Lawrence Berkeley National Laboratory
Recent Work

Title
ACTIVATED HOT PRESSING OF MAGNESIUM OXIDE

Permalink
https://escholarship.org/uc/item/2nq038qm

Author
Hart, Patrick Eugene.

Publication Date
1967-12-01
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
ACTIVATED HOT PRESSING OF MAGNESIUM OXIDE

Patrick Eugene Hart
(Ph. D. Thesis)
December 1967
CONTENTS

ABSTRACT

I. INTRODUCTION ........................................................................................................ 1

II. SURVEY OF DENSIFICATION LITERATURE ......................................................... 2
    A. Pressureless Sintering ............................................................................................ 2
    B. Pressure Sintering ................................................................................................. 3
    C. Densification of Magnesium Oxide .................................................................... 6
    D. Effect of Lithium Compound Additives on Densification of Magnesium Oxide .... 8

III. EXPERIMENTAL PROCEDURE .............................................................................. 13
    A. Apparatus ............................................................................................................ 13
    B. Sample Preparation ............................................................................................. 13
    C. Procedure ............................................................................................................. 14
    D. Chemical Analysis ............................................................................................... 14

IV. RESULTS ................................................................................................................. 16
    A. Densification Behavior ....................................................................................... 16
    B. Lattice Parameter Studies .................................................................................. 27
    C. Annealing ............................................................................................................ 32
    D. Optical and Infrared Transmission .................................................................... 36
    E. Phase Equilibria .................................................................................................. 39
    F. Compressive Creep Experiments ....................................................................... 42

V. DISCUSSION OF RESULTS .................................................................................... 49
    A. First Stage of Densification ............................................................................... 49
    B. Final Stage of Densification ............................................................................... 49
    C. Annealing Stage .................................................................................................. 56
    D. Mechanical Behavior ......................................................................................... 58
VI. CONCLUSIONS .......................................................... 60
ACKNOWLEDGMENTS ....................................................... 63
TABLES ........................................................................... 64
APPENDIX I ................................................................. 67
APPENDIX II ................................................................. 69
APPENDIX III ............................................................... 71
REFERENCES ................................................................. 73
ACTIVATED HOT PRESSING OF MAGNESIUM OXIDE

Patrick Eugene Hart

Inorganic Materials Research Division, Lawrence Radiation Laboratory, Department of Mineral Technology, College of Engineering, University of California, Berkeley, California

ABSTRACT

The densification by pressure sintering of magnesium oxide compacts containing one-half to ten percent lithium fluoride was studied. This investigation gives insight into mechanisms involved in this fabrication process.

Densification may be considered to be a three step process with the first two steps occurring in the fabrication die and the last step, annealing, being performed after pressing. The first stage in the die is a rapid process and is believed to be similar to the rearrangement stage that has been observed by several authors. Depending on fabrication parameters, i.e. temperature, pressure and initial lithium content, this initial stage may take place up to densities as high as 90% of theoretical, relative to pure magnesium oxide. Experimental evidence indicates that the final stage of densification in the die is controlled by flow of a lithium fluoride rich phase along magnesia grain boundaries. Transport of magnesium oxide is by means of a solution-precipitation process. This analysis is valid for samples with densities between 91 and 99.5%. These two stages are separated by a transition or intermediate stage. The annealing stage is controlled by the evaporation of lithium fluoride from the sample surface. Samples having densities of 99.1% or more, become transparent during annealing.
I. INTRODUCTION

Recent emphasis has been placed on the effects of additives on sintering of ceramic materials where additives results in reduction of time and/or temperature required to produce high densities. Additionally, it has been found that application of pressure will result in enhanced densification. The combination of these two techniques has resulted in production of polycrystalline compacts that are essentially fully dense and have optical properties that approach those of single crystals.

Benecke and co-workers, among others, have established the parameters necessary to produce transparent polycrystalline magnesium oxide by pressure sintering magnesium oxide compacts containing minor additions of lithium fluoride.

It is the purpose of this study to investigate the mechanisms involved in pressure sintering of magnesium oxide compacts containing lithium fluoride. By developing an understanding of these mechanisms they may be applied to other systems where it is desirable to obtain high densities at temperatures much lower than those required for either normal or pressure sintering.
II. SURVEY OF DENSIFICATION LITERATURE

A. Pressureless Sintering

Several authors\textsuperscript{5,6} have recently surveyed sintering literature. Current literature indicates that densification in most single phase ceramic systems is controlled by diffusional processes. Grain boundary and bulk or lattice diffusion are often cited as being controlling mechanisms. Plastic flow is thought to operate in some systems although its role is not clearly understood.

1. Effect of Second Phases on Sintering

Thümmler and Thomma\textsuperscript{5} have reviewed the effect of additives on sintering. The effectiveness of the additive will depend on whether or not a reaction takes place between the phases, the physical nature of the phases, and the mutual solubilities of the phases. The second phase can act as a grain growth inhibitor, as a transport media in a solution-precipitation process or, by solution in the primary phase, can create defects resulting in increased diffusion rates. The phase may retard densification by reducing the activity of the surface layer of the primary phase or by acting as a barrier to material transport.

2. Liquid Phase Sintering

Kingery\textsuperscript{7} distinguishes between three separate stages during liquid phase sintering: 1) a rearrangement stage resulting from the formation of a liquid phase and flow of the liquid; 2) a solution-precipitation stage due to solubility of the solid in the liquid phase, and 3) a coalescence stage occurring when the liquid does not penetrate between grains. Equations were derived for the solution-precipitation process
that predict a linear relationship between compact fractional shrinkage, \( \frac{\Delta L}{L_0} \), and time to the one-third power where the process is controlled by diffusion and time to the one-half power where a phase boundary reaction is controlling.

Kingery and Narasimhan have measured sintering rates for the iron-copper system that are in agreement with predicted values for the solution-precipitation process where diffusion through the liquid phase is rate controlling. Thümmler and Thomma note that there is some uncertainty whether or not these models are adequately confirmed.

B. Pressure Sintering

Hot pressing literature has been recently summarized in reviews by Ramqvist\(^9\) and by Vasilos and Spriggs.\(^{10,11}\) Ramqvist comprehensively summarizes pressure sintering work that has been carried out in the last one hundred years.

Vasilos and Spriggs concluded in their critical reviews that stress enhanced diffusion is the principal pressure sintering mechanism operative in most ceramic systems at pressures below 10,000 psi. At greater stresses, plastic flow is considered to be controlling. Other mechanisms considered to be operative during part of the densification process at moderate pressures are: 1) fragmentation, grain-boundary sliding, and rearrangement during early densification and 2) plastic flow occurring at grain contacts.

Evidence of fragmentation occurring during the early stage of calcium fluoride densification has been demonstrated by Hashimoto.\(^{12}\) Chang and Rhodes\(^{13}\) have shown evidence for grain-boundary sliding and fragmentation in hot pressing of uranium carbide at high pressures.
The plastic flow model derived by Murray, Rodgers, and Williams\textsuperscript{14} based on the MacKenzie-Shuttleworth\textsuperscript{15} sintering model predicts a linear relationship between densification rates and porosity. It has been applied with success by Vasilos\textsuperscript{16} to the pressing of powdered fused silica. However, it has also been found to fit data for systems that should not exhibit plastic behavior at the experimental temperatures and pressures. Vasilos and Spriggs rejected the model as the controlling sintering mechanism for most ceramic systems based on the following points: 1) observed particle size effect on densification; 2) non-existence of a true end-point density which the model predicted; and 3) absence of extensive preferred orientation.

Coble and Ellis\textsuperscript{17} analysis of the pressure sintering of large alumina single-crystal spheres indicates that plastic flow cannot be effective in densification at densities above 84\%. Final stage densification of materials that can undergo diffusional creep was suggested as due to a diffusional mechanism.

From alumina, magnesia\textsuperscript{18} and nickel oxide\textsuperscript{19} pressure sintering data, Vasilos and co-workers calculated apparent diffusion coefficients based on Coble's\textsuperscript{20} sintering model and the Nabarro-Herring\textsuperscript{21} viscous diffusional creep model. Results at moderate pressures, using these models, suggest that densification of alumina, magnesia and nickel oxide is a diffusional-controlled process beyond the initial compaction stage.

Rossi and Fulrath,\textsuperscript{22} using a modified Nabarro-Herring equation that predicts a linear relationship between densification rate and porosity, confirmed that final stage densification of alumina is a diffusional process.
It must be noted, however, that in none of these works has any attempt been made to determine the stress dependence of the densification rate.

A pressure-sintering model based on vacancy bulk diffusion fluxes has been derived by Fryer.\textsuperscript{23} Rates were obtained for the densification of alumina that had the predicted porosity dependence of the model. Fryer recalculated Rossi and Fulrath's results for alumina and found them to fit this model also. The previous agreement of Rossi and Fulrath's work with the modified Nabarro-Herring equation was judged to be due to an error in plotting the data.

As discussed by Ramqvist,\textsuperscript{9} several authors have derived various empirical relationships to fit their own data.

