Effect of calcium fluoride additions on the sintering of magnesium oxide

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EFFECT OF CALCIUM FLUORIDE ADDITIONS ON THE SINTERING OF MAGNESIUM OXIDE

By
F. Wayne Calderwood
Dave Wilder

July 1957

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Technical Information Service Extension, Oak Ridge, Tenn.
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Work performed under Contract No. W-7405-eng-82.

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EFFECT OF CALCIUM FLUORIDE ADDITIONS ON THE
SINTERING OF MAGNESIUM OXIDE*

F. Wayne Calderwood and Dave Wilder

ABSTRACT

The effect of additions of calcium fluoride on the sintering of a refractory grade magnesium oxide fired under reducing conditions was studied. Specimens were formed at very low pressures to simulate compaction achieved in the jolt-pack technique, and at higher pressures commonly encountered in powder-pressing of ware. Specimens were fired in an induction furnace and held for pre-determined periods at temperatures ranging from 1300°C. to 1900°C. Shrinkage, bulk density, and grain growth factor were determined and presented as a function of composition and temperature.

Specimens formed with the minimum compaction were found to increase in shrinkage and density with increase of calcium fluoride additive, no maxima occurring over the range 0% to 12 mole %. Specimens formed at higher pressures were found to have

* This report is based on an M. S. thesis by F. Wayne Calderwood submitted July, 1957, to Iowa State College, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.
maximum density, shrinkage and grain growth when four mole-percent calcium fluoride was added. With larger amounts of this additive, bloating occurred, counteracting the sintering forces that tend to consolidate the mass. This mechanism is believed to be a liquid phase formed above a binary eutectic temperature, rather than a solid state reaction. No solid solution or compound formation was found to exist.
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INTRODUCTION

The objective of this research was to determine the effect of calcium fluoride additions on the sintering of commercial magnesium oxide grain as used for the fabrication of refractory ware.

Modern high temperature metallurgical processes demand refractory materials of higher quality than can be attained with traditional clay-silicate ceramics. During recent years progress has been made in commercial bodies with no clay in their structure. These bodies usually do not form a glassy bond but sinter by solid state reactions. Coarse, highly pure particles form a skeleton which is resistant to shrinkage at high temperatures. These coarse particles are bonded together with fine particles of the same pure material. The materials with the widest application are the oxides of aluminum, silicon, magnesium, zirconium, beryllium, and, to some extent, calcium.

Ware made from pure oxides is, in general, more porous than clay-bonded ceramics. The density of ware is known to vary with the amount of compaction received in the forming process. For this reason, ware formed by jolt-packing is less dense than ware formed by powder-pressing. Higher densities may be achieved through the use of finer particle sizes, and in some cases by the use of additives.
It is primarily for the densification of jolt-packed magnesia ware that this study was undertaken. The results may be expected to have a bearing on the density obtained by similar additions to ware formed by other methods.

Calcium fluoride was selected as the particular additive to be studied because of its availability, its well-known fluxing action in silicate-ceramics, and because of the fact that its melting point lies below the sintering temperature usually employed in the firing of magnesia ware.
Properties of Magnesia and Calcium Fluoride

Applications and limitations of magnesia as a refractory material have been described by Runck (32). Magnesia has wide application to metallurgical processes despite high thermal expansion and volatility at elevated temperatures. Its use in reducing atmospheres is limited to about 1700° C. It is slowly soluble in water and mineral acids, but when calcined at a high temperature, it is resistant to water and acid gases. It reacts with carbon and carbides above 1800° C.

Physical and chemical properties of magnesia are available from many sources such as Barnett and Wilson (7), Ephraim (14), Mellor (28), Lange (25), and Rossini and others (31). The melting point of magnesia was found by Kanolt (22) to be 2800° C. The crystal structure of magnesia is face-centered cubic of the sodium chloride type unit cell, with oxygen anions located midway between magnesium cations in six-fold coordination with each other. The unit cell is 4.213 angstroms per side.

Levin, McMurdie and Hall (27) show about sixty phase and melting diagrams in which magnesia is one constituent. The phase diagram for the system magnesia-calcium fluoride is not among those presented. A melting diagram for this system has
been at least partially worked out by Budnikov and Tresvyatskii (9). Although the original of this work is not available, it is reported that a eutectic is formed at 18 mol-percent magnesia, with a eutectic temperature of 1350° C. The liquidus line, up to 51.7 mol-percent magnesia, was obtained by thermal analysis. No information is given about the high-magnesia end of this system.

