C in vacuum (~10 μm Hg) for 22 hr and were processed the same as specimens M to P-1 to study the effect of long time and low temperature calcination and their effect on the sintered microstructures. Also, the hydrogen treatment of the spinel powders allowed further study of the effect of residue sulfate on sintered microstructures.

Because MgO in spinel is fugitive in the sense that it is likely to be reduced by the surrounding tantalum heating element at the sintering temperature, special procedures were followed to minimize MgO vapor loss and to reduce the reaction with tantalum. Specimens A to T were thus loaded in an alumina crucible by spacing them with MgO single crystal chips and bury them in a powder mixture of MgO and MgAl₂O₄,* Fig. 7.

Specimens A to K were sintered in vacuum according to heating schedule 2 which has a short annealing time at 1850°C. For heating schedule 3, in which specimens were annealed at 1850°C for 3 hr, both helium and vacuum atmospheres were used. Helium was used to further reduce the vaporization and reduction of MgO in spinel. Helium was introduced into the vacuum system after the temperature

*Powder mixture of Baker reagent grade MgO and Alcan MgAl₂O₄ calcined at 1750°C in air for 12 hr.
Fig. 7. Specimen arrangement inside an alumina crucible for the sintering runs.
reached 1400°C and was kept at a static pressure a little below the atmospheric pressure. Specimens sintered in vacuum following heating schedule 3, O to T, provided some information on the effect of sintering atmosphere on the microstructures. These specimens were all obtained by calcining the freeze dried powders at 900°C in vacuum with and without milling of the freeze dried powders and the calcined powders. Their microstructural analyses further indicate the effect of different milling techniques on their sintered microstructures.
III. RESULTS AND DISCUSSION

The results and discussion are divided into three parts:

(A) preparation and characterization of the freeze dried powder, correlation with the calcined spinel powders, and modification of the freeze drying process to minimize powder aggregation, (B) calcination of the freeze dried powders and characterization of the calcined powders, and (C) correlation of the powder character with its sinterability and microstructure synthesis.

A. Freeze Dried Powders and Modifications of the Freeze Drying Process

1. Chemical and Physical Criteria for the Preparation of Freeze Dried Powders

One of the purposes for using the freeze drying process to produce reactive oxide powders is to maintain the intimate mixing condition of the chemical species in their solution state to the state when their corresponding oxide is formed by thermal reaction.1 Another purpose, for which not much work was done by previous workers, is to obtain the appropriate physical morphology of the freeze dried powders formed during the freezing and drying stages and to maintain it up to the temperature at which the oxide is formed.

a. Solution Mixing and Its Correlation with Powder Processing.

The first consideration is the chemistry of the aqueous solutions of MgSO₄·7H₂O and Al₂(SO₄)₃·18H₂O. To serve our purpose, there should be no chemical reactions in the individual or mixed solutions. Both hydrates are highly soluble in water at room temperature. Unfortunately, however, the 0.4 M aluminum sulfate hydrate solution showed settling of white precipitates after several months of aging.
The literature indicates\textsuperscript{30} that the hydrolysis of Al(III) is a complicated reaction, both mononuclear and polynuclear species being observed. From other experimental data, it was assumed that the hydrolysis product of Al(III) is either a series of complex \(\text{Al}[(\text{OH})_n\text{Al}_2]^{(n+3)+}_n\) or a single large complex \(\text{Al}_6(\text{OH})_{15}^{3+}\). In this study the structure and composition of the precipitates was not determined. The acidity of the aluminum sulfate solution was increased to pH \(\approx 1\) to prevent the precipitation.

The concentration of the mixed solution effects the melting point of the frozen particles, the reactivity of the thermal reaction to form oxide, the crystallite size of the oxide after calcination\textsuperscript{2} and the strength and physical structure of the freeze dried powders. The more concentrated is the mixed aqueous solution, the lower is the melting point of the frozen particles, and the frozen particles are more likely to suffer melting during the sublimation drying.

In determining the reactivity of the freeze dried powders to form spinel oxide, experimental results indicated that the solution mixed from 0.4 M \(\text{Al}_2(\text{SO}_4)_3\) and 1.14 M \(\text{MgSO}_4\) solutions (solution No. 1), after freeze drying, showed nearly complete reaction of the sulfates after calcination for 1 hr in air at 920°C as compared with other more dilute or more concentrated mixed solutions.\textsuperscript{1} Freeze dried and calcined alumina from aluminum sulfate hydrate aqueous solution indicated a change of about 20% of the determined crystallite size for a ten times change of solution concentration.\textsuperscript{2} A more dilute mixed solution, prepared from 0.267 M \(\text{Al}_2(\text{SO}_4)_3\) and 0.959 M \(\text{MgSO}_4\),
(solution No. 2), was used during the latter part of this research to further prevent the melting of frozen particles during sublimation drying.

b. Quick Freezing and its Correlation with Powder Processing. Quick freezing is the critical step in maintaining the intimate mixing in the solution. In the $\text{MgSO}_4-\text{Al}_2(\text{SO}_4)_3-\text{H}_2\text{O}$ ternary system, the only available information is a partial diagram of the 25°C isotherm. It was used as an approximation for the detailed discussion of the phase relationship during equilibrium and nonequilibrium cooling.\(^1\) Because of the immiscibility of salts and water at low temperatures, ice crystals segregate out as the temperature drops below the liquidus leaving regions of more concentrated solution. The phase transformation of dilute aqueous solutions was studied by Luyet\(^{31}\) on freezing with different cooling rates. He found that increasing the freezing velocity resulted in different types of ice crystals. With further increase of the freezing rate, incomplete crystallization of ice resulted, as verified by X-ray analysis by Meryman.\(^{32}\) In this research, a high freezing rate was desired which resulted in less chemical segregation and fine ice crystals. The physical morphology of the freeze dried powder after sublimation of the ice crystals, is shown in Fig. 8. The radial texture of the freeze dried powders reveals the direction of freezing when the droplet of mixed solution hits the heptane surface at about -50°C. The small voids are in the size range of a few thousand angstrom which indicate the size of the ice crystals segregated out during freezing. Different freezing rates resulted in freeze dried powders
Fig. 11. Size distribution of freeze dried powders.

A FREEZE IN FREON-12
B FREEZE IN HEPTANE
drying process proceeds, from a microscopic viewpoint, and increasing shell thickness of dried material develops. All the water vapor formed by sublimation at the drying boundary has to diffuse through the dried shell. From a macroscopic viewpoint, this water vapor has to diffuse through the bed of the frozen material, especially the bottom layer of the frozen bed.

The critical factor during the drying process is the prevention of melting. The temperature-pressure relationship for ice is shown in Fig. 12. It should be realized that the critical pressure that controls the sublimation is the pressure at the drying boundary of each frozen particle but not the pressure reading of the drying chamber. When melting takes place during the drying process, the porous physical structure is replaced by particles with a rigid surface and joined together through a liquid phase as shown in Fig. 13. This change of powder physical structure becomes the major source of powder aggregation which greatly affects the homogeneity of the sintered microstructures.

A number of steps can be taken to prevent the melting of the frozen particles during drying: dilution of the mixed solution, reduction of the size distribution of the frozen particles, and regulation of the heating cycle so that the upper part of the frozen bed dries first while the temperature of the bottom layer is kept below the melting point of the frozen particles. On following these procedures, melting during drying was affectively prevented.
The physical morphology of the freeze dried powders.
(A) The porous surface of the freeze dried powder.
(B), (C) Cross-sectional views of the freeze dried powder.
of different physical structures as seen in Fig. 9. The importance of the physical morphology of the freeze dried powder will be discussed in a later section.

In order to obtain a fast and uniform freezing rate for each mixed solution droplet, quick freezing conditions were improved. During the early part of this research the solution was sprayed into freon-12 in the same area with vigorous agitation. Because the freon-12 had a higher density than the frozen solution, some of the incoming solution droplets actually impinged on frozen pellets reducing the freezing rate (coarser structure after drying) and causing particle aggregation, Fig. 10. The aggregated particles are much bigger than the non-aggregated particles which persist as an aggregate and gain in strength in subsequent drying and calcining steps, as will be discussed in a later section. Using mixed hexane or heptane which have lower densities than the mixed solution and spraying over a large area resulted in freeze dried powders of finer texture and narrower size distribution than the powders frozen in freon-12, Fig. 11.

c. Sublimation Drying and its Correlation with Powder Processing.
The purpose of the sublimation drying step is to remove the segregated ice crystals while maintaining the chemical and physical integrity of the frozen hydrated particles. As the drying temperature increases, part of the chemically hydrated water is also driven off.

The temperature of the drying specimen is self determined by the rate of heat input, composition of the drying layer, and the rate of removal of water molecules from the drying layer. As the
Fig. 9. Three different freeze dried powders frozen at different freezing rates.
(A) Frozen in freon-12 at -28°C.
(B) Frozen in heptane at about -40°C.
(C) Frozen in mixed hexane at about -60°C.
Freeze dried powders, frozen in freon-12 and dried at 120°C.

(A) An overall view of the powders at low magnification.

(B) A magnified picture of the aggregate showing in the center of (A). This aggregate was the result of frozen particle and solution droplet collision during quick freezing and remelting during drying.

(C) One of the freeze dried particles with porous surface.
Fig. 12. Temperature-vapor pressure relationship for H₂O.
Fig. 13. Freeze dried powders which suffered remelting during drying. Remelting during drying resulting in the join of particles and having a rather solid surface.

XBB 7310-6095
The remaining chemically-combined water content is determined by the final drying temperature. The effect of drying temperature on the X-ray diffraction pattern of the freeze dried powders was studied. The reactivity of the freeze dried sulfates thermally reacted to form spinel was also studied using powders freeze dried from 25 to 140°C. The powder freeze dried at 25°C showed the most complete conversion of sulfates to spinel. The low drying temperature, however, results in highly hydrated salts which usually melt during calcination before the decomposition reaction takes place; this is another source of powder aggregation. To prove that low temperature dried powder would melt before decomposing, a batch of powder freeze dried at 25°C was heated by the electron beam in a scanning electron microscope. Melting of the powders, especially those of large size, was observed on the television screen. The melting took place as soon as the electron beam focused on the powder.