3. Liquid Phase Pressure Sintering

The effect of a liquid phase on pressure sintering of powders has been studied by Kingery and co-workers.\textsuperscript{24} Systems were chosen in which the solid was partly soluble in the liquid phase. The derived time dependence of the solution-precipitation pressureless sintering model is unchanged when the effect of pressure is included. Of the three systems studied: copper-bismuth, sodium chloride-water and ice-methanol, sodium chloride-water and ice-methanol systems showed limited agreement with the predicted $t^{1/3}$ relationship. In the first system, a compact containing 5% water and pressed at room temperature and 10,000 psi, followed this time dependence for the first half minute of pressing. This behavior was not observed for higher pressures and larger water contents. The final stage of densification appeared to be controlled by plastic deformation.
No lower pressures were tried in this system. An ice-methanol compact containing 10% liquid followed the $t^{1/3}$ relationship at -26°C and 1000 psi for 0.8 to 8 hours; however, this relationship was not followed by samples containing 20% liquid. The results suggested that the initial densification stage was pressure enhanced rearrangement and the final was plastic deformation. After the assumed rearrangement stage, densification of copper-bismuth compacts at 600°C and low pressures was found to follow a plastic-flow relationship.

C. Densification of Magnesium Oxide

1. Pressureless Sintering

Brown\textsuperscript{25} has studied the sintering of very pure magnesium oxide between 1300 and 1500°C and found that specimen densities were proportional to $\ln t$. An activation energy of 27 kcal/mole was calculated for densification. Samples containing 0.1% vanadium showed enhanced grain growth and an activation energy of 26 kcal/mole. An activation energy of 18 kcal/mole was found for densification of a sample containing 0.01% vanadium with densification following a $t^2$ relationship. These low activation energies, compared to self-diffusion values,\textsuperscript{*} suggested grain boundary diffusion as the controlling densification mechanism.

Eastman and Cutler\textsuperscript{28} found an activation energy of 80 kcal/mole for the sintering of magnesium oxide in water vapor at pressures below 5 mm and 48 kcal/mole at pressures above 5 mm.

\textsuperscript{*} 79.0 kcal/mole for magnesium; Lindner and Parfitt\textsuperscript{26} 62.4 kcal/mole for oxygen; Oishi and Kingery\textsuperscript{27}
2. **Pressure Sintering of Magnesium Oxide**

Vasilos and Spriggs \(^{18}\) have investigated pressure sintering of magnesium oxide in the range of 4000 to 10,000 psi and 1100 to 1700°C. An activation energy of 78 kcal/mole for the pressure sintering of magnesium oxide, calculated on the basis of the Navarro-Herring creep equation, is in agreement with the calculated activation energy of 79 kcal/mole for magnesium oxide self-diffusion in magnesium oxide single crystals. The analysis appears to be valid up to about 95% of theoretical density where entrapped gases probably decrease the densification rate. Using Coble's sintering equation, an activation energy of 95 kcal/mole was calculated. The absolute values of diffusion coefficients calculated using both models were in good agreement.* Diffusion coefficients calculated for pressure sintering were about two orders of magnitude greater than those calculated in self-diffusion work, and were also greater than those obtained by Spriggs and Vasilos in sintering work that is unpublishd. An activation energy of 112 kcal/mole was calculated in this work. Thus pressure enhanced diffusion was suggested as the controlling mechanism in pressure sintering of magnesium oxide up to nearly theoretical density. Higher pressures were thought to result in grain-boundary sliding, mechanical deformation and/or fracture.

Leipold and Nielsen \(^{30}\) have studied the hot-pressing of magnesium oxide using both very pure magnesium oxide and commercially available magnesium oxide. A density of 3.50 gm/cc was obtained at 800°C and

---

* In reference 18 these curves were shown to be orders of magnitude in variance; however Coble and Gupta \(^{29}\) subsequently reported that an error in use of Coble's sintering model had been made.
10,000 psi using the purer material while a density of 2.56 gm/cc was obtained using the lower purity one. The difference in final density was reduced as the pressing temperature was increased to 1100°C. Specimens prepared from the high purity magnesium oxide showed grain growth 100 times that found in the commercial magnesium oxide. Increase in densification and grain growth was attributed to the smaller grain size of the pure material \(0.017\mu\) for purer material as compared to \(0.05\mu\) for commercial material and higher purity.

3. **Chemically Activated Pressure Sintering**

Morgan and Shaeffer\(^31\) have fabricated high density, fine grain magnesium oxide specimens by using magnesium hydroxide as the starting material in the die. Due to decomposition of the hydroxide on heating and resulting enhancement of densification, specimens approaching theoretical density were fabricated at reduced temperatures and pressures.

D. **Effect of Lithium Compound Additives on Densification of Magnesium Oxide**

1. **Pressureless Sintering**

The effect of lithium compound additives on sintering of magnesium oxide fired in air to 1400°C was first investigated by Atlas.\(^32\) This work was based on the suggestion of Tacvorian\(^33\) that sintering of an oxide would be accelerated by addition of compounds that are weakened models of the oxide. The resulting surface layer solid solution would have a higher diffusivity than the pure oxide. Lithium chloride and bromide were more effective sintering agents than the fluoride. Lithium iodide, sulfate, and carbonate which form lithium oxide at the experimental temperatures were less effective. Chloride and bromide additions resulted
in higher green densities than the fluoride, which may account for the higher fired densities. Lithium chloride and bromide should be less effective than the fluoride on the basis of the weakened structure model. If lithium oxide did form, solution of it into the magnesium oxide lattice should result in increased diffusion rates because of the formation of $O^2-$ vacant sites or interstitial $Li^+$ ions.

Layden and McQuarrie 34 studied the effect of additions of salts on magnesium oxide sintering. It was found that additions of lithium nitrate were effective in enhancing densification.

2. Pressure Sintering

Rice 4 first reported the effect of lithium fluoride additives on pressure sintering of magnesia and outlined processing leading to transparent specimens.

Infrared transmission studies of pressed specimens 35 showed a strong absorption band in the 6.0 to 7.5$\mu$m region that was attributed to lithium and/or magnesium carbonates while a band at 2.8$\mu$m was attributed to entrapped hydroxides. The presence of such impurities was confirmed by mass spectrometric studies.

Lithium fluoride was found to be a lubricating agent for magnesia single crystals in the temperature range of 800 to 1500°C. 4

Benecke, Olson and Pask 1 have characterized the pressures and temperatures necessary to produce transparent polycrystalline magnesium oxide. A hot-pressed density of 99.5%, relative to pure magnesium oxide, was required for transparent specimens to be produced by annealing. Two possible densification mechanisms were proposed: 1) an enhanced grain boundary diffusional creep process and 2) a plastic deformation process.
In the first process, added lithium fluoride was thought to result in an activated layer on magnesium oxide particles through which stress enhanced grain boundary or surface layer diffusion could take place. Although no rate data were reported, it was stated that stress did enhance densification rates.

The second model of plastic deformation was suggested on the basis of an observed particle size effect and the required presence of lithium fluoride. Compacts of coarsely ground magnesium oxide crystals containing lithium fluoride did not densify while fine grained chemically-prepared powders did. This suggested that very fine particles were required to produce transparent specimens. Due to very small contact areas between these fine particles, it was thought that stress concentrations at particle contacts were in excess of the normal yield stress for magnesium oxide at temperatures as low as 600°C. Additionally, lithium fluoride was considered to lubricate magnesium oxide grains and allow favorable particle "arrangements" for flow. Plastic flow was not detected experimentally. In the comparison of results using widely separated particle sizes and character, possible differences in powder characteristics, such as defects and surface area, were not considered.

Liquid phase sintering was rejected as a possible mechanism. Differential thermal analysis of lithium fluoride-magnesium oxide mixtures indicated no endothermic reactions occurring other than the melting of lithium fluoride at 848°C. Interfaces between single crystals of lithium fluoride and magnesium oxide heated at 840°C showed no liquid formation or reactions. Compaction of specimens carried out at constant heating rate and load showed no change in behavior at 848°C, the melting point
of lithium fluoride. Since the densification behavior of specimens appeared to be essentially independent of liquid formation, it was concluded that no liquid phase sintering occurred.

Stress enhanced bulk diffusion was rejected because of unrealistically high diffusion coefficients calculated using the Nabarro-Herring relationship as used by Spriggs and Vasilos. Low concentrations of lithium fluoride in hot-pressed and annealed specimens indicated to Benecke and co-workers that diffusion of either Li\(^+\) and/or F\(^-\) into the lattice resulting in enhanced bulk diffusion was unlikely.

Transparent polycrystalline magnesium oxide has also been fabricated by Sambell and co-workers using lithium fluoride additions. Development of fabrication technique was the main goal of their work; however, they reported unpublished work of Henney and Jones that is pertinent to the magnesium oxide-lithium fluoride system. X-ray diffraction studies indicated a "very limited" solubility of lithium fluoride in magnesium oxide. A highly disordered lithium fluoride lattice was suggested by the diffuse nature of diffraction lines making magnesium oxide solubility in lithium fluoride uncertain.

It was thought that sintering in the lithium fluoride-magnesium oxide system occurred in the presence of liquid. Henney and Jones observed the formation of magnesium fluoride which would form a liquid phase with lithium fluoride at 750°C. Formation of a carrier liquid was thought to be supported by observed concentration gradients of lithium fluoride in the specimens. It was not stated at which temperature this effect was observed. This concentration gradient of lithium fluoride
was considered justified on the basis of a liquid phase being squeezed out of the interstices of the densifying magnesium oxide. Henny and Jones were also reported to have observed formation of a volatile lithium fluoride-magnesium oxide complex which would help remove lithium fluoride from the sample surface during annealing.

Rhodes and co-workers\(^3\) have made gains in the analysis of mechanisms involved in sintering of magnesium oxide compacts containing minor lithium fluoride additions. Two mechanisms were proposed: 1) above the melting point of lithium fluoride, a pressure-enhanced liquid phase sintering mechanisms was suggested, and 2) below the melting point, pressure-enhanced diffusion through a grain boundary phase was suggested.

