

DEVELOPMENT OF POLYCRYSTALLINE SPINEL FOR TRANSPARENT ARMOR APPLICATIONS

March 1972

HAYNE PALMOUR III ENGINEERING RESEARCH SERVICES DIVISION NORTH CAROLINA STATE UNIVERSITY RALEIGH, NORTH CAROLINA 27607

FINAL REPORT

CONTRACT NUMBER DAAG 46-69-C-0097

AD

Approved for public release; distribution unlimited.



Prepared for

ARMY MATERIALS AND MECHANICS RESEARCH CENTER Watertown, Massachusetts 02172

> NATIONAL TECHNICAL INFORMATION SERVICE Springfield, Va. 22151

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

Mention of any trade names or manufacturers in this report shall not be construed as advertising nor as an official indorsement or approval of such products or companies by the United States Government.

.



DOCUMENT CO	and the second	
rSecurity elassification of Hila - hody of abeteact and inday	NTROL DATA - R & D	
IGINATING ACTIVITY (Corporate author)	ing annotation must be entered when	the presail report is classified) SECURITY CLASSIFICATION
Engineering Research Services Divisio	on Un	classified
School of Engineering	26. GROUP	
Raleigh, North Carolina 27607	l	
DEVELOPMENT OF POLYCRYSTALLINE SPINEL	FOR TRANSPARENT ARMOR	APPLICATIONS
SCRIPTIVE NOTES (Type of report and inclusive dates) Final Research Project Report, March	1972	
ThioR(S) (First neme, middle initial, lest neme) Hayne Palmour III		
PORT DATE	78. TOTAL NO OF PAGES	76. NO OF REFS
March 1972	46	32
CNTHACT OF GRANTING DAAG-46-69-C-0097	98. ORIGINATOR'S REPORT N	UMBER(\$)
PHOJECT NO PEMA 4931	AMMRC CTR 72-4	
	96. OTHER REPORT NO(S) (Ar Inia report)	ly other numbers that may be assigned
UPPLEMENTARY NOTES	12 SPONSORING MILITARY A	C TIVIY -
	Army Materials and Watertown, Massach	Mechanics Research Cent usetts 02172
This study was undertaken to det stantial quantities of pure, undoped cursor in a semicontinuous process, a hot molding and/or rate controlled si achieve optical transparency in this a mixed magnesium aluminum sulphate h melting of the starting salts and suf Partially dehydrated precursor was dy dynamically calcined at .1150°C in ar powder production process was not pro- to its basic technology), resulting i ometry and incomplete removal of sulp specimens hot molded from gas-laden, optical properties than had been occo trolled sintering studies produced we	termine the feasibility MgAl ₂ O ₄ spinel powder and thereafter, of dens intering processes on a isotropic material. T mydrate produced on a b osequent solidification ynamically precalcined in inclined rotating tub operly regulated (for r in poor chemical contro obur residues during ca non-stoichiometric pown asionally obtained in p ell documented evidence ormal) linear controlle	of producing sub- from a chemical pre- ifying the powder by best efforts basis to he precursor salt was atch basis by direct by cocrystallization. at ~650°C, and then e furnace. The overall easons almost unrelated l of cation stoichi- lcination. Consequently der displayed poorer rior work. Rate con- of non-Arrhenian d-rate densification

Hall and services.

1!N	CT	AS	CT	E1	TP:
UN	чĿ	คอ	21	. r i	. L L

Security Classification

KEY WORDS	LINK A		LINKS		LINK C	
	ROLE	ΨT	ROLE	WT	ROLE	wт
Lightweight armor Transparent armor						
Spinel		1	Į			1
Hot pressing		1	ł			
Physical properties			Í			
Sintering		ł				
Calcining						
			l i			
		i i				
· · · · · · · · · · · · · · · · · · ·						
					1	
				l		
		· .				
				1	i	
		1	1	1		
		1				
		l			ļ	
	1					
			Í		Í	
			1			
					1	
			1		1	
				Í		
				1		
			1			
		,		CD.		
	<u></u>	UNCL	ASSIFI	ED		

AMMRC CTR 72-4

DEVELOPMENT OF POLYCRYSTALLINE SPINEL FOR TRANSPARENT ARMOR APPLICATIONS

March 1972

HAYNE PALMOUR III ENGINEERING RESEARCH SERVICES DIVISION NORTH CAROLINA STATE UNIVERSITY RALEIGH, NORTH CAROLINA 27607

FINAL REPORT

CONTRACT NUMBER DAAG 46-69-C-0097

D 'A Project1686022AMCMS Code4090.01.6022Title of ProjectDevelopment of Manufacturing Process for Transparent Armor

Approved for public release; distribution unlimited.

Prepared for

ARMY MATERIALS AND MECHANICS RESEARCH CENTER Watertown, Massachusetts 02172

ABSTRACT

This study was undertaken to determine the feasibility of producing substantial quantities of pure, undoped MgAl204 spinel powder from a chemical precursor in a semicontinuous process, and thereafter, of densifying the powder by hot molding and/or rate controlled sintering processes on a best efforts basis to achieve optical transparency in this isotropic material. The precursor salt was a mixed magnesium aluminum sulphate hydrate produced on a batch basis by direct melting of the starting salts and subsequent solidification by cocrystallization. Partially dehydrated precursor was dynamically precalcined at ~650°C, and then dunamically calcined at ~1150°C in an inclined rotating tube furnace. The overall powder production process was not properly regulated (for reasons almost unrelated to its basic technology), resulting in poor chemical control of cation stoichiometry and incomplete removal of sulphur residues during calcination. Consequently specimens hot molded from gas-laden, nonstoichiometric powler displayed poorer optical properties than had been occasionally obtained in prior work. Rate controlled sintering studies produced well documented evidence of non-Arrhenian densification kinetics for (nonisothermal) linear controlled-rate densification over the range 60-90% fractional density. These findings, indicative of plastic flow is the dominant transport mechanis, are considered to be pertinent to successful densification of spinel by both simple and stress-augmented sintering (bot pressing or hot molding).

ii

FOREWORD

This report was prepared by the Department of Engineering Research at North Carolina State University under U. S. Army Contract DAAG-46-69-C-0097. The work was administered under the direction of Capt. D. T. Rankin and Mr. G. E. Gazza.

This report covers the period 16 June 1969 through 31 January 1970, and includes certain follow-up activities which extended through calendar year 1970. University personnel participating in this study included H. Palmour III, W. W. Kriegel, K. O. Beatty, D. R. Johnson, V. A. Dixon, C. E. Zimmer, J. F. Freeman, N. M. Shah, C. Batts, T. Miller, R. E. Haggas, V. Daniel, and M. V. Karia. Helpful assistance by P. F. Becher, M. L. Huckabee, C. H. Kim, E. M. Gregory, E. B. Roberts, W. B. Wilson, T. Banther, and J. P. Kirkland in experimental activities, preparation and analysis, and by Mrs. Ann Ethridge, Miss Anne Young and M. L. Huckabee in report preparation, is gratefully acknowledged.

Finally, it is appropriate to acknowledge helpful discussions with R. Clark and R. J. Weagley (Eastman Kodak Company), J. L. Pentecost, N. Levy, Jr., and D. D. Walczyk (W. R. Grace & Company), W. H. Rhodes (AVCO Corp.), and D. Roy, F. Stermole, D. G. Wirth and D. Sellers (Coors Porcelain Co.).