Properties of calcium fluoride are given by the same sources cited for magnesia. The literature does not agree on the melting point of this material. Lange's Handbook of Chemistry gives a value of 1330° C. without citing the original research. Naylor (29) reports a value of 1418° C. The fluorite structure is a face-centered cubic with fluorine anions at the centers of the eight cubelets into which the unit cell may be divided. The calcium cations are surrounded by eight fluorine ions, and each fluorine anion is surrounded by four calcium ions. The unit cell size is 5.4626 angstroms.

Sintering Phenomena

Much has been written on the phenomena of sintering during recent years. Wilder (39) has described sintering mechanisms in non-mathematical terms. He defines sintering, in the broad sense, to include all processes employed to produce bonding, adhesion, or consolidation of refractory materials.
In a narrow sense, sintering is defined as the mechanism whereby a single, pure material consolidates when subjected to external influences of pressure and temperature, for a time less than sufficient to cause melting. A weak initial bond limited to areas of contact between particles is developed at room temperature. Compaction forces more particles to be in contact, increasing strength. As temperature is increased, sorbed gases are evolved and complex surface phenomena begin. Sintering of ionic materials, such as refractory oxides, is said to be a plastic-flow mechanism. Grain growth may become a factor in the late stages of sintering, when small amounts of impurities may either inhibit or promote grain growth.

Allison and Murray (3) analyzed data on sodium and calcium fluorides in relation to two theories of sintering based on plastic flow and derived the activation energies required. Zvorykin and Timokhina (40) studied sintering of calcium fluoride powders from 400°C to 700°C and found that sintering occurred at discrete points of contact between grains through mutual diffusion. Tacvorian (36) studied acceleration of sintering by minor additions to a single phase. Smothers and Reynolds (34) studied sintering and grain growth of alumina as a function of the type of impurity added. Some additions were found to go into solid solution, straining the lattice and greatly increasing material transport. Other
additives formed a glassy phase, increasing surface diffusion and resulting in grain growth. Some additions which had a large vapor pressure decreased grain growth by sorption of the vapor upon the alumina. Other additives filled anion vacancies, reducing material transport. Cahoon and Christensen (10) also found that impurities may either increase or decrease crystal size and rate of recrystallization. Duwez and others (13) found that recrystallization is a decreasing function of particle size. The term "recrystallization" in much of this work is used where the authors apparently mean grain growth.

Sintering of Magnesia

Schurect and Frechette (33) studied the calcination of crude magnesite over the range 800° C. to 1400° C. and showed by x-ray studies that lightly calcined magnesite is cryptocrystalline with a cubic structure identical with that of periclase and fused magnesia. Eubank (15) studied the effects of temperature, rate of calcination, and impurities on ultimate crystal size. He heated the carbonate, basic-carbonate, and hydroxide at temperatures from 300° C. to 2000° C. for periods ranging from a few minutes to 120 hours. The only structure found was cubic. Gases were liberated from 300° C. to 500° C., and recrystallization and sintering
were found to occur above 900°C. Low temperature calcination yielded a porous structure with great reactivity. Reactivity decreased and particle size increased with increase of calcination temperature until an inert oxide was obtained at 1300°C. Impurities promoted sintering by increasing the amount of liquid phase.

Gregg and others (19) calcined Mg(OH)$_2$ for varying periods over the range 400°C to 750°C. They found that sintering took place, promoted by time and temperature. They postulated that Mg(OH)$_2$ decomposes yielding MgO in a psuedo lattice of Mg(OH)$_2$ which later recrystallizes. Allison and others (2) studied the effect of pre-calcination on sinterability of high-purity magnesia. They state that sinterability decreased with the development of periclase during the calcination.

Clark, Cannon, and White (11), studying the mechanism of flow during sintering, determined isothermal shrinkage curves at various temperatures for magnesia, lime, and other materials. They attempted to fit the shrinkage curves by use of various formulas. Krick and White (24) suggest that additions to magnesia that produce sufficient mobility to promote sintering will also produce crystal growth. Letort and Halm (26) concluded that impurities in magnesia aid in the formation of a liquid phase which is responsible for crystallization. Weyl and Enright (38) explain the difference in
sintering behavior of the oxides of magnesium and zinc by the differences in field strength and polarizibility, and the subsequent effect on the structure.

Fabrication Methods

Magnesia and other refractory oxides are fabricated into ware by methods similar to those used in clay-bonded ceramics. These include powder-pressing, ramming, extrusion, and slip-casting. Hydrostatic pressing, hot-pressing, and jolt-packing methods are also frequently used. Thompson and Mallet (37) have shown that the slip-casting process can be applied to the refractory oxides by development of plasticity through fine grinding and treatment with acids. They found that magnesia could not be cast as an aqueous slip because of hydration but could be cast using absolute alcohol. Greenway (18) modified their method, grinding magnesia in anesthetic ether and casting with absolute alcohol in extrusion thimbles. Allison and Nadler (1) developed a process for casting magnesia as a water suspension, but their slip could be stored for only a short period. Dancy (12) described a unique method of fabricating fused magnesia crucibles by heating powder packed around a graphite former to 3000° C. in an induction furnace and removing the former immediately after shutting off the furnace power. His
crucibles were completely impervious to water, mechanically strong, and resistant to heat shock.