X-ray lattice parameter studies were carried out on specimens pressure sintered at 820°C and originally containing from zero to 100% lithium fluoride. Results indicated that Mg\(^{2+}\) and possibly O\(^{-2}\) were soluble in the lithium fluoride lattice while Li\(^+\) and F\(^-\) were both soluble in the magnesium oxide lattice. Nabarro-Herring bulk diffusion was rejected as the densification mechanism for experiments at 650°C because of high calculated diffusion rates. A second phase at grain boundaries was observed in electron micrographs of samples pressed at 1000°C and at 820°C. Possible liquid phase sintering below the lithium fluoride melting point was rejected on the basis of the work of Benecke, et al. Plastic flow was rejected on the basis of observed grain growth at 820°C which followed a \(t^{1/2}\) relationship.
III. EXPERIMENTAL PROCEDURE

A. Apparatus

Pressure sintering was performed in a vacuum, molybdenum-wound furnace. A heating rate of 25°/hr was used to 450°C; while above 450°C a rate of 500°/hr was used to the final pressing temperature. Temperature was measured by a Pt-Pt 10% Rh thermocouple inserted in the die body. Pressing temperatures were varied between 600 and 1300°C. Loads were applied at the experimental temperature unless otherwise noted. Compaction of specimens was continuously monitored by a Daytronics linear displacement transducer Model 102B-120. Pressure on the die was maintained by a hydraulic ram activated by an S C hydraulic pump model 10-600. Pressures were varied between 1250 and 5250 psi.

B. Sample Preparation

Baker and Adamson reagent grade magnesium oxide Lot No. Yoll (see Appendix for characterization) was used in the preparation of all specimens. Powders were held in a drying oven at 1200°C for 12 to 24 hours prior to use. Lithium fluoride was -125 mesh powder ground from single crystals prepared by Scott and Pask using the Bridgman normal freezing method. Use of reagent grade lithium fluoride resulted in specimens of reduced optical quality. Lithium fluoride content was varied between 1/2 and 10 wt.%. Lithium fluoride and magnesium oxide powders were mixed together in isopropyl alcohol and were then dried in an oven before being placed in the die. Mixed batches contained 30 grams of magnesia.
C. Procedure

Dies were made of reactor grade graphite and were presaturated with lithium fluoride. The bore diameter was one and one-half inches. Pressed specimens were about 0.3 inches in thickness. Plunger faces were re-polished after each run to insure that mechanical bonding between the compact and the plungers was kept to a minimum; this polishing also appeared to result in a reduction in the amount of graphite contamination in the compacts. Powders were loosely loaded into the dies and were precompacted at 1000 psi to insure that all compacts had the same initial density.

The heating cycle was started as soon as the furnace vacuum was below $10^{-4}$ torr. Time at temperature was varied from one half hour to 5 hours. The load was removed as soon as the furnace was turned off. Samples were allowed to furnace cool and were removed from the dies when they had been cooled to room temperature.

Specimen densities were determined using the displacement technique. Two hundred proof ethyl alcohol was selected as the displacement media rather than distilled water. Distilled water was found to result in slightly lowered reproducibilities.

Annealing of specimens was carried out in both air and vacuum using a heating rate of 60°C/hr.

D. Chemical Analysis

Measurement of lithium content in as-hot pressed specimens was performed using flame spectrophotometric analysis. Sample aliquots prepared to contain uniform amounts of magnesium oxide were analyzed against standard lithium aliquots. Readings were taken at $674\text{nm}$. In annealed specimens,
the lithium content was below the limit of detectability using this technique. Accuracy of values is ±10%.
IV. RESULTS

A. Densification Behavior

The densities of specimens fabricated at various temperatures and pressures, and with varying initial lithium fluoride content, are listed in Table I. Samples originally containing 3% lithium fluoride and pressed at temperatures below 670° and above 1100° C had open porosity after being held at temperature for five hours. Analysis of data for these samples is not included in this work.

An attempt was made to analyze compaction data using shrinkage equations derived by Johnson and Cutler for pressureless sintering and Kingery for liquid phase pressure sintering. These equations predict the time dependence of compact fractional shrinkage, i.e. $\Delta L/L_o$. Johnson and Cutler have refined compact shrinkage equations for pressureless sintering models derived previously for bulk and grain boundary diffusion. In all cases, grain boundaries were assumed to be sinks for vacancies, while initial contact points were assumed to have various geometries. As shown in Table II, time exponents of the shrinkage equation $\Delta L/L_o = \alpha t^m$ were derived and found to vary between 0.25 and 0.46 depending on diffusion path and initial contact geometry. Kingery predicted a $t^{1/3}$ time exponent of 0.33 for liquid phase sintering of spherical particles where diffusion within the liquid phase is rate controlling; and an exponent of 0.50, where a phase boundary reaction is rate controlling.

In using this analysis, specimens must be heated very rapidly to experimental temperatures in order to reduce the amount of sintering during heating. Errors in selection of $t_0$, i.e. time zero, for the start of isothermal sintering, can result in shape changes in log fractional shrinkage versus log t curves.
In this work, specimens were held in the furnace during a relatively slow heating process. A specimen, after being heated to 900°C with no applied load, had sintered to a measured density of 84%, while the pre-compacted density was about 54%. Due to this pre-load sintering, the compact had shrunk away from the die walls. After pressing, specimens always filled the die from wall to wall. Therefore, the application of load resulted in lateral flow of material in the die. It is probably incorrect to select the time of load application, \( t_0 \), as the start of isothermal sintering, because of resulting massive particle rearrangement. It would be more meaningful to select the instant where the sample had just flowed out to the die walls as \( t_0 \). However, from the compaction data, it was not possible to judge when this point had been reached.

Figure 1 shows log fractional shrinkage of a specimen pressed at 900°C (Y011-28) plotted versus log \((t-t_0)\) where \( t_0 \) was selected as occurring 5, 10, 30 and 60 minutes after the application of the load. The slopes of these log-log plots are not constant with log \((t-t_0)\) and vary between 0.2 and 0.6; straight lines could be drawn arbitrarily through various portions of the curves. The slopes of these lines fall in the range of values predicted by the various sintering models. Due to the uncertainty in \( t_0 \), an analysis of densification behavior based on these models is not possible.

To account for variations in initial compact weight and in order

* Calculated density of magnesium oxide single crystals using displacement technique is 3.587 gm/cc while lattice parameter determinations yielded a value of 3.583 gm/cc. Where densities are reported in percentages, the value will be relative to the x-ray density.
Fig. 1  Effect of variable $t_o$ on $\Delta L/L_o$. 
to present compaction data on a relative basis, data are reported in the form of specimen density during densification rather than length. Apparent densities during compaction were calculated from the length change during compaction using the final sample length and density as references. This calculation assumes constant sample weight and composition during densification. A compact initially containing 3 wt.% lithium fluoride was heated up to 900°C with no applied load and on cooling to room temperature, contained 0.76 wt.% lithium (corresponding to 2.08 wt.% lithium fluoride). Similar specimens after holding for one hour under a load of 2250 psi, had a lithium content of 0.29 wt.% (0.79 weight percent lithium fluoride); and after holding for 5 hours, 0.31 % (0.85 wt.% lithium fluoride). Thus, within experimental uncertainty, the lithium fluoride content remained unchanged during the last four hours of pressing at 900°C with the reduction in additive occurring only during the first hour of load. In comparison, a sample pressed at 700°C/2250 psi lost slightly less than one-third of the lithium fluoride during five hours at load. Therefore specimen weight and composition remained fairly constant during the latter stage of densification, i.e. the change in sample length during densification is due largely to the removal of voids and not lithium fluoride.

An attempt was made to analyze densification behavior using equations derived by Rossi and Fulrath and by Fryer. Calculated densities, however, did not follow predicted porosity dependencies.

However, for a number of samples, the log of the rate of change in density during the final stage of densification was found to vary linearly with log time with a slope of -7/2; therefore sample density varied
linearly with \( t^{-2/5} \). Densities for typical specimens originally containing 3% lithium fluoride are shown in Fig. 2 plotted against \( t^{-2/5} \). After an initial densification stage, densities are noted to follow:

\[
\rho = \rho_{t=\infty} - \alpha t^{-2/5}
\]  

(1)

Of the samples pressed at temperatures between 670° and 1100°C, only the samples pressed at 800°C/2250 psi did not follow this relationship during the final stage of densification.

From the relationship between density and time, an empirical expression relating densification rate and porosity may be derived. On differentiating (1)

\[
\frac{d\rho}{dt} = \frac{2}{5} \alpha t^{-7/5}
\]  

(2)

by rearrangement and substitution of (2) in (1)

\[
\frac{d\rho}{dt} = \frac{2}{5} \alpha^{-2/5} \rho_{t=\infty}^{-7/2} \left( \frac{\rho_{t=\infty} - \rho_{t=\infty}}{\rho_{t=\infty}} \right)^{7/2}
\]  

(3)

assuming that \( \rho_{\text{relative}} = \frac{\rho}{\rho_{t=\infty}} \) and \( 1 - \rho_{\text{relative}} = \text{fractional porosity} \) yields

\[
\frac{d\rho}{dt} = k \text{ (fractional porosity)}^{7/2}
\]  

(4)

where

\[
k = \frac{2}{5} \alpha^{-2/5} \rho_{t=\infty}^{-7/2}
\]

* Based on the foregoing definition of density during compaction, the actual porosity is inversely related to the volume fraction of the compact that is not occupied by magnesium oxide. This volume of sample is occupied by a second phase which may be pores or lithium fluoride. Density at time equal infinity, \( \rho_{t=\infty} \), is a mathematical value associated with the extrapolation of the straight line portion of the curve; thus fractional porosity as calculated, although related to the actual density, is not a true porosity and will be referred to as apparent porosity.
Fig. 2 Effect of temperature on densification of specimens initially containing 3% lithium fluoride pressed at 2250 psi.
Plotting log of k, the rate constant for samples pressed at temperatures between 670 and 1100°C, versus 1/T, yields an apparent activation energy of 38 kcal/mole.