The purpose of the vacuum thermogravimetric dehydration analysis of the powder freeze dried at 25°C was to understand the structural nature, dehydration kinetics and residue water content. The significance of dehydration kinetics in determining the structure of the freeze dried powders will be discussed in the section on characterization of freeze dried powders. The residue water content was calculated as the average number of water molecules associated with each pair of MgSO₄ and Al₂(SO₄)₃. The results are shown in Table II. Powders dried above 65°C indicated no melting during calcination. The batches prepared for later powder characterization and sintering studies were dried at 120°C.
Table II. Average H$_2$O associated with each MgSO$_4$·Al$_2$(SO$_4$)$_3$ at different freeze drying temperatures.

<table>
<thead>
<tr>
<th>Drying Temperature</th>
<th>Average H$_2$O with each MgSO$_4$·Al$_2$(SO$_4$)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>9.2</td>
</tr>
<tr>
<td>65°C</td>
<td>5.6</td>
</tr>
<tr>
<td>120°C</td>
<td>3.6</td>
</tr>
<tr>
<td>210°C</td>
<td>1.9</td>
</tr>
</tbody>
</table>
2. Correlation of Freeze Dried Powders with the Calcined Spinel Powders

The freeze dried powders prepared from all mixed solutions showed an amorphous X-ray diffraction pattern with two wide diffuse peaks at d spacings of 5.90Å and 3.56Å. With increasing sublimation temperatures, these two peaks increased in intensity. Some of the freeze dried powders showed four sharp peaks superimposed upon the amorphous pattern at d spacings of 2.29Å, 1.99Å, 1.42Å and 1.21Å, which also increased in intensity with increasing drying temperature. These four peaks were not identifiable, but they are probably due to some intermediate phase of aluminum complexes which segregated out as tiny crystallites in the aluminum sulfate aqueous solution and persisted through the drying step.

The X-ray amorphous nature of the freeze dried powders may be explained as being due to either loose aggregates of microcrystals which are too small to diffract X-rays coherently or to completely disordered arrays of ions and molecules in a zeolitic glass. Both explanations indicate an intimate atomic scale mixing of the two starting sulfates. The X-ray amorphous nature of the freeze dried powder is similar to the dehydration of some other crystalline hydrates, such as CuSO$_4$$\cdot$5H$_2$O,$^{32}$ which was explained as being due to the initial formation of a network pseudomorph of the starting crystalline structure which spontaneously rearranges into the amorphous structure upon reaching a critical water content.
Saturated aqueous solutions of an equimolar ratio of the two sulfates were vacuum dried at room temperature and 80°C. The room temperature dried material showed many overlapping peaks of similar intensity while the 80°C dried material had a similar X-ray amorphous pattern as the freeze dried powders. The room temperature dried material after redrying at 80°C in vacuum changed to a completely X-ray amorphous pattern. The amorphous vacuum dried salt mixture recrystallized after being exposed to the atmosphere for a few days. These results indicate that the amorphous nature of the partially dehydrated salt mixture from the concentrated mixed solution is closely associated with its water content.

Scanning electron micrographs, Fig. 14, showed the directional recrystallization of the pipe-like crystals formed from the surface of the freeze dried powders. This pipe-like shape is not understood. The freeze dried powders prepared for this research were all stored in a vacuum desiccator.

Unlike the room temperature vacuum dried saturated aqueous sulfate solution, the powders freeze dried at room temperature exhibited an X-ray amorphous state. Comparison of the dehydration of the saturated sulfate solutions and the freeze dried powders indicates that the X-ray amorphous nature of the freeze dried powder is not just the result of having reached a critical water content. Furthermore, the weight loss curve in Fig. 15 indicates that the freeze dried powder lost its hydrated water gradually as temperature and time increased. The gradual slope and leveling off of the weight loss curve indicates
Fig. 14. Two rehydrated freeze dried powders each at two magnifications.
Fig. 15. Thermogravimetric analysis of a freeze dried powder. XBL 7310-5455
that the freeze dried powder does not have a definite hydrated structure. From the above discussion, it is logical to conclude that the amorphous nature of the freeze dried powder is due to the water content and the lack of long range ordered structure which in turn is due to the rapid freezing of the solution.

The amorphous nature of the freeze dried powders was retained up to about 300°C. Above 300°C, weak crystalline X-ray peaks of anhydrous aluminum sulfate and anhydrous magnesium sulfate began to appear and increased in intensity with increasing temperature. At about 750°C in air or at about 640°C in vacuum (50 μm Hg), the two sulfates began to react to form spinel oxide. Since the amorphous nature of the freeze dried powders indicates an intimate mixing of the two sulfates, it is desirable to maintain the amorphous structure up to the temperature of the thermal reaction. The freeze dried powders were thus calcined by inserting the powders directly into the hot zone of the furnace.

The sulfates decomposed and reacted to form the spinel oxide powders, Fig. 16. A bimodel size distribution is indicated: large aggregates and uniform ultrafine powders. The latter have a platy morphology, as seen in Fig. 17, which is due to the pseudomorphy of the freeze dried powders but not to any preferred growth of the spinel crystallites. The X-ray transmission pinhole photograph of the spinel powders showed uniformly blackened Debye rings which excluded the possibility of preferred orientation.

There is nearly a 60% weight loss when the freeze dried powders decompose to form spinel. The rapid decomposition reaction thus takes
AGGREGATES OF SPINEL POWDERS SCATTERED AMONG FINE PARTICLES.

Fig. 16.

A) CALCINED AT 950°C FOR 1 HOUR IN VACUUM.
B) CALCINED AT 1150°C FOR 2 HOURS IN VACUUM.
Fig. 17. (A) Spinol powders obtained by calcining the freeze dried powder at 1050°C in vacuum for two hours. The freeze dried powder were prepared by freezing the No. 1 mixed solution in mixed hexane at about -60°C and dried without remelting to 65°C. (B), (C), (D) Same powder specimen as (A), showing the pseudomorph relationship between the calcined spinel and the freeze dried powder.
place drastically. The dried powders were broken apart due to the weight loss and the drastic evolution of gas (H\textsubscript{2}O, SO\textsubscript{2} and O\textsubscript{2}). Each platelet which was part of the freeze dried powder became one particle of the calcined spinel. The pseudomorphic relationship between the freeze dried powder and the uniform ultrafine calcined spinel can be seen clearly in Fig. 17. Figure 17A shows the platy shaped uniform spinel powders; Figs. 17B, 17C and 17D show some fine platy particles which are still adhering as if they were part of the freeze dried particle. Each platy spinel particle which consisted of thousands of tiny spinel crystallites tended to aggregate on the coarse scale within the pseudomorphs of the freeze dried powder from which they were derived. Since the freeze dried powders did not have a crystalline structure, it further rules out any possible preferred orientation of the spinel crystallites inside each particle which does happen for other fine oxide powders derived from their salts. Powders A and B in Fig. 16 have approximately the same size of platelets and aggregates, but they have different average crystallite sizes, 95\AA and 280\AA, respectively as measured by the X-ray line broadening technique. Thus, the macroscopic size and morphology of the calcined spinel powders are controlled by the physical structure and morphology of the freeze dried powders, and the individual crystallite sizes are mainly dependent on the calcination temperature and time. The physical structure of the freeze dried powder is controlled by the characteristics of the mixed solution: concentration, freezing rate and the sublimation conditions.
Large aggregates present in the calcined spinel powder have different morphologies. Porous aggregates usually are pseudomorphic after the freeze dried powder, Figs. 18, 19 and 20. The existence of porous aggregates can be attributed to a decomposition reaction that was not drastic enough to break apart the freeze dried particles, to the freeze dried particle having a strong enough structure that would not be broken by the decomposition reaction alone, or to too large a freeze dried particle. The strong structure of the freeze dried powder may be due to powder aggregation during the quick freezing stage, to slightly melting during the drying stage, or to melting during the calcination stage, as discussed before. Usually, melting during the crying stage resulted in freeze dried particles with solid surfaces and thus dense calcined aggregates, as shown in Fig. 20. High temperature and long calcination time form strong bonds between agglomerated fine particlals by partial sintering, Fig. 18.

In general, the nature of the aggregates depends upon the physical structure of the freeze dried powders before calcination. It is expected that dense aggregates are stronger than the porous ones. Johnson et al.\(^6\) compared the size distribution of hard and soft aggregates by wet sieving the aggregated and ultrasonically deaggregated powders. Energy from the ultrasonic probe lowered the fraction of 50-100 µm aggregates in the alum-derived alumina powders. Similar
Fig. 18. TWO MAGNIFICATIONS OF THE SPINEL POWDERS PREPARED BY CALCINING THE FREEZE DRIED POWDER IN VACUUM AT 1150°C FOR ONE HOUR.
Fig. 19. Spinel powder aggregates.
AGGREGATES OF SPINEL POWDERS AT THREE DIFFERENT MAGNIFICATIONS. THE FREEZE DRIED POWDER HAS BEEN DRIED TO AVOID REMELTING AND CALCINED AT 1020°C FOR TWO HOURS IN VACUUM.

AGGREGATE OF SPINEL POWDER PREPARED FROM FREEZE DRIED POWDER WHICH HAS SUFFERED REMELTING DURING DRYING. THE FREEZE DRIED POWDER WAS CALCINED AT 1150°C FOR TWO HOURS.