The jolt-packing method of crucible fabrication has been described by Hauth and Wilhelm (20). The oxide powder is packed in the cavity between a graphite mold and a graphite mandrel and is packed by means of a compressed-air jolter. As the packing progresses, additional powder is added until no further settling occurs. The mandrel is then removed and ware-finished by firing to the proper temperature.

The advantage of this method is the relatively short time required to produce ware. Molds are readily shaped on a lathe from electrode graphite. Fused oxides are available in a fairly pure form and often may be used as purchased. The disadvantage of this method is the low density of the ware produced. Applied pressure between particles is much lower than in pressed ware. A distribution of particles including relatively large grains may be necessary for the proper packing of the raw materials. Since sintering rates decrease with increase of particle size and increase with compacting pressures, it follows that the degree of sintering is less for jolt-packed ware than for pressed ware under the same firing conditions.

Low porosities and high densities are desirable properties in the selection of a refractory. Cost, reaction with the melt and stability must also be considered. A low
porosity body may be expected to be stronger than a high porosity body of the same composition, and will offer less area of contact for reaction with a melt.

Low porosity and high density are a result of improved sintering. Since a distribution of particle sizes is necessary when using the jolt-packing process, there is a limit to the improvement in sintering that can be attained by the use of very fine particles. The other approach to denser jolt-packed ware is through the use of additives.
INVESTIGATION

Scope

This study was limited to additions of calcium fluoride to a commercial grade of electrically fused magnesium oxide.

The firing range studied was from 1300° C. to 1900° C. as measured with an optical pyrometer. All specimens were prepared in an induction furnace and conclusions drawn are limited to this type of firing.

The composition range studied was from zero to twelve mol-percent calcium fluoride. All compositions are given in mol-percent.

Materials

Raw materials for this investigation were:

1. commercial grade electrically fused magnesium oxide grain, produced by the Norton Company, Worchester, Mass., and sold under the trade name of Magnorite 220-F,

2. reagent grade calcium fluoride, produced by Allied Chemical and Dye Corporation, New York.

Chemical analyses of these materials are shown in Table I. It will be seen from the analysis that the magnesia carries some lime and silica impurity. No allowance was made for these impurities in calculating the compositions of the
Table I. Analyses of Materials Used.

<table>
<thead>
<tr>
<th>A. Magnorite 220-F. Typical analysis from company literature.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO........................................ 96.39%</td>
</tr>
<tr>
<td>CaO........................................ 1.91</td>
</tr>
<tr>
<td>SiO₂....................................... 1.21</td>
</tr>
<tr>
<td>Fe₂O₃...................................... 0.23</td>
</tr>
<tr>
<td>Al₂O₃...................................... 0.26</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl........................................... 0.01%</td>
</tr>
<tr>
<td>SO₄.......................................... 0.05</td>
</tr>
<tr>
<td>Fe.......................................... 0.005</td>
</tr>
<tr>
<td>Heavy metals (as Pb)................................ 0.005</td>
</tr>
</tbody>
</table>

various mixtures of magnesia and calcium fluoride. A calculation will show that Magnorite 220-F contains about 68.5 mols of magnesia for each mole of lime present. Calculated compositions are low by an amount contributed by these impurities but the error is quite small.

Preparation of Specimens

Calcium fluoride for each mixture was weighed out on an analytical balance to the nearest milligram. The magnesia was weighed out on a triple-beam balance, care being taken to keep within a half gram of the calculated amount. The error contribution due to weighing alone, ignoring the purity of the materials, was calculated by methods outlined by Beers (8) and found to be ± 0.0012 in the mole fraction of
calcium fluoride for the 12 percent batch and correspondingly smaller in other batches. Table II shows the calculated composition of each batch.

Weighed batches were placed in labeled wide-mouth jars, and clamped to an arm of a rotating mixer which tumbled the powder to opposite ends of the jar thirty-three times each minute. A minimum mixing period of two hours was observed. Two percent by weight of distilled water was then added to each jar. After standing overnight, the moistened powder was granulated by passing it through a 20-mesh sieve.

