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Publication Date
1984-02-01
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S.J. Wu
(M.S. Thesis)

February 1984
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LOW TEMPERATURE SINTERING OF $\text{Al}_2\text{O}_3$-$\text{CaO}$

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This work was supported by the Division of Materials Science, Office of Basic Energy Science, U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.
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ABSTRACT

Pre-eutectic densification phenomena have been studied in recent years. However, there is no research regarding the influence of the second phase on the densification of matrix-additive systems. The purpose of this research is to study the effect of CaO addition on the pre-eutectic densification of alpha-alumina powders. The $\text{Al}_2\text{O}_3$-$\text{CaO}$ system was chosen because of its phase diagram which displays several high melting point intermediate phases between the eutectic composition and that of the $\text{Al}_2\text{O}_3$ matrix.

Two sintering methods were used: (a) constant heating rate sintering and (b) constant temperature sintering. The microstructure evolution was examined extensively by scanning and transmission electron microscopy and by x-ray diffractometry. It was found that the addition of CaO activates several mechanisms affecting the densification rate of $\text{Al}_2\text{O}_3$-$\text{CaO}$ powder compacts. Among them, a solid solution effect and a second phase effect decreased the sintering rate. However, enhanced pre-eutectic densification effect was also observed within a narrow range of composition.
I. INTRODUCTION

When sintering compacted powders, it is advantageous both to lower the sintering temperature and to shorten the sintering time. One common method is to use liquid phase sintering. During such a process, some liquid exists above the melting temperature of the liquid forming phase, and often forms a continuous thin film between the solid particles. Because of the rapid material transport through this liquid grain boundary film and the capillary forces arising from voids, the densification rate of the green compact can be accelerated. Liquid phase sintering has been widely studied. Based on the phenomenological observations of Lenel\(^1\) and Gurland and Norton\(^2\), Kingery\(^3\) summarized the requirements for effective liquid phase sintering as: (a) an appreciable amount of liquid phase; (b) an appreciable solubility of the solid in the liquid and (c) complete wetting of the solid by the liquid.

Although the liquid enhances densification rates significantly, liquid phase sintering may not be the best method for this purpose. Certainly, liquid phase sintering has a number of disadvantages. For example, the liquid film tends to enhance grain growth during sintering. This effect, together with the existence of the liquid forming phase in the grain boundaries, can degrade the high temperature mechanical properties of the sintered products.

In past work on the densification of beta-alumina solid state electrolytes,\(^4\) eutectic additives were used and higher densification rates were observed, as shown in Fig. 1. This could be attributed to the presence of a transient liquid phase during sintering. However,
many experiments also revealed that even below the eutectic temper­
ature of the matrix-additive binary system, when no liquid should
exist, enhanced shrinkage also occurs. Such activated sintering
might be associated with surface property changes, with grain boundary
structure modifications or with enhancement of a transport mechanism.
Early in 1946, Kurtz\textsuperscript{7} reported the effects of nickel additions on
the sintering behavior of tungsten. This work, along with subsequent
investigations by Agte,\textsuperscript{8} Vacek\textsuperscript{9} and Brophy et al.,\textsuperscript{10}
showed that tungsten powders would sinter at a lower temperature due to the addi­
tion of small amounts of nickel. In Brophy et al’s work, it was pro­
posed that a monoatomic layer of nickel, evenly distributed over the
surface of tungsten particles, acted as the carrier phase through
which tungsten atoms would diffuse rapidly. According to this model,
the mechanism of activated sintering resembled that of the liquid
phase sintering with the nickel film acting as the liquid phase in
a completely wetting system. Samsonov and Yakovlev\textsuperscript{11}
ascribed the
activation of sintering to a transfer of electrons from nickel to
unlocalized orbitals in tungsten. This would mean that, as a result
of a solid state reaction, interacting elements could achieve more
stable electron configurations and consequently lower their inter­
atomic bonding strength. Thus, according to Samsonov and Yakovlev,
during the sintering process, the activation energy was lowered and
the sintering rate was increased. In Schintlmeister and Richter’s
work\textsuperscript{12} on the grain boundary diffusion of radioactive tungsten in
pure and nickel-doped tungsten compacts, it was found that the pres­
ence of nickel in the grain boundaries increased the grain boundary
diffusion rate by a factor of 50. Gessinger et al.\textsuperscript{13} concluded that the presence of a great number of nickel atoms in the tungsten grain boundary would diminish the average bond strength, which would explain the enhanced mobility of tungsten atoms in grain boundaries. Exner\textsuperscript{14} studied the WC-Co system and found that more than 95 percent relative density was achieved by activated sintering in the solid state without formation of a liquid phase. Sing-Chung Hu\textsuperscript{15} studied the MgF\textsubscript{2}-CaF\textsubscript{2} system and also found that the sintering rate of MgF\textsubscript{2} was enhanced by CaF\textsubscript{2}, a eutectic forming additive. He concluded that the enhanced pre-eutectic densification kinetics resulted from increased solid state grain boundary transport due to the presence of the eutectic forming phase. The CaF\textsubscript{2}-MgF\textsubscript{2} system was selected because of its simple phase diagram (Fig. 2) and low eutectic temperature (~980°C).