This project has been accomplished as part of the U. S. Army Manufacturing Methods and Technology Program, which has as its objective the timely establishment of manufacturing processes, techniques or equipment to insure the efficient production of current or future defense programs.

iii

TABLE OF CONTENTS

.....

List of Tablesvi
List of Figuresvii
Introduction1
General Scope 3
Detailed Scope
Plan of Work 3
Phase 1: Powder Synthesis 3
Phase IIA: Hot Pressing 4
Phase IIB: Rate Controlled Sintering
Experimental Equipment and Procedures
Phase I 5
Cocrystallization 5
Drying
Crushing and Screening 6
Dynamic Calcination 8
Phase IIA 9
Phase IIB
Rate Controlled Sintering Furnace and
Control Equipment
Materials
Results and Discussion14
Phase I: Synthesis of Precursor14
Stoichiometry14
Purity
Phase I: Dynamic Calcination of Dehydrated Precursor18
Optimizing and Operating the Dynamic
Calcining Furnace
The Calcining Process
Anion (SO3) Removal
Cation Contaminants23
Blending and Milling23

Phase I: Characterization of Product
Phase IIA: Hot Molding of Spinel25
Preliminary Hot Pressings25
Hot Molding25
Hot Pressing Grace S-5570 Spinel
Microstructures
Infrared Transmission
Phase IIB: Rate Controlled Sintering of Spinel
Summary and Conclusions
Literature Cited

v

LIST OF TABLES

Table 1.	Starting Materials for Spinel13
Table 2.	Analysis of Prereacted Spinel Materials14
Table 3.	Comparisons of Analysis for Two Trial Lots
Table 4.	Cation Stoichiometry of Four Production15 Batches of Spinel Precursor
lable 5.	Formulation and Resulting Stoichiometry of
Table 6.	Cation Impurities in Starting Materials and
Table 7.	Typical Operating Conditions for Inclined
Table 8.	Variations in Sulfur Content of Different Spinels22 Attributable to Calcining Conditions and/or Cation Stoichiometry
Table 9.	Characterization of Sulphate - Derived Spinels24
Table 10.	Summary of Hot Molded 2 x 4 x $1/4$ in

LIST OF FIGURES

Figure 1.	Heated 30 gal. mixing vessel for preparation
Figure 2.	Flow chart for synthesis of spinel precusor
Figure 3.	Schematic diagram for dynamic calcining
Figure 4.	Collet grips for inclined rotating mullite tube 9 drive used in dynamic calcining furnace.
Figure 5.	Inlet and exit plenum details for dynamic
Figure 6.	Schematic diagram of programming/controllingll and measuring instrumentation for rate controlled sintering.
Figure 7.	Sectioned schematic of rate controlled sintering12 furnace showing sample holder and shrinkage sensor.
Figure 8.	Thermoanalytical characterizations of starting20 materials; intermediates, and final spinel calcined at 1145°C.
Figure 9.	Relative opacity and/or translucency of
Figure 10.	Relative translucency of Grace S-5570 spinel 26
Figure 11.	Relative translucency of fine plano-plano \dots 31 polished 2 x 4 x 1/4 in. spinel pieces.
Figure 12.	Infrared transmittance curves for various
Figure 13.	Infrared transmittance curves for thin and thick 33 hot pressed spinel pieces.
Figure 14.	lsothermal densification rate as a function of 35 prior constant densification rate in initial stage sintering of spinel

INTRODUCTION

As early as 1961-62, the possibilities of achieving transparency in polycrystalline isotropic spinel ceramics were considered and occasionally even demonstrated (in pertions of small hot pressed specimens) in research studies at North Carolina State University concerned primarily with the structural and mechanical properties of spinel ceramics.¹⁻³ Novel methods for chemical syntheses of spinel starting materials^{1,4} were developed at the University. These materials, when custom hot pressed at moderate temperatures and high pressures *in vacuo* by Eastman Kodak Company, were shown as early as mid-1966⁵ to be capable of producing substantially transparent 1 in. dia discs. During late 1966 and early 1967, still larger shapes, ~2 in. dia by 1/2 in. thick, were custom hot pressed by Kodak for N. C. State University for use in ARO-D sponsored research concerned with strengthening of spinel at high temperatures.⁶

At least a few of the larger specimens produced from starting materials made at the University and subsequently hot pressed by Kodak attained a relatively high degree of transparency. They were, however, reddish in color due to sulfur residues.^{5,6} In mid-May, 1967, the sponsoring agency (ARO-D) was informed that, though much remained to be done in terms of attaining consistent optical quality, transparent polycrystalline spinel appeared to be technically feasible, and that it appeared to have considerable potential as a candidate material for transparent armor.⁷

Subsequent work demonstrated the feasibility of fabricating larger shapes by hot molding, utilizing a proprietary Kodak process (open die hot pressing or *hot molding*) in which the preformed material is subjected to less lateral restraint than in conventional hot pressing. In hot molding, there are far fewer limitations on sizes and shapes which can be successfully formed, in that there is much less dependence upon sizes of available ingots and attainable strength levels for refractory metal die components. Small lots of $\sim 2 \times 4 \times 1/4$ in. finished spinel tiles were successfully custom hot molded by Kodak for the University from two quite different starting materials.

In the first series, sulphate-derived spinel particulates deliberately doped with sapphire whiskers were hot molded, producing blanks from which test specimens were subsequently cut for studies of high temperature strengthening and toughening in whisker-reinforced spinel.^{3,0,9} Some sulfur discoloration (a characteristic maroon red) was present, but, even so, substantial transparency was attained both in the undoped control and in those containing small concentrations of whiskers (0.1 and 1.0 volume %).

Thereafter, a modest quantity of a prototype commercial grade of spinel was made available to the University by its manufacturer, W. R. Grace & Co. This material, identified as Lot S-2 DBM, was also hot molded by Kodak, producing several $2 \times 4 \times 1/4$ in. finished shapes, which were then furnished to Dr. John W. Taylor, Los Alamos Scientific Laboratory¹⁰ for use in dynamic (Hugoniot) yield measurements and related impact studies. The Grace S-2 material was nonstoichiometric (MgO-rich) and had rather 2

different flow characteristics in the Kodak hot molding process. Within the limited number of tries (11 in all), it did not achieve the degree of transparency attained earlier with the N.C.S.U. sulphate-derived material. However, sound, dense pieces verging on transparency were produced having microstructures characterized by very fine grain sizes, typically ~0.2 µm.

In essence, this study has been directed toward achieving transparency in nominally pure (undoped) polycrystalline spinel by hot molding and/or rate controlled sintering. Both methods tend to optimize the densification process at the lowest possible temperatures, and consequently each of them offer the prospect of achieving full densification with minimum grain growth. However, because temperatures are kept as low as possible (thus suppressing diffusional processes responsible for grain growth), success by either method tends to be strongly (perhaps critically) dependent upon the (surface area/energy) particulate properties and high temperature flow characteristics of the starting materials. These powder properties, in turn, are quite sensitive to both chemical constitution and processing history.

