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DEVELOPMENT AND EVALUATION OF TRANSPARENT MAGNESIUM OXIDE

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ABSTRACT

The densification parameters for hot pressing MgO to a theoretically dense polycrystalline body has been studied. Two experimental approaches were followed; using pure MgO powders, and pressing mixtures of MgO plus small amounts of LiF. In the former case specimens having 60% total transmission (adequate for in line observation) were obtained by very precise control of the fabrication conditions followed by a long term anneal in hydrogen. The MgO - LiF process yielded thin specimens having 85% total transmission in the visible, and 3/8 inch thick specimens possessing a maximum transmission of 70%. A post hot pressing anneal at temperatures greater than 1200°C and heating rates less than 28°C/hour were required to produce maximum transparency. Evidence obtained by grain growth studies, weight loss experiments and lattice parameter determinations suggest that the densification mechanism for this process was pressure-enhanced diffusion through a solid solution grain boundary layer and a grain boundary phase. At temperatures above the melting point of LiF a pressure-enhanced liquid phase sintering mechanism probably operates.

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I. INTRODUCTION

The problem of hot pressing theoretically dense MgO has been the subject of this program. The material was characterized and judged by its transmission in the visible spectra. Two experimental approaches were followed toward realizing this goal. The first was an effort to optimize the hot pressing parameters in fabricating the desired material from pure fine particle size MgO. Vasilos and Spriggs[1] have produced specimens approaching transparency by this process, and they believe the densification mechanism to be one of pressure enhanced diffusion. The current program has resulted in specimens of greater transparency by this process, and post hot pressing anneals were shown to be effective in further improving transparency. The second experimental approach incorporated a discovery made by Atlas[2] and recently studied by Rice[3] and Benecke[4] that lithium compounds enhance both the sintering and pressure sintering densification rate of MgO. Benecke[4] suggested that the densification mechanism for pressure sintering is either plastic flow or activated surface pressure enhanced diffusion. The present program utilized additions of up to 2 weight percent of various lithium compounds to produce, under optimum conditions, specimens having 85% transmittance in the visible spectra. New insight into the densification mechanism has been gained, and it has been found that the conditions for the post pressing anneal are a critical part of the overall process.

II. EXPERIMENTAL

A. Apparatus

Much of the initial work was conducted in a small scale vacuum (1×10^{-3} to 1×10^{-5} mm Hg) hot pressing apparatus which is illustrated in Figure 1. Some of the initial pressings were conducted in air in an apparatus similar in principle to that illustrated.

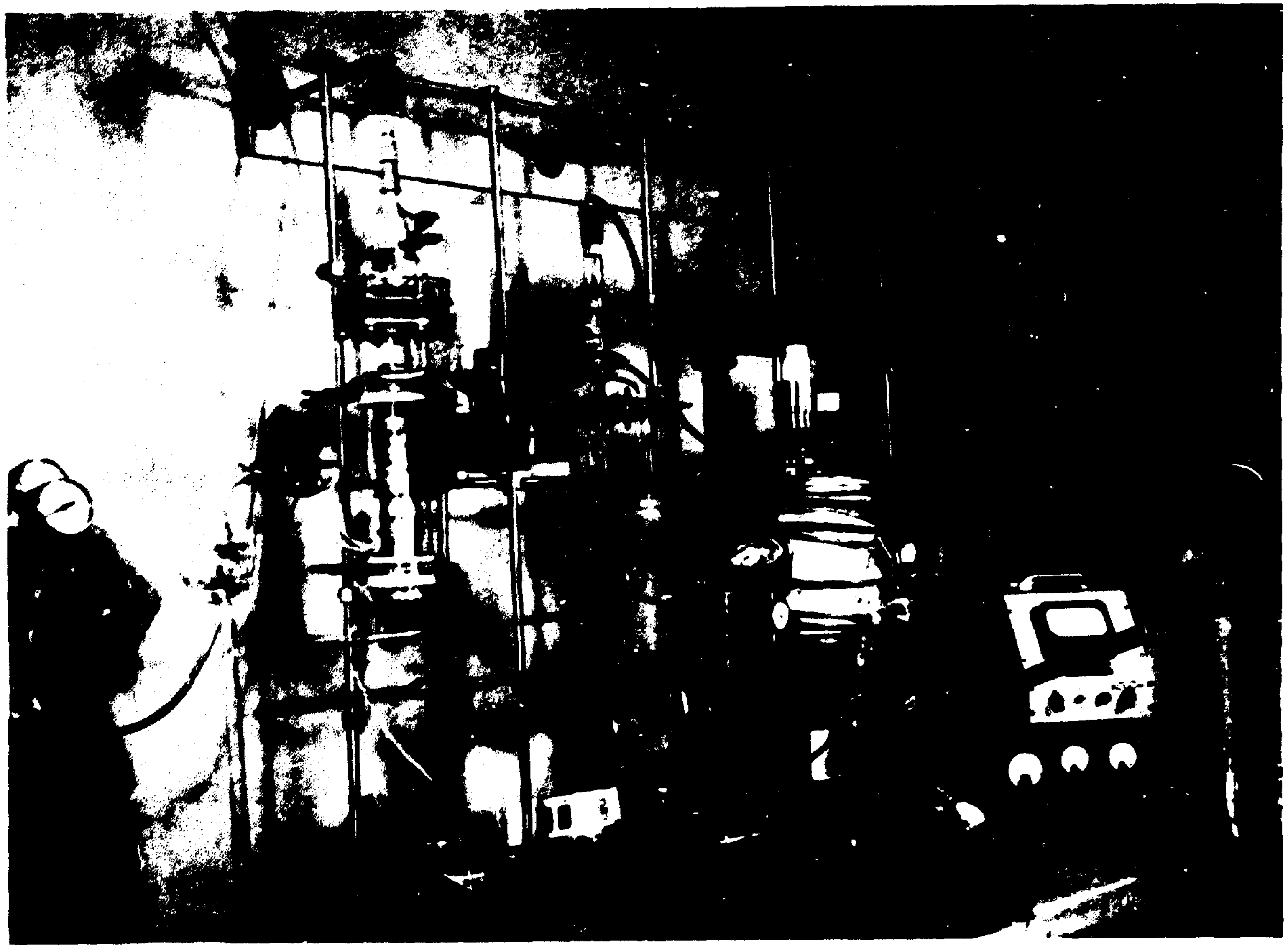

Figure 1 Vacuum High Pressure Sintering Apparatus (40,000 Psi)
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Most fabrication runs for billets larger than 3/4 inch diameter were conducted in a large vacuum chamber shown in Figure 2. Somewhat lower vacuums (3×10^{-2} to 2×10^{-1}) were maintained in this apparatus. Air pressure sintering or press forging runs were conducted in a large graphite furnace illustrated in Figure 3.

Graphite was the hot pressing die material utilized for all but ~10% of the runs, and pressure was limited to 6000 psi. Some of the small scale pressing used SiC punches within a graphite die, and in some cases a press forging configuration (no die wall restriction of lateral movement) developed pressures up to 40,000 psi utilizing W, Al_2O_3 or SiC punches. An all metal die system was constructed from Sylvania MT-104 molybdenum alloy (TZM), and was a cylinder 6 inches O.D., by 3 1/8 inches I.D. by 6 1/2 inches long. A single action plunger was constructed from the same material. The die rested on a 6 inch diameter by 3 inches high nickel base alloy (Waspaloy), and it also acted as a stationary bottom plunger which was in contact with the MgO compact. With this system, hot pressings were conducted up to 20,000 psi at 810°C in vacuum.

B. Starting Powders

Hot pressings were conducted with four grades of MgO powder which have the following characteristics:

		Particle Size, Angstroms		
Grade	**Purity**	**Minimum**	**Maximum**	**Average**
Fisher Electronic Grade	99.6	100	650	400
Baker A.R. Grade	99.6	165	1300	800
Baker and Adamson Reagent Grade	99.3	750	2500	1050
Mallinckrodt Analytical Grade	99.4	700	4000	1000

Figure 2 Four Hundred Ton Press With Vacuum Pressure Sintering Chamber Installed
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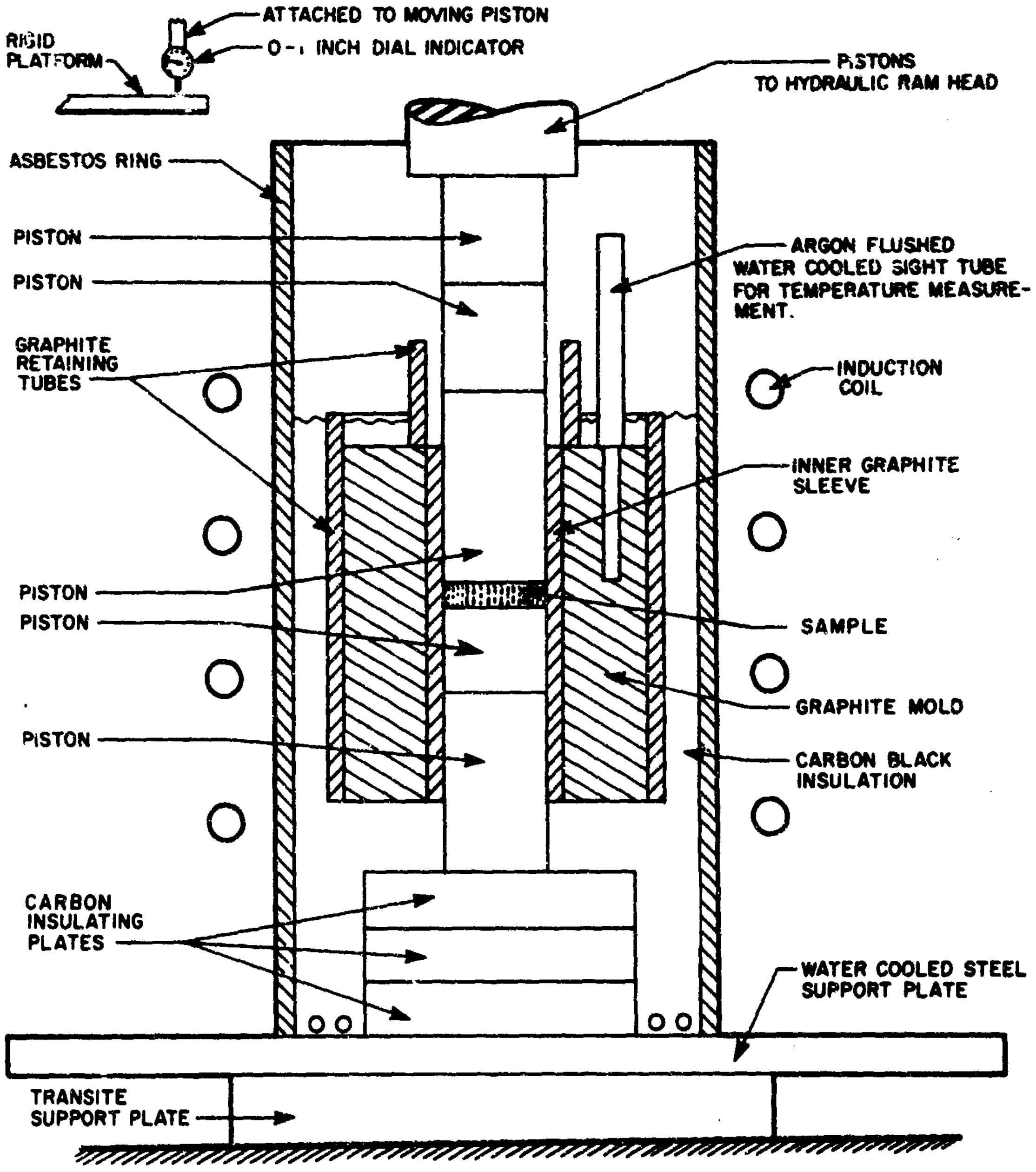

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Figure 3 Large Scale Graphite Hot Pressing Apparatus

The lithium compound additions were made from reagent grade powders of particle size less than 40 µ. The MgO and additive powders were blended in a Waring Blender using ethyl alcohol as a medium. The alcohol was removed through evaporation while the slurry was being agitated.

C. Annealing

Many of the initial anneals were conducted in manually controlled Pt or Mo element furnaces using vacuum, air, oxygen, and hydrogen atmospheres. Controlled heating rate anneals were accomplished in air using a Kanthall furnace programed with a Wheelco Automatic Cam Following Controller.

III. RESULTS AND DISCUSSION

A. Pure MgO

1. Pressure sintering

Ten small scale press forgings (unrestricted lateral deformation) of Fisher Electric Grade MgO were conducted under the conditions listed in Table I. Both SiC and Al_2O_3 punches were employed to press forge 1" diameter discs. Very dense pieces were produced by this process, but they could be considered translucent at best. There is a density gradient in the normal press forged piece where the outer 1/4 of the radius varies from 99.9% dense to ~50% dense. If a forged product was to be utilized, this outer rim would be removed. Sample number 1106 was hot pressed in a graphite die under what had been discovered from a previous study[1] to be the optimum condition for this process, and was uniformly translucent. The densification curve for this pressing is shown in Figure 4 along with curves for doped specimens, and these will be compared in a subsequent paragraph.