Figure 3 shows the change in specimen length during densification where a load of 2250 psi was applied at 275°C. Data were corrected for the thermal expansion of the ram and plungers by monitoring a run made without a sample in the die. The sample (Y011-66) initially contained 3% lithium fluoride. Benecke and co-workers, heating at slower rates, also detected no change in densification behavior at 848°C, the lithium fluoride melting point. They did not report data below 500°C; however, a decrease in compact length at 300°C was observed.

1. Effect of Stress on Densification

Figure 4 shows the effect of stress variation on the densification of specimens originally containing 3% lithium fluoride. Stresses were applied at 900°C and were varied between 1250 and 4250 psi (Y011-42, -22, -41, -39). The density during compaction of these specimens also follows the t^{-2/5} relationship for times greater than 30 minutes. Preliminary results showed like behavior for samples pressed at 1100°C. The densification rate dependence upon stress at 900°C is shown in Fig. 5. The data extrapolate to a zero yield stress.

2. Effect of Lithium Fluoride Content

The effect of varying initial lithium fluoride content between 1/2 and 10% on densification behavior at 900°C/2250 psi (Y011-5a, -3a, -28, -2a, -1a, -4a, -6a) is shown in Fig. 6. All specimens reached a final stage of densification where the density was proportional to t^{-2/5}. 
Fig. 3 Change in length of a sample during pressing as a function of temperature at a stress of 2250 psi.
Fig. 4 Effect of stress on densification of specimens pressed at 900°C.
Fig. 5 Stress dependence of the densification rate of 3% lithium fluoride specimens, calculated at a density of 99%.
Fig. 6 Effect of initial lithium fluoride content on densification of specimens pressed at 900°C/2250 psi.
Specimens containing 5\% or more showed almost linear behavior throughout densification with the initial rate being slightly increased over the final rate. Specimens containing less than 3\% initially densified at a high rate. An intermediate densification stage occurred at a greatly decreased rate prior to the final densification stage.

In Fig. 7, the variation of specimen final density is shown as a function of initial lithium content. The sample initially containing 1/2\% lithium fluoride (0.15\% lithium) had a significantly higher hot-pressed density than samples with higher initial lithium fluoride contents. After pressing, samples initially containing more than 1/2\% lithium fluoride had approximately equal final lithium content (about 0.30\%). The dashed line represents sample theoretical densities based on the assumption that all the lithium in the sample after pressing was present as lithium fluoride and no other phases of either higher or lower density were present. On the basis of this calculation, it cannot be distinguished whether the lithium fluoride is present as a separate phase or whether it is in an ideal solution with the magnesium oxide. This calculation is insensitive to the presence of small amounts of impurities.

B. Lattice Parameter Studies

Variation in the magnesium oxide lattice parameter as a function of fabrication parameters was determined on hot-pressed specimens using a Norelco diffractometer equipped with a crystal monochromator. Copper Kα₁ radiation was used with a 4° beam slit, 4° focusing slit and a 1° detector slit. D-spacings of the 511, 422, 420 and 331 peaks were determined from 2θ values obtained by step scanning at a rate of 0.02°/step with no less than 12,800 counts per step. Spacings were corrected to
Fig. 7 Variation of specimen final density as a function of initial and as hot-pressed lithium content.

- Li content before pressing, 0 Li content after pressing,  △ theoretical density of magnesium oxide.
25°C using Skinner's\textsuperscript{39} thermal expansion data. Calculated lattice parameters for each peak were plotted against $\sin^2 \theta$ and were extrapolated to $\sin^2 \theta$ equal one.

The lattice parameter of the starting magnesium oxide powder was measured at 4.2123 Å. The parameter of a specimen pressed at 900°C/2250 psi for five hours with no lithium fluoride is 4.2122 Å while that of a specimen initially containing three percent lithium fluoride is 4.2114 Å. Therefore the application of stress alone has no effect on the magnesia lattice parameter during pressing. The change in the magnesia parameter depends on the presence of lithium fluoride.

The effect of initial lithium content on the magnesium oxide lattice parameter of several hot-pressed specimens is shown in Fig. 8. In terms of the original lithium content, the lattice parameter changed very little after the first one percent addition of lithium fluoride. When the lattice parameter is considered in terms of lithium content after densification, a fairly linear relationship is noted. The dashed line represents lattice parameters for ideal solutions. For an ideal solution of lithium fluoride in magnesium oxide, a lithium fluoride solubility of 0.4 mole percent (0.075 lithium wt.%) in the magnesia lattice was calculated from lattice parameters of samples pressed with and without lithium fluoride at 900°C/2250 psi (Y011-28 and -47), while by chemical analysis, the sample was found to contain 0.30 wt.% lithium. Therefore, it is indicated that the bulk of the lithium fluoride is located on the grain boundaries.

In Fig. 9, the effect of temperature, pressure, and time on the magnesium oxide lattice parameters of samples initially containing
Fig. 8 Variation of magnesium oxide lattice parameter of specimen pressed for five hours at $900^\circ/2250$ psi

- $\bullet$ original Li content
- $\circ$ pressed Li content
- $\triangle$ no lithium fluoride added.
Effect of temperature on magnesium oxide lattice parameter. Specimens were pressed at 2250 psi. • sample pressed with 3% lithium fluoride; ▲ sample pressed without lithium fluoride.

(b) Effect of time on magnesium oxide lattice parameter. Samples initially contained 3% lithium fluoride and were pressed at 900°C/2250 psi.

(c) Effect of pressure on magnesium oxide lattice parameter. Samples initially contained 3% lithium fluoride and were pressed at 900°C.
3% lithium fluoride is shown. The lattice parameters increased with both increasing temperature and stress. Increased time at temperature has little effect on the parameter after the first hour of pressing.

C. Annealing

Specimen densities after annealing, calculated density of the volatile phase and specimen optical quality after annealing are given in Table III.

1. Annealing in Air

Samples fabricated at temperatures between 830 and 1100°C for 5 hours developed excellent transparency on annealing in air at 1300°C for three hours. All of these samples prior to annealing had densities above 3.551 gm/cc; i.e. in excess of 99.1%. Using normal fabrication techniques, samples pressed at 800°C did not become fully transparent during annealing. A sample that was pressed at 800°C and prepared from magnesium oxide that had been held in a drying oven at 120°C for a much longer time, about 30 days, developed poorer optical quality after annealing at 1300°C.

Densities of the phase that volatilized from the specimens during annealing at 1300°C for 3 hours were calculated from sample weight and volume changes during annealing. Values fall between 2.3 and 2.7 gm/cc while the calculated lithium fluoride X-ray density is 2.64 gm/cc.

Specimen weight loss during annealing is shown in Fig. 10 as a function of lithium content before annealing for samples pressed at 900°C/2250 psi with varying initial lithium fluoride content. The dashed line represents the weight loss that would be expected if all the lithium were present in the form of lithium fluoride and if all of the lithium
Fig. 10 Weight loss of samples after three hours of annealing as a function of lithium content after pressing and before annealing. Specimens were pressed at 900°C/2250 psi for five hours and had varying initial lithium content.
fluoride volatilized during annealing. The close agreement of experimental values with predicted ones infers that the volatile phase is essentially lithium fluoride.

One specimen (Y011-59) was annealed in air at 900°C for a total of 31 hours. The change in density with annealing time is shown in Fig. 11. After three hours of annealing, the specimen was slightly translucent at the edges and had developed a slight pink coloration. The transparency greatly increased during the next eight hours of annealing but was still lower than that of a specimen annealed at 1300°C for three hours. After an additional annealing for 20 hours, the sample was fully transparent; however, the coloration remained. Final density was less than that of the sample annealed at 1300°C. Specimens heated to 1100°C in creep and weight loss experiments also developed this coloration. A section of this sample retained the coloration after it was annealed at 900°C for a total of 120 hours. The specimen became colorless after reannealing in air for three hours at 1300°C; however, this effect was not found to be reversible.

Specimens slowly heated to 1500°C in air and 1750°C in argon, also became transparent during annealing. Heating facilities were not available for 1750°C in air.

The rate of weight loss from a partially densified specimen (Y011-59) was determined in an automatic recording weight loss furnace. The experiment was performed in air at a constant heating rate of 1°/min. If lithium fluoride is considered to be evaporating out of grain boundary channels, the evaporating surface area would be proportional to the
Fig. 11 Change in specimen density as a function of time and temperature during annealing.
amount of lithium fluoride present. The instantaneous rate of weight loss measured at a temperature was corrected for loss of evaporating surface area by dividing by the weight of the unevaporated lithium fluoride. A plot of the log of the corrected weight loss versus $1/T$ is shown in Fig. 12. Linear behavior was observed between $830^\circ$ and $1075^\circ$C. At $1075^\circ$C no further weight loss was observed. From the slope, a heat of evaporation of $54$ kcal/mole at $950^\circ$C was determined. A heat of $60.5$ kcal/mole was calculated for $716^\circ$C which agrees well with the value of $58.3$ kcal/mole reported by Evseev, et al.\textsuperscript{40} for the heat of sublimation of lithium fluoride at $716^\circ$C. Although this work was not carried out under equilibrium conditions, the close agreement of these two values implies that the annealing process above $830^\circ$C is controlled by lithium fluoride evaporation.