On the other hand, fine and uniform grain sizes have consistently been demonstrated to correlate well with increased strength and even ballistic performance in ceramics, ¹¹⁻¹³ generally in accordance with the Petch relationship¹"

 $\sigma_{\rm f} = \sigma_{\rm o} + K \omega^{-1/2}.$

Thus, the methods employed in this study offer, along with the potential hazards of their heightened materials sensitivity, the possibility of direct and significant optimizations of the ultimate mechanical properties of the ceramic shapes being produced. In these respects, the basic direction followed in this investigation has differed substantially from that of others aimed at achieving transparency in polycrystalline spinel by conventional hot pressing, 15,16 arc melting and related fusion techniques, 17 or conventional (isothermal) sintering. 18-20 In these other studies, much higher temperatures generally have been employed, frequently in conjunction with some deliberate doping with additives to serve as sintering aids, e.g., by facilitating liquid phase transport. Transparency has been achieved with various degrees of success by both hot pressing and sintering in some of these studies. However, it is not surprising in view of the temperatures, atmospheric environments and dopants employed, that the resulting grain sizes have tended to be quite large, being typically two to three orders of magnitude greater than that of the N.C.S.U.-Kodak hot molded spinel.

Unfortunately, and for a variety of reasons, the critically important spinel starting materials (calcined spinel powders) did not emerge from the University's synthesis efforts at the intended quality levels. The large quantity of material produced in the final weeks of the active experimental program was substantially inferior in terms of cation stoichiometry and sulphur content to several eirlier smallbatch lots.^{3-5,8} Consequently, the later densification phases of the program had to contend with poor quality, gas-laden material, which created many, unexpected problems in hot molding.

Important new insights were obtained into the kinetics of densification during sintering of spinel under nonisothermal conditions. The kinetic data presently available are confined primarily to the range 60 to 90% of theoretical density, over which linear densification rates could be experimentally maintained. For a variety of reasons, it was not possible under this program to carry out the final experimental optimizations by means of rate control concepts in achieving full densification of spinel by sintering. [It should be noted that such rationales for optimization of sintering have now been successfully demonstrated experimentally for polyphase ceramics and, most recently, as a means of attaining dense high alumina ceramics with exceptionally fine, uniform grain sizes].

It is the purpose of this report to outline the technology, to describe the results, and to examine some of the factors which contributed to the unexpected problems and difficulties encountered. Finally, some interpretations of the technical findings - in consonance with other ongoing research studies - are advanced.

PLAN OF WORK

In keeping with the project scope, experimental effort under this program was organized, and will be described in subsequent sections, in terms of three interrelated phases. The tasks undertaken by the various participating organizations are summarized below.

Phase I: Powder Synthesis

Under the first phase, University personnel undertook to scale up an existing (at that time, patent pending) small-batch process' for chemical synthesis of a suitable spinel precursor, and to provide for its semi-continuous calcinations, thus converting the precursor salt to the mixed oxide, spinel. Since the personal analytical skills and laboratory facilities which had played a significant role in Dokuzoguz's original development of both chloride¹ - and sulphate⁴-derived spinels were no longer available at the University, arrangements for analytical services were made with an experienced outside vendor, widely recognized as a source of reliable wet chemical and spectrographic analyses of ceramics and related materials.

していたとうというないのであるのからいいで

Phase IIA: Hot Pressing

Under Phase IIA, materials generated under Phase I were densified by hot molding (open die hot pressing) at moderate temperatures (~1200°C) and high pressures (~25,000 psi), using refractory metal tooling operating in vacuo. Since very robust equipment (far beyond the University's hot press capabilities) is required to maintain such conditions on a large specimen (>8 in.²), this phase of the work (which to a considerable degree made use of Kodak's existing facilities and proprietary processes) was carried out by Eastman Kodak Company. Larger runs were preceded by and supplemented with a number of trial runs in a smaller (1 in. dia) hot press under comparable conditions, permitting evaluation and some degree of optimization of the densification behavior of specific lots of starting materials.

Phase IIB: Rate Controlled Sintering

Under Phase IIE, effort was focused upon an optional densification method (rate controlled sintering), considered potentially capable of achieving densification (and possibly transparency) in spinel at lower unit costs and with fewer restrictions on sizes and shapes than is the case with hot pressing. This novel approach to sintering stems from earlier theoretical^{5,21} and experimental²² studies in this laboratory. This extension of rate controlled sintering to spinel was carried out by its original co-developer, D. R. Johnson, for whom the work accomplished under this program served as a doctoral dissertation topic.²³ Though it was not possible in the critical last weeks of this project to extend Johnson's investigation of the linear densification rate regime (~60-90% of ρ_{th}) to a fully optimized, multiranged, rate controlled sintering program capable of dealing effectively with final stage densification, such programs have been found effective for other materials. Significant advantages, especially with respect to reduction of fired grain size and grain size distribution, have recently been reported for rate controlled sintering of dense high purity alumina.24

Since it was obvious that material from Phase I would not become available until relatively late in the program, the kinetic studies which formed the principal part of Johnson's work were carried on with a small quantity of a prototype commercial spinel material* having composition and particulate properties generally comparable with earlier "good" lots of sulphate-derived spinel.^{3,6,8}

Spinel powder, presumed to be nitrate-derived, identified as Lot S-2 DBM, made available gratis by Dr. D. G. Wirth, Washington Research Center, W. R. Grace & Co., Clarksville, Maryland.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

Phase I

Three principal functions were undertaken in Phase I: (1) synthesis of a spinel precursor from the respective sulphate salts (MgSO₄ \cdot 7H₂O and Al₂(SO₄)₃ \cdot 18H₂O) by a cocrystallization process (2) initial drying and partial dehydration of the damp, cocrystallized precursor containing mixed sulphate salts together with the double salt, MgAl₂(SO₄)₄ \cdot xH₂O) and thereafter, (3) calcination of the precursor, to remove both the residual water of hydration (as H₂O vapor) and sulphur (presumably as SO₃ gas) and to convert the product into the stable mixed oxide, magnesium aluminate spinel (MgAl₂O₄). The principal problems involved were considered to be:

- (a) Obtaining an intimate initial mixture of the sulfates with an exact stoichiometric ratio. In principle, this is done by proper batching (on the basis of adequate analytical data), than melting (to form a saturated, hot mixed salt solution), and finally, solidifying by rapid cocrystallization.
- (b) Dehydrating the cocrystallized salt mixture without remelting to produce a friable product of reasonably high particle density. This intermediate product must be rather finely divided to allow easy escape of SO₃ during decomposition; however, individual particles should have reasonable density to reduce bulk and dusting.
- (c) Decomposition of the dehydrated sulfates with complete removal of sulfur but without excessive sintering or undue loss of free surface area of the product.
- (d) In all steps, maintaining high purity of material particularly avoiding contamination with metallic ions and/or silica.
- (e) In all steps, maintaining efficient materials handling to achieve reasonably high production rates. In this regard, the calcining stage was considered to be the most time consuming.
- (f) Finally, avoiding air pollution from SO₃ fumes.

Cocrystallization

Figure 1 schematically illustrates the steam heated 30-gallon polyproppylene mixing vessel in which the starting magnesium and aluminum sulphate hydrate salts were batched, intimately mixed, and converted to a hot concentrated aqueous solution prior to cocrystallization. The hot concentrated salt solution was transferred (in initial runs by the drain valve illustrated, and thereafter by ladling) into heavy-duty aluminum foil trays (~20 1/2 x 12 1/2 x 1 1/2 in.) to a depth of ~3/4 in.