Fig. 20.
ultrasonic treatment did not break either the large porous or dense aggregates of the calcined spinel as determined by examination of powders by the scanning electron microscope before and after ultrasonic treatment. For sintering purposes irrespective of the origin of the aggregates, if they do not break down under pressure during the compact forming process, regions of different green densities will be formed which result in nonhomogeneous microstructures. This correlation will be discussed in the microstructure synthesis section.

One batch of nearly aggregate-free ultrafine spinel powder was prepared by spraying the No. 1 mixed aqueous solution into mixed hexane which was chilled by an acetone and dry ice mixture at about -65°C and dried to 65°C without remelting, Fig. 21. This freeze dried powder was calcined at 1000°C for 2 hr in vacuum. The powder specimen was examined by scanning electron microscope consists of uniform platy particles, as shown in Fig. 17. Effects to produce this result were unsuccessful. The reasons that a uniform ultrafine spinel powder was produced and that reproduction was not successful are discussed here. It is apparent from the figure that the freeze dried powder had completely broken down to the ultimate individual pieces during the decomposition reaction. This freeze dried powder had the finest texture in comparison with other batches made from solution mixed solution No. 2 with use of heptane. Even though mixed hexane and heptane were both chilled by acetone-dry ice mixture, the mixed hexane had a much higher thermal conductivity than heptane which resulted in a fast freezing rate. It appears that an appropriate concentration of the mixed aqueous sulfate solution
Fig. 21. Different magnifications of the freeze dried powders prepared by freezing the No. 1 mixed solution in mixed hexane at about -60°C and dried without remelting to 65°C.
freezing at a fast rate is necessary to reproduce the finer texture of the freeze dried powders that would break apart completely upon calcination. Also, during the calcination, freeze dried powders of small size and narrow size distribution would enable the surface and the interior of the powder to reach its decomposition temperature almost simultaneously and cause a drastic evolution of gas to break up the freeze dried powder into uniform ultrafine spinel powders. The chemical engineering details necessary to reproduce this kind of powder in a large batch were not pursued in this research.

Short time dry ball milling was used to further break down the powder aggregates. Ball milling not only broke up the porous structure of the freeze dried powder but also caked the fine particles into dense aggregates as shown in Figs. 22A and B and Fig. 23. Spinel powders calcined from the ball milled freeze dried powders showed individual submicron particles and dense aggregates which were pseudomorphs of the caked aggregates, Figs. 22C and D and Fig. 24. On milling for 7, 10, 15 and 25 min with the same rotation speed, it was found that milling for 7 or 10 min resulted in less caked or unbroken aggregates. Longer time milling increased the aggregation of fine particles. The spinel powders directly calcined from the freeze dried powders and then ball milled indicated uniform size aggregates of fine particles, Fig. 25.
Fig. 22. (A), (B) Four grams of freeze dried powder milled for 10 minutes in alumina planetary mill.
(C), (D) Spinel powders calcined at 900°C in vacuum for one hour from the milled freeze dried powder.
Fig. 23. Freezedried powders ball milled for 15 minutes
(1), (2) Different magnifications at one area
(3) A dense aggregate
Fig. 24. Spinel powders calcined from ball milled freeze dried powders at 900°C in vacuum for one hour.
(1), (2), (3) Different magnifications at one area.
(4) A close look at the dense aggregates.
Fig. 25. SPINEL POWDERS CALCINED AT 1350°C IN AIR FOR ONE HOUR AND BALL MILLED
B. Calcination of Freeze Dried Powders and Characterization of Calcined Powders

The sintering kinetics and the final sintered microstructure is directly related to the properties of the oxide powders prior to sintering. Important characteristics of the oxide powders are crystallite size (or surface area per unit mass), crystallinity, chemical composition, chemical impurities and powder aggregation. For spinel powders derived from the freeze dried mixed sulfate, the calcination process is one of the decisive steps for controlling powder characteristics. Temperature, time and atmosphere are the calcination variables used in this research to correlate the spinel powder's characteristics and their sintering behavior.

The physical morphology of the ultrafine and aggregated spinel powders was discussed in the previous section. The X-ray diffraction phase analysis, crystallite size growth mechanism, and the chemical impurity analysis of the calcined spinel powders are discussed in this section.

1. Crystalline Phases on Calcination

Differential thermal analysis, Fig. 26, and thermodynamic calculations suggest that the reaction forming spinel upon decomposition of the freeze dried powders at one atmosphere pressure is,

\[ \text{MgSO}_4(s) + \text{Al}_2(\text{SO}_4)_3(s) = \text{MgAl}_2\text{O}_4(s) + 4\text{SO}_2(g) + 2\text{O}_2(g) \]

which can be postulated as consisting of the step reactions

\[ \text{Al}_2(\text{SO}_4)_3(s) = \text{Al}_2\text{O}_3(s)_{\text{amorphous}} + 3\text{SO}_2(g) + 3/2\text{O}_2(g) \]
Fig. 26. DTA of freeze dried aluminum sulphate, magnesium sulfate and freeze dried magnesium aluminum sulfate.
and

\[ \text{Al}_2\text{O}_3(s)_{\text{amorphous}} + \text{MgSO}_4(s) = \text{MgAl}_2\text{O}_4 + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \]

In the DTA curve of the freeze dried powder, the first two endothermic peaks corresponding to the decomposition of hydrated water. Before the start of the large endothermic peak at around 370°C, the freeze dried powders have dehydrated and crystallized to a mixture of anhydrous MgSO_4 and Al_2(SO_4)_3. At about 730°C, the spinel phase begins to form at a slow rate; the DTA curve for aluminum sulphate also shows the endothermic decomposition reaction starting at about this temperature. In vacuum (about 50 μm Hg) the reaction temperature to form spinel is about 630°C.\(^1\)

To achieve a complete calcination, either a higher temperature or longer calcination time is required. Freeze dried powders calcined at 650°C in vacuum for different periods of time were studied. After 2 hr, the X-ray diffraction pattern showed shifted spinel peaks and peaks for both sulfates. After 22 hr, the calcined powder showed two minor MgO peaks, a minor sulfate peak (at I/I = 100 for both MgSO_4 and Al_2(SO_4)_3), and all the spinel peaks were again slightly shifted from their standard position. The existence of an intermediate alumina rich monoclinic spinel MgO·3Al_2O_3 has been reported.\(^3\) The shifted peaks, however, do not fit the diffraction lines of this

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\(^*\)Peaks shifted several degrees irregularly from their standard position by Swanson and Fuyat.\(^3\)
monoclinic spinel. The shift of peaks from their normal position can thus only be suggested as being due to the formation of a defect structure spinel at this low calcination temperature.

One gram portions of the freeze dried powders were calcined for 1 hr in air from 900 to 1400°C at 50°C intervals. The 900°C calcined spinel powder showed a minor peak of sulfates (at I/I₀ = 100 for both MgSO₄ and Al₂(SO₄)₃) and a minor peak of MgO. As the calcination temperature increased, the spinel phase increased its crystallinity, the sulfate peak disappeared, and the MgO peak decreased in intensity. The increasing spinel crystallinity was also accompanied by the changing of the relative intensity of the {400}, {440} and {222} reflections with respect to the {311} reflection (I/I₀ = 100), Fig. 27. All peaks at other reflections were essentially constant in their relative intensities with varying calcination temperature. The changing of {400}, {440}, and {222} reflections with calcination temperature has not been reported in the literature. It has shown that the relative intensity for each reflection changed slightly for spinels prepared by different workers. The spinel powders prepared in this research, after 2 hr calcination at 1500°C, had relative intensities of each reflection that closely resembled the latest X-ray standard diffraction pattern.

For the spinel structure, AB₂O₄, the normal or inverse structures, in some cases, are alternated by appropriate heat treatment. If there is sufficient difference between the X-ray scattering power of the A and B ions, it is possible to determine the distribution of these ions by means of their relative integrated intensity from their
Fig. 27. Relative intensities of indicated X-ray diffraction peaks vs temperature.
In magnesium aluminate spinel itself, however, this is not possible because of the similar scattering power of the Mg\(^{++}\) and Al\(^{+++}\) ions. Since the scattering cross section for neutrons of Mg\(^{++}\) is appreciably greater than that of Al\(^{+++}\), it was then possible to determine that the magnesium aluminate spinel has a normal structure. The above discussion excludes the explanation of the changing relative intensity as a result of the distribution of the ions in the close packed oxygen lattice.

From Fig. 27, it is observed that the abnormal high relative intensities of \{222\}, \{400\} and \{440\} reflections, whose standard relative intensities are 3, 58 and 58, respectively, drop sharply after 1200°C and then slowly approach the standard ratio with increasing calcination temperature. At low calcination temperatures, minor MgO or MgSO\(_4\) peaks were observed as an indication of slight segregation of these phases. For freeze dried powders with a starting stoichiometric composition, any separation of MgO or MgSO\(_4\) phase would result in the formation of an Al\(_2\)O\(_3\) rich spinel. MgSO\(_4\) decomposes in air at about 1130°C. The abnormal ratio of the relative intensities of \{400\}, \{440\} and \{222\} reflections can thus be associated with the structure of an alumina rich spinel. As the calcination temperature is increased, the alumina-rich spinel would react with the segregated MgO phase to reach fully crystalline stoichiometric spinel which would have the standard X-ray diffraction pattern.

Summarizing the X-ray diffraction analyses, it can be seen that the freeze dried powders calcined in air above 1200°C for 1 hr had a single fully crystalline spinel phase. Calcination of freeze dried
powders in vacuum lowered the temperature (630°C) needed to form spinel. Long time calcination of the freeze dried powders in vacuum below 750°C yielded a defect structure spinel without observable sulfate peaks. Short time (1-2 hr) calcinations in vacuum below 750°C produced the same defect spinel structure but also showed distinct sulfate peaks. Calcination of the freeze dried powders in vacuum for 1 hr at 900°C yielded a regular but not fully crystalline spinel pattern without any noticeable sulfate peak. The effect of the crystallinity of the calcined spinel powders on their sinterability will be discussed later.