R. M. German\textsuperscript{16} summarized the criteria for effective activated sintering by an idealized phase diagram, as shown in Fig. 3. The criteria were: (a) the liquidus and solidus temperatures should decrease with increasing amount of additive in order for the additives to remain segregated at the grain boundaries and to provide a short circuit diffusion path; (b) the difference in melting temperatures between the additive and the base metal should be large in order to give a high diffusivity due to a low net chemical diffusion activation energy; (3) the additive should have a high solubility for the base metal in order to provide sufficient base metal flux to effect rapid morphological change; however, the solubility of additive in the base metal should be small to prevent alloying or homogenizing, thereby decreasing the amount of the additive phase.
Although German proposed the above requirements for effective activated sintering, there are no discussions to date regarding the solid state reaction between the matrix and additive phase during the sintering process. For example, when the phase diagram has some high melting point intermediate phases between the eutectic and the end phase, as in the $\text{Al}_2\text{O}_3$-$\text{CaO}$ system (Fig. 4), instead of the simple eutectic binary phase diagram as shown in Fig. 2 and Fig. 3, complications might be expected. It is not clear if the activated sintering will still occur or if it will be retarded by these intermediate phases. W. J. Smothers and H. J. Reynolds\textsuperscript{17} investigated the sintering of $\text{Al}_2\text{O}_3$ doped with 1.0 wt.% of various oxide additives. Among those tested, CuO; SnO$_2$; TiO$_2$; Nb$_2$O$_5$ and MnO enhanced the sintering rate below the eutectic temperature. This means that pre-eutectic densification occurred when such oxides were added to $\text{Al}_2\text{O}_3$ powders. The phase diagrams of these $\text{Al}_2\text{O}_3$-oxide binary systems\textsuperscript{18} all have simple eutectic phase diagrams without any high melting temperature intermediate phases. On the other hand, some additives retarded the sintering of $\text{Al}_2\text{O}_3$ powders below the eutectic temperature, e.g. BaO; SrO and Nb$_2$O, all of which have rather complicated phase diagrams with $\text{Al}_2\text{O}_3$;\textsuperscript{18} with high melting point intermediate phases occurring at compositions between that of the eutectic and pure $\text{Al}_2\text{O}_3$. This suggests the hypothesis that intermediate phases may be the cause of the retarding effect observed in the pre-eutectic densification of powder mixtures containing an eutectic forming additive. In Smothers et al's work,\textsuperscript{17} $\text{Al}_2\text{O}_3$-$\text{CaF}_2$ seems to be an exception to this trend since it has a very simple phase diagram (Fig. 5), but showed a retardation of sintering rates. This
exception might be explained by observing that there is a large solubility of CaF$_2$ in Al$_2$O$_3$. This means that CaF$_2$ would be alloyed or homogenized by Al$_2$O$_3$ and would therefore lose its activation effect.

The above discussion suggests that the phase diagram of an Al$_2$O$_3$-additive system should permit a prediction of the additive effect on pre-eutectic densification. Specifically, it is suggested that whenever there are high melting point intermediate phases appearing between the eutectic and the end point compositions, the enhancing effect of the additive will be suppressed and the sintering rate will be decreased by the presence of these second phases. The purpose of this research was to examine this hypothesis by studying the effect of CaO additives on pre-eutectic densification of Al$_2$O$_3$, focusing on the intermediate phases, and put forward a reasonable postulate to explain the retarding mechanism, if pre-eutectic retardation occurred. The Al$_2$O$_3$-CaO system was selected because it contains a number of high melting point intermediate phases.
II. EXPERIMENT

A. Materials

Alpha-alumina from the Baikowski International Corporation (Baikalox Al₂O₃, grade Cr-1) was used in this study. This particular powder has the following characteristics: (a) high purity (99.99%); (b) the powder is deagglomerated, so that further milling is not necessary; (c) the powder is easily made into a slurry, facilitating the introduction of additives and binders. The properties and specifications of the powder are given in Table 1, and chemical analysis of the impurities from the manufacturer is shown in Table 2. The agglomerate size distribution histograms are shown in Fig. 6.

In order to obtain a homogeneous distribution of CaO in Al₂O₃ bulk, calcia preferably should be added in the form of a chemical solution, because complete homogenization is very difficult to achieve by simple mixing of two different kinds of powders. Reagent-grade calcium nitrate (Ca(NO₃)₂ 4H₂O) from Mallinckrodt Inc., purity >99%, was chosen as a sintering additive since it could be dissolved in ethyl alcohol to form a chemical solution. The maximum limits of impurities are shown in Table 3.

Scanning electron micrographs of pressed green compact surfaces are shown in Fig. 7 at two different magnifications. The green density of all specimens was 55.0% of the theoretical density. Micrographs show that the powders were mainly deagglomerated, with a few agglomerates formed by several grains. The maximum agglomerate size was less than 6 μm and conformed to the size distribution histograms quite well.
B. Processing

The procedures followed to prepare samples of Al$_2$O$_3$ powders doped with different amounts of CaO are illustrated by the flowchart in Fig. 8. First, the appropriate amount of calcium nitrate was dissolved in ethyl alcohol; the Al$_2$O$_3$ powder was added and mixed in this solution to yield 0.1 wt.% to 5.0 wt.% CaO in Al$_2$O$_3$. EDAX (Energy Dispersive Analysis of X-Ray) mapping on the fracture surface of a doped, pressed sample showed that CaO was uniformly distributed on the Al$_2$O$_3$ matrix powders (Fig. 9). After mixing, the slurry was stir-dried and ground in a mortar and pestle. The ground mixture was then heated to 400°C for at least 4 hours to decompose calcium nitrate to calcium oxide. Immediately after firing, the powders were ground again in a mortar and pestle. Green compacts were prepared using a Buehler uniaxial hydraulic press, to cold press the powders in a steel die at the pressure of 350 MPa. This high pressure would tend to break up powder clusters, and provided adequate green strength. The samples were 1.27 cm (0.5 inch) in diameter and 0.18 cm (0.07 inch) in thickness, with the same green density of 55.0% of theoretical density. No binder was used in the pressing process; only a small amount of stearic acid was used as the die lubricant. After pressing, the samples were heated at 700°C for at least 1 hour and then stored in a well sealed dessicator connected to a working vacuum pump to avoid moisture pick-up.

Pure Al$_2$O$_3$ samples were made by exactly the same treatments as the CaO-doped samples. Also, untreated Al$_2$O$_3$ powders were pressed directly into samples of the same size in order to examine if the mixing
and calcining treatments would affect sintering in any way. The experimental data showed that there were no differences between these two kinds of samples. So it can be said that the results in this research were free from the influence of sample preparation procedures and depended only on the chemical composition of each sample.

C. Constant Temperature Sintering (CTS)

Samples, taken from dessicator, were put into a quench furnace which was already set at some fixed temperature. In this experiment the firing temperature was between 1320°C and 1440°C, both below and above the eutectic temperature of the Al₂O₃-CaO binary system (1360°C). The samples were put on the pedestal and heated slowly to 900°C for 2 hours to reduce thermal shock, and then pushed into the constant temperature heating zone. The isothermal linear shrinkage (ΔL) was measured with a Starrett micrometer (±2.5 μm) and the sample density was determined by measuring its volume and weight using a Mettler H51 AR balance (±0.01 mg). At least five samples were used for each point on the shrinkage curves.