Figure 2 is a flow chart illustrating the cocrystallization and dehydration steps of the process, as determined on the basis of prior work, ^{3,4,6,8} additional preliminary studies, and early operational experience. The indicated batch size represents a practical working limit for the available facilities, and is designed to yield ~11 lb. of calcined spinel





(including fines). The crushing and screening procedures employed were very inefficient, resulting in as much as 40-50% of the total being screened out as fines in the next-to-last step. With the existing facilities, requiring largely manual operation, one such batch of precursor could be produced in two 24 hr days, but only under maximum effort, consuming at least 2 man-days of labor per day. Drying

Existing cabinet dryers (steam heat for 1st stage, electric for 2nd) were utilized, with the product being handled in the aluminum trays. The soft "cake" which developed during the first drying stage was manually broken into coarse lumps, providing better air circulation, thus facilitating heat and vapor transport. Remelting during drying, with attendant densification (vitrification) which slowed drying and hampered later crushing of the product, was a not uncommon occurrence in these manually controlled dryers. Installation of temperature controllerprogrammers could have eliminated remelting problems, as well as increasing drying efficiency.

Crushing and Screening

Well dried (second stage) material is hard and tough, and the dust generated during crushing and screening is irritating to skin, eyes, and nostrils. These rather time consuming operations were performed manually by personnel who wore protective gloves, goggles and/or breathing masks. Though it would have been very desirable in the interests of efficiency and quality control, it was not feasible within the limits of this program to install an appropriate closed, mechanised materials handling system.



and the second second second second second

1. 2023

7

* Actual quantities depend upon raw material analyses for cation stoichiometry and water of hydration.

** Proper point for on-line verification and/or correction of cation stoichicmetry (if timely analyses are available).



Fig. 3. Schematic diagram for dynamic calcining furnace and effluent gas scrubber.

Dynamic Calcination

A six-foot long Lindberg four zone diffusion furnace was extensively modified to provide an inclined, rotating tube counterflow calcining system. This unit, including a cascaded scrubber system to remove SO3 gases from the stack effluent, is schematically illustrated in Fig. 3. The two-inch I.D. by seven-foot long mullite tube was supported in double collet clamps and bearings designed to accomodate thermal expansion, out-of-roundness, and camber without undue stress on the tube (see Fig. 4). Both the angle of inclination and rotation rate could be varied over wide experimental limits. Inlet and exhaust plenum chambers enclosed both ends of the tube, and provided for controlled introduction of prefiltered, preheated air to sweep products of decomposition through the tube, and for collection and removal at the exhaust end (see Fig. 5). A vibratory feeder (Fig. 5a) introduced predried and sized cocrystallized sulfate feed material at the high end and a collection system permitted gravity removal of the calcined material at the lower end (Fig. 5b). A complete set of working drawings for all components fabricated by N.C.S.U. in modifying this furnace were furnished to the sponsoring agency.



(a)

(b)

Fig. 4. Inclined rotating tube drive details (a) upper thrust/idler bearing-drive unit (left view); (b) lower idler bearingexpansion/camber runout unit (right view). Mullite tube is seven feet long (axis shown horizontal in these views), supported by and centered in the double collet grips. Thick Fiberfrax paper cushions and insulates tube beneath collet, and also is used for iris gaskets through which tube enters plenum chambers.

Phase IIA

All hot pressing and hot molding runs were carried out by Eastman Kodak Company, making use of their own existing facilities and processes. Though they have for obvious reasons wished to protect some proprietary company interests, Kodak personnel have in the past been very cooperative in providing adequate information to permit realitic reporting of processing history^{3,6,8} and in this study, to facilitate planning of future runs and rational reporting and interpretation of results.²⁶⁻²⁹

In view of the marked densification rate sensitivity observed for spinel in comparable temperature ranges in rate controlled sintering studies under Phase IIB²³, it is appropriate to note that Kodak's hot pressing/hot molding facilities do not appear to be instrumented for strain (punch travel) - strain rate data and/or control. For this reason, it has not been possible in this (or in earlier cooperative studies^{6,8,10}) to properly evaluate the concept of rate controlled densification^{2,3,5} during hot molding of this material, even though spinel is known to be a prime candidate for this kind of control because it is both gas-retentive and strongly rate sensitive in its plastic yielding behavior.



(a)



(b)

Fig. 5. Inlet and exit plenum details (a) upper plenum, stack outlet, and vibratory precursor feeder (teilon coated bowl); (b) lower plenum, product discharge (vertical alumina tube), and air preheater. Sightglass (extreme right) permitted visual monitoring of material moving along tube axis.

Phase IIB

Rate Controlled Sintering Furnace and Control Equipment

And the second second

As described by Johnson, "Process control in experimental rate controlled sintering differs from that in conventional sintering by the reversal of the roles of the normally independent (temperature) and dependent (densification rate) variables. In rate controlled sintering, densification rate is independently controlled and the resultant temperatures and time rate of change of temperature are measured. This unique method of process control requires special equipment and instrumentation".²³

The apparatus used (see Figs. 6 and 7) has been under development at N.C.S.U. for several years, and has been described elsewhere, from initial concept,²¹ through development and refinement,^{22,23} and active experimentation.²²⁻²⁴ For the purposes of this program, some new components were added and minor alterations were made, principally to simplify and improve instrumental manipulations, and to provide an alternate high temperature (~1700°C) furnace for achieving very rapid densification rates, and an alternate, slow speed motor for the DataTrak programmer for controlling very slow densification rates.



Fig. 6. Schematic diagram of programming/controlling and measuring instrumentation for rate controlled sintering (After Ref. 21).



Fig. 7. Sectioned schematic of rate controlled sintering furnace showing sample holder and shrinkage sensor (After Ref. 23).

Table 1. Starting Materials

Manufacturer's Designation	Baker and Adamson Magnesium Sulfate Crystals ACS Code 1924	Baker and Adamson Aluminum Sulfate crystals, ACS Code 3241
Chemical Formula	MgSO4+7H2O	Al ₂ (SO ₄) ₃ ·18H ₂ O
Dehydration and	m.p. $(-6H_20)$ 150°C	m.p. (-18H ₂ O) 86.5°C
(Handbook Data)	MgSO4 d. 1124°C	Al ₂ (SO ₄) ₃ d. 770°C
Cation Impurities [*] (spectographic analyses, p	pm)	
A1	-	(Major, >10%)
Ba	-	6
Cu	15	12
Mg	(Major, >10%)	7
Si	6	7
Quantitative Analyses, %†	(Range of 5 samples)	(Range of 7 samples)
A1	- -	8.52 - 8.81
Mg	10.06 - 10.70	-
SO ₄	39.62 - 42.40	47.64 - 48.60
$Al_2(SO_4)_3$, anhydrous	-	56.22 - 59.33
MgSO4, anhydrous	49.68 - 52.90	-
Loss on Ignition at 1300°C, %††	83.48	83.34

* External Analytical Service Laboratory, B 303 (cont.), 9/8/69; † B 303, 8/20/69; †† C 782, 1/7/70.