An attempt was made to form samples by the jolt-pack method in small graphite button-molds, but this was found to be impractical due to difficulty in obtaining identical compaction from specimen to specimen. Instead, specimens

<table>
<thead>
<tr>
<th>Mol-percent CaF₂ in batch</th>
<th>Weight of ingredient</th>
<th>Calcium fluoride</th>
<th>Magnorite 220-F</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0.000 grams</td>
<td>100.0 grams</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.802</td>
<td>96.2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>7.466</td>
<td>92.5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>11.001</td>
<td>89.0</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>14.412</td>
<td>85.6</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>17.707</td>
<td>82.3</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>20.891</td>
<td>79.1</td>
<td></td>
</tr>
</tbody>
</table>
were formed by the powder-press method using two vastly different pressures on two series of specimens. The lowest pressure which appeared to yield a specimen that withstood the necessary handling in the green state was found to be 400 pounds total pressure on a 0.756-inch diameter cross-section, or 890 p.s.i. For the high-pressure series of specimens, a total pressure of 10,000 pounds was employed, or a unit pressure of 22,280 p.s.i.

Specimens were fired, one at a time, in a graphite container in an induction furnace powered by a 6-kilowatt converter. A cylinder of the specimen material was placed between the specimen to be measured and the bottom of the crucible to reduce reaction with the graphite. Another disk of the same material was placed over the specimen to prevent contact with impurities falling through the sight hole. Temperatures were measured by sighting an optical pyrometer on the top disk through a small hole in the lid of the crucible. Coarse zirconia grain was used as insulation between the graphite crucible and a quartz tube. The zirconia permitted enough escape of heat from the system so that fairly low temperatures could be maintained without completely shutting off power to the furnace. Temperature of firing was maintained for a predetermined period of time. Specimens in all cases were allowed to cool in the furnace until well below red heat.
The fired samples were stored in a desiccator until needed for physical measurements.

The initial diameter of the specimens, measured with a micrometer was found to be 0.756 inches. This was checked from time to time and found to remain constant which indicates negligible wear on the hardened steel die. Diameters of the fired specimens were subtracted from 0.756 inches to obtain the linear firing shrinkage. Specimens were weighed on an analytical balance and bulk densities were calculated from the weights and measured diameters and thicknesses.

Apparent densities were obtained by an alteration of the method described by Andrews (6). Considerable difficulty was encountered in obtaining reproducible results when using the conventional method wherein the volume of the specimen minus open pores is obtained from the difference between the saturated weight and the weight when suspended in the saturating medium. Before weighing the saturated specimens, liquid must be wiped from the surface. The difference in the amount of liquid removed during wiping varied from specimen to specimen causing differences in the apparent volume. The density of the saturating medium is a function of temperature and variations in temperature caused by handling could not be accurately determined.

Because of these inaccuracies in the saturated-suspended weight method, another method of obtaining apparent densities
was tried. Volume of the specimens was measured in pycnometers using samples shaped on a cut-off saw to pass through the neck of the pycnometer. The pycnometers used had ground-in thermometers with enclosed scales with a range of 12° C. to 38° C. in intervals of 0.2° and with capillary side tubes with a cap. With this equipment, a close check on the temperature was possible.

True density was measured on some samples before the pycnometers equipped with thermometers were available.

The crystal structure of fired specimens was studied using conventional x-ray powder diffraction methods. Samples were sealed in glass capillaries, mounted in a 11.46-centimeter diameter DeBye-Scherrer camera, and exposed to the radiation of a copper target with a nickel filter. The best value for the lattice constant of magnesia was found by use of an extrapolation described by Nelson and Riley (30).

Before grain growth in the magnesia-calcium fluoride system could be studied, it was first necessary to determine the particle size distribution and the average diameter of the starting materials. This was accomplished by microscopic measurement at a magnification of 562.5X using a filar micrometer. Representative samples of reagent grade calcium fluoride and Magnorite 220-F were mounted on glass slides using the smear technique developed by Green (17). Areas on the slides at regular intervals were selected and every
particle within these areas was measured using Feret's "statistical" diameter, which is defined by Herdan (21) as the mean length of the distance between two tangents on opposite sides of the apparent outline of the particle, parallel to an arbitrary direction and irrespective of the orientation of each particle. About 400 particles were measured on each slide.

Specimens of the various compositions with different firing histories were mounted in bakelite. Rough grinding was done on glass plates with various grades of silicon carbide grain. The final polishing was made wet with aluminum oxide. The polishing agent used was Linde B, a product of Linde Air Products, New York. The polishing was done on a Microcloth on a low-speed polisher, both products of Buehler Ltd., Chicago. No etchant was necessary to bring out grain boundaries.

To determine average grain size of the polished specimens, photomicrographs were made and prints were compared with standard grain size plates published by the American Society for Testing Materials (4). Kehl (23) gives a broad discussion of the use of these plates.

