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PRE-EUTECTIC DENSIFICATION IN MgF$_2$-CaF$_2$

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ABSTRACT
Increased densification rates were found as much as 200°C below the eutectic
temperature (980°C) for MgF$_2$ containing small amounts of CaF$_2$. Constant heat­ing rate and constant temperature sintering data, as well as microstructural
developments indicated that solid state grainboundary transport rates had been
enhanced by the eutectic forming additive. The effect saturated at about 1 wt% CaF$_2$. The results suggest that densification of ceramic powders could be
favorably affected without a substantial increase in the grain growth rate, by
the addition of small amounts of eutectic forming additives, and sintering be­
low the eutectic temperature.

INTRODUCTION
Many densification processes of ceramic powders involve some form of liquid
phase sintering. While these liquids enhance the densification rate very sig­
ificantly, they tend to lead to strongly enhanced grain growth. The process
of liquid phase sintering is usually explained by invoking rapid material
transport through a continuous, liquid grainboundary film, assisted by capil­
lary forces arising from voids in the liquid that resides in interparticle
interstices (Ref. 1). In a study of the transient liquid phase densification
of sodium-beta alumina by an arrested zone sintering method (Ref. 2) it was,
however, observed that significant densification occurred well below the tem­
perature that liquid phases could be present. To clarify the nature of this
effect, possibly occurring near the eutectic temperature of many eutectic form­
ing powder mixtures, the model system magnesium fluoride-calcium fluoride was
examined. In this system the eutectic temperature is 980°C, while the melting
points of calcium fluoride and magnesium fluoride are 1410°C and 1252°C respec­
tively. The mutual solubilities are less than 1 wt%, but have not been deter­
mined accurately (Ref. 3).

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Energy Sciences of the U.S. Department of Energy under Contract Number DE-AC03-
76SF00098.
EXPERIMENTAL METHODS

MgF₂ powder* was sized with an Acucut** air classifier to obtain a uniform agglomerate fraction with a size of 2.5 μm and a primary particle size of about 0.5 μm. Measured amounts of CaF₂† were added to this powder, mixed with anhydrous ethanol. The slurry was stir-dried at 80°C. Both pure and mixed powders were subjected to the same procedures. The powders were die pressed at 48,000 psi to a green density of 55% theoretical. Vacuum drying was carried out under a total pressure of less than 10⁻³ torr, at 350°C, for 1 hour. This removed the water, while minimizing oxidation, hydrolysis, and sintering of the fluorides. A thermobalance experiment showed that no further weight changes occurred in this environment to within the detection limit (~ 10⁻³ wt.%).

Since it might be argued that some pre-eutectic liquid might form as a consequence of undetected oxidation or hydrolysis during densification, CaF₂-MgF₂ eutectic mixtures were prepared containing 5 wt% MgO and CaO. A thermal analysis was performed under conditions identical to those in the dilatometer. No evidence of pre-eutectic liquid formation could be detected.

Dilatometry was carried out at a constant heating rate (CHR) of 4.5°C/min in flowing helium from which the oxygen had been removed by a hot zirconium getter. Constant temperature (CT) sintering was also carried out between 650°C and 850°C in the dilatometer, using a rapid heat up rate. In that case, the specimen reached the sintering temperature in about five minutes.

The microstructures of specimens quenched from particular temperatures during CHR sintering was observed on fracture surfaces of highly porous specimens or on polished and etched surfaces of the denser specimens. The etchant consisted of 100 g boric acid in 200 cm³ of sulfuric acid (Ref. 4) used at 150°C for about 7 min. This removed CaF₂ completely, but only etched grainboundaries in MgF₂.

Data for CaF₂-MgF₂ interdiffusion were not available, so an interdiffusion experiment was performed on an MgF₂ single crystal embedded in CaF₂ powder. The couple was annealed in vacuum, at 950°C, for 96 hours. Afterwards, the MgF₂ crystal was briefly polished, sufficient to remove the CaF₂ particles that stuck to its surface but removing only a few hundred Ångstrom of the crystal itself. A composition versus depth profile was obtained by measuring the relative Ca content as a function of sputtering time in an Auger system equipped with a secondary ion mass spectrometer. The sputtering gas was Ar and the sputtering rate was 400 Å/min. The results permitted a fair estimate of the cation interdiffusion rates at 950°C.

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*Materials Research Corporation, Orangeburg, New York 10962, USA (99.8% pure).
**Majac-Donaldson, P.O. Box 43217, St. Paul, Minnesota 55164 (USA).
†Orion Chemical Company, Hunt Beach, California 92646, USA (99.999% pure).
Auger analysis was also performed on intergranular fracture surfaces of partly sintered compacts in conjunction with Ar-ion sputtering to determine the Ca distribution during the pre-eutectic sintering.