A total of 21 large scale hot pressing runs were made in an attempt to obtain 3", 4", and 5" diameter pieces of transparent MgO, using pure MgO powders previously[1] found favorable for obtaining translucent MgO compacts.

TABLE I

Fabrication Conditions for Hot Pressing Pure MgO

Sample Number Small Scale (3/4" dia.)	Temperature	Time (min.)	Pressure (psi)	ATM.	Relative Density
1029	1100	20	6000	160 μ vac.	
1030	1300	20	4000	10 μ vac.	99.9
1031	1300	15	6000	30 μ vac.	99.9
1032	1200	60	6000	3 μ vac.	99.9
1033	1000	60	6000	8 μ vac.	
1034	1100	3	6000	Air	
1035	1100	65	6000	Air	99.8
1036	1050-1200	30	6000	Air	99.4
1037	1200	20	6000	Air	99.8
1038	1100	40	6000	10 μ vac.	99.9
1106	1150	60	6000	Air	99.9
Large Scale (3-5" Dia.)					
Mg-1	1250	260	4600	Air	99.0
Mg-2	1400	300	4600	Air	99.5
MgV-2	1200	250	4800	Vac.	99.9
MgV-3	1250	240	4800	Vac.	99.9
MgV-4	1320	300	4900	Vac.	99.9
Mg4-1	1425	120	5900	Air	99.8
Mg4-2	1400	180	6000	Air	99.9
Mg4V-1	1200	180	6000	Vac.	99.9
V-30	1200	180	6000	Vac.	99.9
V-39	1100	330	6000	Vac.	99.9
V-41	1200	180	6000	Vac.	99.8
FM-13	1720	35	5100	Air	99.9
FM-14	1700	80	6000	Air	99.9
FM-15	1300	60	7300	Air	99.0
FM-16	1425	120	8500	Air	99.0
FM-17	1400	10	5200	Air	98.0
FM-19	1200	60	6000	Air	98.5
FM-20	1250	120	6000	Air	99.2
FM-22	1600	100	8500	Air	99.9
FM-23	1500	20	9000	Air	99.8
FM-24	1250	150	10000	Air	99.0

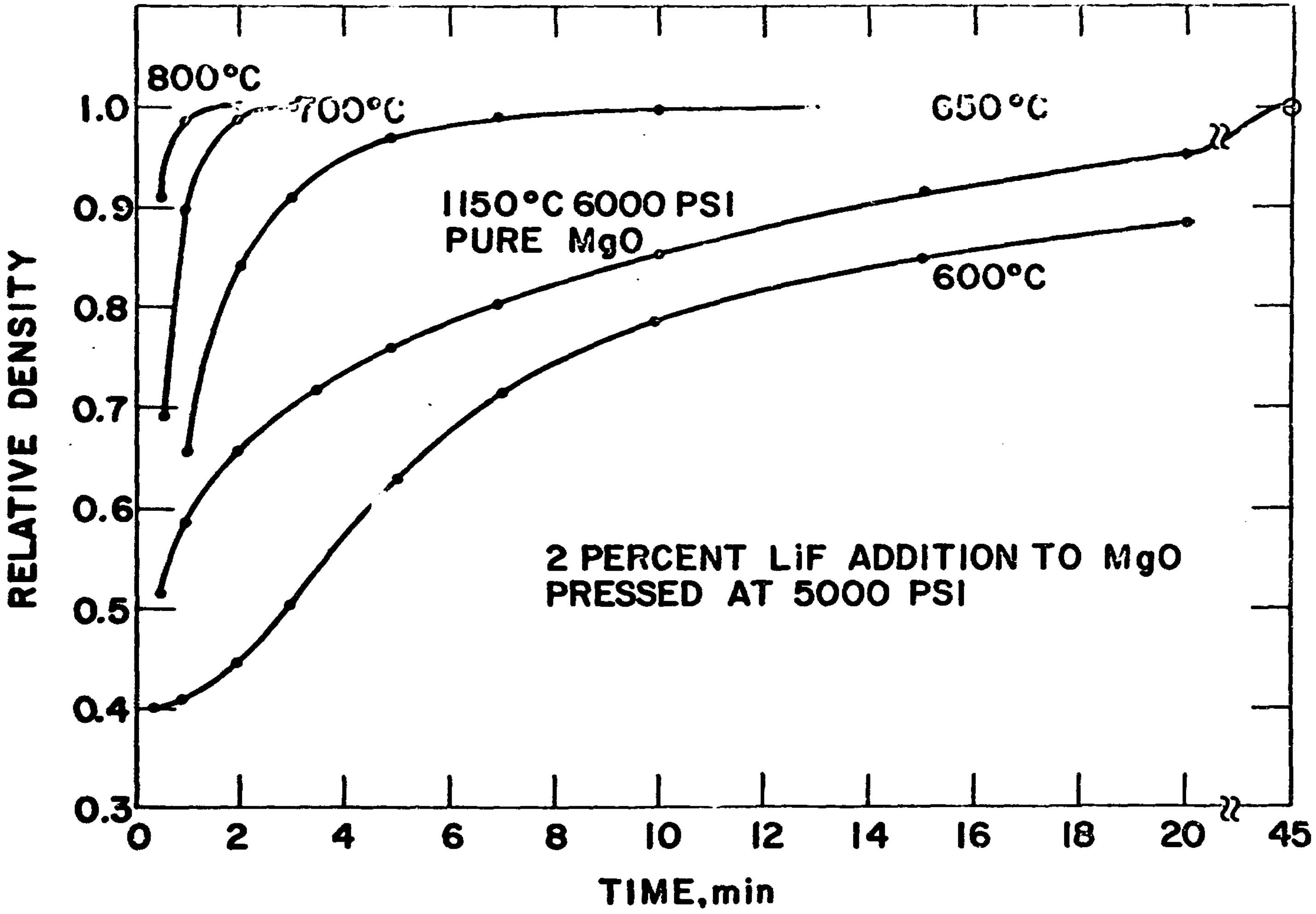

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Figure 4 Densification Curves for 2% LiF - 98% MgO as a Function of Temperature and for 100% MgO at 1150°C

These runs, listed in Table I, encompassed three approaches: 1) vacuum hot pressing, 2) hot pressing in air, and 3) press forging in air. It was found that higher temperatures were necessary to obtain a non opaque specimen when either of the last two methods were used. Five of the runs made under the conditions listed below yielded compacts of very high translucency (several of these could be considered transparent) in the as pressed state (V-30, 39, Mg 4V-1, FM-14, 22).

Pressure sintering of pure MgO proved to be very sensitive to the starting powder particle size, shape, and size distribution. The Fisher and Baker grades of powders described in Section II B had been used previously[1] for extensive densification experiments. The Fisher Electronic Grade MgO possesses the best powder properties for high densification rates. However, there are subtle variations from lot to lot in this powder which effect the densification rate. Weight loss data on the powder shows a 1.3% loss occurring between room temperature and 400°C and 0.2% loss between 400°C and 600°C. The initial loss was probably H_2O. There is a strong possibility that the high temperature loss was CO_2 as the MgO is derived from $MgCO_3$.

2. Post pressing anneal

It has been shown that annealing the pure MgO product affects the visible spectra transmission properties, although this is very sensitive to atmosphere. Air, vacuum or oxygen are completely unsatisfactory because the specimen always becomes more opaque, while specimens annealed in hydrogen undergo microstructural changes which improves light transmission. The annealing treatment generally employed was 160 hours at 1250°C. Five anneals were conducted under these conditions, and the optical properties of the most transparent specimens are given in Section C. Considerable grain growth also takes place during this anneal (from 5 to 40 microns). The degree of H_2 solubility and H_2 diffusion rates in the MgO lattice are unknown, but it is possible that they are high. The mechanism by which the H_2 anneal sweeps away entrapped gases is thought to be worthy of a basic study.

The opacification of MgO during oxygen or air anneals suggested that dissolved or entrapped gases were expanding the pore volume. An effort was made to detect gaseous species being evolved from the surface by annealing MgO in a high vacuum (10^{-8} mm Hg) furnace which was equipped with an omegatron mass spectrometer. The instrument was capable of qualitative analysis of non-condensable species between mass 12 and 44. Background determinations were made with the tungsten filament heater alone and heated single crystal MgO. Vacuum hot pressed MgO (graphite dies) was annealed as high as 1665°C (temperature uncorrected), with the results shown in Table II.

TABLE II

Gas Evolution in Hot Pressed MgO

Mass No.	Probable Molecular Species (specie underlined is most probable)	W Filament	Intensity of Impurity in amps x 10^{10} W Filament + MgO Single Crystal /	\	W Filament + Hot Pressed MgO
44	CO_2	.16	.05	.03	.05
32	O_2	-	.03	-	-
28	CO, N	.85	.36	.31	.64
18	H_2O	.40	.15	.06	.10
17	OH	.10	.05	.04	Trace
16	$\underline{CH_4}$, O	.05	.02	.05	-
14	CH_2, $\underline{N}$	.20	.05	.07	.09
12	C	Trace	-	-	-
Temperature (°C)		1675	1645	1675	1650
Time at Temperature		~5 min.	~5 min.	2 hrs.	2 hrs.
Number of times filament heated above 1600°C		2	3	4	5
Weight of Specimen			0.34 grams		0.24 grams

The W filament gave the highest relative concentrations of impurities. However, it should be noted that this was only the second time at elevated temperature for this filament and the reported results were taken only a few minutes after maximum temperature was obtained. The most meaningful conclusions can be made by comparing the results of runs 4 and 5 which have similar time-temperature histories. It appears that measurable quantities of H_2O, CO (or N) and CO_2 are being evolved from the vacuum hot pressed specimen. This specimen was opaque after this anneal. Previously, the atmosphere of a graphite die was sampled during heating and analyzed by mass spectroscopy[8], and it was concluded that a CO/CO_2 atmosphere was present during hot pressing in a graphite die. The present results indicate that these gases are entrapped and/or dissolved in the MgO structure. As they are entrapped at high temperature under pressure, it is suggested that reheating under the absence of pressure would allow these gases to expand. This opacification might be taken as evidence for a lack of solid solubility of these gas species in the MgO lattice.

B. MgO With Lithium Additions

1. Pressure sintering

The pressure sintering experiments conducted on 1/2 - 1 inch diameter specimens are listed in Table III, and those conducted on 3 - 4 inch specimens are listed in Table IV (all vacuum pressed). The hot pressed specimens were translucent, but it was found that a post pressing anneal greatly improved their optical transmission. The anneal was found to be essential and a qualitative judgment of the optical quality of the heat treated specimens is also included in the above mentioned tables. In the fabrication step pressure was usually applied after the maximum temperature was reached, but the exceptions to this can

TABLE III

Fabrication Conditions for Small Scale Compacts Containing Lithium Compounds

Sample Number	Composition MgO + % x	Temperature °C	Time (min.)	Pressure (psi)	Atmosphere	Relative Density	Post Annealing Optical Quality
PF 1046	2% LiF	800	20	6000	Ambient	100	Ex
PF 1048	¼% LiF	800	10	6000	6 μ vac.	90	O
PF 1049	2% LiF	800	15	6000	1 μ vac.	100	-
PF 1069	2% LiF	800	15	6000	45 μ vac.	100	Ex
1091	2% LiF	800	5	5000	10 μ vac.	98.0	O
1092	2% LiF	700	60	5000	3 μ vac.	98.0	O
1093	2% LiF	750	10	5000	8 μ vac.	96.0	O
1094	2% LiF	800	10	5000	18 μ vac.	98.8	O
1095	2% LiF	800	10	5000	10 μ vac.	100	Ex
1096	2% LiF	800	7	5000	12 μ vac.	100	Ex
1097	2% LiF	750	10	5000	4 μ vac.	100	Ex
1098	¼% LiF	800	30	5000	8 μ vac.	60.0	O
1099	2% LiF	800	20	2000	Ambient	99.1	Ex
1100	¼% LiF	900	30	5000	30 μ vac.	100	Ex
1101	2% LiF	700	5	5000	Ambient	100	Ex
1102	2% LiF	800	30	5000	Ambient	88.0	O
1103	2% LiF	650	15	5000	Ambient	100	Ex
1104	¼% LiF	1000	15	5000	15 μ vac.	100	Ex
1105	2% LiF	1000	10	5000	Ambient	100	Ex
1107	2% LiF	700	10	5000	10 μ vac.	100	Ex
1108	2% LiF	750	18	5000	15 μ vac.	100	Ex
1109	2% LiF	600-800	15	5000	Ambient	100	Ex
1110	2% LiF	800	5	5000	8 μ vac.	100	Ex
1111	2% LiOH	800	19	5000	Ambient	70.5	O
1112	1% LiF	750	5	5000	Ambient	100	Ex
1113	⅓% LiF	800	3	5000	Ambient	99.5	Ex
1114	⅔% LiF	750	5	5000	Ambient	99.8	Ex
1115	2% LiC_2O_4	800	4	5000	Ambient	99.4	Ex
1116	2% LiCl	800	15	5000	Ambient	99.2	O
1117	2% LiC_2O_4	800	15	5000	6 μ vac.	100	Ex
1118	2% LiBr	800	15	5000	Ambient	52	O
1123	1% LiF	500-1000	28	4000	30 μ vac.	100	TP

