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EFFECT OF LITHIUM FLUORIDE ON THE DENSIFICATION OF MAGNESIUM OXIDE

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UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

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EFFECT OF LITHIUM FLUORIDE ON THE DENSIFICATION OF MAGNESIUM OXIDE

Mark William Benecke
(M. S. Thesis)

December 20, 1965

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EFFECT OF LITHIUM FLUORIDE ON THE DENSIFICATION OF MAGNESIUM OXIDE

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December 20, 1965

ABSTRACT

Transparent polycrystalline magnesium oxide can be fabricated by hot-pressing the powder with a small lithium fluoride addition, and a subsequent heat treatment. Compaction-vs-temperature studies have been made of magnesium oxide and magnesium oxide + 2 wt% lithium fluoride have been made up to 1000° C using pressures up to 4000 psi. The lithium fluoride addition allows magnesium oxide to be hot-pressed to near theoretical density at reduced temperatures and stress. The hot-pressed density must be at least 99.5% of the theoretical density of magnesium oxide for the subsequent heat treatment to yield a transparent specimen. Because the densification kinetics vary with the temperature and pressure, the hot-pressing process must be designed to yield this critical density.

Densification during hot-pressing is proposed to occur by a deformation process associated with the small particle size of the magnesium oxide powder with lithium fluoride aiding the process by maintaining the small particle size, or by a diffusional creep process with lithium fluoride enhancing the diffusivity of magnesium oxide.

I. INTRODUCTION

Efforts within ceramic technology have always been directed toward developing processes which yield materials with controlled density and microstructure. Progress toward achievement of theoretical density was realized when it was observed that higher densities could be achieved at lower temperatures by using appropriate sintering additions. In recent years, hot-pressing techniques have been developed which permit higher densification at lower temperatures without the use of additives. More recently, these methods have been combined to achieve further control of as-sintered properties.

It has thus been demonstrated that optically transparent polycrystalline magnesium oxide can be fabricated by hot-pressing magnesium oxide powder with a small lithium fluoride addition, and a subsequent heat treatment.[1,2] The purpose of this study was to determine the hot-pressing conditions for this process which yield a specimen that will become transparent during the subsequent heat treatment, and to determine the predominant densification mechanism.

II. LITERATURE SURVEY

A. Sintering Additions

Densification during the normal sintering of pure materials is generally considered to be controlled by lattice diffusion.[3] Certain sintering additions have been shown to be effective either by creating defects which enhance diffusion, by forming a liquid phase in which the material is soluble, or by inhibiting grain growth.

Tacvorian[4,5] has proposed that a proper sintering addition may activate the surface of refractory particles by forming a solid solution in the surface layers. This surface solid solution will have higher diffusion rates than the pure material and will result in accelerated sintering rates. Eventually, the diffusion process will distribute the additive throughout the refractory material so that the final properties of the sintered powders are nearly the same as those of the pure refractory. In connection with sintering additions, he also stresses the significance of minor impurities on sintering behavior.

The interaction of impurity atoms with the surface and lattice atoms of ionic crystals has been discussed by Weyl.[6] On the basis of ionic polarizability, he has explained the existence of defect structures and described the repulsion of particles due to surface charge. He showed how structures of noble gas-type ions can be made to form defect structures by additions which enter into solid solution with the structure but have ions of different valence. Vacancies must be created within the crystalline solid solution to maintain electroneutrality. On this basis, the enhanced sintering of magnesium oxide

with a ferric oxide addition and the inhibited sintering of zinc oxide containing additions which prevent defect formation were explained.

Sintering in the presence of a liquid phase has been analyzed by Kingery.[7] The driving force for densification is the surface energy of the liquid-gas interface for the pores in the liquid which results in an effective capillary pressure. Densification, or reduction in pore size, occurs by two processes. When rearrangement is complete, solution of the solid particles occurs at contact points which are stress concentrations, and material is transferred away to precipitate on surfaces of lower chemical potential. Experimental evidence of a solution-precipitation process resulting in densification during sintering in the presence of a liquid phase exists for metal-metal systems,[8] carbide-metal systems,[9] and several ceramic systems.

Atlas[10] studied the effect of some lithium compounds on the sintering of magnesium oxide and found that additions of lithium halides particularly aid densification. The relative effectiveness of the different alkali halide additives he used for sintering at 1300° C and 1400° C cannot be determined because the bulk density of the pressed, unfired samples varied with each additive. If differences in unfired density are disregarded, lithium bromide can be considered to be the most effective additive followed by lithium chloride and lithium fluoride. But when the sintering temperature was lowered to 800° C, lithium fluoride was most effective in aiding densification. Atlas postulated that the lithium compounds facilitated sintering by entering into the magnesium oxide structure and creating defects.

Layden and McQuarrie[11] added 14 different metal ions to magnesium oxide in an investigation of the effect of additives on sintering behavior. They found that the effective additions were those which could diffuse into the structure and create defects, or form a liquid phase. Additions which formed compounds with magnesium oxide appeared to hinder sintering.