A print of each photomicrograph was in turn compared with the standard plates and a decision made as to which plate gave the best representation of the grain pattern on the print. After each photomicrograph had been placed
within a particular size range, the group of prints within a particular size range were compared with each other and ranked in the order of decreasing grain size. From this ranking, arbitrary values of average grain number per square inch were assigned.
RESULTS AND DISCUSSION

Shrinkage

The effect of length of time of soak at a given temperature is shown in Figure 1. Specimens formed at 22,280 p.s.i. were held at 1850° C. for varying periods of time up to sixty minutes. These curves indicate rapid shrinkage during the first fifteen minutes of soaking time, and continued shrinkage at a slower rate during the remaining time up to sixty minutes. Specimens having ten and twelve percent calcium fluoride showed excessive bloating when held over fifteen minutes at this temperature and were not measured since they were obviously overfired. Specimens with seven percent calcium fluoride had smooth surfaces when held as long as sixty minutes at 1850° C.

It will be observed in Figure 1 that a measureable amount of shrinkage occurs at zero soaking time. This is shrinkage that takes place due to sintering while the specimens are being heated to the desired temperature. If it were not for thermal shock effects, it might have been possible to have placed the specimens directly in a furnace preheated to the desired temperature, then started the measurement of time. The specimens still would not have immediately reached the temperature of the furnace and part of the
Figure 1. The effect of soaking time and composition upon shrinkage of bodies formed at high pressures.
measured shrinkage would still have been a result of sintering during the brief warm up period.

The observed fact that shrinkage continues during a soaking period agrees with previous observations on shrinkage. The slope of the curve indicates that, with the higher additions of calcium fluoride, continued severe shrinkage during service would be encountered if the service temperature approached the firing temperature.

These curves were the basis for the selection of fifteen minutes as a standard soaking period in the preparation of further specimens.

The effect of composition and firing temperature on the linear firing shrinkage of specimens formed at 22,280 p.s.i. is shown in Figure 2. These specimens were fired at one hundred degree intervals between 1300° C. and 1900° C. and soaked at the temperature for a fifteen minute period. The shrinkage at a given temperature increases with the calcium fluoride content and becomes more pronounced at the higher temperatures. Specimens containing ten percent calcium fluoride bloated too severely to be measured when fired at 1800° C., and those with twelve percent showed a similar condition when fired at 1700° C. Figure 3 shows the same data plotted with firing temperature as the abscissa with curves drawn between points of the same composition. Almost straight lines from 1300° C. to 1900° C. for specimens
Figure 2. The effect of composition upon shrinkage of bodies fired at various temperatures.
Figure 3. The effect of temperature upon shrinkage of bodies with various calcium fluoride additions.
having up to two percent calcium fluoride indicate a linear relationship between shrinkage and firing temperature. Other curves have steeper slopes which tend to rise abruptly at the higher temperatures.

The relationship between forming pressures and shrinkage is illustrated by Figure 4, where shrinkage is plotted against composition for specimens formed at 890 and 22,280 p.s.i. and fired at 1300° C. and 1400° C. The large difference in shrinkage between samples of the same composition is due to the difference in initial compaction. Much void space is eliminated by use of the higher pressure, and densification proceeds more readily.

Density

The effect of composition and firing temperature on bulk density is shown in Figures 5 and 6 for specimens formed at 890 and 22,280 p.s.i., respectively. In Figure 5, specimens formed at 890 p.s.i. show increasing bulk density with increase of firing temperature and with increase of calcium fluoride. In Figure 6, specimens fired at 1800° C. or lower, show increasing bulk density up to an addition of four percent calcium fluoride, and decreasing bulk density for all additions greater than four percent. The greatest bulk density is obtained with a sample having no additive and
Figure 4: The effect of forming pressure and composition upon firing shrinkage at 1300° C. and 1400° C.
Figure 5. The effect of temperature and composition upon bulk density of bodies formed at low pressures.
Figure 6. The effect of temperature and composition upon bulk density of bodies formed at high pressures.
fired to 1900° C.

When one considers what has previously been observed concerning the effect of compaction upon sintering, it is seen that these two curves are not in conflict. The series of specimens formed at 890 p.s.i. are at a lower stage of sintering and still have sufficient open void space to allow escape of the gases evolved. The calcium fluoride additive hastens sintering by providing a liquid phase, and, since it has a higher vapor pressure, it provides more gas to be evolved. The specimens formed at 22,280 p.s.i. have more contact between grains, hence sinter more rapidly and close up the escape paths of the evolving gases.

At first glance, there appears to be a conflict between Figure 6, which shows a decrease of bulk density with increase of calcium fluoride content from four to twelve percent, and Figure 2, which shows an increase of linear shrinkage for the same compositions. Several reactions are occurring simultaneously which result in this apparent discrepancy. Consolidation of the specimens by the forces of sintering is causing shrinkage, while evolution of gases within the specimens is causing bloating. Consolidation forces are great enough so that the shrinkage curves show no evidence of bloating. It is only when the bulk density of the specimens is calculated that the bloating becomes apparent. Another phenomenon that may to a small degree
increase the apparent shrinkage, is sublimation from the surfaces of the specimens.