TABLE III (Cont'd)

	Sample Number	Composition MgO + %x	Temperature °C	Time (min.)	Pressure (psi)	Atmosphere	Relative Density	Post Annealing Optical Quality
PF	1165	1.6 % LiF	825	10	50,000	0.5 µ vac.	100	TP
PF	1166	1.6 % LiF	825	55	15,000	0.04 µ vac.	100	TP
	1167	1.6 % LiF	950	3	5,000	1 µ vac.	99.8	O
PF	1169	1.6 % LiF	825	3	15,000	0.06 µ vac.	100	TP
	1172	1.6 % LiF	825	3	15,000	0.1 µ vac.	98	
PF	1173	1.6 % LiF	825	12	15,000	0.3 µ vac.	100	-
PF	1174	1.6 % LiF	825	6	15,000	0.09 µ vac.	98	
PF	1175	1.6 % LiF	825	7	40,000	0.04 µ vac.	99	
	1179	1.6 % LiF	950	65	5,000	0.07 µ vac.	99.8	TP
	1181	1.6 % LiF	900	1	5,000	0.3 µ vac.		
	1182	1.6 % LiF	500-1000	180	5,000	0.3 µ vac.	100	TP
	1184	1.6 % LiF	1000	30	5,000	1 µ vac.	100	
	1185	1.0 % LiF	100-1000	155	4,000	0.16 µ vac.	99.5	-
	1186	1.0 % LiF	480-1000	24	4,000	0.45 µ vac.	98.4	-
	1187	1.0 % LiF	520-1000	78	4,000	0.17 µ vac.		-

PF = Press forged

HP = Hot pressed in graphite dies

TP = Transparent

TL = Translucent

O = Opaque

Ex = Sectioned for experimental annealing treatments

TABLE IV

FABRICATION CONDITIONS FOR LARGE COMPACTS OF MgO + LiF ADDITIONS

(TP = transparent, TL = translucent, and O = opaque)

Sample	Dimensions	Powder Type + 1% LiF	Temperature °C	Time at Maximum Pressure (min)	Pressure psi	As Pressed Density	Post Annealed Optical Quality
Mg VF-2	3" x 3/8"	Fisher + 2%	820	30	5800		Ex
Mg VF-3	3" x 3/8"	Baker + 2%	820	34	5700		Ex
Mg VF-4	3" x 3/8"	Baker + 2%	820	78	5900		Ex
Mg VF-5	3" x 3/8"	Baker + 2%	1000	15	4200		Ex
Mg VF-6	3" x 3/8"	Baker + 2%	820	60	5900		Ex
Mg VF-7	3" x 3/8"	Baker + 2%	1000	20	5900		Ex
Mg VF-8	3" x 3/8"	Baker + 2%	1200	65	5700		Ex
Mg VF-9	3" x 3/8"	Baker + 2%	820	105	5900		Ex
Mg VF-10	3" x 3/8"	Baker & Adamson + 2%	850	185	5000		Ex
Mg VF-11	3" x 3/8"	Baker + 2%	850	183	5200		Ex
Mg VF-12	4" x 3/8"	Baker + 2%	850	85	5200		Ex
Mg VF-13	4" x 1/2"	Baker + 2%	850	30	4300		TL
Mg VF-14	2 3/4" x 3/8"	Mallinckrodt + 1%	1000	30	5000		Not annealed
Mg VF-15	2 3/4" x 1/2"	Mallinckrodt + 1%	920	5	5000		O
Mg VF-16	2 3/4" x 3/8"	Mallinckrodt + 1%	1000	5	4000		TL
Mg VF-17	3" x 1/2"	Mallinckrodt + 1%	1000	10	3500		O
Mg VF-18	4" x 3/8"	Mallinckrodt + 1%	1000	5	2400		TL
Mg VF-19	3" x 3/8"	Mallinckrodt + 1%	1100	5	2900		TL
Mg VF-22	4" x 3/8"	Baker + 1.6%	900-925	45	3500		TP
Mg VF-25	4" x 3/8"	Baker + 1.6%	850	50	5000		TL
Mg VF-26	4" x 3/8"	Baker + 1.6%	840	100	5000		TL
Mg VF-27	4" x 3/8"	Baker + 1.6%	845	95	5000		TL
Mg VF-28	4" x 3/8"	Baker + 1.6%	820-1010	305	5000	99.5	TP
Mg VF-29	4" x 3/8"	Baker + 1.6%	825-930	115	5000	97.0	TL-TP
Mg VF-30	4" x 3/8"	Baker + 1.6%	850-900	140	5000	97.0	TL
Mg VF-31	4" x 3/8"	Baker + 1.6%	845-1030	300	5000		
Mg VF-32	4" x 3/8"	Baker + 1.6%	820-1000	180	5000	99.0	TP
Mg VF-33	4" x 3/8"	Baker + 1.6%	850-1000	345	5000		TP
Mg VF-34	4" x 3/8"	Baker + 1.6%	830-1000	450	5000	99.5	TP
Mg VF-35	4" x 3/8"	Baker + 1.6%	960	5	5000	99.5	TL
Mg VF-36	4" x 3/8"	Baker + 1.6%	950	15	5000	99.5	TL
Mg VF-37	4" x 3/8"	Baker + 1.6%	850-1000	250	6050		TP
Mg VF-38	3 1/8" x 5/16"	Baker + 1.6%	750	10	14300		TL
Mg VF-39	4" x 3/8"	Baker + 1.6%	850-1000	360	6700		TP
Mg VF-40	4" x 3/8"	Baker + 1.6%	850-1000	225	6500		TP
Mg VF-41	4" x 3/8"	Baker + 1.6%	1000	105	6700		
Mg VF-43	3 1/8" x 3/8"	Baker + 1.6%	810	30	18800		
Mg VF-42	4" x 3/8"	Baker + 1.6%	850-1000	255	6100		

be identified by the dual temperature notation (pressure was applied at the low temperature). Some specimens were fabricated under conditions where they were free to expand laterally during densification, and these are denoted by PF (press forged).

A number of survey hot pressings are included in Table III which were designed to determine the effectiveness of various lithium compounds as densification aids, and Figure 5 illustrates the relative effectiveness of LiF, LiBr, LiOH, and $LiCrO_2$. All pressings were conducted at 800°C and 5000 psi with the exception of the 1% LiF addition which was pressed at the same pressure, but 750°C. Pure MgO would follow a curve quite similar to that shown for the 1/4% LiF addition. It can be concluded that lithium fluoride is a very effective MgO densifying agent when it is present in concentrations of 1/2% or greater. Lithium oxalate appears to be nearly as effective, while LiOH and LiBr are quite ineffective as densifying agents. The densification mechanism forwarded by Atlas[2] was that Li+ occupied grain boundary sites leading to high defect concentrations at these regions which enhanced the mobility of the rate determining MgO ion. This mechanism appears to be invalid or incomplete since several lithium compounds showed no significant densification enhancement.

Specimens were hot pressed under conditions where atmosphere was the only variable; the densification rate was constant for vacuum and ambient. There was apparently some difference in internal chemistry of the ambient prepared MgO since identical annealing treatments failed to produce compacts of comparable transparency. Consequently, after the initial phase of the work all experiments were conducted in vacuum.

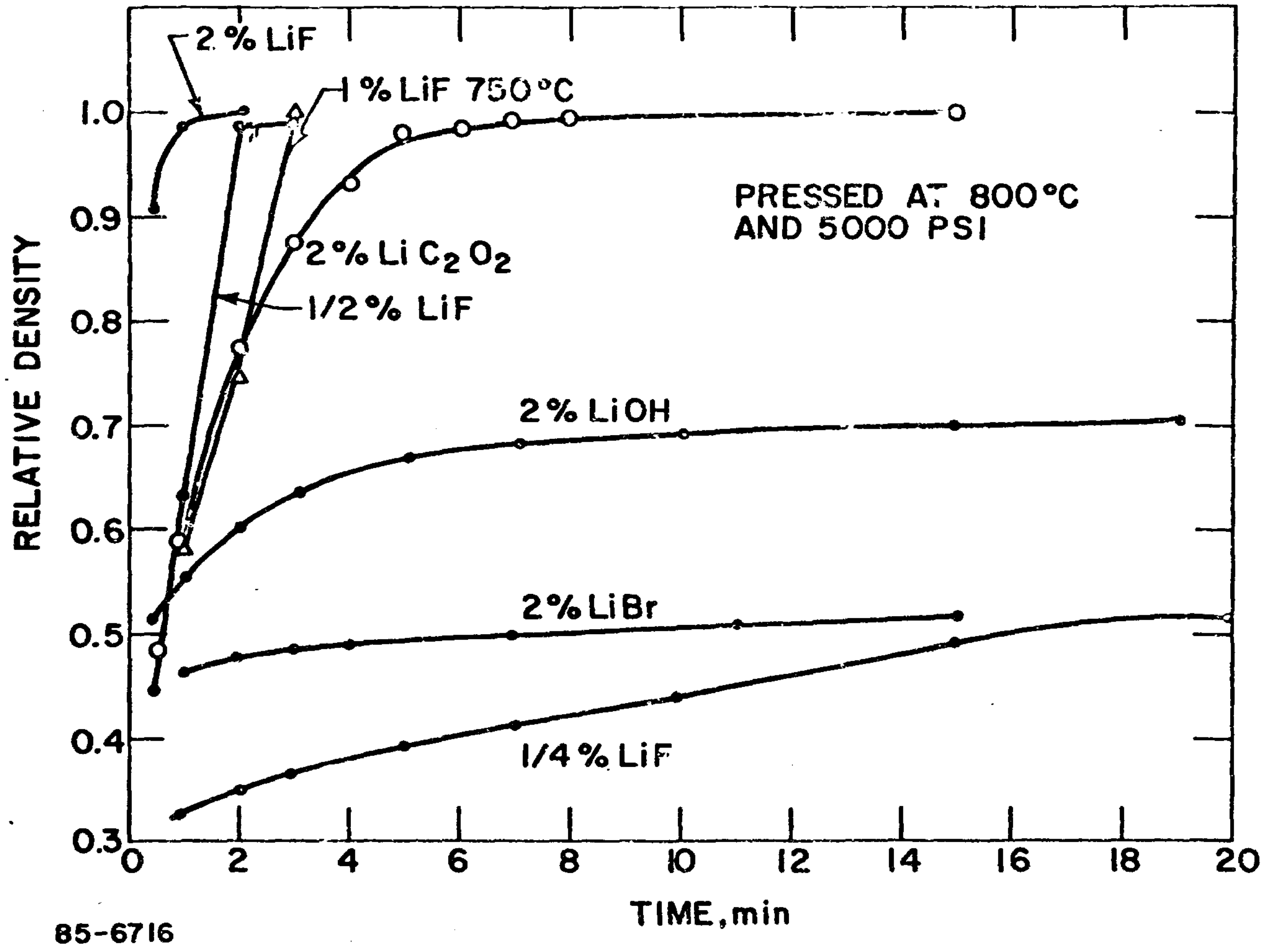

Figure 5 Densification Curves for the Hot Pressing of Various Lithium Compound Additions to MgO.

Figure 4 shows the densification curves of 2% LiF additions to MgO at several temperatures. To illustrate the effectiveness of the additive in the densification process, one curve is presented for pure MgO pressed at a higher temperature and pressure. It appears that 800°C is a sufficient temperature to assure rapid densification using the additive. Two investigators[3,4] hot press with LiF additions at temperatures as high as 1000°C, and it was discovered during this investigation that these relatively high temperatures (900-1000°C) were necessary not for densification, but for a pressurized phase refining process.

Compositions of MgO powder containing from 4.8% to 50% by weight of LiF were blended to provide material for studies on possible LiF loss during fabrication. X-ray studies of peak intensities of these powders and of hot pressed billets made from these powders were made and are presented in Table V as a ratio of the measured crystallographic reflections. At a hot pressing temperature 50°C below the LiF melting point, run (2) showed a LiF loss while run (3) exhibited an unchanged LiF/MgO ratio. (It is thought that an error in reading temperature may be the cause of this inconsistency.) Hot pressing (1) conducted at 920°C (50°C above the melting point of LiF) showed an apparent loss of LiF from 16.7% to ~5% which demonstrates that an applied pressure does not limit the volatilization of LiF, and that significant LiF loss occurred in hot pressing above the melting point of LiF.