Additions which inhibit discontinuous grain growth permit attainment of higher densities because pores are not trapped within grains. Coble has produced theoretically dense aluminum oxide by using a magnesium oxide sintering addition.[12]

B. Hot-Pressing

Densification during hot-pressing is generally considered to occur by some, or all, of three mechanisms: (1) particle rearrangement, (2) plastic flow, and (3) stress-enhanced diffusion.

The first compaction that occurs during hot-pressing has been observed by Felton[13] and Hashimoto[14] to be particle rearrangement and sometimes fragmentation under the influence of the applied stress.

Murray et al.[15] have modified the plastic flow sintering model of Mackenzie and Shuttleworth[16] to describe the behavior of some materials during hot-pressing. They retained the concept that the compact powder deforms as a Bingham solid but replaced the pressure due to pore surface energy by the externally applied pressure for the driving force. An important aspect of their theory is that a characteristic end-point bulk density exists for each combination of temperature and pressure for hot-pressing a particular material. They

concluded that the densification of several oxides and carbides during hot-pressing could be described by a plastic flow model.

The Mackenzie-Shuttleworth model cannot be applied to the hot-pressing of all materials because it requires dislocation motion. A modified Nabarro-Herring[17,18] diffusional creep model has been used to interpret densification during hot-pressing, particularly where plastic deformation is not possible. This diffusional creep mechanism has been used by Vasilos and Spriggs[19,20] to interpret densification of magnesium oxide and aluminum oxide, and by Rossi[21] for aluminum oxide. Activation energies for densification of these oxides during hot-pressing agreed with those for self-diffusion, but calculated diffusion coefficients were several orders of magnitude greater. There is considerable evidence by these investigators that diffusion is enhanced by stress.

C. Hot-Pressing with Additives

Sintering additions often have the same effect, but to a greater extent, in hot-pressing processes as in normal pressureless sintering. Kingery et al.[22] observed that the major effect of applied pressure on densification of some solid-liquid systems was to increase the initial rearrangement of the solid particles. The applied stress level determined the mode of densification subsequent to rearrangement. At low pressures solution-precipitation processes occurred and at high pressures plastic deformation was observed.

Rice[1] has produced fairly transparent polycrystalline magnesium oxide by hot-pressing magnesium oxide powder with a small lithium

fluoride addition and a subsequent heat treatment. He suggested that lithium fluoride might aid densification by increasing rearrangement and consolidation due to lubrication of the magnesium oxide particles, and that it possibly contributes to the continued sintering which occurs during the subsequent heat treatment by creating defects in the magnesium oxide structure. He did not comment on how lithium fluoride affects densification after the initial consolidation has occurred in hot-pressing.

III. EXPERIMENTAL PROCEDURE

A. Apparatus

Pressing was done in graphite dies presaturated with lithium fluoride in a vacuum hot-press furnace shown schematically in Fig. 1. The 1.5 in. i.d. dies were heated by radiation from a Kanthal coil wound on a ceramic core. Two Pt-Pt 10% Rh thermocouples were used: one near the furnace windings for control purposes, and another in the die wall to measure the sample temperature. The accuracy of the temperature measurements was estimated to be within ±5°C. A vacuum of about 100μ of mercury was used only to protect the graphite dies from oxidation.

Pressure was applied by a manually operated hydraulic jack which moved against the water-cooled copper ram. Compaction of the powders was recorded continuously with a linear variable differential transformer which measured translation of the hydraulic ram with respect to the furnace top.

Further heat treatment was done in a small Kanthal-wound vertical tube furnace.

B. Sample Preparation

Batches were prepared from Baker and Adamson reagent grade MgO, Lot No. Y011, and J. T. Baker reagent grade LiF, Lot No. 2380. (Using the electron microscope, the smallest magnesium oxide particles were determined to be approximately 0.1μ in diam.) Two percent lithium fluoride was mixed with 30.0 gm magnesium oxide by tumbling the powders

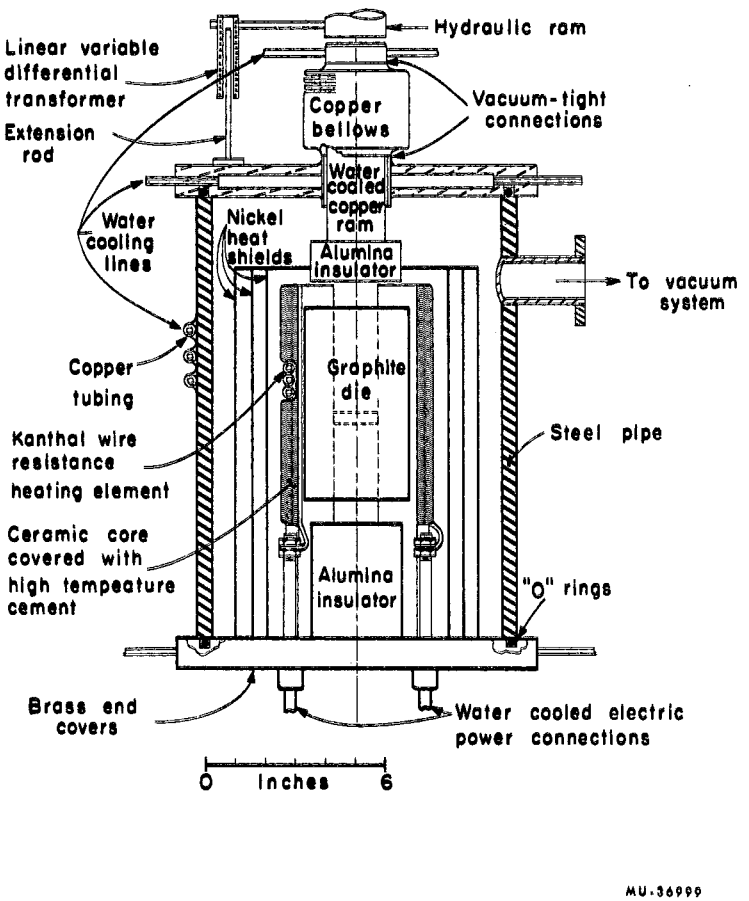
Hydraulic ram
Linear variable differential transformer
Extension rod
Copper bellows
Vacuum-tight connections
Water cooled copper ram
Water cooling lines
Nickel heat shields
Alumina insulator
To vacuum system
Copper tubing
Graphite die
Kanthal wire resistance heating element
Steel pipe
Ceramic core covered with high tempeature cement
Alumina insulator
"O" rings
Brass end covers
Water cooled electric power connections
0 Inches 6
MU-36999