The effect of firing temperature and composition upon the apparent density is shown in Table III.

Table III. Apparent Densities as Obtained with Pycnometers.

<table>
<thead>
<tr>
<th>Mol percent of CaF$_2$ in specimen</th>
<th>Firing temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1400$^\circ$ C.</td>
</tr>
<tr>
<td>0</td>
<td>3.56</td>
</tr>
<tr>
<td>4</td>
<td>3.30</td>
</tr>
<tr>
<td>8</td>
<td>3.46</td>
</tr>
<tr>
<td>12</td>
<td>3.40</td>
</tr>
</tbody>
</table>

The calculations of apparent density were made using the following equation:

$$D_A = \frac{W - P}{\frac{W_1 - P}{d_1} - \frac{W_2 - W}{d_2}}$$

(Equation 1)

where

$D_A$ = apparent density in grams per cc.

$W$ = weight of pycnometer and sample

$P$ = weight of pycnometer

$W_1$ = weight of pycnometer filled with water

$W_2$ = weight of pycnometer plus sample plus water

$d_1$ = density of water in $W_1$

$d_2$ = density of water in $W_2$. 
It was observed that $W$ and $P$ could be repeatedly measured to agree within less than 0.0005 grams from weighing to weighing. Several observations were made to obtain the best values for $W_1$ and $W_2$ for each determination. The absolute density of water was taken from Lange's Handbook of Chemistry (25). A mean value and standard deviation were calculated for each volume, and the standard deviations in the different quantities were combined to obtain a standard deviation in the apparent density. These deviations were of the order of 0.014 grams per cubic centimeter.

It will be observed that for samples containing no additive, apparent density appears to decrease slightly as specimens are fired at increasing temperatures. Specimens with four percent additive increase in density as firing temperature increases, while those with eight percent and twelve percent decreased. The decrease of apparent density with increase of firing temperature would mean that these samples contain an increasing amount of closed pores that cannot be filled by water.

Results of true density calculations, using data taken with pycnometers not equipped with thermometers, are shown in Table IV.

Since the specific gravity of calcium fluoride is 3.18 according to Lange (25), it would be expected that a mechanical mixture of magnesia and calcium fluoride would have a lower true density than magnesia.
**Table IV. True Density of Specimens Formed at 22,280 p.s.i.**

<table>
<thead>
<tr>
<th>Mol percent CaF₂ in sample</th>
<th>Firing temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1400°C</td>
</tr>
<tr>
<td>0</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>3.51</td>
</tr>
<tr>
<td>4</td>
<td>3.52</td>
</tr>
<tr>
<td>6</td>
<td>3.52</td>
</tr>
<tr>
<td>10</td>
<td>3.51</td>
</tr>
</tbody>
</table>

**X-Ray Investigation**

Comparison of the lines found in the x-ray diffraction pattern of the various specimens with the lines listed for magnesia and fluorite by Swanson and Tatge (35) revealed that no new compound was present. The region between two and twelve percent calcium fluoride is therefore a two-phase region. Impurities listed in Table I were not detected by x-ray diffraction methods due to their low concentration.

The presence of two phases rules out solid solution of fluorite in magnesia in this region. This may be predicted by the differences in unit cell types and dimensions. To discover if more limited solubility existed somewhere below two percent, apparent lattice constants were calculated for the magnesia lines on several of the films using the
relationship

\[ a_0 = \frac{\lambda}{2 \sin \theta} \sqrt{h^2 + k^2 + l^2} \]  \hspace{1cm} (Equation 2)

where

- \( a_0 \) = apparent lattice constant,
- \( \lambda \) = wavelength of radiation,
- \( \theta \) = Bragg angle,
- \( h, k, l \) = indices of line.

The wavelength of the radiation for each line is dependent upon whether or not the Ka doublet is resolved. For resolved copper Ka_1 and Ka_2 radiations, the wavelengths are 1.54050 and 1.54134 angstroms, respectively. For the unresolved radiation, a weighted average of 1.54178 angstroms is used. The Bragg angle \( \theta \) for each line was obtained by measuring the distance between the line and the calculated front center of the beam. A correction was made for film shrinkage by multiplying each observed angle \( \theta \) by the quotient obtained by dividing the film length between front and back centers into 180 centimeters, the original length had no shrinkage occurred.

The best value for the lattice constant was found by using an extrapolation described by Nelson and Riley (30), in which the apparent lattice constant is plotted against the function \( \frac{1}{2} \left( \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right) \) and extrapolated back to the zero value of this function. Values of this function are tabulated in the work cited at each tenth of a degree.
from 0° to 90°.