2. Residue Sulfate Chemical Analysis

One gram portions of the freeze dried powder were calcined for 1 hr in air from 900 to 1400°C at 50°C intervals. The sulfate content of the calcined powders was chemically analyzed* in terms of wt% residue sulfur and plotted against temperature, Fig. 28. The data were also plotted against temperature on a semilog plot, Fig. 29. The residue sulfur data for powders calcined at 1000 and 1300°C for different periods of time were plotted against time on a log-log basis, Fig. 30; the slope is the order of the sulfate decomposition reaction.** Figure 30 indicates that the reaction order changes with

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*Coors Spectrochemical Laboratory, Golden, Colorado.
**Al2(SO4)3 and MgSO4 decompose in air at about 725 and 1130°C. The residue sulfate being measured is thus more likely to be due to the unreacted MgSO4; therefore, the reaction order measured here is with respect to MgSO4.
Fig. 28. Crystallite size and sulfur residue in spinel powders vs temperature.
Fig. 29. Log of wt% sulfur residue vs temperature for 1 hr calcinations.
Fig. 30. Log-log plot of sulfur residue vs time for calcinations at 100 and 1300°C.
temperature* and time; therefore, it is impossible to determine the apparent activation energy of the decomposition reaction. Figure 29 indicates a nearly straight line empirical relationship between the residue sulfur and temperature:

\[ C_s = K e^{aT} \]

where \( C_s \) = wt\% residue sulfur, \( a \) = slope, and \( T \) = temperature. This nearly straight line relationship can not be evaluated from a chemical kinetics approach; it only serves as an empirical relationship for this particular system.

As indicated, the complete removal of residue sulfate is kinetically dependent on the calcination time and temperature and thermodynamically dependent upon the calcination atmosphere. Long time and high temperature calcinations not only remove the sulfate but also aggregate the fine particulates. Vacuum calcination reduces the partial pressure of the gases evolved during calcination and, therefore, enhances the sulfate decomposition reaction. Another atmospheric approach is to remove residue sulfate during calcination by a chemical reduction reaction.

Thermodynamic calculations indicate that either magnesium sulfate or aluminum sulfate can be reduced by hydrogen at temperatures as low as 200°C. The kinetics of the reduction reactions of freeze

*For the 1000°C calcination, the different slope before and after 1 hr calcination may be due to the fact that both aluminum and magnesium sulfates were decomposing before the 1 hr period.
dried Al$_2$(SO$_4$)$_3$ and MgSO$_4$ were studied by thermogravimetric analysis with a constant heating rate and positive hydrogen pressure of 1/3 psi. The percent cumulative weight loss of surface was plotted against time for aluminum sulfate in Fig. 31, and for magnesium sulfate in Fig. 32. Figure 31 indicates that a fast rate of weight loss due to the reduction reaction occurred at around 580°C for Al$_2$(SO$_4$)$_3$, and Fig. 32, at about 700°C for MgSO$_4$. An incomplete experiment with 2/3 psi H$_2$ indicated that the sharp weight loss took place for MgSO$_4$ at about 650°C. A comparison of calculated weight loss and experimental weight loss data indicated that both sulfates were completely reduced. The X-ray diffraction analysis of the reduced products indicated that the major phase is gamma alumina or magnesia, and that both had some unidentified minor peaks.

Chemical analysis results for the freeze dried powders calcined in vacuum at 700°C for 14 hr before and after an additional H$_2$ (1/3 psi) treatment at 750°C for 30 min are 1.12 and 0.072 wt% residue sulfur. Results for freeze dried powders calcined in vacuum at 1160°C for 1 hr before and after the H$_2$ treatment are 0.327 and 0.055 wt% residue sulfur. These results do not quite fit the data shown in Fig. 29,* but they do show the effective removal of residue sulfate by H$_2$ treatment at low temperature prior to calcination.

From the foregoing discussions, it can be seen that for 1 hr calcination the residue sulfate concentration decreases exponentially

* Samples were sent to the Coors Spectro-Chemical Laboratory at different times, some differences were thus expected.
Fig. 31. Reduction of $\text{Al}_2(\text{SO}_4)_3$ in 1/3 psi flowing $\text{H}_2$. 

$\text{Al}_2(\text{SO}_4)_3$ REDUCTION REACTION IN $\frac{1}{3}$ PSI $\text{H}_2$

TIME, min. 

PERCENT CUMULATIVE WEIGHT LOSS

TEMPERATURE, °C

0 20 40 60 80 100 

0 20 40 60 80 100 

XBL753-6024
Fig. 32. Reduction of MgSO₄ in 1/3 psi flowing H₂.
with calcination temperature. The order of the decomposition reaction is temperature and time dependent. The high calcination temperature needed to remove the trace amount of residue sulfate would seriously aggregate the fine spinel crystallites by partial sintering. If the trace of residue sulfate is not removed prior to sintering, trapped gases would be retained inside the microstructure. TGA experiments show that both aluminum and magnesium sulfates can be reduced to their oxide at low enough temperature to avoid powder aggregation. Chemical analysis results indicate that H₂ treatment at 750°C of already calcined powders greatly reduces the residue sulfate content. The effect on the spinel crystallite growth and sintered microstructure will be discussed later.

3. Spectrographic Analysis

A qualitative X-ray fluorescence analysis indicated that Mo, Pb, Zn, Cu, Fe are the major impurities of the freeze dried powder. Based on this analysis, a spectrographic analysis* was made on the precursor sulfates, the freeze dried powders and the calcined spinel powders, Table III. From indicated data no significant increase of impurity level occurred during the freeze drying process.

4. Spinel Crystallite Growth during Calcination

The average spinel crystallite size as a function of calcination temperature, time and atmosphere was measured by the X-ray line broadening technique assuming that the calcined powders were essentially 

*American Spectrographic Laboratories, Inc., San Francisco, CA
Table III. Spectrographic analysis.

<table>
<thead>
<tr>
<th></th>
<th>Freeze Dried Powder</th>
<th>MgSO₄·7H₂O</th>
<th>Al₂(SO₄)₃·18H₂O</th>
<th>Calcined Spinel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>5.0 %</td>
<td>0.001%</td>
<td>8.0</td>
<td>20.</td>
</tr>
<tr>
<td>Al</td>
<td>7.0</td>
<td>8.5</td>
<td>1.75</td>
<td>12.</td>
</tr>
<tr>
<td>Si</td>
<td>0.006</td>
<td>0.002</td>
<td>0.002</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe</td>
<td>0.005</td>
<td>0.002</td>
<td>0.002</td>
<td>0.015</td>
</tr>
<tr>
<td>Cu</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.002</td>
</tr>
<tr>
<td>Ni</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.002</td>
</tr>
<tr>
<td>Ca</td>
<td>0.003</td>
<td>0.003</td>
<td>0.001</td>
<td>0.004</td>
</tr>
<tr>
<td>Cr</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.001</td>
</tr>
<tr>
<td>Na</td>
<td>0.1% in each sample (not detected).</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.15% in each sample (not detected).</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.005 in each sample (not detected).</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.002% in each sample (not detected).</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>0.007% in each sample (not detected).</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Balance of each sample—not found.
strain free. This method only allows the determination of the average thickness of crystallites in certain crystallographic orientations which satisfy the Bragg condition. The crystallite size was measured at \( \{220\} \) and \( \{511\} \) orientations because these two orientations were not overlapped by diffraction peaks of other related compounds and their relative intensities were less affected by the crystallinity of the calcined powder. One gram portions of freeze dried powder, formed from aqueous solution No. 1 and dried at 120°C, were calcined isothermally in air for 1 hr from 900 to 1400°C at 50°C intervals. The average crystallite size is plotted vs calcination temperature in Fig. 28. One gram portions of the same batch freeze dried powder were calcined in air isothermally at 1000°C and 1300°C for different periods of time and the measured average crystallite sizes were plotted against calcination time on a log-log (Fig. 33) and linear (Fig. 34) scale.

The large increase of the spinel crystallite growth rate above 1200, as seen in Fig. 27, indicates that either different growth mechanism exist or the rate of crystallite growth is inhibited below 1200°C. Similar crystallite growth curves were shown for other oxides without explanation. The linear plot of crystallite size against time shows a rapid increase of crystallite size for both temperatures during the first several hours.

To explain the spinel crystallite growth phenomena, it is necessary to consider the effect of calcination temperature on the dehydration and crystallization of anhydrous sulfates of the freeze
Fig. 33. Log-log plot of crystallite size vs time for powders calcined at 1000 and 1300°C.
Fig. 34. Crystallite size vs time for powders calcined at 1000 and 1300°C.
dried powder before decomposition, the effect of temperature on the crystallite growth rate and mechanism, and the effect of residue sulfate on the spinel crystallite growth.

From the DTA curve and X-ray analyses, it was determined that crystallites of both anhydrous sulfates began to appear at the end of the dehydration reaction and grew in size at higher temperatures up to the spinel reaction temperature and longer times. Isothermal calcination at a higher temperature raised the powder temperature at a faster rate. The faster the freeze dried powder reaches its decomposition reaction temperature, the smaller the size of the anhydrous sulfate crystallites, since the spinel crystallite formed more easily through the diffusional movement of the reacting atoms. The faster reaction to form spinel crystallites minimizes the compositional segregation and results in a more homogeneous composition powder. After reaching the reaction temperature, a layer of spinel formed between adjacent MgSO₄ and Al₂(SO₄)₃ crystallites. The growth of the spinel layers continued by chemical interdiffusion between Al₂O₃ and MgSO₄ (or MgO, depending on the calcination temperature) grains. As the sulfates were consumed, the spinel crystallites impinged on each other and further increase of their size was due to grain growth.* Figure 34

*The activation energy for forming MgAl₂O₄ from single crystal Al₂O₃ and MgO is 125 k cal/mole below and 88 k cal/mole above 1750°C. The activation energy for spinel grain growth is 110 kcal/mole and the sintering by volume diffusion has an activation energy of 118 k cal/mole. Those reported activation energies are not quite applicable to this system because we are dealing with very small crystallites which have a different vacancy concentration compared with large single crystals.
indicates that for 2 hr of calcination the spinel crystallite size is much larger for the 1300°C calcination than for the 1000°C calcination; this figure also shows that both crystallite growth rates slow down after 2 hr of calcination. From the log-log plot of the same data, Fig. 32, the data points for both calcination seem gradually developed into a straight line relationship after 2 hr of calcination. This straight line relationship is characteristic of grain growth phenomena for both ceramic and metallic materials. The data indicate that the higher temperature calcination allows the crystallites to grow to a larger size before the grain growth mechanism takes place. Also, from the data it is seen that the initial growth of the spinel crystallites is much faster than the subsequent grain growth. The different growth rates are logical if one considers that the atomistic state of the powder before the reaction to form spinel is full of structural defects and, therefore, would require a low activation energy for a diffusional reaction.