Fig. 1

in isopropyl alcohol to insure even distribution. The slurry was dried in an oven and the resultant cake was broken and hand-stirred with a spatula, and placed in a dessicator under vacuum for several hours.

C. Procedure

For most experimental runs full pressure was applied at room temperature. Pressures ranged from 570 to 4000 psi and the heating rate was 5.5° C per min. Heating under pressure was continued until the desired final temperature was reached which ranged from 775 to 975° C. The length of time the sample was held under pressure at the final temperature varied from zero to 5 hrs.

The hot-pressed samples were slowly heated overnight to 1300° C and held there for 3 hrs. This firing was done in air.

IV. RESULTS AND DISCUSSION

Densification behavior under various hot-pressing conditions was analyzed to determine the necessary conditions which yield a magnesium oxide specimen which will become transparent during the subsequent heat treatment. Possible densification mechanisms are also discussed.

A. Phenomenological Aspects of Hot-Pressing Process

The effect of lithium fluoride on the densification of magnesium oxide is shown in Fig. 2. When 1705 psi is applied at room temperature and the heating rate is 5.5°C per min, densification (based on the linear change in the specimen length) begins near 570°C and is essentially complete by the time melting point of lithium fluoride is reached (846).[23] Figure 3 shows how densification is affected by varying the applied pressure. Increasing or decreasing the pressure reduces or extends the time required to complete densification during hot-pressing. Note that complete densification was not achieved with 580 psi within the temperature limit of 925°C of the experiment and that no discontinuity occurred in the densification curve at the melting point of lithium fluoride. The temperature corresponding to the beginning of rapid densification was approximately between 560 and 575°C.

The dependence of the heat-treated appearance on the hot-pressing conditions is indicated in Fig. 4. The powder compacts in this case were heated under pressure to the final desired temperature and held at this temperature for 3 hrs before the pressure was released and

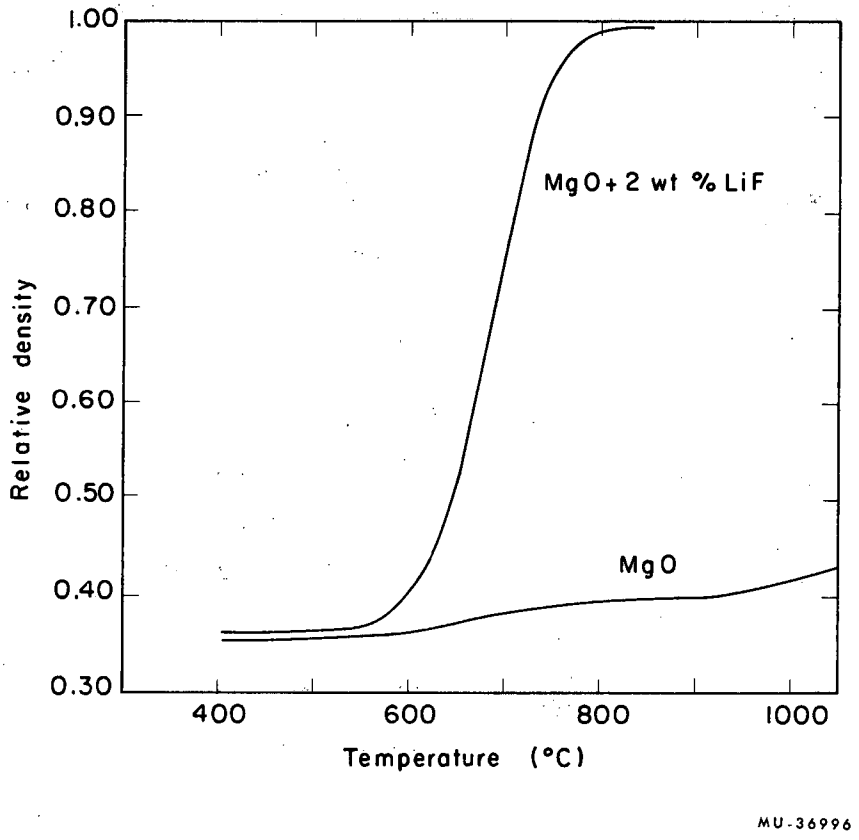
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
Relative density
MgO + 2 wt % LiF
MgO
400
600
800
1000
Temperature (°C)
MU-36996