D. Constant Heating Rate Sintering (CHR)

A Harrop dilatometer (model TDA-HI-PPG) was used for constant heating rate sintering. The samples were placed in an alumina tube and contacted with a constant pressure alumina push rod to measure the sample shrinkage during the sintering process. The furnace used a platinum alloy heating element which was divided into five sections in order to provide a uniform hot zone of approximately 10 cm in length. The dimensional change during sintering was transmitted by the push rod to a linear variable differential transformer (LVDT).
Both shrinkage and sintering temperature (measured by an S-type thermocouple) were recorded on a two-pen X-Y chart recorder.

During the experiment, samples were separated from both the alumina push rod and alumina holder by platinum foil to prevent the dilatometer from reacting with the samples at high temperature. The linear heating rate was 5°C/min. and temperature was raised from room temperature to 1420°C, held for 4 hours at that temperature and then cooled at the same rate.

E. Microstructure Examination

(a) Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used to examine the morphological change during sintering. The procedures use to polish and etch samples were as follows: First, samples were cold mounted in epoxy resin and roughly polished with SiC abrasive papers from 120 to 600 grit, then fine polished with a series of diamond pastes (6, 1, and 1/4 μm) with kerosene as the lubricant. After polishing, samples were removed from their mounts and ultrasonically cleaned in acetone. Thermal etching was done in air at 1250°C for 2 hours. Etched samples were gold coated using a Polaron Sputter Coater to eliminate charging effects during SEM observation. An ISI-DS 130 SEM was used in most of this research. An AMR SEM equipped with EDAX was used to examine the distribution of calcium in the Al₂O₃ matrix by means of a mapping technique.

(b) Transmission Electron Microscopy (TEM)

Transmission electron microscopy was used to examine the grain boundary structure of sintered samples. Thin foils were sliced from sintered samples with a diamond saw and ground to a thickness of 50 μm.
on a diamond wheel. Small pieces having a 3 mm diameter were cut from these foils with an ultrasonic cutter, then glued on a copper oval-shape specimen holder and thinned by a double-gun ion mill at 6 kv, 1 mA and a 15° tilting angle, until perforation occurred.

The EM 1500 high voltage transmission electron microscope, and the Atomic Resolution Microscope were used in this research.

F. Diffusion Experiments

The alumina powders were loaded into a graphite die with the die wall lined with graphite foil. The loaded die was placed in a vacuum hot press. A tungsten mesh resistance element was used to heat the die, and an oil diffusion pump was used to maintain vacuum. The chamber was evacuated to \(<10^{-4}\) torr and the die heated to 1000°C, then a pressure of 80 MPa was applied until the temperature reached 1320°C. These conditions were maintained for 8 hours to obtain fully dense \(\text{Al}_2\text{O}_3\) compacts.

CaO powders were cold pressed into pellets and the hot pressed polycrystalline \(\text{Al}_2\text{O}_3\) was sandwiched between two CaO pellets. The ensemble was heated in a quench furnace at 1330°C for periods of up to 2 weeks. After cooling, the \(\text{Al}_2\text{O}_3\) sample was separated from the CaO pellets and the cross section of the \(\text{Al}_2\text{O}_3\) sample, perpendicular to the contact surface, was examined. The scanning electron microscope was used to examine the morphological changes in the diffusion zone. Also, AEM (Auger Electron Microscopy) was used to obtain the depth profile of calcium in the \(\text{Al}_2\text{O}_3\) matrix, so that the concentrations of calcium corresponding to intermediate phases, if present, could be determined from this profile.
G. X-Ray Analysis

The Picker x-ray diffractometer, with 40 kv, 14 mA and copper as target, was used to examine the evolution of intermediate second phases in CaO-doped Al₂O₃ compacts during isothermal experiments.

H. Auger Electron Microscopy (AEM)

A scanning Auger electron microscope, made by Physical Electronics Inc. and equipped with a secondary ion mass spectrometer, was used. Samples being tested were fractured to obtain a clean fracture surface and directly introduced into the microscope under ultra high vacuum condition. The constituents of the first few atomic layers of the exposed intergranular fracture surface were examined. The depth profile of Ca at the grain boundary was determined by the Auger ion sputtering technique to strip off atomic layers at a constant sputtering rate of about 40 Å/min. Auger analysis was also performed in conjunction with the diffusion experiment by means of a line scanning technique to determine the concentration change of Ca ions in the diffusion direction, inside the Al₂O₃ polycrystal.
III. RESULTS AND DISCUSSIONS

A. Diffusion Experiment

In order to verify the development of intermediate phases during the solid state reaction between $\text{Al}_2\text{O}_3$ and $\text{CaO}$ powders in the sintering process, a diffusion experiment was conducted.

From the phase diagram, the binary system of $\text{Al}_2\text{O}_3$–$\text{CaO}$ has five intermediate phases ($\text{CA}_6$, $\text{CA}_2$, $\text{CA}$, $\text{C}_{12}\text{A}_7$, $\text{C}_3\text{A}$, $\text{C}=\text{CaO}$, $\text{A}=\text{Al}_2\text{O}_3$) together with the terminal $\text{Al}_2\text{O}_3$ and $\text{CaO}$ phases. When a diffusion couple is formed by contacting a pure $\text{Al}_2\text{O}_3$ polycrystal to a pure $\text{CaO}$ polycrystal, then, after firing at 1330°C for up to 2 weeks, it should show successive layers corresponding respectively to the $\text{CA}_6$, $\text{CA}_2$, $\text{CA}$, $\text{C}_{12}\text{A}_7$ and $\text{C}_3\text{A}$ phases. Each of these single-phase areas would appear with a finite thickness while those two-phase regions (such as $\text{Al}_2\text{O}_3+\text{CA}_6$, $\text{CA}_6+\text{CA}_2$, ...) would appear as dividing surface. The reason why the two-phase areas should appear as surfaces of zero thickness instead of layers of distinct thickness, after solid state diffusion reaction, can be explained by considering chemical potentials. To allow diffusion to proceed, a chemical potential gradient must exist along the diffusion path. This means that continuous diffusion across the couple can occur only if the partial molar free energy of the diffusing species decreases continuously with distance. However, in a two-phase region, the molar free energy, as defined by common tangent on the free energy vs. composition curve, is constant and therefore contradicts the foregoing requirement. So the only way for diffusion to proceed is to minimize the thickness of the two-phase region until it vanishes to zero thickness (surface) in the diffusion couple.
Because each intermediate phase has a certain concentration gradient of CaO and each two-phase region appears as an interface surface, it is reasonable to expect that, in the Al₂O₃-CaO diffusion couple, if intermediate phases did occur during solid state reaction, the curve of Ca concentration as a function of diffusion distance should show steps instead of a smooth penetration curve. In such a plot, near horizontal lines would correspond to the intermediate phases and vertical lines would correspond to the two-phase area. This is because each intermediate phase appears as a line in the phase diagram and thereby its composition is nearly fixed.