The major chemical impurity is residual sulfate. Adsorbed phosphate inhibited the crystallite growth of beryllium oxide. The residual sulfate appears to inhibit the grain growth of sintered specimen H of this research.* To further prove the inhibition of spinel crystallite growth by sulfate, two 1 gram portions of freeze dried powders were calcined: one at 1000°C in air for 12 hr, the

* This specimen was sintered from spinel powders calcined in vacuum for 2 hr at 750°C. The residual sulfate formed a secondary grain boundary phase resulting in a grain size much smaller than that for specimen E, which was sintered under the same heating condition using the same calcined spinel powder with an additional H₂ treatment to remove the residual sulfate.
other in air at 1000°C for 2 hr and then treated with H₂ at 800°C with 2/3 psi positive pressure for 1 hr and then recalcined for 10 hr in air at 1000°C. The crystallite size of the two calcined powders was 160Å and 300Å. The H₂ treated powder showed an increasing growth rate which confirmed that the residual sulfate is inhibiting the spinel crystal growth.

Based on the above discussions, the spinel crystallite growth can be explained. When the powder temperature reached the decomposition temperature, a layer of spinel formed a crystallite contacts of MgSO₄ and Al₂(SO₄)₃. The diffusional growth of this spinel layer is temperature dependent, i.e., a faster growth for high temperature calcination. Because of the faster initial growth of the spinel crystallites, high temperature calcination allows the crystallites to coalesce to a bigger size than the low temperature calcination before normal grain growth starts. Because MgSO₄ decomposes at around 1130°C in air, a small amount of the segregated and unreacted MgSO₄ would inhibit the coalescence of the crystallites at calcination temperatures below 1200°C.

C. Powder Sinterability and Microstructures

1. Effect of Crystallite Size and Packing Uniformity on Powder Sinterability

The sintering kinetics of powder compacts vary with the sintering conditions (temperature, heating schedule, atmosphere, etc), crystallite size, crystallinity, impurity level, packing homogeneity, and packing density of the powder. The non-isothermal sintering kinetics for powders of different crystallite size and packing uniformity was
studied by directly monitoring the linear shrinkage of powder compacts in the hot stage of a scanning electron microscope. Some of the powder characteristics which affect the sintering kinetics are inter-related, and therefore it is difficult to study the sintering kinetics with only one powder characteristic changing at a time. For the powders calcined at three different temperatures to obtain different crystallite sizes, their residue sulfate content, powder aggregation, packing density and sintering conditions were kept the same as much as possible in order to obtain significant results.

a. Packing Uniformity. Powders from the same batch of ball milled freeze dried powder were calcined at 750°C in vacuum for 2 hr (powder A), 900°C in vacuum for 1 hr (powder B), and 1300°C in air for 1 hr (powder C); all of the powders were treated with H₂ at 750°C for 1/2 hr to control their residue sulfate content. The scanning electron micrographs of the calcined powders, shown in Figs. 35, 36 and 37, indicate that powders A and B have similar particle and aggregate distribution, but the powder calcined at 1300°C is more aggregated and the aggregates are much stronger. A portion of powder C was ball milled (powder C-1), shown in Fig. 38, to study the effect of powder packing uniformity on sintering kinetics. To determine the uniformity of powder compaction, fracture surfaces of cold pressed pieces made from powders A, B, C and C-1 were examined by SEM. Figure 39 indicates that compacts made of powder A and B were very uniformly packed without any micron size pores throughout the fractured green bodies. On the other hand, the fractured specimen made of powder C, Figs. 39C and 40, showed
Fig. 35.  Spinel powders calcined at 750°C in vacuum for two hours from the freeze dried powders which were ball milled for 10 minutes.
(A), (B) Overall view at low magnifications
(C) Some fine particles from center of (B)
(D) An aggregate consists of fine particles from (B)
Fig. 36. Spinel powders calcined at 900°C in vacuum for one hour from the freeze dried powders which were ball milled for 10 minutes.
(A), (B) Overall view at low magnifications
(C) Some fine particles from center of (B)
(D), (E) Two magnifications of an aggregate shown in (B)
Fig. 37. Spinel powders calcined at 1300°C in air for one hour from the freeze dried powders which were ball milled for 10 minutes.
(A), (B) Overall view at low magnifications
(C), (D) Aggregates of fine particles
Fig. 38. Spinel powders milled by agate pestle and mortar. The spinel powders were calcined at 1300°C in air for one hour from freeze dried powders which were ball milled for 10 minutes.
Spinel powders calcined from ball milled freeze dried powders and treated with H$_2$ at 750°C for half hour were pressed into green compacts.

(A) Calcined at 750°C in vacuum for 2 hours and pressed into 52.5% theoretical density
(B) Calcined at 900°C in vacuum for 1 hour and pressed into 54% theoretical density
(C) Calcined at 1300°C in air for 1 hour and pressed into 54.5% theoretical density.
Spinel powders calcined at 1300°C in air for 1 hour from ball milled freeze dried powders were pressed to 54% theoretical density.

(A, B) Powder compact made of unmilled calcined powders as shown in figure (C).

(C, D) Powder compacts made of milled calcined powders as shown in figure.
scattered porous areas. Since these three compacts were pressed to a similar bulk green density, the dense area of compact C in Figs. 39 and 40 should have higher density than the bulk green density of powder A and B. Compacts made from powder C-1, Figs. 39C and D indicated that ball milling had improved the packing uniformity and that they were comparable with the compacts made of powder A and B.

b. **Powder Crystallite Size and X-Ray Diffraction Analysis.** The crystallite size for powders A, B and C were measured as 50, 90 and 630Å respectively. The X-ray diffraction pattern for powder A before H₂ treatment indicated several weak sulfate peaks and strong MgO peaks. After the H₂ treatment, the sulfate peaks were gone but the MgO peak increased in intensity. X-ray diffraction patterns of powders B and C showed a minor MgO peak in the former and fully crystalline spinel in the latter. The H₂-treated powder B showed a slight decrease of the relative intensity of the {222} reflection; and powder C showed no change after H₂ treatment.

c. **Correlations with Sintering Kinetics.** Powders A, B, B-1, (B with H₂ treatment), C and C-1 (C with additional ball milling) were made into compacts of similar green density and sintered under similar conditions in the hot stage of the SEM. The percent linear shrinkage was plotted against temperature for each powder compact as shown in Fig. 41. The linear shrinkage curve for powder A leveled off at 1080, 1300, 1380 and 1470°C. A portion of powder A was subsequently annealed isothermally in air for 20 min at 1080, 1300 and 1380°C progressively, and X-ray analyzed after each calcination. The MgO phase disappeared and the spinel showed increased crystallinity
Fig. 41. Shrinkage vs temperature for several powders calcined under different conditions, listed in order of powders A, B, B-1, C and C-1.
after calcining at 1300°C. The reaction of magnesia and alumina to form spinel is accompanied by a volume expansion of approximately 5%. Also, for alumina rich spinels, the lattice parameter decreases with increasing mole percentage of alumina. The volume expansion accompanying the reaction between MgO and Al₂O₃ rich spinel should be compensated by the sintering shrinkage causing the linear shrinkage curve to level off. The reactivity of powder A due to its small crystallite size is thus counteracted by its multicrystalline nature.

The shrinkage curves for powders B and B-1 showed the fastest sintering rate. One experiment indicated that, before 1000°C, compacts B and B-1 had linear shrinkages of 5.4 and 4.6%, respectively. The behavior of powder above 1250°C is not understood. The shrinkage curves for powder C and C-1 showed a significant difference. The more uniformly packing of the powder and the higher green density of the compact for powder C-1 due to ball milling of the spinel powder and may be responsible for the enhanced sintering.

Since constant heating rates were used, the temperature axis is equivalent to a time axis; the slope of the shrinkage curve specimen point thus is the densification rate of the powder at that temperature. If a tangent is drawn for curve B-1 at 1035°C, parallel tangents can be drawn for the other curves which would indicate the temperature at which equivalent densification rates existed. 1140, 1215 and 1280°C are the temperatures for curves C-1, A and C. It is regretful that the experimental equipment condition did not permit an extension of the curves. Such shrinkage-temperature plots enable the determination of the sintering time, or temperature, if a certain
shrinkage is desired for a certain powder.

2. Correlation of Powder Characterizations and Microstructures

Spinel microstructures were prepared by sintering spinel powder compacts prepared differently in order to correlate the powder characteristics and their sintered microstructures.