Fig. 2

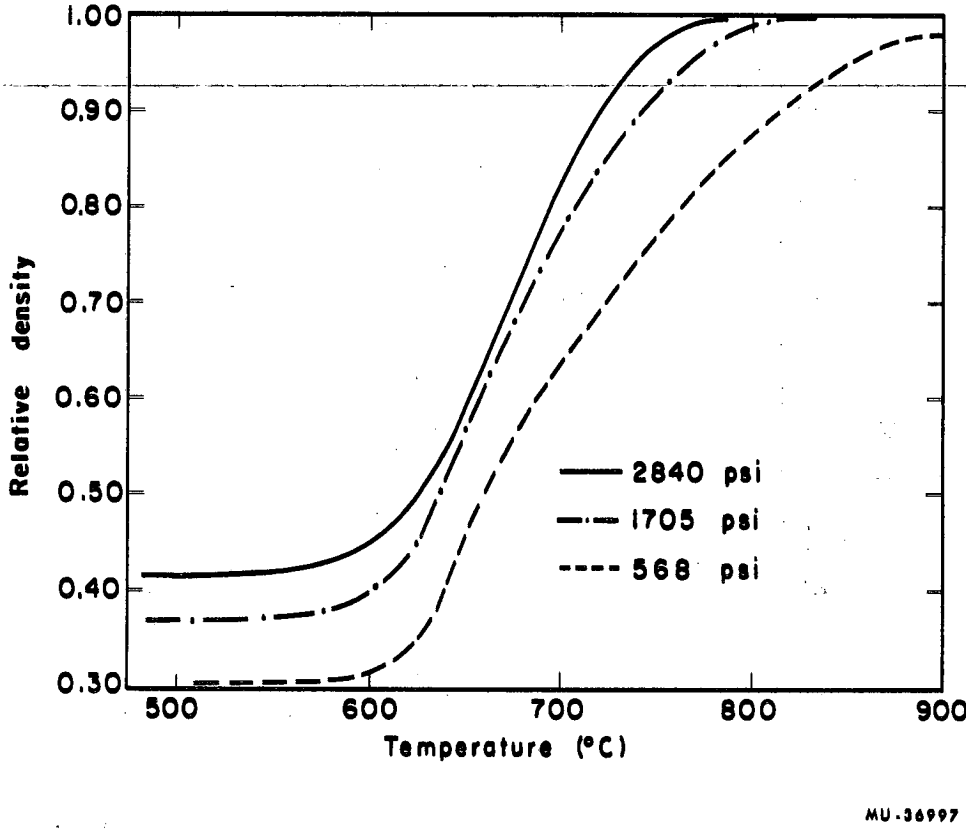
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
Relative density
500
600
700
800
900
Temperature (°C)
2840 psi
1705 psi
568 psi
MU-36997

Fig. 3

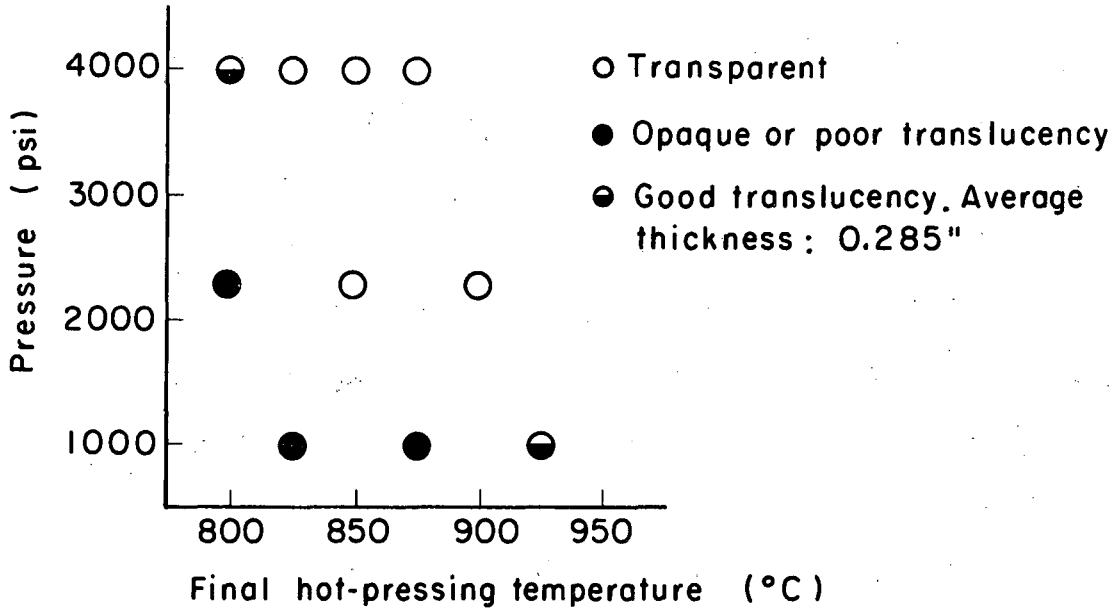

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Fig. 4

the furnace cooled. From Figs. 3 and 4 it is evident that this is a kinetic process and that there is a proper combination of temperature, pressure, and time required to produce a specimen which will become transparent during the subsequent heat treatment.