Figure 10 was taken by SEM, which proved the existence of a layered structure, probably corresponding to the successive intermediate phases in the phase diagram, which were parallel to the reaction surface. Figure 11 shows the result obtained by Auger electron microscope by line scanning on Al₂O₃ surface which was vertical to the reaction surface of the diffusion couple. The diffusion distance was measured from the contacting surface. It is encouraging to observe the appearance of some steps along the diffusion curve. As discussed above, these steps should correspond to the intermediate phases. The reason why Fig. 11 did not show a definite step profile is that the thickness of some intermediate phases is relatively small and the electron beam size used for Auger line scanning is about 5000Å in diameter, so it might analyze two successive intermediate phases at the same time. This curve, together with Fig. 10 and the work by Iwao Kohatsu et al.²⁰ and Suketoshi Ito et al.,²¹ validate the underlying assumption of this research that in mixed powders of Al₂O₃ and CaO,
the intermediate phases would develop during the sintering process. It is the purpose of this research to explore in more detail the effects of these phases on the densification of $\text{Al}_2\text{O}_3$ compacts.

B. Constant Heating Rate Sintering (CHR)

Constant heating rate sintering was used to: (a) examine the continuous dimensional changes during the sintering process of both pure $\text{Al}_2\text{O}_3$ and CaO-doped compacts in order to discover when enhanced densification rates occurred; (b) study the initial portion of the sintering process where the most rapid shrinkage occurred; (c) verify the effects of either pre-eutectic densification below the eutectic temperature ($1360^\circ\text{C}$) or transient liquid phase sintering above eutectic temperature.

Three different samples were used in the CHR sintering experiments: pure $\text{Al}_2\text{O}_3$; 0.1 wt.% CaO-doped and 1.0 wt.% CaO-doped powders. The shrinkage data obtained by dilatometry are shown in Fig. 12. Since there was no significant shrinkage below 900°C, the temperature scale began at this temperature. Two observations can be made from Fig. 12: first, for the heating rate used the addition of either 0.1 wt.% or 1.0 wt.% CaO results in a smaller total shrinkage at all temperatures investigated both above and below the eutectic temperature. Reference to the $\text{Al}_2\text{O}_3$-CaO phase diagram (Fig. 4) shows that a likely reason for the retarding effect might be found in the solid state reaction of CaO with $\text{Al}_2\text{O}_3$ to form calcium aluminate intermediate phases. The development of the reaction products had been indicated by the diffusion experiment, as discussed in part A. Their effects upon densification can be summarized into three categories: (a) if some intermediate
phases formed below the eutectic temperature, then the amount of the
eutectic forming phase would decrease significantly, thus decreasing
the effect of pre-eutectic densification; (b) in order to form a liq-
uid phase when the firing temperature reached the eutectic tempera-
ture, the composition would have to be between that of the CA and
$C_{3}A$ phases; therefore if the reaction proceeding to form intermediate
phases, like $CA_2$ or $CA_6$, was faster than the reaction to form the trans-
ient liquid phase, then the effect of the liquid phase on the sintering
rate would be lost; (c) also, other effects can be caused by the mor-
phological distributions of calcium aluminate, as discussed later.

Second, the addition of $0.1 \text{ wt.}\% \text{ CaO}$ decreased the densification
of $Al_2O_3$ compacts to a greater extent than the addition of $1.0 \text{ wt.}\% \text{ CaO}$. This result indicates that the retarding force was not simply propor-
tional to the amount of CaO added, even at small percentages of CaO.
The second observation implies that we cannot interpret the effect of
CaO on densification simply by one mechanism, because in this case the
densification curves should show a monotonic change with increasing
amounts of added CaO. So, it was assumed here that more than one
mechanism was active during the sintering process in $Al_2O_3$-CaO systems.
The mechanisms operative during the sintering process will be discussed
in more detail in conjunction with the CTS experiments.

C. Constant Temperature Sintering (CTS)

From CHR curves, it can be concluded that the addition of CaO to
$Al_2O_3$ decreased the sintering rate both below and above the eutectic
temperature where eutectic liquid phase might be present. Constant
temperature sintering was used in order to provide more information
about the role of CaO doping in the initial stage sintering of Al₂O₃ powders. The purposes of CTS experiments are: (a) to study the effect of CaO additives on the low temperature isothermal sintering of Al₂O₃; (b) to study in detail the relationship between the amount of CaO added and the densification of Al₂O₃ below the eutectic temperature, with focus on the existence of pre-eutectic densification.

(a) Low Temperature Isothermal Sintering

The isothermal shrinkage curves of pure Al₂O₃, 1.0 wt.% CaO and 5.0 wt.% CaO doped Al₂O₃ powders vs. firing temperature are shown in Fig. 13. From these curves it is obvious that: (1) the addition of CaO retarded the sintering rate of Al₂O₃ powders; (2) the retarding effect of 5.0 wt.% CaO was greater than that of 1.0 wt.% CaO.

From metallographic examination of these samples, Fig. 14., it can be seen that all samples contained open porosity, and there is essentially not much difference in pore distribution among these samples. Figure 15 shows the same microstructure as Fig. 14 at a higher magnification. In this figure most grains were equiaxed, but some large grains could also be found in all three samples. Average grain size was measured by counting the number of grain boundaries intersected by random straight lines, and the grain size was taken as by the average distance between intersections multiplied by 1.5. Using this method, the grain size of pure Al₂O₃ (1.8 ± 0.2 μm) was found to be a little larger than the grain size of CaO-doped samples (1.5 ± 0.2 μm).