The effect of powder aggregation was studied by controlling the freeze process to eliminate powder aggregation, and by ball milling the freeze dried powder or the calcined spinel powder. To study the effect of residue sulfate on the sintered microstructure, spinel powders which varied only in the amount of residue sulfate were sintered under the same condition. The residue sulfate content was controlled by $\text{H}_2$ treatment, calcination temperature and time. Spinel powders of different crystallite size were sintered for two different periods of time to study the crystallite size effect on their sintered microstructures. Besides the powder characteristics, the effect of powder packing density (green density) and sintering atmosphere on microstructure was also studied. For all the microstructure studies, the processing details for each specimen are listed in Table I.

a. Effect of Powder Aggregates on Microstructure. Specimens 1, 2, 3 and 4 prepared from powders calcined as indicated in Figs. 42 and 43 were sintered for 3 hr at 1550°C in air (schedule A). An examination of the polished sections at a low magnification in Fig. 42, indicates a nonhomogeneous microstructure of a continuous dense matrix with pockets of porous regions. Figure 43, at a higher magnification, shows the microstructures of the continuous dense
Fig. 42. SINTERED SPINEL MICROSTRUCTURE PREPARED FROM FREEZE DRIED POWDERS CALCINED IN VACUUM.

1 950°C FOR ONE HOUR
2 950°C FOR TWO HOURS
3 1150°C FOR ONE HOUR
4 1150°C FOR TWO HOURS.
Fig. 42. SINTERED SPINEL MICROSTRUCTURE PREPARED FROM FREEZE DRIED POWDERS CALCINED IN VACUUM.

1. 980°C FOR ONE HOUR
2. 980°C FOR TWO HOURS
3. 1150°C FOR ONE HOUR
4. 1150°C FOR TWO HOURS.
matrices. The packets of porous areas (Fig. 42) were undoubtedly due to the presence of large aggregates which did not sinter as readily as the fine loose powder which was densely packed in pressing. It would be expected that the amount and strength of these aggregates would increase with temperature and time of calcination as verified by the microstructures. The micrographs also suggest that some crushing of the aggregates occurred in cold pressing, resulting in elongation and alignment of the porous areas perpendicular to the vertical pressing direction. Since all four specimens were pressed to similar bulk green densities, it is expected that specimen 4 which has the greatest amount of strong aggregates should have the highest green density for the matrix between the porous regions which resulted in a denser microstructure (Fig. 43).

The sources of aggregate formation as discussed in an earlier section were eliminated progressively by freezing the solution into a big area of freon-12 or, mixed hexane, or heptane, by preventing melting during the drying stage, and by drying at a high temperature. The freeze dried powders with decreasing amounts of aggregates were calcined and pressed to a low green density in order not to crush the aggregates; the powder compacts were then sintered following schedule No. 1. Microstructures 5, 6, 7 and 8 are shown in Figs. 44 and 45. Comparing Figs. 41 and 43, by preventing the aggregate formation during the freezing and drying processes, the big porous regions have been eliminated. Freezing in mixed hexane eliminated the powder aggregation due to collision of incoming solution droplets and already frozen particles. The resulting microstructure 7 shows
SINTERED SPINEL MICROSTRUCTURE PREPARED FROM FREEZE DRIED POWDERS CALCINED AT 1020°C FOR TWO HOURS IN VACUUM. THE FREEZE DRIED POWDERS WERE PREPARED AT DIFFERENT FREEZING AND DRYING TEMPERATURE AND BYPASSING REMELTING DURING DRYING.

1. FROZEN AT -28°C AND DRIED AT 25°C
2. POWDER A REDRIED AT 65°C
3. FROZEN AT -40°C AND DRIED AT 25°C
4. POWDER C REDRIED AT 65°C.
Fig. 45. SINTERED SPINEL MICROSTRUCTURE PREPARED FROM FREEZE DRIED POWDERS CALCINED AT 1020°C FOR TWO HOURS IN VACUUM. THE FREEZE DRIED POWDERS WERE PREPARED AT DIFFERENT FREEZING AND DRYING TEMPERATURE AND BYPASSING REMELTING DURING DRYING:

1. FROZE AT -28°C AND DRIED AT 25°C
2. POWDER A REDRIED AT 65°C
3. FROZEN AT -40°C AND DRIED AT 25°C
4. POWDER C REDRIED AT 65°C
an increased homogeneity as compared with microstructure 5. The effect of eliminating aggregates which were formed because of calcination during melting due to a higher water content in the freeze dried powder shown by comparing microstructure 5 with 6, and 7 with 8. It thus is evident that aggregates were formed at different steps of the freeze drying process and were strengthened during the calcination process. The results also indicate that the aggregates can be effectively eliminated by controlling the critical steps of the freeze drying process.

b. **Effect of Green Density on Microstructure.** The polished sections of microstructures A, B, C and D are shown in Fig. 46. A general trend is a decreasing grain size with increasing green density and an increasing amount of trapped pores inside the grains with decreasing green density. A comparison of microstructures C and D, and also microstructures L, M, N, O, P, L-1, M-1, N-1, O-1 and P-1, indicates that grain size does not vary a great deal for green densities higher than 55% of theoretical density for a given heating schedule.

The large grain size and large amount of entrapped pores for low green density microstructure were due to the nonhomogeneous green packing which initiated exaggerated grain growth. Because of the presence of a small amount of aggregates among the fine powders, the low green density powder compacts would be less homogeneously packed and cause local fluctuation of packing density, Figs. 47 and 48. Upon sintering, the denser areas of the low green density body form grains much larger in size than the gains in the porous regions, and
Sintered spinel microstructures prepared from freeze dried powders calcined at 900°C in vacuum for one hour and treated with hydrogen at 750°C for half hour. The specimens were sintered to 1850°C following heating schedule No. 2.

Spinel powders were pressed to different green density:
(A) 45% theoretical density
(B) 28% theoretical density
(C) 55% theoretical density
(D) 61% theoretical density
The green compacts of spine powders calcined at 900°C in vacuum for one hour from ball milled freeze dried powders. The calcined spine was treated with H₂ at 750°C for half hour.

1. 28% theoretical density
2. 45% theoretical density
3. 54.5% theoretical density
4. 61% theoretical density
The green compacts of spinel powders calcined at 900°C in vacuum for one hour from ball milled freeze dried powders. The calcined spinel was treated with H₂ at 750°C for half hour.

(1) 28% theoretical density
(2) 46% theoretical density
(3) 54.5% theoretical density
(4) 61% theoretical density
the larger grains grow in size by an exaggerated grain growth mechanism. The exaggerated grain growth proceeded with breaking away from grain boundaries from pores resulting in trapped pores inside the grains. Typical microstructures of sintered MgAl$_2$O$_4$ exhibiting exaggerated grain growth have been shown in previous papers by Bailey$^{43}$ and Jorgenson.$^{44}$ If the fluctuation of packing density was uniform inside the specimen, the large grains formed during sintering which served as centers for exaggerated grain growth were also uniformly distributed inside the specimen. After a certain period of sintering time, all small grains in the neighboring porous area of the large grains (first generation grain*) were all consumed by the exaggerated growth of the large grains and resulted in large grains of comparable size with uniformly distributed trapped pores inside the grain (second generation grain). Because the adjacent grains are comparable in size, the vacancy concentration gradient across the grain boundary becomes small and the exaggerated grain growth proceeds to completion. The low green density specimens A and B in Fig. 46 show the result of second generation grain growth as described above. For specimens of uniform and densely packed green compacts, the normal grain growth mechanism was followed upon sintering which resulted in small grain size and less entrapped pores inside the grains. The big dark areas in specimens C and D are grain pullouts.

*For convenience of explaining the sintered microstructures in the following sections, the terminology of first, second and third generation grains used by Rossi and Burke$^{16}$ will be used in this thesis.
c. **Effect of Residue Sulfate on Microstructure.** Spinel specimens were formed by sintering powders of different residue sulfate content to study the effect of residue sulfate on sintered microstructures. Also, from the sintered microstructures, an evaluation can be made of the different approaches of calcination used for the removal of sulfates. It was indicated in previous discussions, that residue sulfates due to incomplete calcination are mainly magnesium sulfate. Vacuum calcination, low temperature-long time calcination, high temperature-short time calcination, or hydrogen reduction were the methods used for sulfate removal.

The pairs of specimens E and H, F and J and G and K show microstructures made from the same powder with and without hydrogen treatment, Figs. 49 through 52. Comparison of specimens F with J and G with K indicates that the specimens with hydrogen treatment have fewer trapped pores inside the grains. Specimen F was made the same way as specimen C, but specimen F has a bimodel grain size distribution and is nearly free of trapped pores, Fig. 53. The difference is not understood. Comparison of specimens E and H indicates that microstructure H has a much smaller grain size and a grain boundary second phase, Fig. 54. The grain boundary second phase had inhibited the grain growth for specimen H as compared with specimen E. The grain boundary second phase disappeared after specimen H was annealed in air at 1500°C for 12 hr (specimen HA), Fig. 55. Determination of the chemical composition of the second phase was not successful because the beam size of the available electron microprobe was too large to scan over
Fig. 49. Spinel microstructures sintered to 1850°C following heating schedule No. 2. All calcined powders were treated with hydrogen at 750°C for half hour.

(E) Freeze dried powders calcined at 750°C in vacuum for two hours and pressed to 52% theoretical density.

(F) Freeze dried powders calcined at 900°C in vacuum for one hour and pressed to 53% theoretical density.

(G) Freeze dried powders calcined at 1300°C in air for one hour and pressed to 54.5% theoretical density.
Fig. 50. Spinel microstructures sintered to 1850°C following heating schedule No. 2. All calcined powders were treated with hydrogen at 750°C for half hour.

(E) Freeze dried powders calcined at 760°C in vacuum for two hours and pressed to 52% theoretical density.
(F) Freeze dried powders calcined at 900°C in vacuum for one hour and pressed to 53% theoretical density.
(G) Freeze dried powders calcined at 1300°C in air for one hour and pressed to 54.5% theoretical density.
Spinel microstructures sintered to 1850° C following heating schedule No. 2.

(H) Freeze dried powders calcined at 750° C in vacuum for two hours and pressed to 52% theoretical density.

(J) Freeze dried powders calcined at 900° C in vacuum for one hour and pressed to 53% theoretical density.