MATERIALS

Since spinel constitutes only about one sixth of the weight of original starting material, for Phase I it was necessary to obtain substantial quantities, 200 lb. and 500 lb. respectively, of the required reagent grade magnesium and aluminum sulfate hydrates. The basic chemical data pertinent to these specimens is given in Table 1. Upon receipt, these very hygroscopic materials were carefully transferred to tightly sealed plastic bags in convenient quantities for storage, hepefully minimizing atmosphere-related variations in water content. The magnitude of such variations, and their potential deleterious influence upon precision batching to obtain an exact MgO:Al₂O₃ stoichiometry, is indicated by the range of values reported for five and seven samples, respectively, of these bagged materials. Prereacted spinel materials produced by another process, presumably from nitrates, were made available gratis by the manufacturer, W. R. Grace & Co., for use in portions of the work undertaken in Phases IIA and IIB. Table 2 summarizes the available analytical data for these materials.

Table	2,	Prereacted	Spinel	Materials	Obtained	from	W.	R.	Grace	&	Co.,
			C	larksville	, Maryland	1					

	Lot S-2*	Lot S-? DBM*	<u>Lot S-5570+</u>
Mg0:Al ₂ O ₃ mol ratio	1.086	1.062	1.003
Impurities, ppm			
Fe ₂ 0 ₃	140	110	Fe 66 - 79
MnO	2	2	_
S102	40	320	Si 6 - 10
CoO	nd (<10)	nd (<10)	-
Na ₂ 0	30	30	nd (<500)
T102	50	80	-
2r0 ₂	nd (<40)	nd (<40)	-
B203	3	3	-
NiO	40	· 40	-
N	< 50	<50	-
			Cu 6 - 10

* External Analytical Service Laboratory, A 248, 6/10/69; † Analysis courtesy W. R. Grace & Co.

RESULTS AND DISCUSSION

Phase I: Synthesis of Precursor

Stoichiometry

From Fig. 2, it is obvious that, apart from accidental contamination, the cation components of the chemical constitution of the spinel and, thereafter, of the densified spinel ceramic essentially become fixed at the time the hot molten salt is cocrystallized. In later stages, cation stoichiometry cannot be changed significantly, except possibly by blending of batches which differ in MgO:Al₂O₃ ratio. It is also apparent that very precise and reliable analyses of the starting materials are required if the desired stoichiometry is to be attained reproducibly. However, as indicated by Table I and its associated text, a considerable spread in the available data was encountered; presumably, such variations can be attributed to (1) the materials, (2) the sampling procedures and/or (3) the accuracy and reproducibility of the analyses. As often is the case, even after much work has been done, it is not really possible in this instance to be certain which of the three factors dominate. However, it is clear that, for whatever reasons, uncertainties associated with the

Table 3. Comparisons of Analyses for Two Irial Lots of Cocrystallized Spinel Precursor

	Sampl	.e A	Sample B			
SO3 MgO AlO MgO/Al2O3 ratio % solids (ignited	<u>Analysis 1</u> * 53% 8.9% 17.8% 1.28	Analysis 2 ⁺ 61.2% 5.36% 19.5% 0.696 25.01%	Anilysis 2* 54.02 7.7% 18.5% 1.065	Analysis 2+ 55.69% 7.58% 18.05% 1.069 25.87%		
Agreement between Analyses	Po	or	Goc	bd		

* External Analytical Service Laboratory, B 882, 10/10/69; corrected 11/10/69; † Check analyses courtesy Dr. N. Levy, Jr., W. R. Grace & Co., 11/10/69.

actual quantitative oxide content (MgO and Al2O;, respectively) of the starting sulphate salts - and of the resultant stoichionatries (see Table III) - persisted throughout this study. These uncertainties, coupled with other operational factors, ultimately led to overcompensation for apparent prior errors in batch formulations, and contributed to unexpectedly poor control of cation stoichiometry. The first large lot of precursor salt, identified as Batch 8, was formulated for 1:1 stoichiometry on the basis of all analytical data then avilable. However, ss shown by Table 4, it was found to be quite alumina-rich: again, bacch yields were in apparent disagreement with batch formulations. At this juncture, fresh specimens of the starting saits (which had been stored in plastic bags in the open laboratory environment for about five months) were sent for new analyses, to include loss on ignition at 1300°C (see Table 1), [In addition, a new lot (Batch 9) was made, with the formulation having been shifted toward magnesia, apparently compensating for the aluminarich report from Batch 8.]

Table 4. Cation Stoichiometry of Four Production Batches of Spinel Precursor

	Batch 8*	Batch 9t	Batch 117	Batch 12†
	(calcined)	(precalcined)	(precalcined)	(precalcined)
MgO	24.87%	9.39%	9.55%	8.867
A1.0,	75.88%	20.74%	20.74%	20.38%
Mg0:A1 ₂ 0 ₃ mol ratio	0.829	1.155	1.164	1.100

* External Analytical Service Laboratory, C 782, 1/7/70; + D 154, 2/13/70.

日本学生などのないないのないでも見

Section of the Albert of Ball and

Date	Identity	Batch Wei	ghts, 1b.	Initial Weight Ratio	Final Mol Ratio
	}	Magnesium Sulphate	Aluminum Sulphate		
12/8/69	Batch 8	17.59	46.506	0.3782	0.829
12/30/69	Batch 9	18.738	46.416	0.4037	1,155
1/7/70	Batch 10	* 19.19	46.506	0.4126	
1/16/70	Batch 11	18.84	46.133	0.4084	1.164
1/21/70	Batch 12	18.84	46,645	0.4039	1.100

Table 5. Formulation and Resulting Stoichiometry of Large Production Lots of Spinel Precursor.

* During ladling of the hot melt, the operator noted undissolved "nodules" of material in the bottom of the vessel; he quite properly recommended it not be analyzed, calcined, or used. From its initial weight ratio, it seems likely that Batch 10 was supersaturated with magnesium sulphate; graphical estimates (see text) indicate that the final mol ratio would have exceeded 1.20.

In evaluating the additional analytical information, the operator responsible for the cocrystallization process concluded that stored aluminum sulphate had remained essentially inchanged, whereas magnesium sulphate had changed (presumably by equilibrating with atmospheric moisture) during the storage period. It is now apparent from the records that, lacking additional analyses and being under considerable time pressure, the operator arrived at a 2.46% additive correction factor which was applied to the magnesium sulphate content of all remaining runs (Batches 10-12).

Table 5 summarizes the initial formulations and the resulting stoichiometric ratios (from *post facto* analyses) for Batches 8-11. Recent reevaluations of these data have shown that, when treated graphically (not illustrated), they correspond rather well with a simple linear relationship of the form

y = a + bx

where x initial weight ratio y = final mol ratio a = intercept constant (~5.905)

b = slope constant (~17.77).

Based upon this admittedly empirical analysis,* to achieve the desired 1.00 mol ratio the initial weight ratio should have been ~ 0.391 ($\pm \sim 0.0025$).

* The observed linear relationship appears to support the relative reliability of the earlier stoichiometric analyses (see Table 3); the trends (slopes) appear to be correct, but offsets may well exist for quantitative values.

Call Call A Details

This value is in reasonable accord with a revised weight ratio of 0.3988 recommended on Jan. 16, 1970 by the cognizant staff scientist on the basis of his review of the Jan. 7, 1970 analytical data (Table 1). His calculations indicated that the starting materials were actually $MgSO_4 \cdot 6.87H_2O$ (not $\cdot7H_2O$) and $Al_2(SO_4)_3 \cdot 15.3H_2O$ (not $\cdot 18 H_2O$). Unfortunately, these more precise calculations and the recommended weight ratio of starting materials did not reach the operator concerned in time to influence the formulation of any of the large production batches.