However, it is interesting to note that the curves of both 1.0 wt.% CaO and 5.0 wt.% CaO in Fig. 13 were not straight lines, but rather were slightly bent towards the pure Al₂O₃ densification curve, with
the peak point A corresponding to 1.0 wt.% CaO and the peak point B corresponding to 5.0 wt.% CaO, both occurring at about 1360°C. This means that the difference of densification between pure Al₂O₃ and doped Al₂O₃ was a minimum at that temperature. Coincidentally, this is the eutectic temperature of the Al₂O₃-CaO system. This phenomenon can be explained by postulating that the enhancing effect of the transient liquid phase was likely to occur, but then was retarded at the same time by other adverse effects, and could not function as effectively as in other systems,⁴⁻⁶ so that the final densities of CaO-doped compacts were lower than those of the pure Al₂O₃ compacts.

The Al₂O₃-CaO phase diagram is somewhat complicated and shows a succession of intermediate phases in the sequence of CaO/C₃A/C₁₂A₇/CA/CA₂/CA₆/Al₂O₃. Among them, C₃A, C₁₂A₇ and CA have random orientations, but CA₆ and CA₂ are strongly oriented with respect to the reaction surface and can be identified by their columnar appearances, even in very small amounts. Figure 16 shows intermediate phases formed in CaO-doped compacts after isothermal sintering at 1330°C for 20 hours. The first two samples contained 0.1 wt.% CaO while the latter sample contained 0.5 wt.% CaO. Figure 17 shows the high voltage TEM picture of 0.5 wt.% CaO sintered sample which confirmed the second phase to be the CA₆ phase. In Fig. 16, the CA₆ phase was uniformly distributed in the Al₂O₃ matrix and showed a tabular shape, with an average length of less than 10 microns.

In order to determine the relationship between the density change and the evolution of sample composition during the sintering process, x-ray diffraction analysis was used and the results are shown in
Fig. 18 and Fig. 19. In these diagrams, $\Delta D$ denotes the difference between the relative densities of pure $\text{Al}_2\text{O}_3$ and of 5.0 wt.% CaO-doped samples after isothermal sintering at 1330°C (Fig. 18) and at 1440°C (Fig. 19), for times up to 20 hours. The second phases occurring during the solid state sintering were verified by x-ray diffractometry, and the amount of each second phase was represented by the peak height of the $\{112\}$ reflection for the $\text{CA}_2$ phase and the $\{114\}$ reflection for the $\text{CA}_6$ phase.

In Fig. 18, $\Delta D$ increased rapidly for the initial 2 hours, concurrently with the rapid formation of the $\text{CA}_2$ second phase, then continued to increase but at a lower rate at longer times. The maximum amount of $\text{CA}_2$ phase was obtained after about 4 hours and then subsequently decreased due to the formation of the $\text{CA}_6$ phase. The newly formed $\text{CA}_6$ phase reached the saturation amount after about 13 hours. These data imply that for 1330°C isothermal sintering, both $\text{CA}_6$ and $\text{CA}_2$ second phases formed and were responsible for the retardation of densification of $\text{Al}_2\text{O}_3$ compacts.

In figure 19, $\Delta D$ vs firing time at 1440°C is presented; $\text{CA}_6$ was formed at this temperature. Although there may be some small amount of $\text{CA}_2$ phase present, no evidence for the existence of this phase was found by x-ray diffractometry. By comparing these two curves, it is seen that in Fig. 18, with the formation of $\text{CA}_6$ second phase, the $\Delta D$ curve was flat after 2 hours. That is, after 2 hours, the difference between the relative densities of doped and of undoped $\text{Al}_2\text{O}_3$ was approximately constant. This means that the retarding effect resulting from
the presence of the $CA_2$ phase (and also partly from the $CA_6$ phase) saturated gradually after isothermal sintering for 2 hours. In contrast, as indicated in Fig. 19, $\Delta D$ continues to increase even after 20 hours. This means that the $CA_6$ phase retards densification even after long sintering times. So, it is clear that both $CA_2$ and $CA_6$ second phases decrease the sintering rate, but that the $CA_6$ phase is more effective than the $CA_2$ phase.

(b) Pre-Eutectic Densification Studies

Figure 20 and Fig. 21 show the influence of CaO additives on the densification of $Al_2O_3$ compacts after isothermal sintering at 1330°C (below the eutectic temperature) for 1 hour, 8 hours, and 20 hours. Figure 20 shows the linear shrinkage, $\Delta L/L_0$, as a function of the amount of CaO added, and Fig. 21 shows the relative density as a function of the amount of CaO added for the same samples. All three curves show an s-type profile. With a small amount of CaO (less than 0.15 wt.%) sintering was noticeably retarded, then as the amount of CaO increased, the density went back up and reached a maximum corresponding to 0.7 wt.% for all three curves. When the amount of CaO was gradually increased, the density went down again monotonically. So, it is appropriate to discuss these shrinkage curves in three regions:

1. Initial decreasing densification region.
   (pure $Al_2O_3$ - 0.15 wt.% CaO)
2. Intermediate increasing densification region.
   (0.15 wt.% CaO - 0.7 wt.% CaO)
3. Final decreasing densification region.
   (above 0.7 wt.% CaO)
Figure 22 and Fig. 23 consist of a series of micrographs which show the evolution of the microstructure during isothermal sintering of pure $\text{Al}_2\text{O}_3$ (Fig. 22) and 0.1 wt.% CaO (Fig. 23) at $1330^\circ\text{C}$ for 1 hour, 12 hours, and 20 hours. Figure 24 and Fig. 25 show microstructures of three samples with different amounts of CaO additives (pure 0.1 wt.% CaO and 0.5 wt.% CaO), after isothermal sintering at $1330^\circ\text{C}$ for 12 hours. These micrographs reveal several features: (a) all samples contained open porosity, (b) individual agglomerates seemed to sinter quickly, leaving a network of coarse porosity between them; (c) there was not much difference in pore distribution among the three samples.

(1) Initial decreasing densification region.