(K) Freeze dried powders calcined at 1300° C in air for one hour and pressed to 54.5% theoretical density.
Spinel microstructures sintered to 1850°C following heating schedule No. 2.

(H) Freeze dried powders calcined at 750°C in vacuum for two hours and pressed to 52% theoretical density.

(J) Freeze dried powders calcined at 900°C in vacuum for one hour and pressed to 53% theoretical density.

(K) Freeze dried powders calcined at 1300°C in air for one hour and pressed to 54.5% theoretical density.
Fig. 53. Sintered spinel microstructures at two different magnifications prepared from freeze dried powders calcined at 900°C for one hour in vacuum, treated with H₂ at 750°C for half hour and pressed to 53.5% theoretical density. This specimen was sintered to 1850°C following heating schedule No. 2.
Fig. 54. (H1) Freeze dried powder calcined in vacuum at 750°C for 2 hours, packed to 51.5% of theoretical density and sintered following heating schedule No. 2. Microstructure exhibit grain boundary second phase.
(H2) Same microstructure as (A), with grain boundaries showing no distinguishable second phase.
(H3) Higher magnification of the center part of (A).
Fig. 55. Freeze dried powder calcined in vacuum at 750°C for two hours, packed to 51.5% of theoretical density, sintered following heating schedule No. 2 and annealed in air at 1500°C for twelve hours. Two different areas of the specimen each at two magnifications.
the grain boundary between two grains.\(^*\) However, from other sulfate derived material, it was reported\(^{45}\) that incomplete calcination caused a second phase on the boundary and a sulfur K\(_\alpha\) display obtained with the electron microprobe demonstrated that sulfur is concentrated at the grain boundary. Because of the size of the SO\(_4\) group, it is not possible for a significant concentration MgSO\(_4\) to stay in solution in spinel. Depending on the kinetics, segregated MgSO\(_4\) (may have a different chemical formula and structure) could be trapped inside the grain or along the grain boundary. The trapped sulfate will then decompose to form pores filled with gas inside the grain. The grain boundary phase can be removed either by annealing after sintering or during sintering as indicated by the fact that the microstructure near the surface region did not show a distinguishable second phase, photograph H2 of Fig. 54. The effect of residue sulfate is again shown by comparing specimen M with M-1, N with N-1, O with 0-1 and P with P-1, Figs. 56 through 59. The starting spinel powders were calcined under similar conditions as the powders for the spinel crystallite size growth study, Fig. 28. Part of each of the calcined powders was hydrogen treated and packed to similar green density and sintered in He. On comparing corresponding microstructures, it can be seen that the number of pores clustered inside the grains decreases with H\(_2\) treated specimen. The remaining porosity inside

\(^*\) A solid state X-ray spectra in the scanning electron microscope is appropriate for the identification of the second phase composition at the grain boundary. This equipment is not available.
Spinel microstructures sintered following heating schedule No. 3. The spinel powders were calcined from freeze dried powders and ball milled.

<table>
<thead>
<tr>
<th>Calcination</th>
<th>Temp. °C</th>
<th>Time hr.</th>
<th>Atmosphere</th>
<th>Green Density % Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>650</td>
<td>22</td>
<td>Vacuum</td>
<td>57.5</td>
</tr>
<tr>
<td>M</td>
<td>950</td>
<td>1</td>
<td>Air</td>
<td>58.1</td>
</tr>
<tr>
<td>N</td>
<td>1150</td>
<td>1</td>
<td>Air</td>
<td>59.6</td>
</tr>
<tr>
<td>O</td>
<td>1250</td>
<td>1</td>
<td>Air</td>
<td>60.5</td>
</tr>
<tr>
<td>P</td>
<td>1350</td>
<td>1</td>
<td>Air</td>
<td>54.4</td>
</tr>
</tbody>
</table>
Fig. 57.

Spinel microstructures sintered following heating schedule No. 3. The spinel powders were calcined from freeze dried powders and ball milled.

<table>
<thead>
<tr>
<th>Calcination</th>
<th>Temp °C</th>
<th>Time hr</th>
<th>Atmosphere</th>
<th>Green Density % Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>650</td>
<td>22</td>
<td>Vacuum</td>
<td>57.5</td>
</tr>
<tr>
<td>M</td>
<td>950</td>
<td>1</td>
<td>Air</td>
<td>58.1</td>
</tr>
<tr>
<td>N</td>
<td>1150</td>
<td>1</td>
<td>Air</td>
<td>59.6</td>
</tr>
<tr>
<td>O</td>
<td>1250</td>
<td>1</td>
<td>Air</td>
<td>60.5</td>
</tr>
<tr>
<td>P</td>
<td>1350</td>
<td>1</td>
<td>Air</td>
<td>54.4</td>
</tr>
</tbody>
</table>
Fig. 58. Spinel microstructures sintered following heating schedule No. 3. The spinel powders were calcined from freeze dried powders, balled, milled and treated with H₂ at 750° C for half hour.

<table>
<thead>
<tr>
<th>Calcination</th>
<th>Temp. °C</th>
<th>Time hr</th>
<th>Atmosphere</th>
<th>Green Density % Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-1</td>
<td>650</td>
<td>22</td>
<td>Vacuum</td>
<td>55.4</td>
</tr>
<tr>
<td>M-1</td>
<td>950</td>
<td>1</td>
<td>Air</td>
<td>58.7</td>
</tr>
<tr>
<td>N-1</td>
<td>1150</td>
<td>1</td>
<td>Air</td>
<td>60.4</td>
</tr>
<tr>
<td>O-1</td>
<td>1250</td>
<td>1</td>
<td>Air</td>
<td>55.6</td>
</tr>
<tr>
<td>P-1</td>
<td>1350</td>
<td>1</td>
<td>Air</td>
<td></td>
</tr>
</tbody>
</table>
Spinel microstructures sintered following heating schedule No. 3. The spinel powders were calcined from freeze-dried powders, ball milled and treated with H$_2$ at 750°C for half hour.

Calcination

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp, °C</th>
<th>Time hr.</th>
<th>Atmosphere</th>
<th>Green Density % Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-1</td>
<td>650</td>
<td>22</td>
<td>Vacuum</td>
<td>55.4</td>
</tr>
<tr>
<td>M-1</td>
<td>950</td>
<td>1</td>
<td>Air</td>
<td>58.7</td>
</tr>
<tr>
<td>N-1</td>
<td>1150</td>
<td>1</td>
<td>Air</td>
<td>58.7</td>
</tr>
<tr>
<td>O-1</td>
<td>1250</td>
<td>1</td>
<td>Air</td>
<td>60.4</td>
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<tr>
<td>P-1</td>
<td>1350</td>
<td>1</td>
<td>Air</td>
<td>55.9</td>
</tr>
</tbody>
</table>
the grain of H\textsubscript{2} treated specimen are thought to be the result of the early stage secondary grain growth and entrapped He (to be discussed later). Figure 60 supports the He entrapment argument as the microstructure near the surface of the specimen, photo Ne, has less pores inside the grain as compared with the interior microstructure, photo Ne. This study indicates that presintering H\textsubscript{2} treatment of the calcined powder has removed the residue sulfate which is detrimental for a homogeneous dense microstructure.

A comparison of specimens M, N, O and P shows that specimens formed with increasing calcination temperature have finer entrapped pores inside grains.

Microstructures prepared from spinel powders calcined at a low temperature for a long time are shown by specimens L and L-1. The spinel powders were calcined at 650°C in vacuum for 22 hr and L-1 had an additional hydrogen treatment. The microstructures show very few trapped pores and large grain sizes. The microstructure indicates that the long time calcination had removed most of the sulfate so that the H\textsubscript{2} treatment does not have a significant effect. (Other features of this microstructure will be discussed later.) Specimens Q and R were made from the same calcined powder except specimen R had H\textsubscript{2} treatment prior to sintering (same as specimen J and C except for the sintering schedule). The long time vacuum sintering produced very dense specimens nearly free of entrapped pores for both specimens, Figs. 61 and 62.

It is concluded that residue sulfate will for a second phase in the microstructure along the grain boundary and form entrapped pores
Fig. 60. Polished microstructure at 80°C specimen N, near the center Nc and edge Ne of the specimen.
Spinel microstructures sintered following heating schedule No. 3 in vacuum. The spinel powders were calcined from freeze dried powders for one hour.

<table>
<thead>
<tr>
<th>Calcination</th>
<th>Ball Milling</th>
<th>Green Density % Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q Vac.</td>
<td>Freeze dried powders</td>
<td>55.8</td>
</tr>
<tr>
<td>R Vac. + H₂</td>
<td>Freeze dried powders</td>
<td>55.0</td>
</tr>
<tr>
<td>S Vac.</td>
<td>No</td>
<td>52.5</td>
</tr>
<tr>
<td>T Vac.</td>
<td>Spinel powders</td>
<td>55.8</td>
</tr>
</tbody>
</table>
Fig. 62. Spinel microstructures sintered following heating schedule No. 3 in vacuum. The spinel powders were calcined from freeze dried powders for one hour.

<table>
<thead>
<tr>
<th>Calcination Atmosphere</th>
<th>Milling</th>
<th>Green Density % Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q Vac.</td>
<td>Freeze dried powders</td>
<td>55.6</td>
</tr>
<tr>
<td>R Vac. + H₂</td>
<td>Freeze dried powders</td>
<td>55.0</td>
</tr>
<tr>
<td>S Vac.</td>
<td>No</td>
<td>52.5</td>
</tr>
<tr>
<td>T Vac.</td>
<td>Spinel powders</td>
<td>55.8</td>
</tr>
</tbody>
</table>
inside the grain. \( \text{H}_2 \) treatment of calcined spinel powder or low
temperature long time calcination and vacuum sintering can effectively
eliminate the residue sulfate.

d. **Effect of Crystallite Size on Microstructures.** For long time
sintering under schedule 3a, specimens M, N, O, P, M-1, N-1, O-1 and
P-1, have nearly the same grain size and similar microstructure
except for the amount of pores entrapped inside grains. It indicates
that for a non-defect structure single phase crystalline spinel, the
initial powder crystallite size only affects the sintering kinetics
but not the final microstructure.