Purity

As mentioned in the preceding section, the condition at cocrystallization not only determines stoichiometry, it also has a major role in determining purity. In general, subsequent handling can only add cation contaminants, not remove them (this point is discussed again in a later section). Therefore, it was of some concern to determine impurities present in starting materials, and if possible to eliminate them prior to cocrystallization.

The spectrographic data given in Table 1 relate to the respective sulphate hydrate salts, (i.e., a very dilute form of the final product) and constitute a rather insensitive measure of the impurities which will be found in the much more concentrated oxide forms. For this reason, additional analyses of cation impurities were obtained on starting materials which had been ignited at 1300°C; the results are given in Table 6. It is evident that the magnesium sulphate is much cleaner than the aluminum sulphate, and that the latter, making up the bulk of the batch, dominates the impurity content of the calcined product. Sodium (Na) appears to be the only significant process-related contaminant. The operator noted that the aluminum sulphate contained readily visible insoluble "trash"; this had been previously observed in earlier studies,⁶⁸

MgSO4 $A1_{2}(S0_{4})_{3}$ Element* ACS 1924 ACS 3241 (Batch 8, IRTCF 13) ignited @ 1300°C ignited @ 1300°C Ag 1 1 3 A1 5 Major Major В 25 10 1 10 5 Ca -Cr 5 5 _ 10 25 Cu 10 250 Fe 250 Major 100 Mg Major Mn 10 10 50 Na 500 5 Si 50 25 :

Table 6. Cation Impurities in Starting Materials and Calcined Spinel.

Concentration in ppm unless otherwise noted; C 782, 1/7/70.

.

working with salts of comparable quality obtained from another vendor. Whereas in earlier work it had been possible to remove the "trash" by filtration,* there was very little hope of doing so from the directmelted batches produced in this program.

Phase I: Dynamic Calcination of Dehydrated Precursor

Optimizing and Operating the Dynamic Calcining Furnace.

The inclined rotating tube calcining furnace (IRTCF), described earlier, is a relatively complex device with a number of independent controls, e.g., for temperature, rotation rate, stack draft, air counterflow, etc. Under dynamic conditions, they give rise to a whole set of interdependent operating parameters which combine to influence markedly the local conditions to which the material is subjected at various points along the tube length, the stability of its patterns of movement through the furnace, as well as what is done to it in terms of thermochemical treatments. These parameters were studied in a series of preliminary runs of a few minutes to at most a few hours duration. It was found rather quickly that a favorable set of conditions existed (described later) wherein the whole dynamic system could be operated under essentially stable conditions. When dynamic stability was attained, the principal preturbations of concern (which could be detected and cleared by the operator) were occasional sticking or jamming of feed materials in the feed tube or near the upper (entrance) end to the rotating tube itself. To attain this much-needed stable mode of operation, two conditions relating to the feed material had to be satisfied: (1) the material had to be sized relatively coarsely, ~-6 mesh, and substantially free of fines $(\sim -20 \text{ mesh})$, and (2) the material had to be precalcined to ~650°C. This latter condition which removed most of the water of hydration, was necessary to avoid forming an almost unmanageable, highly corrosive effluent, equivalent to fuming sulphuric acid, which had devastating effects upon the upper plenum chamber and stack components.

Since no other suitable facility for precalcination was available, the dynamic tube furnace (IRTCF) was employed; thus each lot of material made two separate trips through the tube, (1) to precalcine, removing $H_{20} @ ~650°C$, and thereafter (2) to remove nominally anhydrous SO₃ @ ~1145°C. Typical operating conditions for each case are given in Table 7.

Weight loss (principally H_2O) in precalcining is about 33%; for final calcination the loss (principally SO_3) is ~80%. These very substantial weight losses are accompanied by (1) a solid-to-vapor change of state, (2) expansion of the vapor as it comes into equilibrium with

^{*} The Palmour-Dukuzoguz patent teaches (1) preparation of a cold, dilute aqueous solution of the starting salt, (2) filtration to remove tramp impurities, (3) concentration by evaporation (simmering), and finally, (4) cocrystallization by chilling.

Slope	RPM	lope RPM Temperatures, °C						Avg. Feed Bate	Avg. Product Rate
Stohe	RIH	Zone 1	Zone 2	Zone 3	Zone 4	Air Preheater	g/hr	g/hr	
				Preca	alcining				
1:12	6	360	370	500	660	~ 950	625	416	
				Calc	ining				
1:12	3	740	880	1130	1145-1150	0 ~ 950	585	147	

Table 7. Typical Operating Conditions for Inclined, Rotating Tube Calcining Furnace.

PROFESSION OF

the heated tube. Under dynamic conditions, both factors contribute to very large volumes of expanded vapor, which move up the tube at relatively high (at times almost explosive) velocities, sufficient to entrain and blow back fines at the upper (feed) end. By contrast, the lower portion of the tube, in the hottest zone, is relatively quiescent, marked by gentle thermal convection currents. Best handling of the counterflowing gases was obtained by keeping the entire system (plenums, tube, and product collection bag) under moderate negative pressure through proper regulation of the forced draft scrubber fan damper and the excess air inlet at the upper plenum stack. Under these conditions, sufficient air (filtered through a glass wool plug) was aspirated through the air preheater, so that pressurized air was not required.

With properly sized feed material, excellent tumbling action was obtained; the rolling, tumbling material covered an almost ideal ~120° segment of the tube circumference. This vigorous action provided for very rapid thermal equilibration and repeated exposures of each granule to the "free surface" of the bed, directly in contact with the countercurrent gas stream. Transit times through the furnace varied somewhat with granule size, faster for large grains, slower for small. On the average, under calcination conditions, transit times were in the 25-30 minute range, resulting in hot zone (peak temperature) residence times estimated at 5-8 minutes. Optical pyrometer readings taken directly on granules within the hot zone were consistently within a few degrees (i.e., within the limit of observer error) of those measured by thermocouple on the appropriate (idicator_controller.

In general, the IRTCF unit worked very well, with only minor mechanical adjustments being required; most of them related to the small vibratory feeder and its associated feed tube components. The very corrosive nature of the sulphur-laden exhaust gases created some problems in the upper plenum chamber and eventually, in the scrubber system. The 4 in, dia cross-section of the pyrex pipe components of the scrubber resulted in high gas velocities at the strong negative drafts required for stable furnace operation. Scrubbing efficiency probably would have been improved by — larger column cross-sections, denser packings, and slower local velocities.

19

شميانا يميك يعدالهما ممالطهم ممامسهم

The unit was operated continuously, 24 hours per day, for a period of more than seven days (January 26-February 1, 1970) in precalcining and calcining ~30 lb. of spinel from Batches 8, 9, 11 and 12. The furnace was manned by two-man crews (who also performed some crushing and acreening tasks) for 16-18 hrs per day and by an experienced person operating alone for the remaining hours.



Fig. 8. Thermoanalytical characterizations of starting materials, intermediates, and final spinel calcined at 1145°C. Material from Batch 11. Dynamic differential calorimetry to 1200°C @ 10°C/min, sapphire (Al₂O₃) reference; curves corrected for baseline drift.