For maximum accuracy, the radiation used should be of such a wavelength that at least one line has an angle greater than 80°. This will place a point of the data near the limit of extrapolation. The largest angle obtained for magnesia when using copper radiation is less than 73°, placing the closest point somewhat further from the extrapolation point than is preferred.

Figure 7 shows typical extrapolation plots. All values found for the lattice constant of magnesia are between 4.211 and 4.214 angstroms, which are in good agreement with the published value of 4.213 angstroms. This supports the belief that solid solution of fluorite in magnesia does not occur even at low concentrations.

Grain Growth in Magnesia-Fluorite Specimens

Figure 8 shows a photographed area on the slides, taken at a magnification of 125X. The fact that only a small portion of the particles is in focus indicates a wide range of sizes and indicates some of the tedious work in measuring all particles within the resolving power of the microscope.

The particle size distribution of the raw materials is presented graphically in Figure 9 where cumulative percent finer is plotted against diameter in microns. From this
Figure 7: Extrapolation of apparent lattice constant values by the Nelson-Riley method.
Figure 8. Particles mounted on glass slides. Magnesia is at the left and calcium fluoride at the right. Magnification 125X.

It will be seen that fifty percent of the observed particles of calcium fluoride are finer than 2.4 microns, fifty percent of the observed particles of magnesia are finer than 1.35 microns. This cannot take into account any particles finer than the resolving power of the microscope, which, according to Kehl (23), is about 0.2 to 0.3 microns.

Specimens formed at 890 p.s.i. did not possess enough bond strength to be successfully polished, even when fired at 1900° C. for fifteen minutes. Specimens formed at 22,280
Figure 9. Particle size distribution of starting materials as determined by microscopic measurement.
p.s.i. had to be fired higher than $1600^\circ C$ before the bond strength was great enough to permit polishing. One exception to this was the sample with twelve percent calcium fluoride, fired fifteen minutes at $1600^\circ C$. The uniform fine grain structure is of interest for it points out the growth that was observed in samples fired at higher temperatures. A photomicrograph of this sample is shown in Figure 10.

Specimens fired at $1700^\circ C$ were polished with a fair degree of success despite some tear-out of individual grains. Specimens fired at higher temperatures and for longer periods of time were successfully polished.

A few typical photomicrographs that span the composition range studied under different firing conditions are shown in Figures 10 through 21. Figure 22 shows a plot of grain growth factor against composition of samples in the region studied. The factors were obtained by dividing the average grain size obtained from the photomicrographs by the average grain size of the starting materials. All computations were based upon an initial grain size of 1.35 microns, the size where the fifty percent finer line meets the curve for particle size distribution of magnesia.

These curves bear out the fact that when grain growth does occur, it is a function of time, temperature and composition. Specimens soaked sixty minutes at $1850^\circ C$ showed larger grains than did specimens held at $1900^\circ C$ for fifteen
Figure 10. Photomicrograph of specimen with 12 mol-percent calcium fluoride addition, fired at 1600° C. with a fifteen minute soaking period. Magnification 125X.

Figure 11. Photomicrograph of specimen with no additive, fired at 1800° C. with a fifteen minute soaking period. Magnification 125X.

Figure 12. Photomicrograph of specimen with 4 mol-percent calcium fluoride addition, fired at 1800° C. with a fifteen minute soaking period. Magnification 125X.

Figure 13. Photomicrograph of specimen with 12 mol-percent calcium fluoride addition, fired at 1800° C. with a fifteen minute soaking period. Magnification 125X.
Figure 14. Photomicrograph of specimen without calcium fluoride addition, fired at 1900° C. with a fifteen minute soaking period. Magnification 125X.

Figure 15. Photomicrograph of specimen with 4 mol-percent calcium fluoride addition, fired at 1900° C. with a fifteen minute soaking period. Magnification 125X.

Figure 16. Photomicrograph of specimen without calcium fluoride addition, fired at 1850° C. with a thirty minute soaking period. Magnification 125X.

Figure 17. Photomicrograph of specimen with 4 mol-percent calcium fluoride addition, fired at 1850° C. with a thirty minute soaking period. Magnification 125X.
Figure 18. Photomicrograph of specimen without calcium fluoride addition, fired at 1850°C with a sixty minute soaking period. Magnification 125X.

Figure 19. Photomicrograph of specimen with 12 mol-percent calcium fluoride addition, fired at 1850°C with a sixty minute soaking period. Magnification 125X.

Figure 20. Photomicrograph of specimen with 4 mol-percent calcium fluoride addition, fired at 1850°C with a sixty minute soaking period. Magnification 125X.