To produce a specimen which will become transparent during the final heat treatment, it appears necessary to achieve or at least come close to the theoretical density for the two-phase system of magnesium oxide and lithium fluoride during hot-pressing. Table I lists the hot-pressed densities and final heat-treated appearance for a number of hot-pressing conditions. Every specimen which did develop the desired transparency had a relative density of 99.5% or greater after hot-pressing, based on the theoretical density of magnesium oxide. Also, a certain degree of translucency in the as-hot-pressed specimens was found to be a necessary but not sufficient condition for eventual transparency.

Most of the lithium fluoride is thus removed during hot-pressing. For example, a specimen which began with 4 wt% contained only 0.2 wt%* after this step of the process. Much of it is squeezed out of the compact, and some escapes by vaporization.

It has also been observed that some grain growth occurs during the hot-pressing process as shown in Figs. 5, 6, and 7. The hot-pressing conditions and grain size after hot-pressing were, respectively: 2840 psi applied at 850°C and held 10 min - 0.3μ; 2275 psi applied at room temperature, heated to 850°C, and held 3 hrs - 1.2μ;

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*Reported as lithium oxide. Determined by American Spectrographic Laboratories, Inc., San Francisco, California.

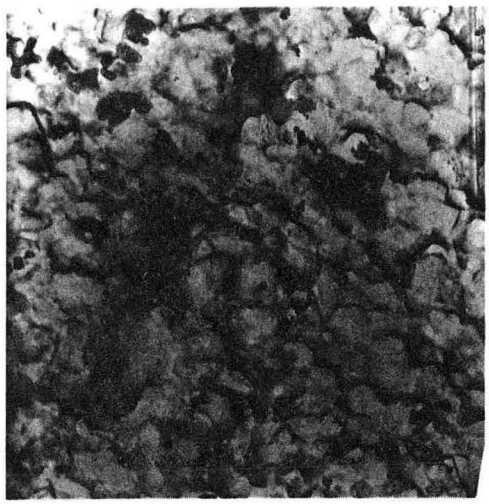
Table I. Hot-pressing conditions and density after hot-pressing, and heat-treated appearance.

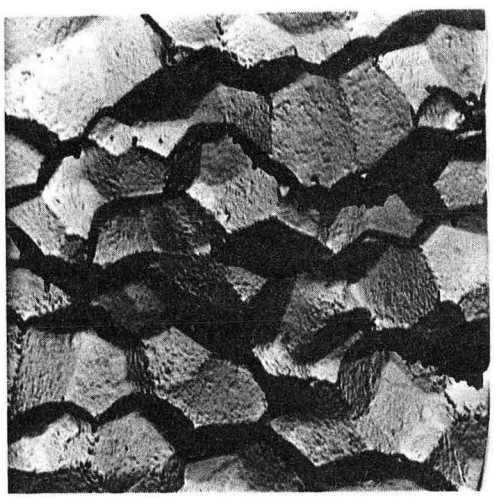
Hot-pressing conditions	Relative density (%)*	Heat-treated appearance†
4000 psi to 875° C, held 3 hrs	99.6	○
4000 psi to 850° C, held 3 hrs	99.6	○
4000 psi to 825° C, held 3 hrs	99.6	○
4000 psi to 800° C, held 3 hrs	99.5	⊖
2275 psi to 900° C, held 3 hrs	99.6	○
2275 psi to 850° C, held 3 hrs	99.5	○
2275 psi to 800° C, held 3 hrs	99.1	○
1000 psi to 925° C, held 3 hrs	99.3	⊖
1000 psi to 875° C, held 3 hrs	99.3	○
1000 psi to 825° C, held 3 hrs	98.9	○
1705 psi to 875° C, held 5 hrs	99.6	○
1705 psi to 875° C, held 1 hr	99.4	⊖
1705 psi to 825° C, held 5 hrs	99.2	○
2275 psi at 900° C, held 1 hr	99.5	○
2275 psi at 850° C, held 1 hr	99.0	○
2275 psi at 800° C, held 4.6 hrs	98.9	○

*Based on theoretical density of 3.581 gm/cm^3. Densities were measured by displacement in ethanol using an automatic analytical balance. The accuracy and reproducibility of these measurements was ±0.1%.

† ○ = transparent; ○ = opaque or poor translucency; ⊖ = good translucency. Specimens were approximately 0.280 in. thick.