The Calcining Process

For the material in question, calcination continues and completes the process begun in Fig. 2. It relates to high temperature chemistry: (1) dehydration of the remaining water of crystallization in the starting salts, (2) decomposition of the resultant anhydrous sulphates, and (3) solid-state reaction of the remaining oxides to form the mixed oxide spinel. The sequence of events occurring during thermal treatment is indicated by the superposed thermoanalytical (DDC) traces shown in Fig. 8. The initial salts show strong endotherms at ~100°C, and later at ~250°-300°C, all associated with dehydration. The decomposition of sulphur is denoted in aluminum sulphate by an endotherm at $\sim 800^{\circ}$ C, and in magnesium sulphate by a more complex endotherm from about 750-1000°C. being substantially complete by 1100°C. The cocrystallized and partially dehvdrated material shows a dehvdration endotherm at $\sim 300^{\circ}$ C, a strong sulphate decomposition endotherm at ~800°C, and a less prominent one at ~950°C. After precalcination at 650°C, only the sulphate decomposition exotherms remain. Material dynamically calcined at 1145°C appears to be substantially free of any thermal activity which might be indicative of further reaction; on the basis of these data alone one would conclude that calcination was complete. A similar conclusion would be reached on the basis of x-ray diffractometer studies (not illustrated), which for this material calcined at 1145°C- indicated well crystallized but very fine grained spinel containing some free MgO.

However, other criteria, including both chemical analyses and discolorations occurring in hot molding evaluations, clearly show that sulphur was incompletely removed. This topic is discussed in some detail in the following section.

Anion (SO3) Removal

As indicated in the preceding section, both x-ray crystallographic and DDC analyses indicated that calcination was essentially complete at 1145°C in the dynamic calcining furnace. Table 8 shows that the elemental sulphur content of Batch 8, IRTCF 13 (initially thought to be <0.01% at the time the process was considered to be optimized and the seven day calcining run was started) was actually in the range 0.25-0.35% by weight, equivalent to almost 1 wt. % SO₃. Had the true sulphur content been known at that decisive moment, further experiments capable of really optimizing the process at higher calcining temperatures would have been easy and timely to make, well within the thermal capabilities of the calcining furnace (max. temperature ~1400°C).

Table 8 includes data from several earlier dynamic runs, and for comparison, Zimmer's⁸ static-calcined spinel having a sulphur content of 0.08%. There is no clearly discernable temperature dependence in this limited spread of data; however, there are some indications that the ease of sulphur removal may possibly depend upon the cation stoichiometry ratio, with magnesia-rich spinels being more sulphur-retentive.

			LO TOUTOMETLY		
Material	Mg0:Ai ₂ 03 mol ratio	Calcining Procedure	Temperature °C	Sulfur Content (2S)	Source of Analysis
Zimmer spinel	~1.00	Static, deep bed	1080 (24 hr)	0.08 (0.048 after hot molding)	Table 1 of Ref. 8
Johnson spinel #2	~1.00	Precalcined,	700	6.03	*C 458, 11/24/69
(ŗrecalcined,-20 mesh)	~1.00	static Dynamic (IRTCF #2)	1075	0.423	C 458, 11/24/69
Batch 2 (-6 mesh)	1.056	Dynamic	1075	0.46	*C 501, 12/11/69
Batch l (-6 mesh)	1.086	(IRICF #0-11) Dynamic (IRTCF #7-11)	1085	0.71	C 501, 12/11/69
Batch 8 (-6 mesh)	0.829++	Dynamic (IRTCF #13)	, ,	0.361†	*C 782, 1/7/70
Batch 8 (-6 mesh)	<u> </u>	Dynamic (IRTCF #13)	1140	<0.01 +	*C 782 (corrected) 1/7/70
Lot 08015020/11016018 (Blend of Batches 8 and 11)	.091++	Dynamic (TRTCF #18 #20)	1145-1150	0.245	*D 771, 5/20/70
Lot 08015020/11016018 (Blend of Batches 8 and 11)	1.1729+†	Dynamic #20) (IRTCF #18, #20)	1145-1150	0.235	AMMRC, cited in Table 1 of Ref. 24
* Analysis by External Analy † In a routine check of analy sulfur content was erroniou likelihood of much higher s personnel involved until m	tical Servic ysis reports isly reporte sulphur cont ich later.	e Laboratory at the external a d to N.C.S.U. by t ent in this pivota	nalytical serv elephone. Writ l sample were	tice laboratory ten reports in not received b	r, a very low idicating the oy the University
<pre>++ Lot #08015020/11016018 was rich) and Batch 11 (magnesi</pre>	carefully b ia-rich) on	lended to achieve the basis of analy	l:l cation sto ses given in T	ichiometry fro able 4. Analys	<pre>mm Batch 8 (alumina- ies of the actual</pre>

blend show it to be quite magnesia-rich. Evidently Batch 8 was appreciably less alumina-rich- or Batch 11 more magnesia-rich - then the analyses indicated.

Cation Contaminants

The final products, as well as all earlier intermediates, were handled with great care to avoid as much as possible the pickup of accidental contaminants; disposable plastic gloves (protecting product and producer) were used in manual operations, and plastic bags were employed to collect, transfer, and store the product in all stages. Product purity was considered to be vulnerable to (1) airborne laboratory dirt and dust which could have been incorporated during drying, crushing, screening and other "open" operations, (2) pickup of silica from Fiberfrax debris or from the hot mullite furnace tube, and (3) other accidental sources. Since neither iron nor silicon contents increased as a consequence of handling and firing (Table 6), possibilities (1) and (2) apparently did not occur to any significant degree. However, soda content (as Na) did increase significantly. No conclusive evidence for attribution of a sodium source is available, but the best candidates are thought to be (1) airborne transport of sodium carbonate dust (even though a dense, nondusting grade was being used) from the supply tank for the second scrubber column to the precursor feeder on the furnace during periodic recharging and mixing of the sodium carbonate solution; (2) soluble salt "drip" from within the steam dryer during humid conditions; or (3) a cleaning agent residue in process equipment.

Phase I: Blending and Milling

The granular calcined product derived from batches of differing stoichiometry) was blended to achieve uniform stoichiometry and milled to break up agglomerates. Briefly, the procedure consisted of (1) dividing a given quantity of granular product - in a sample splitter to avoid size segregation - to the approximate quantity needed for blending, (2) accurately weighing and batching in 300g quantities to achieve the best attainable stoichiometry from the requisite number of lots, (3) tumbling 2 hr in a twin shell blender - with added 96% Al_2O_3 balls and $\sim 0.27 \text{ml}$ triethanolamine as a milling aid - to break down the friable granules, (4) combining two 300 g tumbled lots. then fine milling for 2 hr in a 96% Al_2O_3 jar mill (1 gal, capacity) with a 4:1 ball:charge ratio, (5) tumbling again for 15 minutes to break up and disperse any "caked" material from the ball mill, and (6) screening through -20 mesh hylon to remove any remaining coarse agglomerates. This sequence, yielding .600g of milled material, was repeated as needed to make up the required total.

Two different blends were prepared, each designed - on the basis of the available analyses - to achieve 1:1 Mg0:Al_2O_3 stoichiometry. The first, identified as Lot 08015020/11016018-DBM-T-1 through 4, a blend of Batches 8 and 11, was forwarded to Eastman Kodak Co. for use in Phase IIA. The second, identified as Lot 811129B-T-DBM-1 through 17, totalling 20 lb., was drawn from Batches 8, 9, 11 and 12, and was forwarded to AMMRC^{30,11} in compliance with a contractual requirement under Phase I.