Figure 21. Photomicrograph of specimen with 12 mol-percent calcium fluoride addition, fired at 1700°C with a fifteen minute soaking period. Magnification 125X.
Figure 22. The effect of firing conditions upon growth factor of grains in magnesia-calcium fluoride bodies.
minutes. Among the specimens held at 1850°C for the longer periods of time, a maximum grain growth was observed with four percent calcium fluoride in the body. This is the same composition that showed a maximum in the bulk density curve when fired at or below 1800°C.

Specimens soaked fifteen minutes at 1800°C and at 1900°C show an increase in growth factor up to four percent and no change in growth factor at higher calcium fluoride contents. Specimens held fifteen minutes at 1700°C show a similar curve with smaller growth factors due to the influence of temperature. The one sample fired for fifteen minutes at 1600°C shows a factor considerably smaller than that of similar specimens fired at a higher temperature.

The only specimen that appears to have approached a uniform grain size is the specimen containing four percent additive and fired one hour at 1850°C.

A complete and accurate phase diagram for the magnesium oxide-calcium fluoride system would aid in clarifying the mechanism by which grain growth has proceeded. In the absence of a complete diagram, and with the information reported by Budnikov and Tresvyatskii (9), plus the fact observed in the x-ray study of this investigation that a two-phase system consisting of magnesia and fluorite exists in the region being studied, a possible phase diagram may be sketched as shown in Figure 23.
Figure 23. Possible phase diagram for the magnesium oxide-calcium fluoride system.
Since no solid solution has been found to exist, the mechanism for material transport causing grain growth must be liquid formed above the eutectic temperature. By simple lever-law relationships, the amount of liquid phase increases with increase in calcium fluoride content at any given temperature in the magnesia plus liquid field. Likewise, at any constant composition in the range of this study, the liquid content increases as temperature increases above the eutectic temperature. If no other phenomenon were taking place, grain growth should increase with both temperature and calcium fluoride content at constant time. Other phenomena do occur, such as vaporization of both materials, and formation of gas pockets in the structure. The over-all composition must therefore be changing. It is the interaction of these and other phenomena that determines the rate of grain growth and the size of the equilibrium grains.

An examination of the photomicrographs in Figures 10 through 21 will give some indication of bleb structure caused by the failure of entrapped gases to escape as rapidly as they are evolved. The dark spots on the photomicrographs of specimens fired at higher temperatures are voids in the structure caused by this phenomenon. The dark areas on photomicrographs of specimens fired at lower temperatures are a result of tear-out of grains during polishing of the specimens.
CONCLUSIONS

This study has shown that additions of calcium fluoride to a particular commercial grade of magnesium oxide hastened the sintering of product when fired in an induction furnace.

The optimum amount of calcium fluoride to be added to a magnesia body will depend upon several factors, including the method of fabrication of the ware and the amount of compaction involved.

Since jolt-packed ware undergoes a relatively small amount of compaction by comparison to powder-pressed ware, the results obtained on the series of specimens formed at the lower pressure give an indication of what would be expected with jolt-packed ware. With the lower forming pressure, the degree of densification was observed to increase with increase of calcium fluoride at all firing temperatures within the range 1300° C. to 1900° C. There was then no optimum calcium fluoride content as far as bulk density is concerned in the temperature-composition range covered. The linear shrinkage was observed to rise sharply with increase of temperature and calcium fluoride content; deformation of the faces of the specimens began to appear at 1900° C. for samples containing ten mol-percent additive.

The high-pressure series gives results that have more application to powder-pressing of ware than to formation by
jolt-packing. If ware can be fired to 1900° C., there is no advantage to be gained by additions of calcium fluoride, since the densest sample was a pure magnorite sample fired at 1900° C. and soaked fifteen minutes. Additions of calcium fluoride in any quantity reduced the density of high-pressed, high-fired magnesia specimens. If, on the other hand, the ware is to be fired at 1800° C. or at some lower temperature, additions of calcium fluoride up to four percent increase the density of the ware. The density of this ware will be below that of ware fired at 1900° C. Calcium fluoride additions greater than four percent were found not to be beneficial to high-pressed ware under any firing conditions. This is believed to be because internal bloating increases rapidly with calcium fluoride content.

Presence of calcium fluoride in magnesia ware should require closer control of firing conditions such as temperature, temperature distribution on large pieces, and time at temperature, since this additive has been observed to be quite active in promoting sintering.

The mechanism by which sintering is promoted is believed to be a liquid-phase reaction which is formed above a binary eutectic temperature, rather than a true sintering in the narrow sense, which is a solid-state reaction.

Although densification can be obtained under certain
conditions, it must by no means be concluded that the strength of the product is improved. Since some liquid phase is postulated, strength of ware made of these bodies will at high temperature be dependent upon the amount and viscosity of the liquid formed.
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