RESULTS AND DISCUSSION

Some dilatometry data, converted to % shrinkage (\(= 100 \frac{\Delta L}{L_0}\); where \(\Delta L\) is the length change and \(L_0\) is the initial sample length) are shown in Fig. 1 for CHR sintering of samples containing up to 5 wt% CaF\(_2\). It is evident that enhanced densification rates are observed as much as 200°C below the eutectic temperature. The enhancing effect of the CaF\(_2\) appears already noticeable when as little as 0.1 wt% is added to the MgF\(_2\), and saturates above 1 wt% of CaF\(_2\). This behavior is difficult to bring in agreement with, at present, the only quantitative treatment of liquid phase sintering (Ref. 1), and argues for a different mechanism of pre-eutectic densification.

![Graph showing shrinkage and grain size vs temperature](attachment:fig1.png)

**Fig. 1.** Shrinkage and grain size vs temperature for pure MgF\(_2\), 0.1 wt%, 1 wt%, and 5 wt% CaF\(_2\) containing MgF\(_2\). The heating rates are 4.5°C/min. The eutectic temperature is 980°C. Theoretical density corresponds to 20.1% shrinkage.

Grain growth rates are increased as a result of the CaF\(_2\) addition, but at 900°C, Figure 1 shows that they are still relatively modest. The microstructures of samples quenched from 900°C and 1000°C are compared in Figures 2 and 3,
while the grain sizes at other temperatures are listed in Table 1. The grain size of the pure MgF$_2$ at 1000°C is about four times that of the 1 or 5 wt% CaF$_2$ containing MgF$_2$ at 900°C, while their densities are about equal (89% theoretical). Thus, the grain growth rates have not been increased sufficiently to overcompensate for the faster densification kinetics. One might rationalize this behavior qualitatively by the following type of simplified argument: according to Coble and Burke (Ref. 5) one might express the shrinkage of a powder compact as:

\[ L = K_L D_L G^{-p} \]  

(1)

and

\[ G = K_G (D_G t)^n + G_0 \]  

(2)

where \( L = d(\Delta L/L_0)/dt \), with \( \Delta L = \) shrinkage, \( L_0 = \) initial length, \( K_L, p, K_G, \) and \( n \) constants, \( G_0 = \) initial grain size, \( D_L = \) diffusion coefficient of the dominant transport mechanism for densification, \( D_G = \) diffusion coefficient of the dominant transport mechanism for grain growth. Under the assumption that \( G_0 \ll G \), Eqs. (1) and (2) give

\[ L = K_L D_L t^{(1-np)/(1-np)}(K_G D_G)^{np} \]  

(3)

Since \( L \) increases with increasing time we must have

\[ np < 1 \]  

(4)

in the interval of densification where Eqs. (1) and (2) hold. This is a very large part of the densification process, and only excludes the final stage. In this interval the presence of an additive would succeed in producing a smaller grain size at constant density if, from combining Eqs. (1) and (2),

\[ D_G^*/D_L^* < D_G/D_L \]  

(5)

where \( D_G^* \) and \( D_L^* \) refer to the additive containing and \( D_G \) and \( D_L \) refer to the pure powder compact. Such a situation would arise if volume diffusion controlled impurity drag governed grain growth, and grainboundary transport controlled densification. This type of argument can be thought of as providing an upper limit estimate of the grain size after impurities are added. If the pre-eutectic solubility limit were exceeded, additional second phase particle drag would tend to lower \( D_G^*/D_L^* \) even more. Above the eutectic temperature, when
an intergranular liquid phase increases the grainboundary mobility dramatically, a larger grain size should be expected at constant density. Significant enhancement of the grain growth rate can also be found above the eutectic temperature of the MgF$_2$-CaF$_2$ system, as can be seen in Fig. 2 and 3, and in Table 1.

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**Fig. 2.** Scanning electron micrographs of powder compacts quenched from 900°C, after CHR sintering at 4.5°C/min. The calcium fluoride contents are indicated in wt% in the lower left corners.
Fig. 3. Scanning electron micrographs of powder compacts quenched from 1000°C, after CHR sintering at 4.5°C/min. The calcium fluoride contents are indicated in wt% in the lower left corners.