Many billets developed small pockets of porosity either in the hot pressing process or during annealing, and variations of time, temperature and pressure within the range attainable with graphite were employed in an attempt to eliminate these pockets. (The porosity was not uniformly dispersed in a manner leading to general opacification, but it was limited to nests of high

TABLE V

Diffraction Intensity Ratios - MgO/LiF for Various Crystallographic Planes

A. Blended Powders

Composition (wt. % LiF)	(111)	(200)	(220)	(420)	(422)
4.8	2.1	29	38	55	>60
9.0	1.5	15	18	>25	>20
16.7	0.8	8.0	11	22	10
26.8	0.46	4.3	5.0	6.7	5.7
50	0.18	1.7	2.2	3.0	3.5

B. Hot Pressed Powders

						Estimated LiF Content
16.7(1)	7.0	87	230	30	40	<5%
26.8(2)	0.59	5.9	7.5	16	12	20-22%
50(3)	0.19	1.6	2.2	2.2	3.0	≅50%

(1) Hot pressed at 920°C, 10 minutes, 4000 psi

(2) Hot pressed at 820°C, 40 minutes, 4000 psi

(3) Hot pressed at 820°C, 60 minutes, 4000 psi

porosity spaced 0.5 - 3 mm apart). Both weight loss and x-ray studies showed that LiF was lost during the hot pressing process, so it appeared that the pore nests might be associated with LiF volatilization. Run number 1167 and run number 1179 were pressed for minimum time (3 minutes) and extended (65 minutes) times at 950°C respectively, and resulted in as pressed specimens of equal density. Annealing under the best conditions developed in this program resulted in an opaque specimen for 1167 and a specimen of high transparency (Figure 6) for 1179. Similar results were noted for large billets; MgVF 15-19 which were processed for a short time in the 900-1100°C range, were not transparent while MgVF-22, and MgVF-28 through MgVF-34 approached good transparency after heat treatment. It is hypothesized that the LiF vapor pressure is high enough to cause porosity generation during the annealing step; therefore the long soak under an applied pressure removes a large fraction of the free LiF phase while insuring intimate MgO grain to grain contact.

Seven press forging runs were conducted at pressures between 15 - 50 kpsi (Table III). Most of these specimens were very dense and annealed to a transparent body, but several cracked during annealing; presumably a result of residual strain from forging. Two hot pressings were conducted in the 3 inch diameter TZM system, and only one of these (Mg VF-38) was annealed; the finished product was again translucent indicating that LiF must be volatilized while pressure is applied in order to insure a transparent specimen upon annealing. It was thought that high pressure hot pressing would provide a very fruitful area for research in this system.

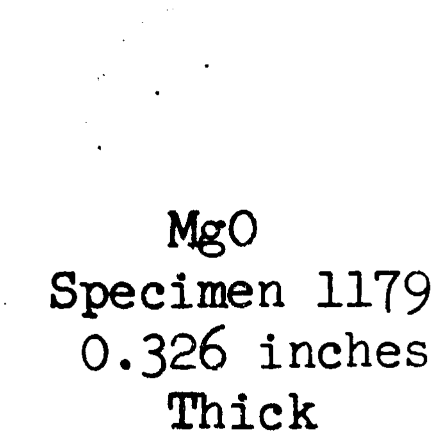

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Figure 6 Run Number 1179 Showing High Transparency in Thick Specimen

2. Densification mechanisms

The mechanisms by which LiF could enhance the hot pressing densification rate of MgO are briefly summarized as follows:

a. The additive could inhibit grain growth thereby allowing MgO to densify by a lattice diffusion mechanism without entrapping porosity within grains.

b. Second phase or solid solution grain boundary films could be formed with the MgO - LiF components. Mg^{+2} or O^{-2} ions may possess increased diffusion rates in these solid phase grain boundary regions thereby increasing densification rates by a diffusion mechanism.

c. LiF or a LiF - MgO eutectic composition may form a liquid phase which would promote densification by the transfer of MgO ions from region of high to low chemical potential via the liquid phase. Diffusion is much more rapid in liquids than in solids hence densification rates are high.

d. Densification could occur by plastic flow with MgO providing a lubricating film which allows MgO grains to become aligned for slip on the $\{110\}$ $\langle 110 \rangle$ preferred slip system.

Benecke[4] has investigated densification mechanisms in this system, and he suggests either mechanism (b) or (d) as the most likely possibilities. His conclusions, however, were based on evidence against mechanism (a) and (c) rather than evidence for his favored mechanisms. He recognized this point and recommended that the work be continued. Several studies in this program have answered some of the questions about possible densification mechanisms, and these studies are described in the following three sections.

a. Grain growth

A knowledge of grain growth during the hot pressing operation was thought to be particularly important for deciding whether or not a plastic flow mechanism (d) operated. Grain sizes were determined by electron microscopy replica techniques for the hot pressings summarized in Table VI.

TABLE VI

Process Conditions for Grain Growth Study on Vacuum Hot Pressed MgO + 2% LiF

Specimen Number	Pressure (psi)	Time (min)	Temperature °C
MG VF-2	5800	30	820
Mg VF-4	5900	78	820
Mg VF-9	5900	105	820
Mg VF-11	5200	183	850
Mg VF-3	5150	320	850

The inclusion of runs Mg VF-11 and Mg VF-3 was thought to be valid as the increased temperature was somewhat counteracted by lower pressures and the grain sizes increased in the expected manner (Figure 7).

The driving force for grain growth whether it occurs by solid state diffusion or via a liquid phase is the lowering of chemical potential; this is proportional to the radius of curvature of a grain size and therefore it is portional to the grain diameter. The rate of grain growth is therefore inversely proportional to the grain diameter giving

$$dD/dt = k/D \qquad (1)$$

which, upon integration becomes,

$$D - D_o = k' t^{\frac{1}{2}} \qquad (2)$$

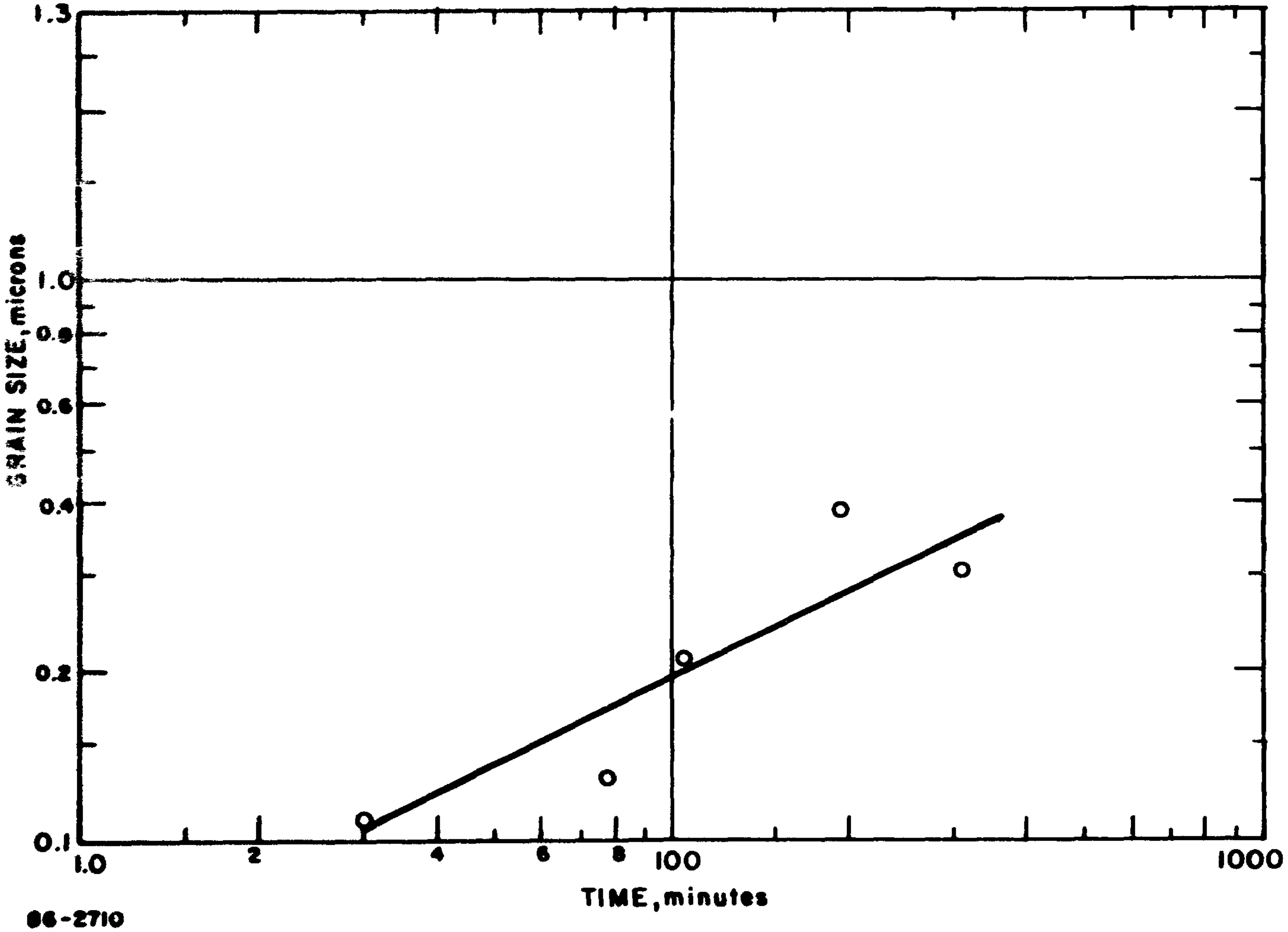

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Figure 7 Grain Growth During Hot Pressing of MgO + 2% LiF at 820° C where D_o is the grain diameter (in microns) at time, t, equal to zero and k' is a constant. Although considerable scatter exists, the data adequately fits relation (2) with the following equation

$$D = 1.94 \times 10^{-2} t^{\frac{1}{2}} \qquad (3)$$

and demonstrates that grain growth takes place at the predicted rate.

Electron microscopy also revealed a grain boundary film in specimen Mg VF-9 (Figure 8) used in this grain growth study, and a clearer example of this film is shown in Figure 9 of sample Mg VF-5 hot pressed at 1000°C for 15 minutes. The grain growth data and the evidence for a LiF or LiF-MgO grain boundary film suggest that Mg^{+2} and O^{-2} are diffusing to regions of low chemical potential through this film and apparently have extremely high difucivities at 820°C.

b. Solid solubility

The grain growth kinetics and the microscopic evidence for a grain boundary film suggests that a finite solubility exists between LiF and MgO. Benecke[4] conducted DTA studies on mixtures of these materials and he detected no liquid formation below the melting point of LiF (870°C). An X-ray diffraction lattice parameter study was conducted to determine if direct evidence (other than grain growth) could be obtained for solid solubility.

Diffractometer scans were made on billets containing various amounts of LiF and hot pressed at 820°C for 60 minutes (50°C below the melting point of LiF), and lattice parameters were calculated from these (Table VII). Although some discrepencies appear in the constant variation of a_o values (possibly due to inadequate mixing, LiF volatilization or experimental scatter, the values reveal an expansion of the LiF lattice accompanied by a contraction of the MgO lattice.

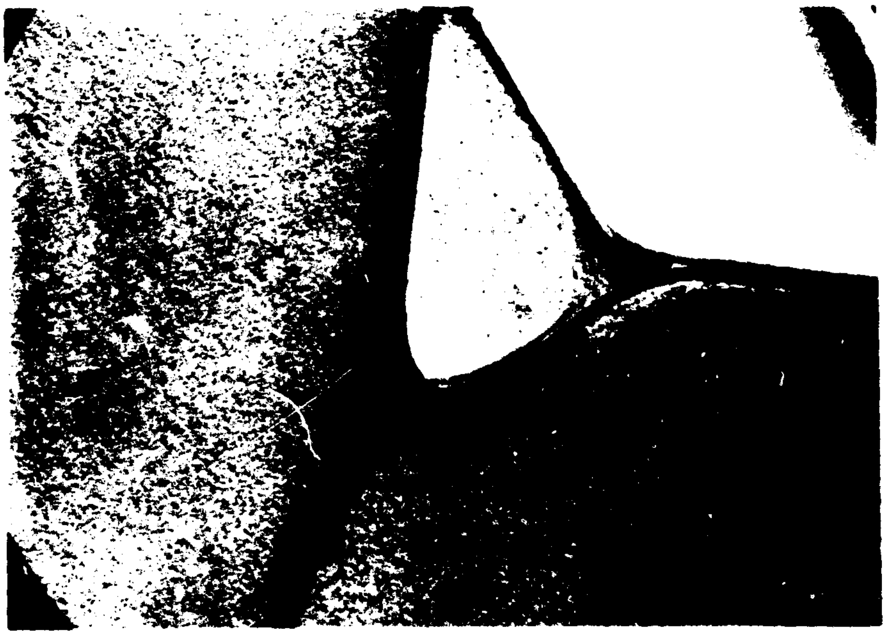

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Figure 8 Electron Micrograph Showing Grain Boundary Phase in As Hot Pressed Specimen MG VF-9

#66090

Figure 9 Grain Boundary Phase in MgO + 2% LiF Pressure Sintered at 1000°C for 15 minutes.