Fig. 5





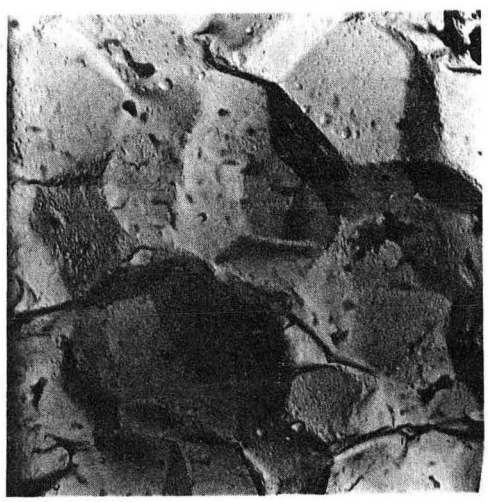


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Fig. 6.

Fig. 7

2275 psi applied at room temperature, heated to 900° C, and held 3 hrs - 1.9μ. The specimen in Fig. 6 did become transparent during the subsequent heat treatment. If it is assumed that its density of 99.5% of the theoretical density of magnesium oxide is due to the presence of a lithium fluoride phase which exists only as a film surrounding each magnesium oxide grain and that the grains are spherical, the calculated thickness of the film between the grains becomes about 60 Å. The actual thickness, however, is less because there are scattered inhomogeneities that appear as pores after the final heat treatment. Therefore, the apparent inclusions at the grain boundaries in the photograph are probably the result of the surface replicating technique. If too much lithium fluoride remains as a result of inadequate hot-pressing conditions, the porosity which develops as the additive is removed during the subsequent heat treatment may not be removed by the additional sintering which occurs during this step; this final porosity results in a translucent specimen. If the lithium fluoride is present as a thin film and is not concentrated in pockets at grain boundary triple points, etc., its further removal during final heat treatment does not result in porosity; the specimen is then transparent.

B. Densification Mechanisms During Hot-Pressing

For lithium fluoride to be so effective, it must be evenly distributed throughout the magnesium oxide powder. Since 2% of relatively coarse particles is an insufficient amount to have all magnesium oxide particles in contact with lithium fluoride particles

(assuming ideal mixing), there must be some process which distributes it throughout the powder compact.

The formation of a eutectic liquid at the temperature where densification begins could aid rearrangement of the powder by lubrication of the magnesium oxide particles and could lead to a liquid sintering mechanism as well as distribute the lithium fluoride. However, DTA studies of various mixtures of the two materials detected no liquid formation other than the melting of pure lithium fluoride. Also, there was no evidence of any liquid formation or reaction between single crystals of the two materials that were in contact at 840° C for one-half hour. If a eutectic does exist, its composition and temperature must be very close to that of lithium fluoride and its melting point. Because densification can occur at temperatures where no liquid was observed and it apparently was not enhanced by the presence of a liquid at temperatures where liquid is known to exist, a liquid phase sintering mechanism does not appear to be operative.

At the lower temperatures lithium fluoride must then be distributed throughout the powder compact through its vapor phase or by surface diffusion. Its equilibrium vapor pressure near 575° C is about 10^{-7} atm[24] which is sufficient for distribution throughout the system since the vapor tends to occupy all available volume. Vapor coming in contact with the surface would be expected to interact with the surface because sessile drop experiments indicated a contact angle of about 20°.

Stress enhanced bulk diffusion is often considered to be the densification mechanism following the initial rearrangement during

hot-pressing. Also, there is evidence that some mass transport process does occur since grain growth did occur during the hot-pressing process. Consequently, using the Nabarro-Herring relation

$$D = \frac{\dot{\epsilon}\ k\ T\ d^2}{40\ \Omega\ \sigma_e},$$

where D = diffusion coefficient (cm^2/sec),

$\dot{\epsilon}$ = strain rate (sec^{-1}),

k = Boltzmann's constant (1.38×10^{-16} ergs/°K),

T = absolute temperature,

d = grain diameter (cm),

Ω = vacancy volume (cm^3), and

σ_e = effective stress (dyn/cm^2),

in conjunction with the density-vs-time curve shown in Fig. 8 for the sample pressed at 800°C with 2275 psi, the calculated values of the diffusion coefficient were of the order of 10^{-4} to unity for densification up to about 95% theoretical density. These values are many orders of magnitude larger than the apparent diffusion coefficients calculated by Vasilos and Spriggs from hot-pressing data for magnesium oxide without any additives.[19,20]

If the densification mechanism requires diffusion, then these abnormally large calculated diffusion coefficients indicate that lithium fluoride must enhance diffusion in some way. Diffusion of Li^+ and/or F^- into magnesium oxide would increase its bulk diffusion coefficient by creating vacancies in order to maintain electroneutrality.