(pure $\text{Al}_2\text{O}_3$ - 0.15 wt.% CaO)

The addition of small amount of CaO decreased the $\text{Al}_2\text{O}_3$ sintering rate in this region, which could be explained by the influence of CaO upon the rate-controlling diffusion coefficient. In Johnson and Cutler's work, it was proposed that the following equation described isothermal sintering in the early stage:

$$\frac{\Delta L}{L_0} = \frac{K \gamma a^3 D}{k T r^p} t^m$$

similar expression have been obtained for later sintering stage, so that in general we have $\Delta L/L_0 = t^m$ where $\Delta L/L_0 =$ fractional shrinkage under isothermal condition; $K =$ rate constant which can be calculated for the different geometries; $\gamma =$ surface energy; $a^3 =$ vacancy volume; $D =$ self-diffusion coefficient; $k =$ Boltzmann's constant; $T =$ absolute temperature; $r =$ particle size; $P =$ size-effect constant; $t =$ time and
m = constant. When taking the logarithm of both sides in this equation the shrinkage curve of \( \Delta L/L_0 \) vs. sintering time \( t \) should be a straight line with the slope equal to \( m \). Figure 26 is the result of isothermal sintering data from two identical shrinkage experiments, conducted at 1330°C of pure \( \text{Al}_2\text{O}_3 \) and 0.1 wt.% \( \text{CaO} \)-doped compacts and plotted in a logarithm shrinkage vs. logarithm time chart. It is again clear that the addition of \( \text{CaO} \) retarded the sintering of \( \text{Al}_2\text{O}_3 \) powders. The curves appearing in this figure were straight lines with the same slope of 0.2 \( (m = 0.2) \). Although it is not possible to draw unambiguous conclusions about the transport mechanism from the value of \( m \) along, it is reasonable to assume that if \( m \) is invariant, the transport mechanisms are the same. Thus the same values of \( m \) exhibited by the different samples implies that the addition of \( \text{CaO} \) did not change the diffusion mechanism during sintering of \( \text{Al}_2\text{O}_3 \) compacts. Instead, \( \text{CaO} \) additions only influenced the rate of the dominant transport mechanism.

Thus, the decrease of shrinkage by the addition of 0.1 wt.% \( \text{CaO} \) may be explained by the change of the values of \( D \) or \( \gamma \) in the above equation. So, as follows from the vertical distance between the two lines, a decrease by a factor of two in the surface energy, \( \gamma \), or in the self-diffusion coefficient, \( D \), of the rate controlling aluminum ion\textsuperscript{23,24} could account for this reduction.

The effect of \( \text{CaO} \) additives on the grain boundary defects of \( \text{Al}_2\text{O}_3 \) can be hypothesized, by analogy with bulk defect chemistry, as follows:
(a) two Ca\(^{++}\) ions substitute for two Al\(^{+++}\) ions.

\[
\begin{align*}
\text{Al}_2\text{O}_3 & \\
2 \text{CaO} \quad \xrightarrow{} \quad 2 \text{Ca}_\text{Al}^{+} + 2 \text{O}_0 + \text{V}_0^\ast
\end{align*}
\]

(b) three Ca\(^{++}\) ions substitute for two Al\(^{+++}\) ions.

\[
\begin{align*}
\text{Al}_2\text{O}_3 & \\
3 \text{CaO} + \text{V}_{\text{Al}}^{+++} \quad \xrightarrow{} \quad 3 \text{Ca}_\text{Al}^{+} + 3 \text{O}_0
\end{align*}
\]

In case (a), an additional oxygen vacancy is produced. From the equilibrium relationship

\[
K_S = [V_{\text{Al}}^{+++}]^2 [V_{0}^\ast]^3
\]

where \(K_S\) = Schottky constant, it follows that the aluminum vacancy concentration is related to oxygen vacancy concentration by:

\[
[V_{\text{Al}}^{+++}]^2 = K_S/[V_{0}^\ast]^3
\]

Thus an addition which increases the oxygen vacancy concentration \([V_{0}^\ast]\) will decrease the aluminum vacancy concentration \([V_{\text{Al}}^{+++}]\). In case (b), the extra calcium ion will fill an aluminum vacancy site so that the aluminum vacancy concentration will be decreased. In either case, the diffusion rate of aluminum ion is expected to decrease with the addition of CaO. Since sintering of Al\(_2\)O\(_3\) is controlled by Al\(^{+++}\) diffusion through grain boundary,\(^{23,24}\) the sintering rate will be decreased.

So far the discussion applied mainly to the subject of solid solution of CaO in Al\(_2\)O\(_3\). However, it is well known that Ca\(^{++}\) ions will segregate to grain boundaries of Al\(_2\)O\(_3\).\(^{24,25}\) The segregation may be attributed primarily to the distortion energy when a Ca\(^{++}\) resides on an Al\(^{+++}\) lattice site. This is because the Ca\(^{++}\) ion size is about twice as
large as the Al+++ ion size (0.99 Å vs. 0.5 Å). Figure 27 is the depth profile of Ca concentration in Al₂O₃ matrix by Auger analysis on a fracture surface of a 0.1 wt.% CaO sample, after isothermal sintering at 1330°C for 1 hour. It shows that Ca was highly localized on grain boundaries in a layer with a thickness of less than 40 Å. The solubility of calcium in the Al₂O₃ matrix is likely to be low, also due to the large misfit between the Ca++ ion and the Al₂O₃ lattice site. So, the excess calcium is expected to form a second phase along the grain boundaries of an Al₂O₃ polycrystal. By referring to the phase diagram of Al₂O₃ - CaO, the equilibrium phases will be Al₂O₃ and CA₆ in this region. Because the added amount of CaO (up to 0.15 wt.% in this region) should be higher than the solid solubility of CaO in Al₂O₃ bulk, CA₆ will then form as the second phase. Therefore the mechanism for retarded sintering in this initial decreasing densification stage can not be explained solely by solid solution effect. The influence of the CA₆ second phase should also play an important role in retarding the sintering rate of Al₂O₃. However, the details of the second phase mechanism will be discussed in the following sections.