2. **Annealing in Vacuum**

Vacuum annealing at $1300^\circ$C for three hours produced specimens of excellent optical quality while annealing at $900^\circ$C produced inhomogeneous specimens with areas of high transparency. The sample annealed at $900^\circ$C for three hours in vacuum was colorless and not pink as was the case for the sample annealed in air at $900^\circ$C.

D. **Optical and Infrared Transmission**

The infrared transmission of typical hot-pressed and annealed specimens was determined using a Beckman IR 4 spectrometer. The absorbance of typical hot-pressed and annealed specimens and a magnesium oxide single crystal are shown in Fig. 13. The absorption peaks of unannealed specimens at $3.0\mu$ and $6.7\mu$ were also noted by Rice and are attributed
Fig. 12 Rate of weight loss from a partially densified specimen (Y011-59) as a function of temperature.
Fig. 13 Absorbance in the infrared region of typical unannealed and annealed specimens.

--- Single crystal --- Hot-pressed specimen
----- Annealed specimen.
to hydroxides and carbonates of lithium and/or magnesium, respectively.

Using a Cary 14 spectrometer, the absorbance of specimens annealed at 900 and 1300°C in air was determined in the region of 0.25 to 2.1µm. No sharp absorption peaks were noted that would explain on the basis of di- or tri-valent ions the coloration of the specimen annealed at 900°C.

E. Phase Equilibria

Several techniques were used to study phase equilibria between lithium fluoride and magnesium oxide. Cooling curves for samples containing from one to ten percent lithium fluoride were followed in graphite cells using Pt-Pt 10% Rh thermocouples. On heating and cooling, only the plateaus associated with melting and solidification of lithium fluoride were noted between 500 and 900°C.

Controlled thermal gradient firings were performed on one inch diameter specimens pressed at 1000 psi containing from zero to nine percent lithium fluoride. In this technique a constant thermal gradient is maintained across a sample during heating by controlling the furnace heating rate. Variations in the heating rate indicate either endo- or exothermic reactions and changes in thermal conductivity due to specimen sintering. An endothermic peak was noted at about 300°C which correlates with first observed compact shrinkage and start of sample weight loss. A second endothermic peak near the lithium fluoride melting point was observed for specimens containing three to nine percent lithium fluoride. The break in the curve was independent of the original lithium fluoride content and the size of the thermal gradient used. The measured temperature of the break was $835°C \pm 5°C$. A gradual change in heating
rate occurred between 300 and 800°C indicating that the sample was densifying.

Differential thermal analysis was carried out on samples containing 10 and 20% lithium fluoride. Results are shown in Fig. 14. Both firings showed the previously observed endothermic peak at 300°C and a second peak starting to appear at about 820°C where the furnace was turned off.

Diffusion studies were performed on lithium fluoride-magnesium oxide couples. Lithium fluoride and magnesia single crystals were lapped together using 1000 grit diamond paste. The couple was weighted with a 75 gm piece of platinum rod to insure good contact between the crystals and was heated in a closed graphite cell at 800°C for 24 hours. Qualitative studies using a Material Analysis electron probe showed that diffusion of magnesium into the lithium fluoride lattice took place. This diffusion zone was about 10μ. Due to the broad beam width for fluorine analysis, the determination of any diffusion of fluorine into the magnesium oxide lattice was uncertain. Attempts were made to study diffusion above the lithium fluoride melting point; however, these tests proved to be inconclusive.

The contact angle between liquid lithium fluoride and a cleaved surface of magnesium oxide single crystal was measured in vacuum at 850°C. A contact angle of 30° was formed when the lithium fluoride first melted with the angle appearing to decrease with time. Lithium fluoride evaporated rapidly without any change in the diameter of the drop resulting in a reduced height of the drop and apparent reduction in the contact angle.
Fig. 14 DTA curves of compacts heated in air.
F. Compressive Creep Experiments

Compressive creep experiments were carried out on specimens that had received various pressing and annealing treatments. Apparatus that has been described by Hulse and Copley \(^4\) was used to perform the experiments. Specimens were cut into right rectangular parallelepipeds that had length to width ratios of less than 1.7. \(^3\)

Initial experiments were performed on two specimens; both had been hot-pressed at 900°C/2250 psi for only 2 hours (Y011-59). One sample was strained in the as-pressed state while the other was strained after it had been annealed at 1300°C for 3 hours in air. \(^*\)** The strain behavior of the two samples at 750 psi and a heating rate of about 250°F/hr is shown in Fig. 15. The sample that was annealed at 1300° exhibited thermal expansion behavior that compares well with Skinner's expansion data for magnesium oxide. The unannealed sample developed a total true strain of about 50% during the test. In preliminary tests, one unannealed specimen was strained in excess of 75% at 900°C and a stress of 1000 psi. Strain for the unannealed samples was observed to first deviate from the expansion curve of the annealed specimen at about 630°C with a large increase in the strain rate occurring at about 830°C. Both of the unannealed specimens which were translucent before annealing became fully transparent during the test.

A sample that had been annealed at 900°C for 31 hours \(^***\) was also tested under the same heating rate and load as the previous samples. Strain behavior closely followed the expansion behavior of the specimen.

\(\text{\* Density 3.564 gm/cc}\)
\(\text{\** Density 3.564 gm/cc}\)
\(\text{\*** Density 3.581 gm/cc}\)
Fig. 15 True strain of annealed and unannealed specimens under a stress of 750 psi.
that had been annealed at 1300° for 3 hours. The lower annealing temperature was chosen to reduce the amount of grain growth during the annealing process. A comparison of the microstructure of the annealed specimens is shown in Fig. 16. Grains in the unannealed specimen were too small to be resolved using optical techniques. At 1000°C the stress on the annealed specimen was increased at a rate of about 20 psi/sec to 21,000 psi. As shown in Fig. 17, a total strain of 0.96% resulted of which 0.09% was elastic as indicated on unloading. A calculated elastic modulus of $2.3 \times 10^7$ psi agrees well with reported values for polycrystalline magnesium oxide at 1000°C.

Further experiments were carried out at constant temperature to determine the stress dependence of the strain rate. The incremental stress technique was employed to determine the value of the exponent. Creep experiments were performed on two specimens: one sample had been pressed at 900°C/2250 psi for two hours (Y011-59) and was strained at 850°C; while the other had been pressed at 770°C/2250 psi for 2 hours (Y011-63) and was strained at 770°C. The measured strain showed a rapid response to stress changes indicating that little or no primary strain occurred during the test. Loads were changed after the sample had been deformed about 2%.

Ratios of the strain rates before and after stress changes and ratios of the stresses were used to determine the stress dependence of the strain rates rather than actual strain rates and stresses. The advantage of using ratios is that the sample need not be in true structural independent creep in order to determine the stress dependence. Changes in structure throughout the experiment are believed to occur due to
Fig. 16  Microstructure of annealed specimens after straining.
Fig. 17 Stress strain behavior at 1000°C of a specimen annealed at 900°C for 31 hours.
lithium fluoride loss and limited grain growth during the tests.

Figure 18 shows a log plot of the ratios of the strain rates versus the ratios of the stresses. A slope of unity indicates that both samples deformed in a viscous manner during creep. This behavior, thus, is not dependent on the melting temperature, 848°C, of lithium fluoride.
Fig. 18 Ratios of strain rates and stresses for compressive creep behavior of unannealed specimens.
V. DISCUSSION OF RESULTS

The densification of magnesium oxide compacts containing small lithium fluoride additions may be considered as a three step process: 1) the first or rearrangement stage, 2) the final or flow stage which is aided by solution-precipitation, and 3) annealing after hot pressing. Stages one and two take place in the die during hot pressing.

A. First Stage of Densification

Compacts sintered away from die walls during heating to pressing temperatures with subsequent load application resulting in flow of material out to the die walls. During the first five to fifteen minutes of compaction, sample strain rates were on the order of one in/hr, which were too rapid to be accurately measured. Such a rapid densification rate is attributed to flow and rearrangement of particles and is comparable to the rearrangement process discussed by several authors. In this case, the presence of a second phase in the system provides lubrication for particle rearrangement. Rice has reported that lithium fluoride, above its melting point, reduces the coefficients of static and dynamic friction between magnesium oxide single crystals. Depending on test parameters, i.e., temperature, pressure's initial lithium fluoride content, the rearrangement stage may continue to be the predominate mechanism up to densities as high as 90 percent.

B. Final Stage of Densification

During the final densification stage, specimen densities were found to be proportional to \( t^{-2/5} \). Correspondingly, the rate of densification was linear with the \( 7/2 \) power of apparent porosity. The
range of densities in which these relationships were followed depended on test parameters. During this stage, the amount of porosity was reduced and magnesium oxide was probably distributed by a solution-precipitation process. Undoubtedly, a transition period exists between this and the rearrangement stage.

The lack of theoretical density in pressed specimens is due to the presence of lithium fluoride and not porosity. Measured densities (Fig. 7) suggest that lithium fluoride is present in the hot-pressed specimens either as a separate second phase or in an ideal solution with the magnesium oxide. Lattice parameter studies (Fig. 9), however, indicate that very little of the lithium fluoride is tied up in solid solution in magnesium oxide. The amount in solution decreases with temperature (Fig. 9). The excess material, therefore, appears to form a second phase at the magnesia grain boundaries.