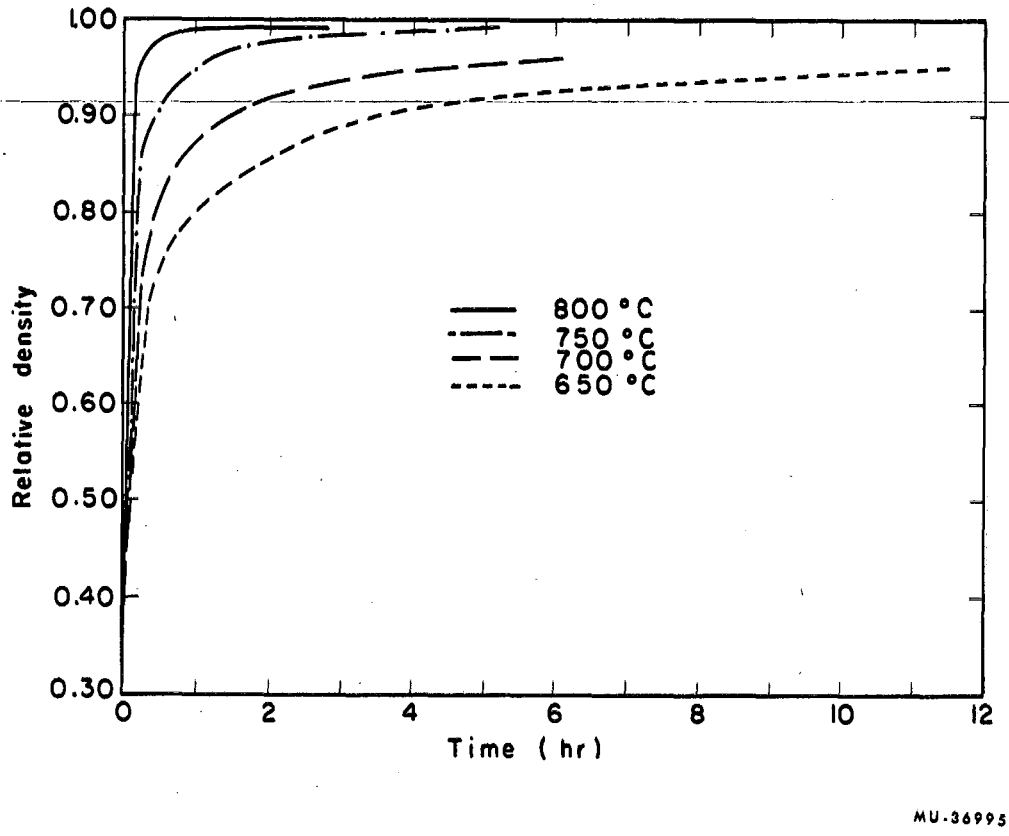
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
Relative density
0
2
4
6
8
10
12
Time (hr)
800 °C
750 °C
700 °C
650 °C
MU-36995

Fig. 8

To determine if there is any interdiffusion of magnesium oxide and lithium fluoride, some single-crystal magnesium oxide was ground in a mortar to -200 +325 mesh and hot-pressed with 20 wt% lithium fluoride so that the microstructure could be observed and the electron beam microprobe utilized. Unexpectedly, this sample did not densify at all when heated to 950°C under 2000 psi. The microprobe was set to analyze Mg-K_α radiation to determine if there was any interdiffusion of Mg^{++} and Li^{+}, particularly in the lithium fluoride phase. No diffusion was detected by either microscopic or electron probe examinations. Although no diffusion was detected, the data from the microprobe, however, were somewhat inconclusive because of the difficulty in obtaining a polished flat surface due to the great difference in hardnesses of magnesium oxide and lithium fluoride.

The final low content of lithium fluoride in the hot-pressed specimen and the further decrease in amount after the heat-treatment stage also argue against a bulk diffusion mechanism. However, the formation of an "activated surface" layer of the type proposed by Tacvorian, within which diffusion can occur, is a possibility. Because of the very fine magnesium oxide particle size, the effective thickness of such a layer may include a significant amount of the particle. Surface diffusion coefficients can be several orders of magnitude larger than bulk diffusion coefficients and possibly the diffusivity in this layer could be as large as the values calculated using the Nabarro-Herring diffusional creep model. The enhanced densification (approximately 80% of theoretical density) Atlas observed after 2 hrs at 800°C when a lithium flouride addition was used[10] may have been

due to the formation of a layer of increased diffusivity, or possibly to the result of rearrangement of particles which was aided by a lubricating film of lithium fluoride.

The rapid densification which occurs at relatively low temperatures and stress suggests that some type of deformation process may be operative. The stress levels, however, appear to be too low in the temperature range where densification is observed to begin. General bulk plastic deformation of completely constrained particles would require dislocation motion on both the {110} <110> and {100} <110> slip systems.[2] Yield stresses measured in compression for magnesium oxide at 600°C are about 8000 psi for the {110} <110> slip systems[25] and nearly 40,000 psi for the {100} <110> slip systems.[26] Nevertheless, some plastic deformation may be possible before compaction of the particles occurs. Constraints at this stage would be at a minimum and lubrication of the particles by lithium fluoride could allow some favorable rearrangement of particles for flow. Furthermore, stress concentrations at contact points probably exceed the critical shear stress for the {100} <110> slip systems, but it is expected that the amount of deformation would be limited because as the particles deformed the contact area would increase and the stress would decrease. Also, in an investigation on the mechanical behavior of polycrystalline lithium fluoride, dislocation movement was observed near grain boundaries on slip systems which required nearly ten times the calculated shear stresses on these systems.[27] But these stress concentrations should exist whether lithium fluoride is present or not and lithium fluoride is necessary for densification. Lithium fluoride could also

aid deformation by removing or displacing an adsorbed surface layer which prevents dislocations from forming or from passing out of the particles, but there was no densification when the coarse powder ground from single-crystal magnesium oxide was used.