(2) Intermediate increasing densification region

(0.15 wt.% CaO - 0.7 wt.% CaO)

Pre-eutectic densification has been observed in many systems. In fact, the enhancing effect could also be seen in this region by observing that the shrinkage rate increased in proportion to the amount of CaO. In Fig. 20 and Fig. 21, all three curves showed this trend and reached the maximum density (or linear shrinkage) at about 0.7 wt.% CaO. After 1 hour of isothermal sintering, the linear shrinkage
or density of samples with this composition was even higher than that of the pure Al₂O₃ sample (point A in Fig. 20 and Fig. 21). This means that with an addition of 0.7 wt.% CaO, the sintering rate of Al₂O₃ was enhanced in comparison to that of pure Al₂O₃. This indicates that pre-eutectic densification did occur in a limited way during the sintering process. This is because by increasing the amount of CaO phase, the amount of eutectic forming phase was also increased; therefore the enhancing effect would become large enough to overcome the retarding effect, as discussed above. However, the enhancing effect did not persist for extended sintering times. When the isothermal time was prolonged, for example from point A to point B or point C, the amount of the CA₆ second phase increased, and its retarding effect then masked the pre-eutectic enhancing effect, decreasing the sintering rate.

(3) Final decreasing densification region
(above 0.7 wt.% CaO)

As the amount of CaO increased, the amount of CA₆ second phase formed also increased, as confirmed by both SEM pictures and x-ray analysis of sintered samples. CaO was assumed to be uniformly distributed on the grain boundaries initially. However, high resolution TEM could not provide definite evidence of second phases along the grain boundaries (Fig. 28). The reason why CA₆ did not appear as a grain boundary phase, but rather as the individual column-like phase in the Al₂O₃ matrix (Fig. 16), may be that the grain growth of Al₂O₃ grains, early in the sintering process, caused calcium to be rejected from the grain boundaries which then led to the formation of CA₆ second phase.
As discussed before, the CA₆ phase appeared to be the main reason for the retardation of densification when either the sintering time or the amount of CaO was increased. Two reasons might explain this retarding effect: (a) the quick formation of CA₆ phase decreased the amount of eutectic forming phase and so decreased the effect of pre-eutectic densification; (b) the preferred direction of crystal growth of the CA₆ phase, once formed in the early stage of sintering, might impede the rearrangement of Al₂O₃ grains and retard the sintering rate.

However, there still needs to be an explanation as to why such small amounts of CA₆ should induce so large a difference in shrinkage between the doped and undoped Al₂O₃ compacts. Figure 29 is a typical morphological image of the CA₆ second phase in polycrystal line Al₂O₃. One thing to be noted from these pictures is that the CA₆ phase not only existed intergranularly, but also intragranularly. This means that when the CA₆ phase formed in the early stage of sintering, it would penetrate the surrounding alumina grains which were located in front of the direction of CA₆ crystal growth. In this case, the CA₆ second phase could "pin" the surrounding Al₂O₃ grains and inhibit local densification in the direction as shown by arrows in Fig. 29.
IV. CONCLUSION

CaO additions to Al₂O₃ caused several mechanisms to influence the sintering rate of Al₂O₃ compacts. Enhanced pre-eutectic densification appeared to occur to some extent, but was opposed by solid solution effects and by second phase formation.

When a small amount of CaO was added, the Ca in solid solution would decrease sintering rate, more likely by lowering the surface energy and/or the self-diffusion coefficient of aluminum ions. When more CaO was added, an enhanced pre-eutectic densification effect could be observed, but this enhancing effect saturated at about 0.7 wt.% CaO content. The suppression of the enhanced pre-eutectic densification could be ascribed to the formation of the CA₆ second phase. Competition between two mechanisms thus occurred: when the enhanced pre-eutectic densification started to compensate for the adverse defect chemistry, the shrinkage rate would increase; however, when the added amount of CaO exceeded 0.7 wt.%, the second phase retarding effect dominated and a decreasing sintering rate was observed.
ACKNOWLEDGEMENTS

I wish to express my acknowledgement to Professor L. C. De Jonghe for his guidance and encouragement in this research work. I am also grateful to K. A. Gaugler and Erlene Fong for their technical assistance.

The help of my fellow graduate students through this work is greatly appreciated.

Finally, I would like to express my special thanks to my parents and my wife Chia-Chu for continuous love and encouragement.

This work was supported by the Division of Materials Science, Office of Basic Energy Science, U. S. Department of Energy, under contract No. DE-AC03-76SF00098.
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8. C. Agte, Hutnicke Listy, 8, P227 (1953).
Table 1.

The properties and specifications of Baikowski aluminum oxide powders. (Baikalox Al₂O₃, grade CR1).

<table>
<thead>
<tr>
<th>Property</th>
<th>Specification</th>
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<tr>
<td>Purity, Al₂O₃</td>
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<tr>
<td>Major phase</td>
<td>alpha</td>
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<tr>
<td>Major phase</td>
<td>97%</td>
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<tr>
<td>Hardness, Mohs</td>
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<tr>
<td>Crystal density, gm/cm³</td>
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<tr>
<td>Bulk density, gm/cm³</td>
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<tr>
<td>Ultimate particle size, microns</td>
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<tr>
<td>Mean agglomerate size, microns</td>
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<tr>
<td>Specific surface area, B.E.T., m²/gm</td>
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Table 2.

Chemical analysis data of impurities of alpha-alumina from Baikowski International Corporation.

<table>
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<th>Element</th>
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<tbody>
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<tr>
<td>Fe</td>
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<td>V</td>
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</tr>
<tr>
<td>Cu</td>
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Table 3.

Maximum limit of impurities of calcium nitrate Ca(NO₃)₂·4H₂O, from Mallinckrodt Inc.

<table>
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<th></th>
<th>wt.%</th>
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<tr>
<td>Barium (Ba)</td>
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<tr>
<td>Chloride (Cl)</td>
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<tr>
<td>Heavy metals (as Pb)</td>
<td>0.0005</td>
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<tr>
<td>Insoluble and NH₄OH Ppt.</td>
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<tr>
<td>Iron (Fe)</td>
<td>0.0005</td>
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<td>Magnesium and alkali salts</td>
<td>0.2</td>
</tr>
<tr>
<td>Sulfate (SO₄)</td>
<td>0.002</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Fig. 1. Linear shrinkage $\Delta L/L_0$ as a function of position during zone sintering of sodium beta alumina. A: eutectic additive sample; B: additive free sample. The eutectic temperature is about 1575°C. (XBL 815-9725)

Fig. 2. Phase diagram of CaF$_2$-MgF$_2$.