In room temperature X-ray studies of hot-pressed specimens, broad, very weak lithium fluoride peaks were detected. The broadness of the peaks suggests that the lithium fluoride is present in the samples in a very finely divided state, e.g., a thin film, or with a highly defected structure. Rhodes and co-worker observed a second phase at grain boundaries in electron micrographs of replicas of specimens pressed at 800°C for 105 minutes and at 1000°C for 15 minutes. Specimens initially contained two percent lithium fluoride; final content was not reported. In this work, grain size of about one micron was observed by examination of replicas of specimens pressed at 900°C. Assuming spherical particles and a lithium content of 0.31 weight percent, the corresponding lithium fluoride film thickness would be about 60 Å and was
therefore difficult to resolve. Landon and Pask have examined thinned sections of transparent annealed specimens produced by this author and observed no second phase at the grain boundaries at magnifications up to 6000x.

Phases other than lithium fluoride and magnesium oxide were not detected in X-ray analysis of hot-pressed specimens. Infrared transmissions, however, indicated that carbonates and hydroxides of magnesium and/or lithium are present in specimens after hot-pressing (Fig. 13). In annealed specimens, absorption corresponding to these compounds was not detected. Overall cation impurity content is reduced during hot-pressing with little or no further reduction occurring during annealing (see Appendix for chemical analysis of a typical specimen).

The lithium fluoride-lithium carbonate eutectic is reported as occurring at 604°C. Simple eutectic behavior would result in increased liquid content with increasing temperature above 604°C. The presence of lithium hydroxide and the corresponding magnesium salts could further reduce this temperature. The amount of liquid formed by the lithium fluoride-lithium carbonate eutectic reaction, or by a similar reaction between lithium fluoride, magnesium oxide or impurities, is expected to be relatively small since the starting powder was relatively pure. The heat of reaction associated with the formation of a very small amount of liquid would be difficult to detect in the DTA and controlled thermal gradient experiments. Changes in sample thermal conductivity, due to the onset of sintering at the reaction temperature, could mask the peak corresponding to such an endothermic reaction.

Magnesium oxide powders containing three present lithium fluoride
were observed normally (Fig. 5) to begin rapid densification at temperatures between 550 and 600°C. The compressive strain of a partially densified specimen (Fig. 15) first deviated from the magnesium oxide thermal expansion curve at about 600°C. These changes in strain behavior correlate well with the expected low temperature eutectic.

The eutectic between pure magnesium oxide and lithium fluoride is estimated (see Appendix II) as occurring at 846°C and 0.05% magnesium oxide-99.5% lithium fluoride. The presence of impurities in the lithium fluoride or on the magnesium oxide particle surfaces would result in the reduction of this temperature. The endothermic reaction, observed in both the controlled thermal gradient and in the DTA work, at 835°C may represent the reduced eutectic temperature. In the compressive creep experiments, onset of very rapid strain was observed at about 850°C.

No discontinuity in sample compaction behavior (Fig. 6) was observed at 830°C, where the sample had reached a density of about 92%. In a high density body, the formation of additional liquid would probably cause little change in the densification rate.

Sample densities increased slightly at about 300°C. This temperature correlates with the endothermic reaction noted in DTA and controlled thermal gradient firings and the onset of rapid weight loss from the starting magnesium oxide powder. This temperature probably represents the onset of magnesium hydroxide and/or carbonate decomposition.

Changes in densification and creep behavior and the endothermic reactions noted in the phase equilibria study correlate well with each other. If a lithium fluoride-rich film did surround the magnesia grains, then specimens would deform when liquid first formed.
The dependence of the densification rate on the 7/2 power of apparent porosity may be explained on the basis of a second phase being squeezed through passages along magnesium oxide grain boundaries. The rate of flow of material through a capillary is proportional to the fourth power of the radius of the capillary, while the rate of flow through a narrow channel is proportional to the third power of the channel width (see Appendix III for derivation). If grain size and capillary length are constant during this densification stage, then the amount of lithium fluoride in the sample will be proportional to the width of the channel or to the square of the radius of the capillary. If densification is controlled by flow of material through such paths then the densification rate would be proportional to either the second or third power of the apparent porosity depending on flow path configuration. A porosity dependence of 3.5 may mean that the grain boundary paths are behaving as neither pure channels nor capillaries, but the dimensions are decreasing more rapidly in one direction than in the other. Uniaxial loading in the die could cause such an effect. It is of note that the porosity dependence 7/2 is followed at temperatures both above and below the lithium fluoride melting point and by samples having both partially unfilled and filled pores. For example, the sample pressed at 700°C/2250 psi followed this relationship at relatively low densities where there was not enough lithium fluoride to fill all voids. The flow of the liquid phase through the intergranular channels could be either into voids or out of the sample proper. Both phenomena would result in the same changes in sample length and calculated apparent densities.
Contact points between magnesia grains have high radii of curvature and are active sites relative to other areas of the grains. These points should tend to dissolve preferentially in a liquid phase. Stress concentrations at the contact points would also enhance the solubility. The precipitation of the dissolved material at sites of less stress results in a distribution of magnesium oxide.

The application of load could, however, result in the squeezing of all of the liquid out from grain contact points. A thin film of liquid, however, should remain between grains because of the wetting of the grains by the liquid. Solution of solid into the liquid would result in an increase of the volume of the liquid at the contact points. The applied load causes the excess liquid to flow out of the contact area with the grain centers moving closer together resulting in an increase in sample density. In normal liquid phase sintering, densification ceases when all voids become completely filled with liquid. In pressure sintering, external pressure becomes the driving force for flow of excess liquid to the compact surfaces. As the liquid phase is squeezed through the compact, dissolved magnesium oxide should tend to deposit at lower energy sites on magnesia grain boundaries.

The initial lithium fluoride content affects the length of time that the $t^{-2/5}$ relationship is followed. Samples initially containing one half, one, and three percent lithium fluoride did not follow the relationship immediately after the initial rapid densification stage. The low densification rate in this intermediate stage may indicate that there is not enough second phase present to maintain a film around each grain in the compact. This would result in magnesia grain to grain contacts
resulting in a slowing down of the densification process. After further reduction in grain boundary area by a relatively slow sintering process, a stage may be reached where there is enough lithium fluoride present to allow the solution process to then continue throughout the sample. The stage where the \( t^{-2/5} \) relationship is followed goes to shorter times and lower densities as the amount of lithium fluoride is progressively increased. Therefore, for a lower initial lithium fluoride starting content, the sample must reach a higher density and thus lower grain boundary area before the \( t^{-2/5} \) relationship is followed.

Samples pressed at 800°C did not follow the \( t^{-2/5} \) relationship at any time during the densification process. The shape of the density versus \( t^{-2/5} \) curve for this specimen is very similar to those of the initial densification stage of samples initially containing one-half and one percent lithium fluoride. At this temperature, below the lithium fluoride melting point, the amount of liquid phase present in the compact may depend upon the concentration of carbonates and hydroxides. With increasing time, the concentration of these impurities would decrease due to increased decomposition with a resulting decrease in the amount of liquid present. Samples pressed at 850°C and above followed the \( t^{-2/5} \) relationship for the latter period of hot-pressing because of liquid formation at the lithium fluoride magnesium oxide eutectic.

Samples pressed at 1200° (Yoll-55) and 1300°C (Yoll-51) were porous after pressing at 2250 psi for five hours. Due to the high vapor pressure of lithium fluoride, at these temperatures, the specimens were probably depleted of lithium fluoride resulting in not enough liquid phase to sustain the densification process. Note that the lattice parameter of
the sample pressed at 1300°C with 3% lithium fluoride is equal to that of the starting powder indicating no lithium fluoride solution in the magnesium oxide lattice.

In Fig. 7, the final lithium content in a pressed specimen is seen to be independent of the starting lithium content past the initial 0.16 percent (one-half percent lithium fluoride). Within experimental accuracy, samples containing one-half and one percent lithium fluoride lost no lithium during the first five hours of pressing at 900°C. Samples initially containing more lithium reached a steady state lithium concentration of about 0.31 percent. The excess material is removed during the latter stage of densification in hot pressing.

Little emphasis is placed on the activation energy of 38 kcal/mole calculated for the densification stage where the $t^{-2/5}$ relationship was followed. According to the above analysis, it should represent the activation energy for plastic flow of the lithium fluoride rich phase. This value is lower than ones reported for self-diffusion of magnesium and oxygen in magnesium oxide single crystals and for normal sintering and pressure sintering of magnesium oxide measured by Vasilos and Spriggs. However, it is higher than that reported by Brown for the sintering of very pure magnesium oxide.

C. Annealing Stage

Optical quality of hot-pressed specimens normally improved during the annealing process with most specimens developing excellent transparency. Improvement in optical quality is explained by the removal of the second phase from the grain boundaries. If the second phase had an index of refraction different than that of the magnesia, then light would
be refracted or scattered at the grain boundaries, resulting in a reduction in light transmission. Removal of grain boundary phases during annealing would result in reduction of light scattering and a corresponding increase in transmission.

The activation energy of 54 kcal/mole calculated from specimen weight loss during annealing suggests that above 850°C, lithium fluoride removal can be controlled by evaporation. In hot-pressing, however, due to the tight fit between plunger and die walls, the presence of graphite and magnesia particles between the plunger and die walls, and the saturation of graphite with lithium fluoride, vaporization of lithium fluoride from the specimen would be prevented. If this were the case, then loss of lithium fluoride during hot pressing could only occur by pressure induced flow and the interior of the specimen would be expected to clear first during pressing. It was found that the center of a specimen (Y011-45) pressed at 1100°C/2250 psi for five hours was optically transparent while the edges were only translucent.