The microstructures for specimen M, N, O, P, M-1, N-1, O-1 and
P-1 all have the same features: angular large size grains, small
pores clustered in the center of the grains, and big pores at grain
intersections. These microstructures (third generation grain) are
the result of normal grain growth proceeding after the formation
of second generation grains (as a result of exaggerated grain growth
of the first generation fine grains). Since the second generation
grains had similar grain size, the driving force for grain growth,
vacancy concentration gradient across grain boundaries, was small
so that the grains grew normally. The grain boundary movement of
normal grain growth annihilated the pores and left behind pore free
regions between the center pore clusters and the grain boundaries.
The above explanation is further supported by the grain-like shape
of the center pore clusters and the sizes of the center pore clusters
are in the range of the second generation grains. The average
distance between the pore clusters is 60 to 70 \( \mu \text{m} \); this indicates that
the "nucleus grains" which initiated the exaggerated grain growth
to form the second generation grains are spaced on a 60 to 70 \( \mu m \)
distance in the powder compacts. Similar microstructures have been
shown for alumina with different additives.\(^{26}\) The big pores at
grain intersection are due to pore coalescence. The powders used for
specimens F, J and G, K were of different crystallite size and
sintered a short time, schedule No. 2. The difference in their
microstructure may not be due to the difference of the crystallite
size of the starting spinel powders. A comparison of their micro­
structures in Figs. 49 through 52 provides a similar explanation as
that for specimens A, B, C and D. Specimen F, G, J and K were pressed
to the same green density, but because the 1300\(^\circ\)C calcined powders
would have aggregates of denser structure than the powders calcined
at 900\(^\circ\)C exaggerated grain growth occurred much more readily for
specimens G and K than for F and J.

e. Effect of Ball Milling, Heat Schedule and Atmosphere on
Microstructure. On comparing specimens Q, S and T, specimen Q, formed
from powder calcined at 900\(^\circ\)C for 1 hr in vacuum, shows the densest
uniform microstructure as seen in Figs. 61 and 62. The differences
between the powders are in milling procedure; in the case of Q, the
freeze dried powder was milled. Reproducing this essentially
aggregate-free powder was unsuccessful. Efforts of eliminating aggregates
by carefully controlling the freeze drying process, although not
completely successful, however, were effective since the porous area
shown for specimen S only occurs occasionally inside the specimen. A
comparison of specimens Q and R with T indicates that milling of the
freeze dried powder is more effective than milling of the calcined powders.

The major differences of the microstructures produced from schedule 2 compared with 3a and 3b are the nature of the grain boundaries and surfaces. The longer time firing with schedule 3 produces microstructures with angular grain boundary morphology. This morphology suggests that the longer firing time produces cleaner grain boundaries, and develops anisotropy in the surface energies. The shorter firing time probably leaves an adsorbed sulfate which makes the grain boundary surface energies more isotropic. Another critical feature in the difference of the firing schedules is the long period of 800 to 1420°C for schedules 3a and 3b which could permit the gaseous impurities to leave the sintering compact more effectively.

Specimens M-1 and R received the same processing treatment except the calcining and sintering atmosphere: air and vacuum, respectively, in calcining and helium and vacuum, respectively, in sintering. Comparing them, it is obvious that the vacuum sintered specimen is nearly free of pores entrapped inside the grains. It is expected that the vacuum atmosphere during sintering is the most critical in this case. The helium atmosphere could inhibit the diffusion of gaseous impurities outside of the grains.
IV. SUMMARY AND CONCLUSION

Reactive magnesium aluminate spinel powders were prepared using the freeze drying technique followed by calcination.

Ending that the freeze drying technique yields intimate mixing of magnesium and aluminum sulfate hydrates is the fact that the freeze dried powder was X-ray amorphous. Residue water content at different drying temperature was studied by thermogravimetric analysis which further indicated that the freeze dried powder did not have a crystalline structure. The freeze dried powder has a sponge-like structure; and the faster is the freezing rate, the finer is the network structure. Among the different freezing media, freon-12, mixed hexane and heptane, a small batch powder frozen in mixed hexane at about -60°C produced the finest network structure. When this freeze dried powder with the finest structure was inserted into the hot zone of the calcination furnace, because of the drastic decomposition reaction, the structure shattered into uniform ultrafine (1-2 μm) spinel powders which were pseudomorphs of the fine network structure of the freeze dried powder. The freon-12 and heptane processed powder did not completely shatter into individual particles. In large batch powders frozen in freon-12 and heptane, large aggregates of strong structure were present. The freeze drying process was improved by producing sprayed droplets of a narrow size distribution, drying at high temperature, and avoiding melting during drying to eliminate aggregate formation.

From analysis of DTA and thermodynamic data, it was postulated that the spinel formation at 750°C was due to the chemical reaction
of the mixed sulfates. The crystallinity of the reacted spinel powder increases with calcination temperature and approaches full crystallinity above 1250°C as indicated by X-ray relative intensity measurement of the diffraction patterns.

Chemical analysis indicates that the residue sulfate content decreases exponentially with temperature. Long time-low temperature, short time-high temperature, and vacuum calcination were shown to be effective approaches to remove sulfate from the spinel powder. Thermogravimetric analyses of the freeze dried magnesium sulfate and aluminum sulfate mixture in a positive hydrogen atmosphere indicated that the sulfates can be removed successfully by the hydrogen reduction reaction.

The growth of spinel crystallites for different temperature and time periods was measured by the X-ray line broadening technique. The crystallite growth was inhibited by residual sulfate below 1250°C. Two mechanisms were postulated for the growth of spinel crystallites. The first growth mechanism is chemical diffusion of the reaction species through the spinel layer which is immediately followed by a grain growth mechanism.

Nonisothermal sintering kinetics of different spinel powder compacts were studied in the hot stage of a scanning electron microscope. The results indicate that the powder of nearly single phase spinel and the finest crystallite size has the fastest sintering rate. Increase of the packing homogeneity also increases the sintering rate of powders that have the same crystallite size.
Microstructures prepared from powders having strong aggregates show regions of different densities; the low density regions are characterized by large pores with small grains. Improvement of the freeze drying process as previously described effectively eliminated this microstructural inhomogeneity. Powder packing homogeneity also depends on the packing density. Low green density powder compacts are less homogeneous and show exaggerated grain growth during sintering. If exaggerated growth takes place uniformly, the large grains impinge on each other and grain growth then proceeds in a normal way.

Excess residue sulfate results in a grain boundary second phase for short time sintering. This phase was removed by annealing in air at 1500°C leaving a porous grain boundary. Small amounts of residue sulfate form entrapped pores inside the grains during subsequent grain growth. Post calcination hydrogen treatment improved the microstructure by reducing the amount of entrapped pores. Vacuum atmosphere sintering was found to be effective in producing an entrapped pore free microstructure.

One set of sintering experiments showed that the final grain size was in the same size range even though the starting powders had different crystallite sizes.

A major effort was made to produce a large batch of powder free of aggregates. Improvements in the freeze drying technique were not completely successful in realizing this goal. Ball milling of the freeze dried powder in a desiccated condition for a short period of time was found to be a more effective way to produce uniform calcined powders free of aggregates than ball milling the calcined spinel powder.
In summary, it was found that the most uniform and reactive spinel powder was produced by the following procedure: quick freezing the mixed salt solution in mixed hexane at about -60°C, sublimation drying at 120°C, ball milling prior to calcination if necessary, calcination in the temperature range of 950°C for 1 hr in vacuum atmosphere, and post calcining in flowing hydrogen at 750°C to remove residue sulfate. The best sintering schedule in the study was a slow heating rate from 800°C to 1850°C in a vacuum atmosphere.
ACKNOWLEDGEMENTS

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Finally, I am especially indebted to my wife, Ken-lin, for her clerical assistance and prolonged moral support.

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APPENDIX

Mixed Hexane*

Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Vol. PCT</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal paraffins</td>
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<td></td>
</tr>
<tr>
<td>Isoparaffins</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>Naphthenes</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Total Aromatics</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

Thermal Conductivity 60°F

0.101 BTU/HR/FT/°F

or

0.493 Cal/SEC/CM/°C

Specific Heat, BTU/lb/°F

<table>
<thead>
<tr>
<th>Temperature (°F)</th>
<th>Specific Heat</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°F</td>
<td>0.4103</td>
</tr>
<tr>
<td>100°F</td>
<td>0.4637</td>
</tr>
<tr>
<td>200°F</td>
<td>0.5172</td>
</tr>
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</table>

Freezing Point

-100°F

Density, gm/ml

<table>
<thead>
<tr>
<th>Temperature (°F)</th>
<th>Density (gm/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>68°F</td>
<td>0.6628</td>
</tr>
<tr>
<td>77°F</td>
<td>0.6582</td>
</tr>
<tr>
<td>100°F</td>
<td>0.6466</td>
</tr>
<tr>
<td>130°F</td>
<td>0.6314</td>
</tr>
</tbody>
</table>

*Chevron 5 degree hexane, supplied by Standard Oil Company of California
## Thermal Conductivity cal/sec/cm/°C*

<table>
<thead>
<tr>
<th>Substance</th>
<th>Conductivity</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>0.0003287</td>
<td>(30-100°C)</td>
</tr>
<tr>
<td>Heptane</td>
<td>0.0003354</td>
<td>(30°C)</td>
</tr>
<tr>
<td>Freon-12</td>
<td>0.0002310</td>
<td>(0-75°C)</td>
</tr>
</tbody>
</table>

*From Handbook of Chemistry and Physics, 48th edition.*
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