TABLE VII

Lattice Parameters of MgO and LiF Hot Pressed at 820°C

Composition	Condition	MgO, Å	LiF, Å
1.000 MgO	Powder	4.21245	
1.000 MgO	Hot Pressed	4.21407	
0.990 MgO - 0.010 LiF	Hot Pressed	4.21213	
0.952 MgO - 0.048 LiF	Hot Pressed	4.21118	
0.908 MgO - 0.092 LiF	Hot Pressed	4.21154	
0.714 MgO - 0.282 LiF	Hot Pressed	4.20891	
0.500 MgO - 0.500 LiF	Hot Pressed	4.20685	4.03124
0.200 MgO - 0.800 LiF	Hot Pressed		4.03049
0.100 MgO - 0.900 LiF	Hot Pressed		4.02952
0.050 MgO - 0.950 LiF	Hot Pressed		4.02962
0.030 MgO - 0.970 LiF	Hot Pressed		4.02972
0.01 MgO - 0.990 LiF	Hot Pressed		4.02885
1.000 LiF	Hot Pressed		4.02917
1.000 LiF	Powder		4.02622

These changes in lattice parameter upon hot pressing at 820°C are taken as evidence of solid solution of both LiF in MgO and MgO in LiF. The extent of solution is not known, but some predictions can be made concerning the chemistry of the solution and the effect on the host lattice and lattice parameter. The observation of grain growth during pressure sintering indicates that both Mg^{+2} and O^{-2} are transported in LiF, hence the following reactions are written:

MgO in LiF

$$Mg^{+2}\text{ (in MgO)} + Li^{+1} + O^{-2}\text{ (in MgO)} + F^{-1} = Mg^{+2} + O^{-2} + \square_{Li} + \square_{F} + Li^{o} + F^{o} \qquad (4)$$

or

$$Mg^{+2}\text{ (in MgO)} + Li^{+1} + O^{-2}\text{ (in MgO)} + F^{-1} = Mg^{+2} + O^{-2} + Li_{i}^{+1} + F_{i}^{-1} \qquad (5)$$

The ion sizes are; $Mg^{+2} = 0.65$ Å, $Li^{+1} = 0.60$ Å, $O^{-2} = 1.40$ Å, and $F^{-1} = 1.36$. Reaction (5) would definitely expand the lattice in agreement with the experimental observation, but it is not easily predicted whether reaction (4) would expand or contract the lattice; the preferred reaction cannot be chosen with certainty. For the solid solution of LiF in MgO the following reaction can be written:

LiF in MgO

$$Li^{+1}\text{ (in LiF)} + 2Mg^{+2} + 2O^{-2} + F^{-1}\text{ (in LiF)} = Li^{+1} + 2Mg^{o} + \square_{Mg} + F^{-1} + O_2 + \square_{O}^{-2} \qquad (6)$$

or

$$2Li^{+1}\text{ (in LiF)} + Mg^{+2} + O^{-2} + 2F^{-1} = Li^{+1} + Li_{i}^{+1} + Mg^{o} + F^{-1} + F_{i}^{-1} + \tfrac{1}{2}O_2 \qquad (7)$$

Reaction (6) would contract the lattice while reaction (7) would undoubtedly cause an expansion. In view of the experimentally observed contraction, it is thought that reaction (6) occurs during the solution of LiF in MgO. A high vacancy concentration would be caused by this reaction which could be responsible for high diffusion rates for Mg^{+2} and O^{-2} in a solid solution zone that may well be microns wide.

c. Diffusion rate

The densification mechanism for hot pressing pure MgO was considered to be particle rearrangement in the early stage followed by pressure enhanced solid state diffusion.[1] The Nabarro Herring equation of pressure enhanced diffusion is

$$D = \frac{\dot{\epsilon} \, K \, T \, G^2}{10 \, \Omega \, \sigma} \tag{8}$$

where D = diffusion rate

$\dot{\epsilon}$ = strain rate

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

T = absolute temperature

G = grain size

Ω = vacancy volume

σ = stress

Considering that a diffusion mechanism may operate (mechanism a or b) a sample calculation for the diffusion coefficient was made for specimen 1103 (densification curve appears in Figure 4) hot pressed at 650°C. For the rate limiting species $D = 4.5 \times 10^{-12}$ cm^2/sec.* This diffusion coefficient is

---

* Benecke[4] made a similar calculation giving D's equal to between 1.0 and 10^{-4} cm^2/sec leading him to conclude that pressure enhanced diffusion was not a possible mechanism, but it is thought that his calculation was incorrect.

reasonable for any kinetic process, but it is between 10^7 and $10^{9.5}$ faster than the extrapolated values of the lattice diffusion coefficients[5,6] at 650°C. It is not uncommon[1] to find differences from 10 to 10^3 in diffusion coefficients calculated from kinetic models and directly measured self-diffusion coefficients although these differences are the subject of much current study. It is unlikely, however, that the densification mechanism incorporates diffusion through the MgO lattice, but diffusion through some other phase or high diffusivity layer is certainly possible.

d. Proposed model

The evidence for or against a specific densification model (a, b, c, or d) is summarized in Table VIII. The facts greatly favor densification by diffusion of Mg^{+2} and O^{-2} through a LiF containing film. Since the lattice parameter of both LiF and MgO change upon doping with the solute, high point defect concentrations with associated high diffusivities are most probably controlling densification. LiF also increases the densification rate for sintering, but the kinetic data for Wappner and Coble[7] shows the rate to be orders of magnitude less than that observed for hot pressing. Therefore, it is thought that below 870°C the densification mechanism can be considered as pressure enhanced diffusion (Nabarro-Herring) through a high diffusivity grain boundary region or film. Above 870°C a liquid phase sintering mechanism probably becomes operative.

3. Post Pressing Anneal

Approximately seventeen exploratory annealing experiments were conducted where temperature ranged between 1235°C - 1700°C, atmosphere was either

TABLE VIII

Summary of Diffusion Mechanism Evidence

	Model	Evidence Against	Evidence For
a)	MgO pressure enhanced diffusion	Diffusivity too high Grain boundary film	
b)	MgO pressure enhanced diffusion in second phase (or S. solution)		Diffusivity reasonable grain growth, solid solution evidence, grain boundary film.
c)	Liquid phase pressure sintering	No liquid formed[4]	
d)	Plastic flow aided by LiF film	Grain growth	

vacuum (10μ), air, oxygen, or hydrogen, and heating rate varied between 0.2°C/min and 100°C/min. Samples 1046 - 1123 were quartered and used for these annealing experiments. Also sections of the larger billets Mg VF2-12 were used in these experiments.

These anneals resulted in twenty seven specimens having a high degree of transparency. Twelve showed an increase in transparency but were still considered translucent. Forty-four samples were opaque after annealing. The opaque samples showed post anneal expansions due to "bloating" of between 1.8% and 41.9%.

None of the vacuum annealed samples developed a high degree of transparency while over one half of them showed significant bloating. There was no detectable difference between the air and oxygen anneals, however. In both air and oxygen, samples annealed near the low end of the temperature scale re slightly pink unless they were annealed 25 hours, while those annealed above 1550°C were colorless. Samples heat treated in hydrogen retained a gray cast, so both hydrogen and vacuum were abandoned as annealing atmospheres.

From this annealing program, two common factors consistently resulted in opaque samples. Samples hot pressed in air were always opaque after the heat treatment. Also most samples heated at a rate > 10°C/min. in the critical range 500°C to 1200°C were opaque, although a few thin specimens were not. The anneal with the lowest heating rate (0.2°C/min - 0.8°C/min.) yielded the largest number of transparent samples. Figure 10 shows four quarters of a 1% LiF - MgO specimen hot pressed at 1000°C in vacuum and heat treated under the conditions illustrated.

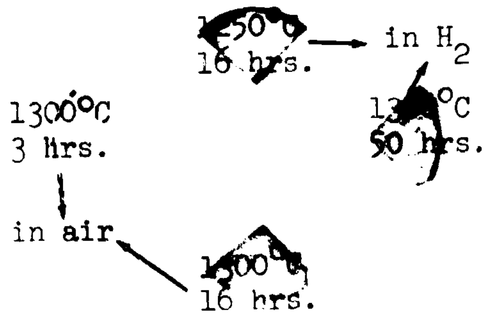

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Figure 10 Transmission Through 1% LiF - 99% MgO Specimen No. 1123 After Various Heat Treatments.

It would appear that the 1300°C - 16 hour air anneal should have greater transparency than the 1300°C - 3 hour air anneal. There were two major differences in the 3 hour anneal which may be responsible for the increased transparency; 1) the heating rate averaged 0.6°/min. as opposed to 1.2°/min. in the 600°C - 1300°C range; and 2) the 3 hour anneal was above the melting point of LiF (870°C) for 45 hours as opposed to 25 hours for the 16 hour anneal. The H_2 anneals also underwent different heating rate cycles. It is quite apparent that one or both of these variables are the most sensitive factors controlling the transparency of LiF - MgO hot pressed material.

Several weight loss experiments were conducted to obtain quantitative information on the conditions for volatilizing LiF from MgO. In the first experiment sample 1110 (MgO + 2% LiF) was monitored as a function of temperature between 600°C and 1300°C at a heating rate of 1.8°C/min, and the weight loss is shown in Figure 11.

Two points are significant from these data; namely, the fact that at least 0.2% weight is lost below the melting point of LiF (870°C), and no further weight was lost beyond 1.44% after reaching 1300°C. The zero point for recording weight loss was taken at 600°C, and at this temperature impurities from handling and physically adsorbed H_2O should have been evaporated. Some chemisorbed H_2O may be included in the 0.2%+ weight loss between 600°C and 870°C, but it is most probable that LiF diffuses to and evaporates from the surface below its melting point giving rise to a significant portion of this weight loss. This sample was hot pressed at 800°C and 5000 psi for 5 minutes in a 5 μ vacuum, and in view of these results it is probable that some weight loss occurred during hot pressing. This, of course, would account for the fact that only 1.44% LiF was driven off while the sample originally contained 2% LiF.

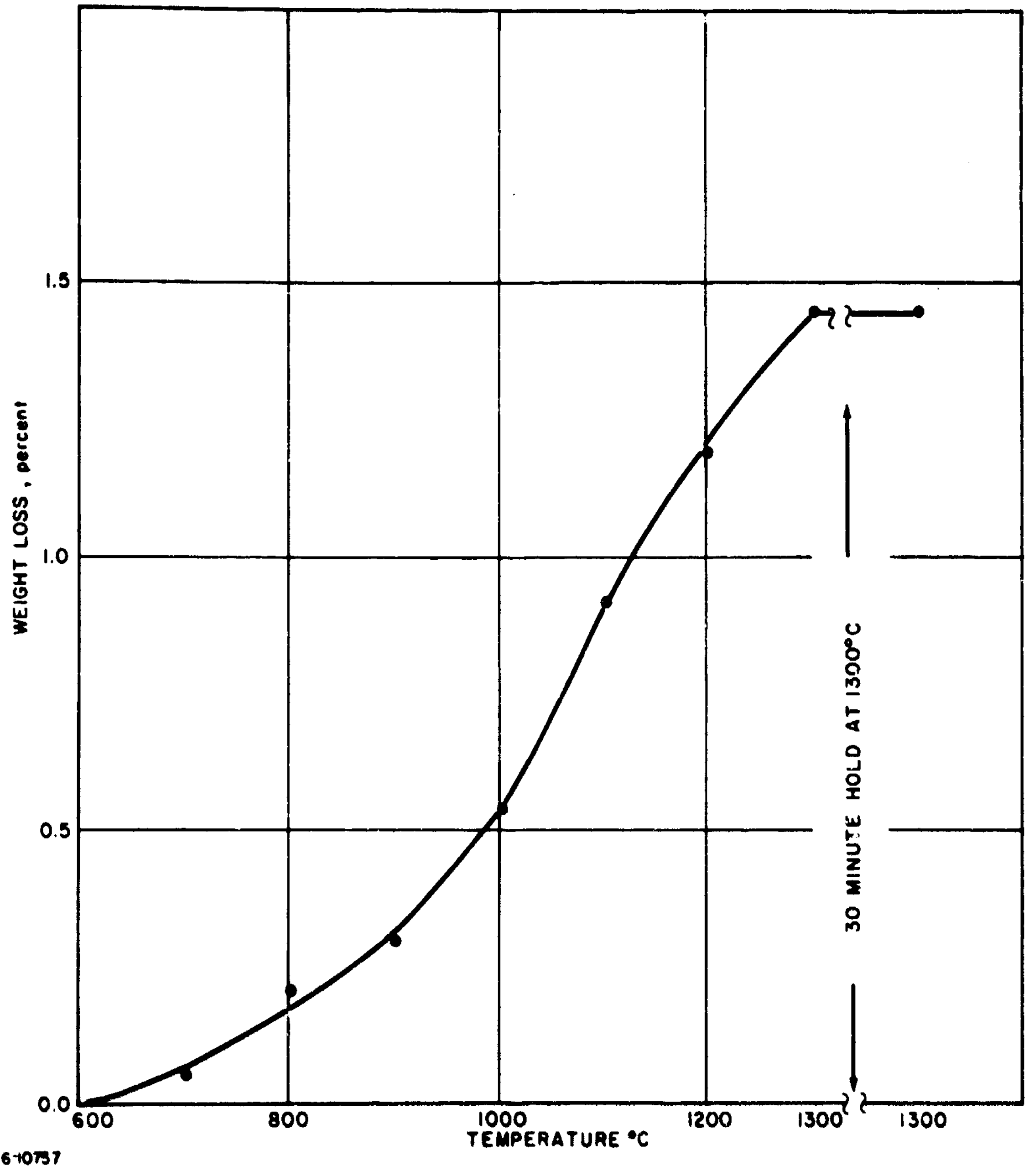

Figure 11 Weight Loss of MgO + 2% LiF as a Function of Temperature

An isothermal weight loss experiment was conducted at 1050°C by heating to this temperature in as short a time as possible (90 minutes) and holding until weight loss was halted. Again, the weight loss was zeroed at 600°C, and these results are given in Figure 12.