Fig. 3. Idealized phase diagram of activated sintering after G. M. German.

Fig. 4. Phase diagram of CaO-Al$_2$O$_3$.

Fig. 5. Phase diagram of CaF$_2$-Al$_2$O$_3$.

Fig. 6. Agglomerate size distribution of Baikowski Al$_2$O$_3$.

Fig. 7. Scanning electron micrographs taken from pressed compact surface. (a) low magnification, (b) high magnification.

Fig. 8. Flowchart of sample preparation of pure Al$_2$O$_3$ and CaO-doped powders.

Fig. 9. (a) Ca mapping by EDAX of 0.1 wt.% CaO-doped sample. (b) Scanning electron fractographs of EDAX analysed surface.

Fig. 10 Scanning electron picture of diffusion zone, showing layered structure parallel to the reaction surface.

Fig. 11. Calcium concentration vs depth in diffusion test by Auger electron microscope line scanning technique.

Fig. 12. Linear shrinkage vs temperature curve in dilatometer by constant heating rate sintering at 5°C/min.

Fig. 13. Theoretical density vs temperature curve in isothermal sintering.
Fig. 14. Microstructure of doped and undoped samples, isothermally sintered at 1415°C for 20 hours. (a) pure Al₂O₃, (b) 1.0 wt.% CaO, (c) 5.0 wt.% CaO.

Fig. 15. Same samples as in Fig. 14 with higher magnification.

Fig. 16. Intermediate phases formed in Al₂O₃ matrix after isothermally sintered at 1330°C for 20 hours. (a) pure Al₂O₃, (b) 0.1 wt.% CaO, (c) 0.5 wt.% CaO.

Fig. 17. TEM picture of sample after isothermal sintering at 1330°C for 20 hours.

Fig. 18. The relationship between the amount of intermediate phases and the difference in density of 5.0 wt.% CaO samples after isothermal sintering at 1330°C.

Fig. 19. Same meaning as in Fig. 18, except samples were isothermally sintered at 1440°C.

Fig. 20. Linear shrinkage vs the amount of CaO additive, isothermally sintered at 1330°C for successive hours.

Fig. 21. Relative density vs the amount of CaO additives, isothermally sintered at 1330°C for successive hours.

Fig. 22. The evolution of microstructure during isothermal sintering of pure Al₂O₃ at 1330°C for (a) 1 hour, (b) 12 hours and (c) 20 hours.

Fig. 23. The evolution of microstructure during isothermal sintering of 0.1 wt.% CaO samples at 1330°C for (a) 1 hour, (b) 12 hours and (c) 20 hours.
Fig. 24. Different microstructures of three samples (a) pure $\text{Al}_2\text{O}_3$, (b) 0.1 wt.% CaO, (c) 0.5 wt.% CaO, isothermally sintered at 1330°C for 20 hours.

Fig. 25. Same meaning as in Fig. 24 with higher magnification.

Fig. 26. Log $\Delta L/L_0$ vs log t of pure $\text{Al}_2\text{O}_3$ and 0.1 wt.% CaO samples sintered by CTS method at 1330°C.

Fig. 27. Auger electron microscope depth profile of Ca concentration on fracture surface of 0.1 wt.% CaO sample after isothermally sintered at 1330°C for 1 hour.

Fig. 28. High resolution TEM picture of grain boundary of 0.5 wt.% CaO-doped sample, after isothermal sintering at 1330°C for 20 hours.

Fig. 29. The formation of $\text{CA}_6$ second phase in $\text{Al}_2\text{O}_3$ matrix after isothermally sintered at 1330°C for 20 hours.
Fig. 1
Fig. 2
Large Melting Point Difference

High Solubility

Decreasing Liquidus and Solidus

Examples: Liquid Phase Activated

Low Solubility

Additive

Base

Fig. 3
Fig. 4
Figure 5

Solid Sol'n

A = SS Al₂O₃ in CaF₂
B = SS CaF₂ in Al₂O₃

Solid Sol'n B
+ Melt

Solid Sol'n A
+ Melt

Solid Sol'n A

Solid Sol'n B

CaF₂ vs. Al₂O₃

Temperature, °C

Wt. %

XBLB312-6640

Fig. 5
Fig. 6
Fig. 7
\[ \text{Al}_2\text{O}_3 \text{ as received} \]
\[ \text{Ca(NO}_3\text{)}_2 \cdot 4 \text{H}_2\text{O as received} \]

\[ \text{Magnetic Stirring} \rightarrow \text{Dissolve} \]

\[ \text{Magnetic Stirring} \rightarrow \text{Mixing} \rightarrow \text{Drying} \]

\[ \text{Decompose} \]
\[ 400^\circ\text{C, 4 Hours} \]

\[ \text{Cold Press} \]
\[ 0.5'' \text{dia., 0.07'' height} \]

\[ \text{Constant Heating Rate} \]
\[ \text{Sintering} \]
\[ (\text{CHR}) \]

\[ \text{Constant Temperature} \]
\[ \text{Sintering} \]
\[ (\text{CTS}) \]

\[ \text{Sintered Samples for Analysis} \]

\text{Fig. 8}
Fig. 10
Fig. 11
Fig. 12

Linear shrinkage, $\Delta L / L_0$ (%) vs. temperature, °C

- Pure $\text{Al}_2\text{O}_3$
- 1.0% CaO
- 0.1% CaO
Isothermal sintering 20 hours

Theoretical Density, %

Temperature, °C

Fig. 13
$\Delta D =$ the difference between relative density of pure $\text{Al}_2\text{O}_3$ and 5.0 wt. % CaO

1330°C

Fig. 18
\( \Delta D = \) the difference between relative density of pure \( \text{Al}_2\text{O}_3 \) and 5.0 wt. % \( \text{CaO} \)

1440°C

\( \Delta D \)

\( \text{CA}_6 \)

Relative amount of second phase

Time hours

Fig. 19
Fig. 20
Fig. 21

Theoretical Density, %

CaO (wt. %)
Sputtering rate ~ 40 Å min

Fig. 27