During annealing, as material evaporates from the sample surface, the lithium fluoride-rich phase is pulled toward the surface along the magnesia grain boundaries by capillary action. In order to prevent creation of liquid vapor interfaces within the compact, these capillary forces could pull the grain closer together to compensate for material loss from the sample surface.

If densification during annealing is controlled by evaporation, the process should be more rapid in vacuum than in air. In air annealing, a lithium fluoride atmosphere would build up near the surface of the specimen that would tend to inhibit the loss of lithium fluoride. A sample
that was pressed at 900°C/2250 psi for two hours developed much higher transparency when annealed at 900°C for three hours in vacuum than in air.

The rate of weight loss during annealing (Fig. 12) is not linear with 1/T below about 830°C. In a hot-pressed specimen, below the lithium fluoride-magnesium oxide eutectic there would probably be not enough liquid phase to maintain a continuous film between grains. Evaporation would no longer occur at the sample surface. This could result in a change in the mechanism controlling weight loss and an accompanying change in activation energy.

Samples pressed at 1000°C and 1100°C densified at a reduced rate after the first 40 to 60 minutes of hot-pressing, i.e., sample density no longer followed the t^{-2/5} relationship. These samples had reached densities approaching theoretical density. This region of slower densification may represent a stage where material loss is no longer controlled by a pressure induced flow process, and is dependent upon an evaporation process as in annealing. Such a change in mechanism could account for a reduction in the densification rate.

D. Mechanical Behavior

The presence of a liquid film on the magnesia grain boundaries would also explain the observed difference in compressive creep behavior of annealed and unannealed specimens. The strained unannealed specimens yielded a stress exponent of unity at temperatures both below and above the lithium fluoride melting point, i.e., at 770 and 850°C, but both above the first appearance of liquid at about 600°C. The presence of a liquid phase in which magnesium oxide is soluble is used again to explain the apparent viscous behavior of unannealed specimens. As in
the hot-pressing densification process, the flow of the liquid phase out of the contact points rather than a solution-precipitation process is indicated as rate controlling; a solution-precipitation process, however, must be going on concurrently to maintain grain boundary integrity. Even though unannealed specimens were strained in excess of 75 percent, they became optically transparent during the tests. Transparent annealed specimens when strain to failure became opaque. Relatively small strains in the absence of an adequate mechanism for material transport result normally in the creation of cavities at the grain boundaries which lead ultimately to failure of the specimens.

In order to maintain translucency throughout the specimen, continuity between particles must be maintained. On the basis of the von Mises analysis of uniform plastic deformation of polycrystalline bodies, magnesia must have five active independent slip systems in order that grain to grain continuity is maintained during plastic deformation. This criterion is not met by magnesium oxide at 1000°C for low stresses. Not only did cavities not open up at grain boundaries during creep but the specimens actually became transparent. A solution-precipitation process occurring at the grain boundaries could serve to maintain grain to grain continuity. Annealed specimens, with no liquid phase present, did not exhibit plastic behavior at low stresses.
VI. CONCLUSIONS

The densification of magnesium oxide compacts containing small lithium fluoride additions by hot-pressing at temperatures between 670 and 1100°C is considered to be a two-step process. Transparency is attained by a following annealing step which is the final step in the densification process.

The first stage is a rapid particle rearrangement process resulting primarily from a lateral flow of material to the die walls. This stage is enhanced by the presence of lithium fluoride which acts as a lubricant between particles. A kinetic analysis of this stage was not carried out.

The final stage of densification is controlled by flow of a lithium fluoride-rich phase through intergranular channels during which stage calculated sample densities followed a $t^{-2/5}$ relationship. The actual mode of magnesium oxide transport, however, is by a solution-precipitation process in the lithium fluoride-rich phase. The criterion, as generalized by Kingery, for the solution-precipitation processes are met, i.e., 1) lithium fluoride, above the melting point, wets magnesium oxide,* and 2) each phase magnesium oxide appears to have a limited solubility in the other lithium fluoride. Below the lithium fluoride melting point, the presence of the liquid phase appears to be dependent on salt impurities. At 800°C, due to decomposition of these impurities, insufficient liquid phase is present to sustain the process and the $t^{-2/5}$ relationship is not followed. Due to loss of lithium fluoride from the compact, samples fabricated at 1200 and 1300°C also did not follow this relationship.

* A lithium fluoride rich phase should also wet magnesium oxide.
For most specimens, the rapid rearrangement stage and the final stage were separated by an intermediate transition stage. In samples with low liquid content this stage is more extensive in reaching a configuration that finally follows the kinetics of the final stage of hot-pressing.

An activation energy of 38 kcal/mole was determined for the final densification process. This value may represent the activation for the flow of the lithium fluoride rich film.

The annealing process is controlled by the evaporation of lithium fluoride from the compact surface. Loss of lithium fluoride results in a closing of the intergranular channels. An activation energy of 54 kcal/mole for weight loss during annealing above 830°C indicates that the annealing process is controlled by evaporation of the lithium fluoride phase. The density of the phase that volatilized from the sample was calculated to be near that of lithium fluoride for a number of samples annealed at 1300°C.

From chemical analysis of pressed specimens, a starting lithium fluoride content of between one and two percent appears to be the optimum amount of additive for the production of dense specimens. Amounts in excess of one percent are squeezed out of the specimen during hot-pressing.

On the basis of the preceding proposed model and experimental observation, the following criterion are suggested for the selection of additives that will result in enhancement of the oxide densification by hot-pressing: 1) the solid must be soluble to some degree in the liquid, but should not form a compound with the oxide, 2) the liquid must wet the solid, 3) the vapor pressure of the additive must, at
pressing temperatures, be low enough that there is not excessive escape from the compact during heating to the fabrication temperatures. Yet the vapor pressure must be high enough to insure uniform distribution of the additive throughout the sample.
ACKNOWLEDGMENTS

The author is indebted to Professor J. A. Pask for his guidance during this research project. Thanks are extended to T. G. Langdon, D. R. Cropper and R. B. Atkin for their assistance in performing experimental work and helpful counsel.

This work was done under the auspices of the United States Atomic Energy Commission.
Table I. Densification results.

<table>
<thead>
<tr>
<th>Run</th>
<th>Lithium fluoride content, percent</th>
<th>Pressure, psi</th>
<th>Temperature °C</th>
<th>Time at temperature, hrs</th>
<th>Density, gm/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y011-28</td>
<td>3</td>
<td>2250</td>
<td>900</td>
<td>5</td>
<td>3.562</td>
</tr>
<tr>
<td>29</td>
<td>3</td>
<td>2250</td>
<td>900</td>
<td>5</td>
<td>3.563</td>
</tr>
<tr>
<td>30</td>
<td>3</td>
<td>2250</td>
<td>800</td>
<td>5</td>
<td>3.483</td>
</tr>
<tr>
<td>31</td>
<td>3</td>
<td>2250</td>
<td>1000</td>
<td>5</td>
<td>3.579</td>
</tr>
<tr>
<td>38</td>
<td>3</td>
<td>4250</td>
<td>1000</td>
<td>5</td>
<td>3.581</td>
</tr>
<tr>
<td>39</td>
<td>3</td>
<td>4250</td>
<td>900</td>
<td>5</td>
<td>3.572</td>
</tr>
<tr>
<td>40</td>
<td>3</td>
<td>4250</td>
<td>800</td>
<td>5</td>
<td>3.539</td>
</tr>
<tr>
<td>41</td>
<td>3</td>
<td>3250</td>
<td>900</td>
<td>5</td>
<td>3.572</td>
</tr>
<tr>
<td>42</td>
<td>3</td>
<td>1250</td>
<td>900</td>
<td>5</td>
<td>3.562</td>
</tr>
<tr>
<td>44</td>
<td>0</td>
<td>2250</td>
<td>1100</td>
<td>5</td>
<td>--</td>
</tr>
<tr>
<td>45</td>
<td>3</td>
<td>2250</td>
<td>1100</td>
<td>5</td>
<td>3.576</td>
</tr>
<tr>
<td>46</td>
<td>3</td>
<td>5250</td>
<td>900</td>
<td>5</td>
<td>3.539</td>
</tr>
<tr>
<td>47</td>
<td>0</td>
<td>2250</td>
<td>900</td>
<td>5</td>
<td>1.924</td>
</tr>
<tr>
<td>49</td>
<td>3</td>
<td>2250</td>
<td>750</td>
<td>5</td>
<td>3.583</td>
</tr>
<tr>
<td>50</td>
<td>3</td>
<td>2250</td>
<td>860</td>
<td>5</td>
<td>3.558</td>
</tr>
<tr>
<td>51</td>
<td>3</td>
<td>2250</td>
<td>1300</td>
<td>5</td>
<td>3.557</td>
</tr>
<tr>
<td>53</td>
<td>3</td>
<td>2250</td>
<td>700</td>
<td>5</td>
<td>3.411</td>
</tr>
<tr>
<td>55</td>
<td>3</td>
<td>2250</td>
<td>1200</td>
<td>5</td>
<td>3.575</td>
</tr>
<tr>
<td>56</td>
<td>3</td>
<td>2250</td>
<td>830</td>
<td>5</td>
<td>3.551</td>
</tr>
<tr>
<td>57</td>
<td>3</td>
<td>2250</td>
<td>670</td>
<td>5</td>
<td>3.013</td>
</tr>
<tr>
<td>59</td>
<td>3</td>
<td>2250</td>
<td>900</td>
<td>2</td>
<td>3.564</td>
</tr>
<tr>
<td>63</td>
<td>3</td>
<td>2250</td>
<td>770</td>
<td>2</td>
<td>3.506</td>
</tr>
<tr>
<td>1a</td>
<td>5</td>
<td>2250</td>
<td>900</td>
<td>5</td>
<td>3.566</td>
</tr>
<tr>
<td>2a</td>
<td>4</td>
<td>2000</td>
<td>900</td>
<td>5</td>
<td>3.565</td>
</tr>
<tr>
<td>3a</td>
<td>1</td>
<td>2000</td>
<td>900</td>
<td>5</td>
<td>3.567</td>
</tr>
<tr>
<td>4a</td>
<td>7</td>
<td>2000</td>
<td>900</td>
<td>5</td>
<td>3.565</td>
</tr>
<tr>
<td>5a</td>
<td>1/2</td>
<td>2000</td>
<td>900</td>
<td>5</td>
<td>3.573</td>
</tr>
<tr>
<td>6a</td>
<td>10</td>
<td>2000</td>
<td>900</td>
<td>5</td>
<td>3.567</td>
</tr>
</tbody>
</table>
### Table II. Values of time exponents.