The kinetics of the weight loss will not be analyzed in detail since other temperatures and longer times would be required to reach any conclusions concerning the mechanism of the LiF diffusion and evaporation. The weight loss appears to be complete at 1.56% which is below the level of LiF added to the original MgO powder. Again, this indicates that LiF is lost in the hot pressing. However, the sample did not become transparent while a companion sample from the same billet had fair transparency after annealing 91 hours at 1250°C. This would indicate that some LiF still remains in the weight loss sample or more likely the LiF is lost and the opacity is caused by internal volatilization of LiF during the rapid heat up.

Based on these annealing and weight loss experiments a cycle was adopted as standard which was utilized on the billets listed in Tables III and IV after Nos. 1123 and Mg VF-14 (except Mg VF-22, 25, 26 which were heated to 1250°C in air for several hours followed by ~ 50 hours in H_2 at 1250°C). A Kanthall wound furnace was heated at 0.46°C/min to 1250°C, and temperature was maintained for a minimum time of 27 hours. Several billets listed after Mg VF-14 were annealed in this furnace for longer times (up to 96 hours), but this did not result in noticeably improved transparency.

Directly after hot pressing a LiF containing phase exists in the grain boundaries (Figure 9), and the annealing process presumably allows LiF to diffuse to the surface and volatize into the atmosphere. A high heating rate apparently does not allow the LiF to diffuse sufficiently to the surface

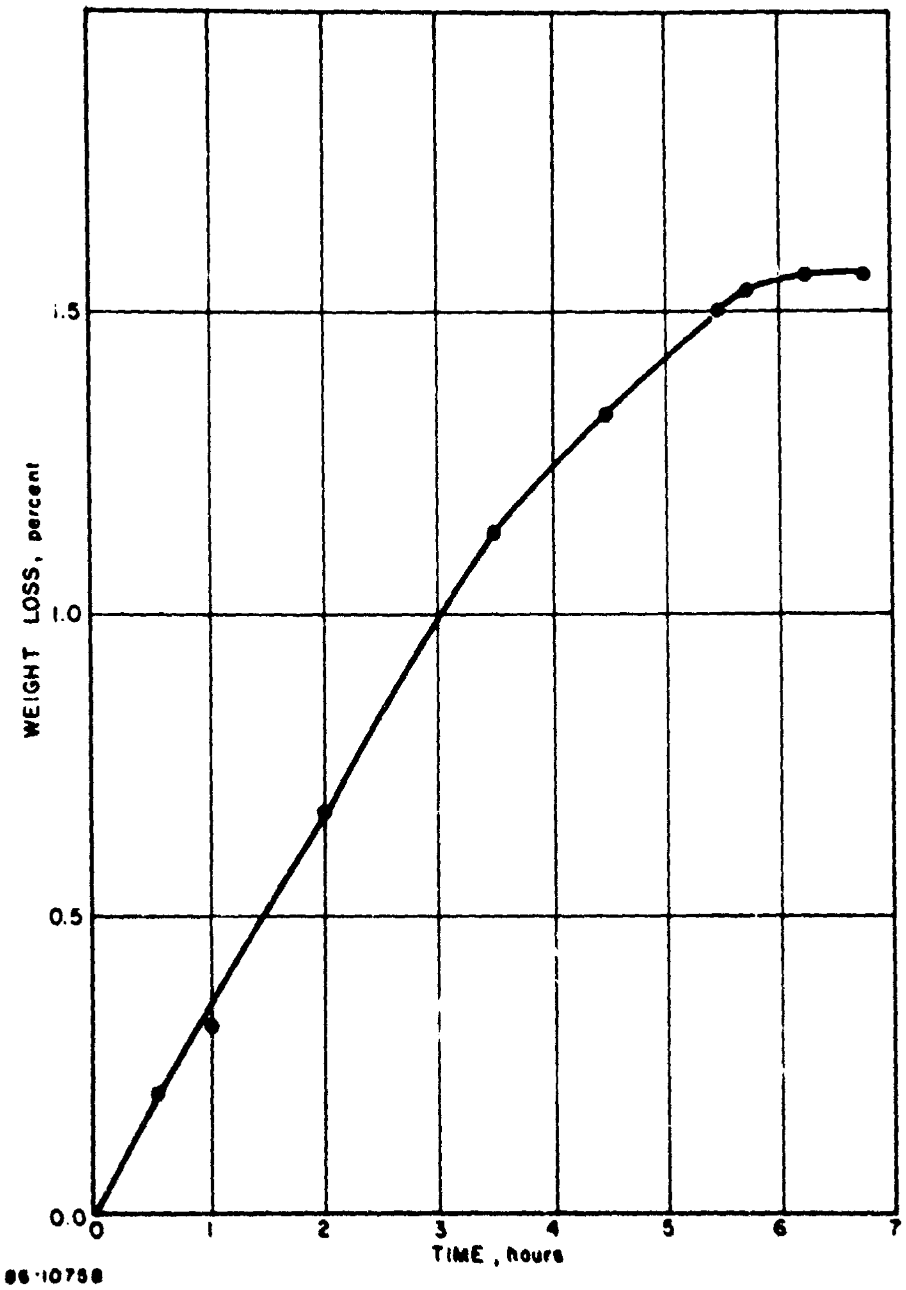

Figure 12 Weight Loss of MgO + 2% LiF at 1050°C as a Function of Time

prior to developing a high vapor pressure which will cause porosity generation. A slow heating rate combined with a long high temperature hold in the hot pressing cycles are apparently necessary to give the pore free microstructure illustrated in Figure 13.

C. Optical Properties of MgO

Total transmission curves for several of the most transparent small and large specimens are shown in Figures 14 and 15 respectively. Figure 15 shows the transmittance data for the most transparent specimens made by hot pressing pure MgO (V-30) while the remaining specimens were made by the MgO - LiF process. Macroscopic photographs of some of these same specimens and several produced near the end of the program are shown in Figures 16 through 19. The transmission data was taken on an extended range Beckman DK-2 ratio recording spectrophotometer with attached integrating sphere. The transmission curve for National Bureau of Standards Didymium glass was employed as a calibrating reference.

This transmittance data is for specimens of different thicknesses which makes a comparison between specimens difficult. The absorption of a transmitting electromagnetic wave is given by Lambert's equation:

$$I/I_o = e^{-u\,x} \qquad (9)$$

where I_o is the initial intensity, u is the absorption coefficient, and x is the specimens thickness. The absorption coefficient was determined by cleaving a series of MgO single crystals to different thicknesses. Care was taken to utilize surfaces which showed few cleavage steps, and to utilize crystals of the same color (presumably the same purity).

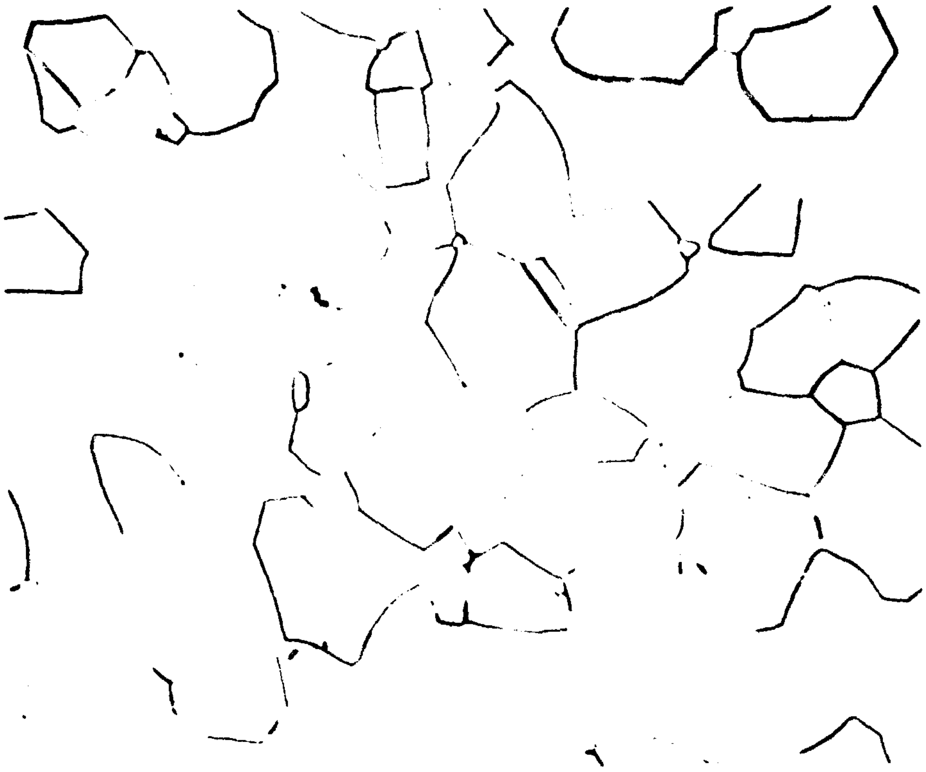

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Figure 13 Microstructure of Specimen: Mg VF-5
Heat Treated 91 Hours at 1550°C in Air.

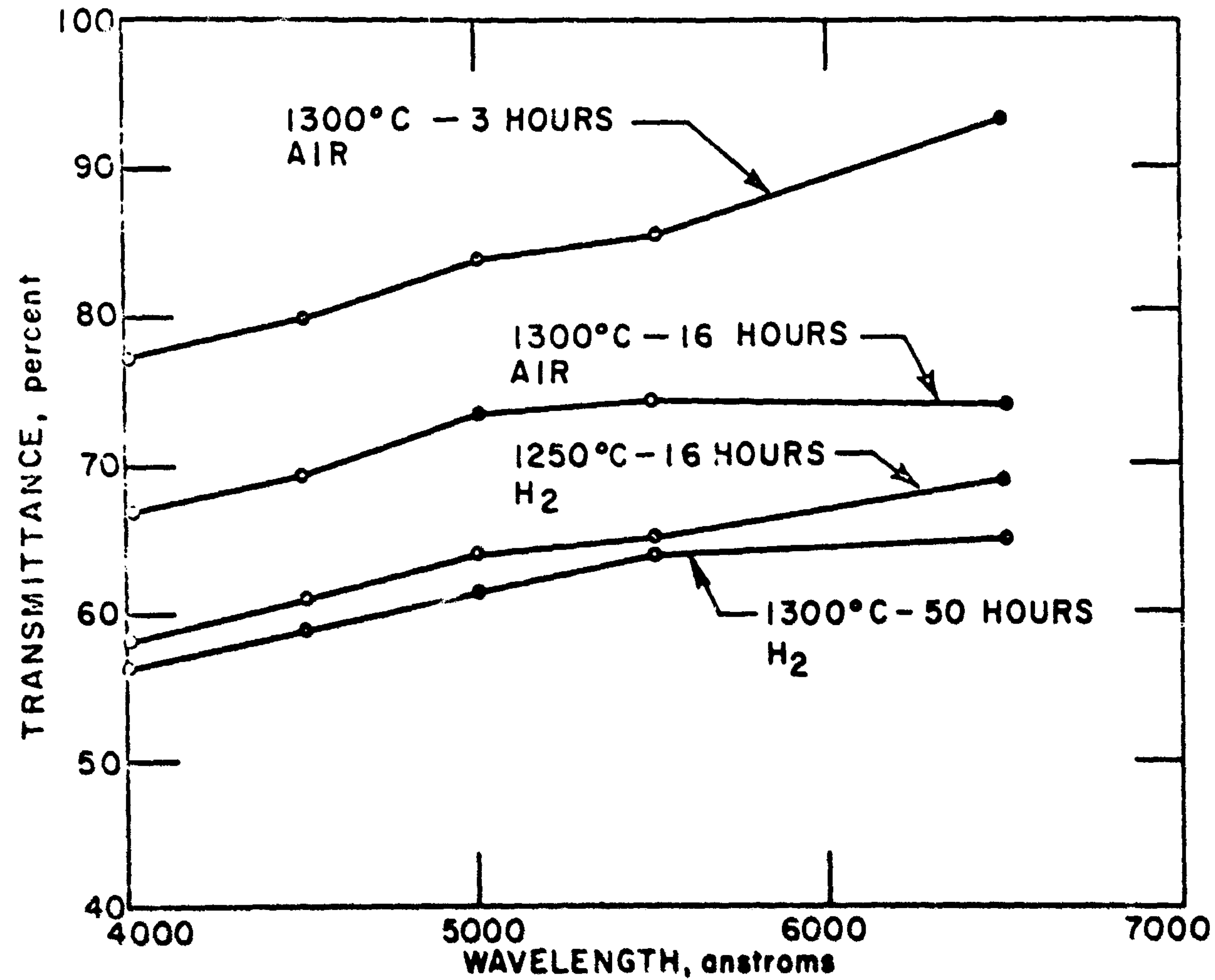

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Figure 14 Total Transmission in the Visible Spectra for Specimen Number 1123.
(.18 inches thick)