The difference in densification behavior of the powder ground from single crystal and the powder from Baker and Adamson, when hot-pressed with a lithium fluoride addition, must be due to some difference in the magnesium oxide powders. The only differences between the two powders are the particle size and perhaps a structural difference because the powder from Baker and Adamson was probably formed by a decomposition or precipitation process. Some of the reagent powder was presintered before being hot-pressed with lithium fluoride so the effect of particle size could be observed. Unfortunately, the partial sintering also anneals structural defects and thus the variables of particle size and defect structure were not separated. Figure 9 shows that densification is delayed until higher temperatures are reached by using presintered powder. Rice[1] also observed that calcining the magnesium oxide powder prior to hot-pressing with lithium fluoride was detrimental to the final density.

Based on the analysis of the experimental evidence, two possible densification mechanisms are proposed, each requiring a very fine magnesium oxide particle size:

(a) The very small size particle of the chemically prepared powder permits deformation of the particles at reduced temperatures and stresses; and the primary function of lithium fluoride is to form a lubricating film on the magnesium oxide particles which prevents them

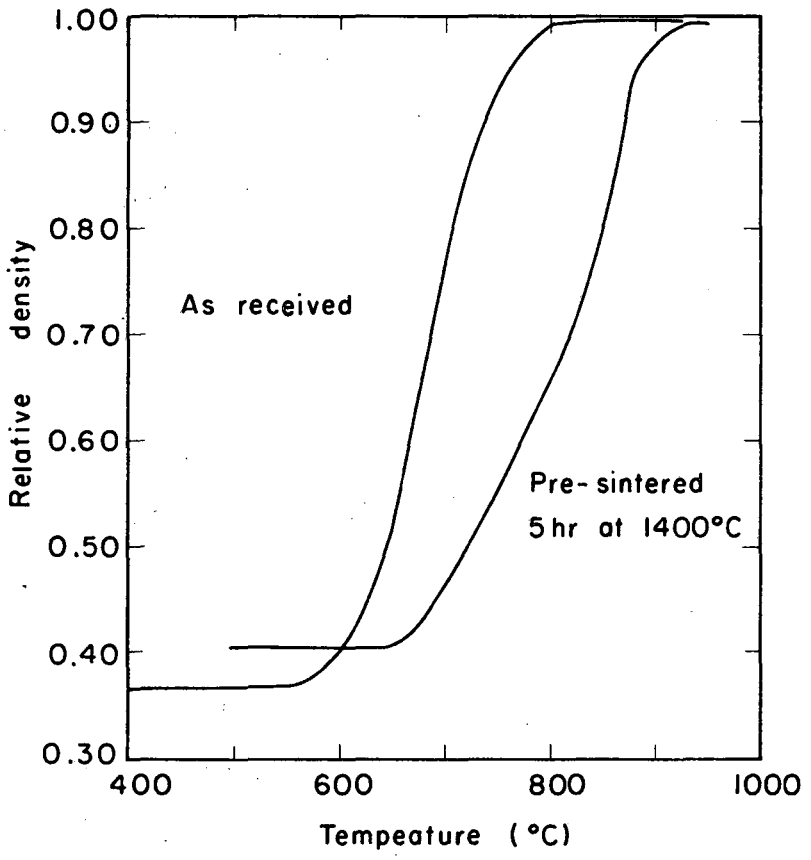

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Fig. 9

from friction welding together. In the absence of lithium fluoride the particles weld together and the resulting agglomerate behaves under the applied stress as if they were large particles, and higher stresses are required for deformation.

(b) Lithium fluoride interacts with the magnesium oxide surface and creates a layer of greatly enhanced diffusivity. This "activated surface" comprises a significant amount of the bulk material because of the high surface-to-volume ratio associated with the very fine magnesium oxide particle size. Then, densification occurs by a diffusional creep process which is enhanced by pressure.

V. CONCLUSIONS

Transparent polycrystalline magnesium oxide can be fabricated by hot-pressing the powder with a small lithium fluoride addition, and a subsequent heat treatment. The hot-pressed density must be at least 99.5% of the theoretical density of magnesium oxide for the final heat treatment to yield a transparent specimen. Because the densification kinetics vary with the temperature and pressure, the hot-pressing process must be designed to yield this critical density. Using temperatures as low as 825°C with 4000 psi, magnesium oxide powder with 2 wt% lithium fluoride can be hot-pressed to near theoretical density and become transparent during a subsequent heat treatment at 1300°C.

Densification during hot-pressing of magnesium oxide powder containing a small lithium fluoride addition requires that the powder be of very fine particle size which is maintained by the presence of lithium. Then, densification occurs by a deformation process associated with the small particle size of the magnesium oxide, or by a diffusional creep process in which lithium fluoride also enhances diffusion in magnesium oxide. If densification occurs by diffusional creep, lithium fluoride probably enhances diffusion by creating a surface layer of high diffusivity and not by enhancing bulk diffusion.

It is recommended that this study be continued. A mathematical analysis of dislocation behavior in small crystals should be undertaken to determine the validity of the hypothesis that deformation of very fine submicron particles is easier than deformation of larger crystals. It is also recommended that the problem of the possible diffusion of lithium fluoride in magnesium oxide be further investigated.

ACKNOWLEDGMENTS

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