<table>
<thead>
<tr>
<th>Diffusion path</th>
<th>Initial contact</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>Spherical</td>
<td>0.46</td>
</tr>
<tr>
<td>Bulk</td>
<td>Paraboloid</td>
<td>0.46</td>
</tr>
<tr>
<td>Bulk</td>
<td>160° cone on a plane</td>
<td>0.33</td>
</tr>
<tr>
<td>Bulk</td>
<td>Spherical, grooved neck</td>
<td>0.46</td>
</tr>
<tr>
<td>Grain boundary</td>
<td>Spherical</td>
<td>0.31</td>
</tr>
<tr>
<td>Grain boundary</td>
<td>Paraboloid</td>
<td>0.31</td>
</tr>
<tr>
<td>Grain boundary</td>
<td>160° cone on a plane</td>
<td>0.25</td>
</tr>
<tr>
<td>Grain boundary</td>
<td>Spherical, grooved neck</td>
<td>0.31</td>
</tr>
</tbody>
</table>
### Table III. Annealing results.

<table>
<thead>
<tr>
<th>Run</th>
<th>Temp. °C</th>
<th>Atmos.</th>
<th>Time at temp. hrs</th>
<th>Volatilized phase density gm/cc</th>
<th>$\rho$, after annealing gm/cc</th>
<th>Optical quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y011-28</td>
<td>1300</td>
<td>Air</td>
<td>3</td>
<td>2.6</td>
<td>3.576</td>
<td>excellent</td>
</tr>
<tr>
<td>-31</td>
<td>1300</td>
<td>Air</td>
<td>3</td>
<td>2.5</td>
<td>3.584</td>
<td>excellent</td>
</tr>
<tr>
<td>-40</td>
<td>1300</td>
<td>Air</td>
<td>3</td>
<td>2.7</td>
<td>3.574</td>
<td>inhomogenous</td>
</tr>
<tr>
<td>-42</td>
<td>1300</td>
<td>Air</td>
<td>3</td>
<td>2.6</td>
<td>3.585</td>
<td>excellent</td>
</tr>
<tr>
<td>-45</td>
<td>1300</td>
<td>Air</td>
<td>3</td>
<td>2.6</td>
<td>3.584</td>
<td>excellent</td>
</tr>
<tr>
<td>-46</td>
<td>1300</td>
<td>Air</td>
<td>3</td>
<td>2.5</td>
<td>3.581</td>
<td>excellent</td>
</tr>
<tr>
<td>-49</td>
<td>1300</td>
<td>Air</td>
<td>3</td>
<td>2.3</td>
<td>3.579</td>
<td>excellent</td>
</tr>
<tr>
<td>-53</td>
<td>1300</td>
<td>Air</td>
<td>3</td>
<td>2.5</td>
<td>3.571</td>
<td>opaque</td>
</tr>
<tr>
<td>-56</td>
<td>1300</td>
<td>Air</td>
<td>3</td>
<td>2.5</td>
<td>3.585</td>
<td>excellent</td>
</tr>
</tbody>
</table>
APPENDIX I

I. Results of spectrographic analysis of magnesia powder before and after pressing, and after annealing.

<table>
<thead>
<tr>
<th>Impurities</th>
<th>Before pressing, percent</th>
<th>After pressing, percent</th>
<th>After pressing, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.01</td>
<td>0.004</td>
<td>0.007</td>
</tr>
<tr>
<td>Al</td>
<td>0.03</td>
<td>0.005</td>
<td>0.003</td>
</tr>
<tr>
<td>Li</td>
<td>&lt; 0.005</td>
<td>0.2</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Ca</td>
<td>0.04</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe</td>
<td>0.002</td>
<td>0.002</td>
<td>0.003</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0008</td>
<td>0.001</td>
<td>0.0007</td>
</tr>
<tr>
<td>Na</td>
<td>0.05(?)</td>
<td>0.05(?)</td>
<td>--</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt; 0.002</td>
<td>&lt; 0.002</td>
<td>&lt; 0.002</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt; 0.002</td>
<td>&lt; 0.002</td>
<td>&lt; 0.002</td>
</tr>
<tr>
<td>Ba</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Sr</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Analysis performed by American Spectrographic Laboratories, San Francisco, California.

II. A surface area of $9 \pm 2 \text{ m}^2/\text{gm}$ for the magnesium oxide powder was determined using a Perkin-Elmo-Shell sorptometer, corresponding to a BET particle diameter of 0.19 $\mu$. 
III. Attempts were made to fabricate transparent specimens out of several commercially available reagent magnesium oxide powders. However, use of some of these powders did not consistently result in transparent specimens on annealing. Chemical analysis showed that these powders had significantly higher calcium and sodium concentrations. Preliminary electron microscope examination of these powders showed no significant differences in particle size or shape. Differences in impurity content may only be a symptom of the cause of differences in behavior and not in themselves the cause. More careful electron microscope work as outlined by Moodie and co-workers\textsuperscript{51} may give more insight into this problem.
APPENDIX II

Approximation of LiF-MgO eutectic

Reaction at eutectic on heating:

\[ \text{LiF}(c) + \text{MgO}(c) \rightarrow \text{LiF}(l) \cdot \text{MgO}(l) \]

Assumptions: 1) no or very little solid solution
2) ideal solution

At eutectic \( \Delta F = 0 = \Delta H - T \Delta S \), \( T = \frac{\Delta H}{\Delta S} \)

On melting:
\( \Delta H \text{ LiF} = 6.57 \text{ kcal/mole} \)
\( \Delta H \text{ MgO} = 18.5 \text{ kcal/mole} \)
\( \Delta S \text{ LiF} = 5.774 \text{ eu.} \)
\( \Delta S \text{ MgO} = 6.4 \text{ eu.} \)

\[ n = \text{ moles of MgO} \]
\[ \Delta H_t = 6.474 (1-n) + 18,500 n \]
\[ \Delta S_t = 5.774 (1-n) + 6,400 n + R \sum ni \ln ni \]

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \Delta H_t )</th>
<th>( \Delta S_t )</th>
<th>( \Delta T_t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>.99</td>
<td>6.594</td>
<td>5.8916</td>
<td>1119.2</td>
</tr>
<tr>
<td>.98</td>
<td>6.715</td>
<td>5.9813</td>
<td>1122.6</td>
</tr>
<tr>
<td>.97</td>
<td>6.835</td>
<td>6.0605</td>
<td>1127.8</td>
</tr>
<tr>
<td>.96</td>
<td>6.953</td>
<td>6.1327</td>
<td>1133.8</td>
</tr>
<tr>
<td>.995</td>
<td>7.075</td>
<td>5.8396</td>
<td>1118.9</td>
</tr>
</tbody>
</table>
Fig. 19  Eutectic temperature as a function of assumed eutectic composition.
APPENDIX III

Derivation of rate of densification porosity dependency for flow paths behaving as capillaries and channels.

Case I. Paths having circular cross sections with the radius being reduced as material is removed from the compact. According to Poiseuille's equation, the flow rate through the capillary is:

\[
\frac{dV}{dt} = \frac{\pi \Delta P R^4}{8 \eta}
\]

where 
- \( V \) = volume of material
- \( \rho \) = viscosity
- \( \Delta P \) = pressure drop along channel
- \( R \) = capillary radius
- \( l \) = capillary length

For a flow path shrinking radially, apparent porosity = \( \alpha R^2 \) if path length remains constant with time.

\[ \therefore \frac{dV}{dt} = \alpha (\text{Porosity})^2 \]

\[ \frac{d\rho}{dt} \alpha \frac{dV}{dt} \alpha (\text{Porosity})^2 \]

Case II. Paths having a rectangular cross section with only one dimension \( X \) changing with time.

Poiseuille's equation derived for a channel of constant length \( l \), and width \( a \), but variable height \( X \) is

\[
\frac{dV}{dt} = \frac{2a \Delta P X^3}{3 \eta l}
\]
porosity = \alpha x

\therefore \quad \frac{dV}{dt} \alpha (\text{Porosity})^3

\frac{dp}{dt} \alpha \frac{dV}{dt} \alpha (\text{Porosity})^3
REFERENCES


38. M. W. Benecke, private communication.


41. Technique developed in this laboratory by Prof. R. M. Fulrath.


This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.