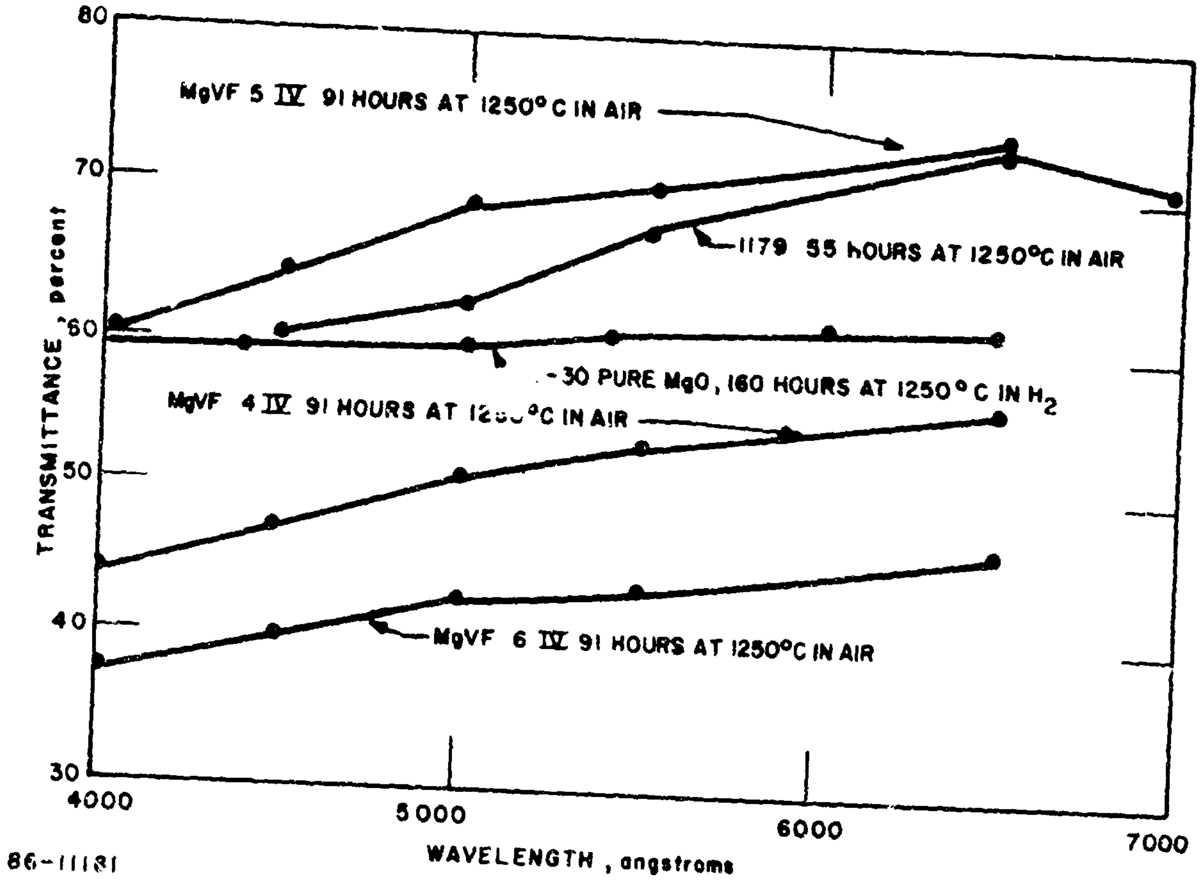

Figure 15 Total Transmission of Thick Sections of MgO in the Visible Spectra
(Thickness between 0.246 - 0.416 inches)

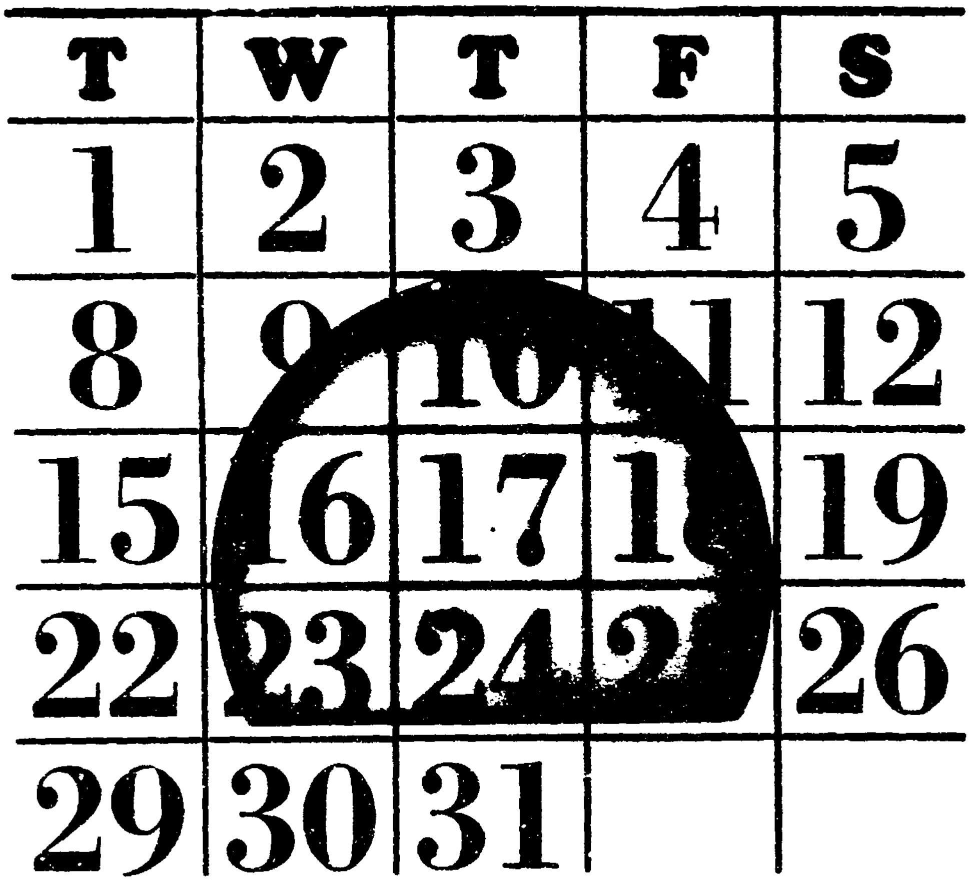

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Figure 16 Polished Specimen V-30, Pure MgO Pressure Sintered at 1200°C - 180 minutes - 6000 psi and Annealed at 1250°C - 160 hours in H_2.

Figure 17 Polished Specimen MgVF-28 Pressure Sintered at 820°C - 1010°C - 305 minutes - 5000 psi and annealed for 99 hours at 1250°C in Air.

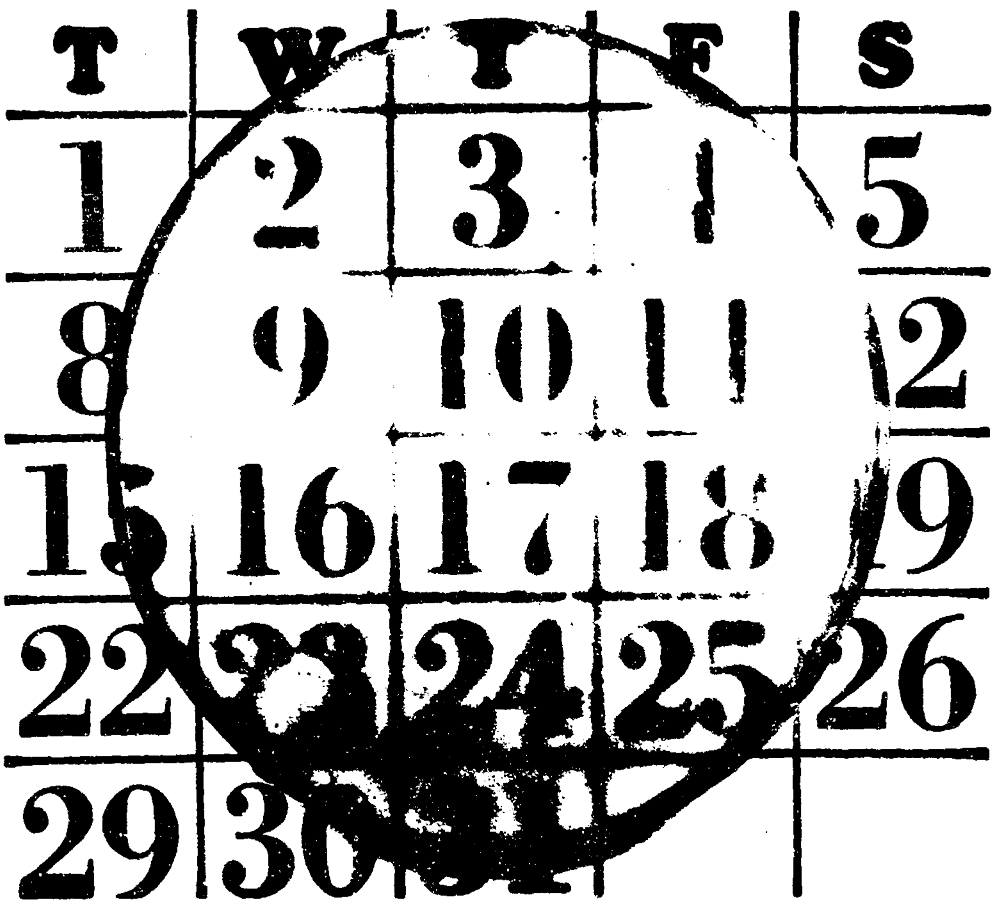

Figure 18 Unpolished Specimen MgVF-34 Pressure Sintered at 830°C-1000°C - 450 minutes - 5000 psi and annealed for 55 hours at 1250°C in air.

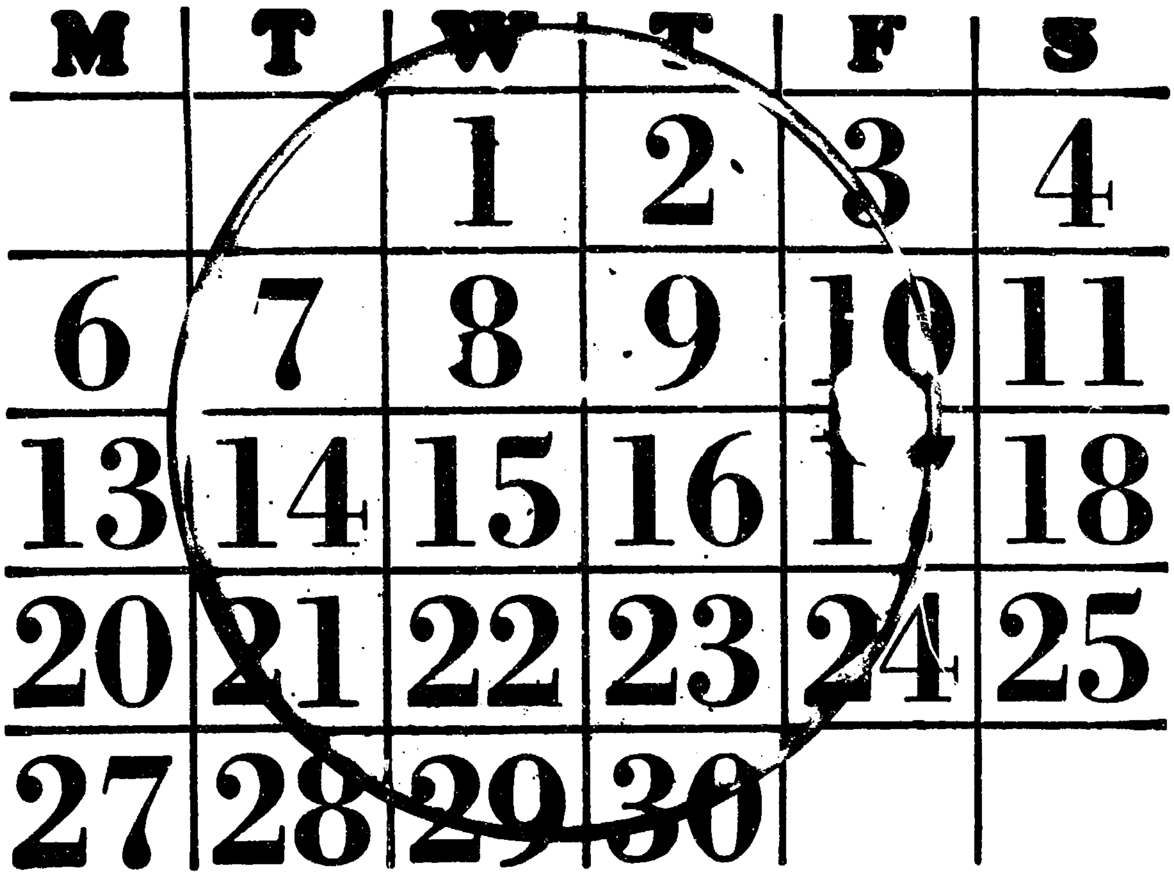

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Figure 19 Polished Specimen MgVF-34 Showing Contrast In Light Transmission Between This and Unpolished Surface (See Figure 18)

Six spectral relative transmittance determinations as a function of specimen thickness are shown in Figure 20. The absorption coefficients were calculated from the slope of these lines, and this parameter is shown as a function of wavelength in Figure 21. The total transmission data for the large and small scale specimens having the highest transmittance were corrected to a common thickness (3/8 inch = 0.952 cm) using equation (9) and the calculated absorption coefficients. The corrected transmittance curve is shown in Figure 22, where the specimen number 1123 d was small scale specimen having an actual thickness of 0.275 cm and specimen number Mg VF-5-IV was a 0.983 cm thick section of a 4-inch diameter billet. This calculation shows that the small scale specimen possesses a higher absolute transmittance.