The experiments on CaO-MgO-MgF₂-CaF₂ mixtures showed that no liquid forms below the eutectic temperature. At the same time, densification and grain growth behavior below 980°C is not in agreement with what would be expected if a liquid phase sintering mechanism were active. It is therefore concluded that the enhanced pre-eutectic densification kinetics are due to a solid state transport mechanism with a rate increased by the eutectic additive. While the CHR experiments permit a convenient and rapid evaluation of the sintering behavior of different powder mixtures, a detailed analysis of the kinetics (Ref. 6) is not reliable due to possible interference from non-densifying mechanisms (Ref. 7). A possible indication of the sintering mechanism may come from a comparison of diffusion rates derived from CT experiments, assuming a single rate controlling mechanism, with those obtained from the diffusion couple experiment.
TABLE 1
Grain sizes in µm of specimens quenched after CHR sintering at 4.5°C/min.

<table>
<thead>
<tr>
<th>Temperature(°C)</th>
<th>CaF\textsubscript{2} content in wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>0</td>
</tr>
<tr>
<td>900</td>
<td>0.4</td>
</tr>
<tr>
<td>1000</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
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<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
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<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>50</td>
</tr>
</tbody>
</table>

Some CT densification data are shown in Fig. 4. A time correction, \(\Delta t\), was necessary to take into account the densification that took place in the heat-up cycle, by forcing the data to obey a relationship of the type \(\log\left(\frac{A}{L/L_0}\right) = n \log (t - \Delta t) + B\), where \(B\) is a constant. This is the type of relationship that should be expected for isothermal sintering (see e.g. Ref. 8). Approximate volume diffusion coefficients were derived from these data employing the expressions developed by Johnson and Clarke (Ref. 9), assuming exclusive volume diffusion control. This coefficient was compared to the volume interdiffusion rate derived from the MgF\textsubscript{2}-CaF\textsubscript{2} couple. The relative concentration versus distance is shown in Fig. 5. The mean penetration distance is about 1 µm after 96 hours at 950°C making \(D = 3 \times 10^{-14} \text{ cm}^2/\text{sec}\).

![Graph](XBL 815-5785)

Fig. 4. Log \(\frac{A}{L/L_0}\) versus log (t - \(\Delta t\)) for MgF\textsubscript{2} containing 1 wt% CaF\textsubscript{2} additive, sintered at the indicated temperatures. The heatup time was about 5 min leading to a small amount of densification before temperature equilibrium was reached; this was corrected for by the time correction, \(\Delta t\).
Fig. 5. Relative Ca concentration as a function of sputtering time in the Auger analysis of the MgF₂-CaF₂ interdiffusion couple. The sample was annealed for 96 hours at 950°C. The mean Ca penetration depth is about 1 μm.

The activation energy for interdiffusion is estimated to be equal or higher than for Ca self-diffusion in CaF₂ (Ref. 9). This is to be expected since Ca⁺⁺ is larger than Mg⁺⁺, and since a similar trend is observed for other fluorides, e.g., Sr⁺⁺ in CaF₂ (Ref. 9). This puts a lower bound on the activation energy for interdiffusion of 95 kcal/mol. It is then found that the volume diffusion rates necessary to account for the enhanced pre-eutectic densification rates are 3 to 4 orders of magnitude higher than those determined from the interdiffusion experiment.

Additionally, the Auger analysis of intergranularly fractured specimens indicates that the grain boundaries are significantly enriched in Ca to a depth of less than 100 Å, as shown in Fig. 6.

All the obtained results thus strongly indicate that enhanced pre-eutectic densification rates can be attributed to increased solid state grain boundary transport rates caused by the presence of an additive that can form a eutectic liquid at a higher temperature. This phenomenon might be understood if one considers that diffusion rates scale approximately as the absolute temperature of the melting point of a solid (Ref. 10). If the grain boundaries are rich in the eutectic forming additive then their relative melting points should be
considerably below that of the matrix, and their transport rates should be accordingly enhanced.

The results, therefore, suggest that densification of ceramic powders could be favorably affected, without an undue increase in the grain growth rate, by the addition of small amounts of eutectic forming additives, and sintering below the eutectic temperature.

![Auger electron depth profile on intergranular fracture surface of a CHR sintered specimen with an average CaF₂ content of 1 wt%. The specimen was sintered at 4.5°C/min to 900°C. The eutectic composition has a Ca/F ratio of about 0.25.](image)

Fig. 6. Auger electron depth profile on intergranular fracture surface of a CHR sintered specimen with an average CaF₂ content of 1 wt%. The specimen was sintered at 4.5°C/min to 900°C. The eutectic composition has a Ca/F ratio of about 0.25.

ACKNOWLEDGMENTS

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