Summary and Conclusions

1. Translucent MgO can be produced from pure MgO by hot pressing in vacuum under carefully controlled conditions. A body having 60% total transparency, adequate for in line visual observation, can be obtained by annealing in H_2 at 1250°C for 160 hours. This process is very critical to conditions and starting material; consequently a very high reject rate presently exists, and while this reject rate could be lowered a major fabrication refinement program would be required.

2. MgO specimens having 85% total transmission in the visible range can be fabricated by low pressure (4-6 kpsi) hot pressing followed by an anneal utilizing a slow heating rate and prolonged soak at 1250°C. A prolonged soak ($>$1 hour) at 950°C in the hot pressing step aids the final transparency presumably because LiF is volatilized during this soak making LiF removal during the annealing step less disruptive to the structure. In sections 3/8"

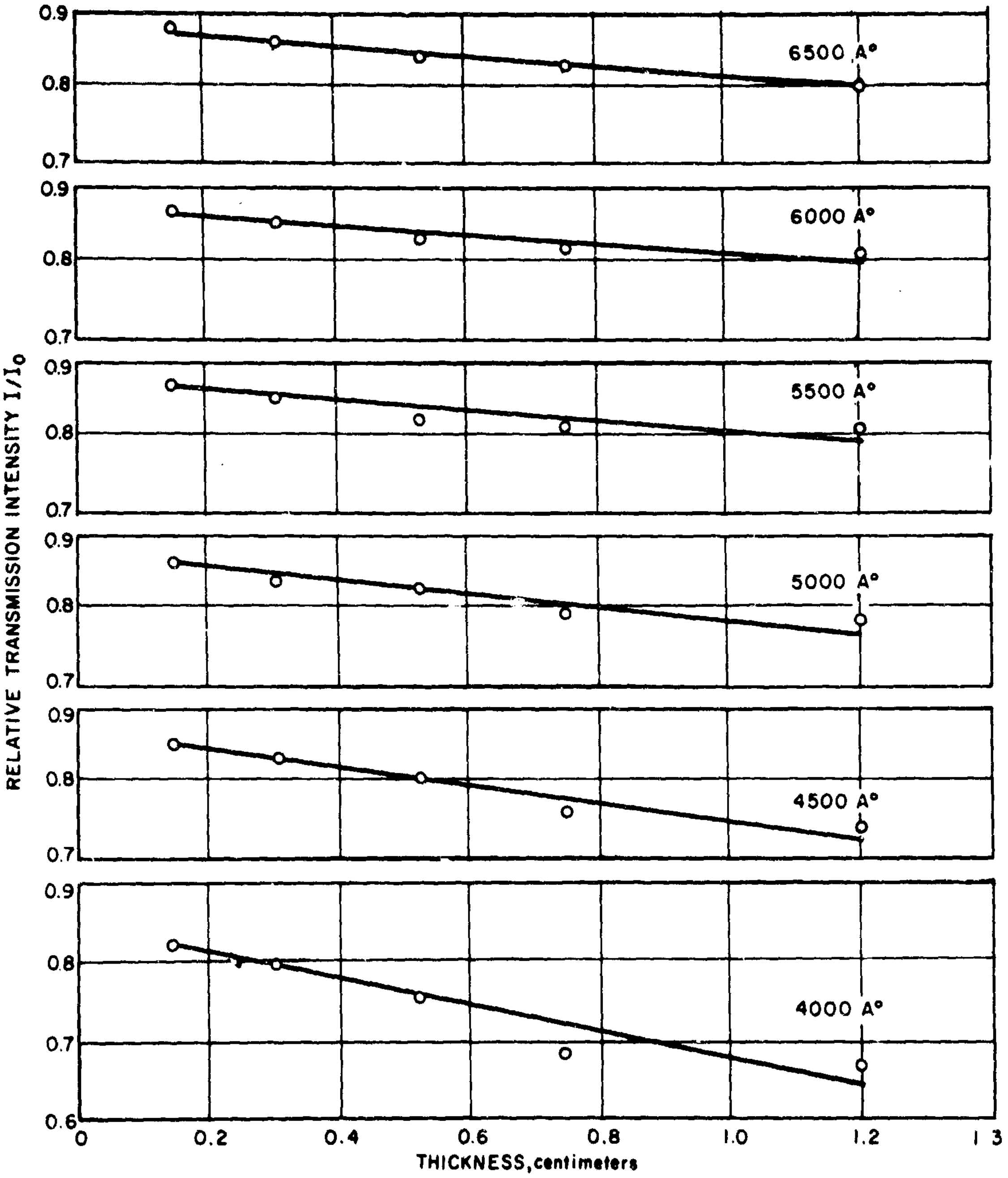

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Figure 20 Relative Transmittance in Single Crystal MgO as a Function of Thickness and Wavelength.

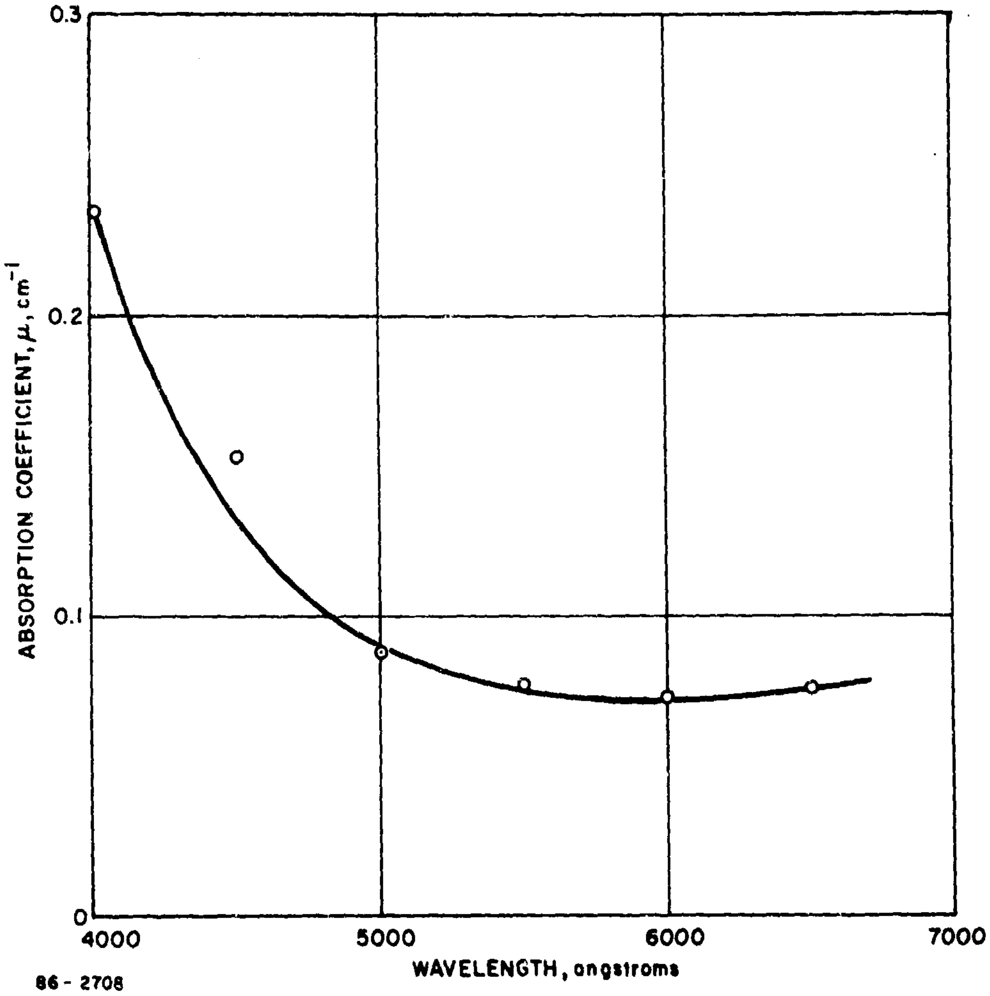

Figure 21 Absorption Coefficient for Single Crystal MgO as a Function of Wavelength.

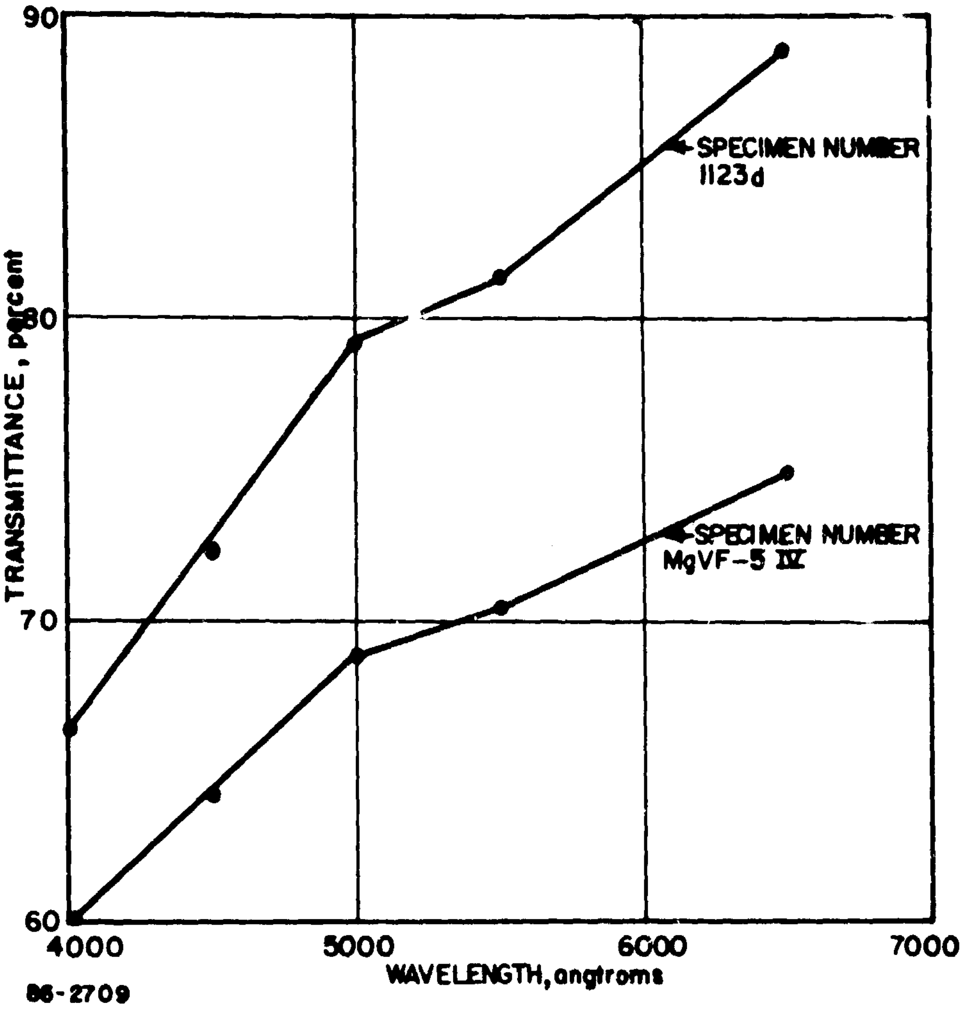

Figure 22 Spectral Transmittance for Two Hot Pressed Polycrystalline MgO Specimens Corrected to a Common Thick..ess (3/8 inch)

thick 70% transmission was obtained, and it appears that the increased diffusion distance for LiF removal causes internal volatilization resulting in pore generation. Evidence was obtained for less critical fabrication conditions by high pressure (> 15 kpsi) hot pressing, but this fabrication regime was not refined to the extent necessary to adequately define the conditions.

3. Densification in the MgO - LiF process is thought to occur by pressure enhanced diffusion in a solid solution grain boundary layer. At temperatures above 870°C (the melting point of LiF) liquid phase pressure enhanced sintering is the probable mechanism.

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13 ABSTRACT

The densification parameters for hot pressing MgO to a theoretically dense polycrystalline body has been studied. Two experimental approaches were followed; using pure MgO powders, and pressing mixtures of MgO plus small amounts of LiF. In the former case specimens having 60% total transmission (adequate for in line observation) were obtained by very precise control of the fabrication conditions followed by a long term anneal in hydrogen. The MgO - LiF process yielded thin specimens having 85% total transmission in the visible, and 3/8 inch thick specimens possessing a maximum transmission of 70%. A post hot pressing anneal at temperatures greater than 1200°C and heating rates less than 28°C/hour were required to produce maximum transparency. Evidence obtained by grain growth studies, weight loss experiments and lattice parameter determinations suggest that the densification mechanism for this process was pressure-enhanced diffusion through a solid solution grain boundary layer and a grain boundary phase. At temperatures above the melting point of LiF a pressure-enhanced liquid phase sintering mechanism probably operates.

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UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Magnesium Oxide						
Transparent						
Optical Properties						
Hot Pressing						

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