Phase I: Characterization of Product.

For reasons discussed in the foregoing section, the quality of the product (spinel powder) fell far short of expectations. The results are compared with an earlier small-batch sulphate-derived spinel^{4,4} in Table 9.

Table 9. Characterization of Sulphate-Derived Spinels

	*Zimmer <u>Powder</u>	spinel Hot Molded	⁺ Lot 08015	020/11016018-1 Powder	8M-1
	Va	lues in per cer otherwise no	nt unless oted		
Al	>10	>10	(A1 ₂ 0 ₃)	69.48	
В	0.01	0.004	$(B_2 \bar{O}_3)$	0.015	
Ca	-	-	(Ca0)	0.01	
Cu		<10ppm	(Cu0)	0.0025	
Fe	0.02	0.01	(Fe_2O_3)	0.011	
Ga	nd	0.006			
К	<3ppm		(K ₂ 0)	0.003	
Mg	>10	>10	(MgO)	29.96	
Mn	nd	nd	(MnO)	0.01	
Na	0.04	<10ppm	(Na20)	0.10	
Ni	30ppm	-		-	
S	0.08	0.048		0.245	
Si	0.01	0.004	(SiO_2)	0.02	
Sn	60ppm	-	•	-	
Ti	-	-	(Ti0 ₂)	<0.005	
Zn	-	0.08		-	
Zr	-	0.05		-	
mol ratio	(est)~1.00			1.091	
(BET)	$25 \text{ m}^2/\text{g}^+$			$\sim 55 \text{ m}^2/\text{g}^+$	

*Table 1 of Ref. 8

+External Analytical Service Laboratory, D 771, 5/20/70. +Surface area measurements (Aminco Sor-BET), N.C.S.U.

Phase 2A: Hot Molding of Spinel

Preliminary Hot Pressings

Figure 9 illustrates relative opacity and/or translucency in discs hot pressed by Kodak in preliminary evaluations of the sulphate-derived spinel (identified as T-1 through T-4) from Phase I and of the alternate material, Grace S-5570. As might be expected, the high sulphur content (at least 0.6 wt % SO₃) of the Phase I material greatly hinders densification by normal hot pressing procedures; it also produces strong coloration, particularly when hot pressed in the presence of carbon. When rehot-pressed (press-forged) the degree of translucency is much improved, though far short of the rather good transparency attained in some comparable earlier hot pressings of small-batch produced sulphate-derived spinels (S ~0.05%).^{3,5,6,8}

Hot Molding

Table 10 summarizes Kodak's efforts at hot molding $2 \times 4 \times 1/4$ in. shapes from these materials. Regretably, four of the best pieces



Fig. 9. Relative opacity and/or translucency of selected hot pressed spinel discs: ²5²7²9</sup> (a) #52-53 (T-1)"Carnall method", 1200°C @ 10 tons; opaque; (b) #60 (T-1) cold pressed @ 10 tons, heated to 2200°F @ 10 tons, maintain 10 tons @ 2200°F for 30 min, very dark, opaque, microhardness K₅₀₀ ≈1385 ± 65, polished; (c)#63 (T-1) same procedure as (b), maintain 10 tons @ 2200°F for 30 min, semi-opaque, less dark, polished; (d)#118FR66 (T-2), procedure same as (b) and (c), but rounded to 0.975 in. and rehot-pressed (press - forged) at 10 tons @ 2300°F for 30 min, contains healed cracks, translucent, red, polished; (e) same as (d), but without carbon spacers, broken in two pieces, highly translucent, much less red, polished; (f)#177 (Grace Lot S-5570; as received, cold pressed and reground) 10 tons @ 2300°F for 30 min, polished, 0.063 in. thick, translucent. Specimens in contact with ruled horizontal lines, back lighted.



Fig. 10. Relative translucency of Grace S-5570 spinel (a) hot molded (ODHP-12, Table 10), and (b) hot pressed in 4.6 in. dia, 200 tons @ 2300°F for 60 min (NB-1-194²³). Back lighted.

(ODHP-3/4, 5, 6, and 11) were accidentally ruined during grinding on a Blanchard machine during finishing at Kodak.²⁸ These whole blanks were crushed, released from the work holder, and broken into many pieces.

Hot Pressing Grace S-5570 Spinel

Since an insufficient quantity of comparable material from Phase I for fabrication of additional samples remained either at Kodak or at the University, arrangements were made to acquire, gratis, a modest quantity of Grece spinel identified at Lot S-5570. Its behavior in preliminary pressings is described in Fig. ^o and Table 10. Since this material (unmilled) was not very amenable to hot molding, it was processed in a large conventional refractory metal hot pressing die, 4.6 in. dia, in the final attempts to obtain one more sound $2 \times 4 \times 1/4$ in. piece. Fig. 10 compares the results of the first hot molding and hot pressing attempts with Lot 5770 material.

Thereafter, an additional specimen identified as NB-2-197 was successfully hot pressed under these conditions:

Charge: 310g Lot S-5570, screened thru 100-mesh Cold Press: 80 tons, top and bottom carbon spacers Temperature-Pressure Sequence: Heat to 600°F, no load; load to 200 tons, hold for 1 min, release; continue heating to 2300°F, no load; load @ ~10 tons/min to 200 tons, maintain 200 tons @ 2300°F for 60 min; end run, releasing load and heat.

The specimen was opaque and white at the periphery, but whole and translucent within. A 2 x $4\times1/4$ in. blank of moderately high translucency was cut and polished, which, with ODHP-7, -8, -9, and -10,

	Connents	Central portions translucent, red; outer sections opaque. Broken due to sticking to mold parts.	Corners and pe- riphery opaque, central area trans- lucent, red. Bro- ken due to stick- ing, less severely than UDHP-1.	Sample whole, white, opaque. Repressed - see ODHP-4.	Sample whole. 1 1/2 x 3 in. central area translucent, red; remainder, white, opaque. 22
ín. Specimens	Bulk Density	not determined As	not determined or	est. 80 - 85% of P _{th}	3.366 g/сm ³ (~93.9%) 30
ary of Hot Molded 2 x 4 x 1/4	Pressure-Temperature Sequence	10 tons @ $1850^{\circ}F$, building to 75 tons @ $2200^{\circ}F$ in ~ 1 hr, increase to 100 tons in ~20 min., cool to $2000^{\circ}F$ at 100 tons, increase to 115 to @ $2000^{\circ}F$ for 5 min; end run, releasing load and heat	Load slowly to 115 tons @ 2000°F, while still heating; maintain 115 tons @ 2200°F f 30 min., end run, releasing load and heat.	Load slowly to 115 tons @ ~1750° (still heating); run aborted @ ~2100°F and 75 tons due to power failure.	Load @ ~5 ton/min to 115 tons (stili heating), main- tain 115 tons @ 2200°F for 3 min.; and run, releasing load and heat.
Table 10. Summ	Pretreat	Coldpress @ 10,000 psi; hcat to 1850°F no load	Coldpress @ 10,000 psi; heat to 2000°F no load	Coldpress @ 10,000 psi; heat to 1750°F no load; graphite cloth parting layers top & bottom	Heat to 1750° c no load sth strs
	Charge	185g (T-1)	185g (T-2)	185g (T-1)	Partly den- sified blani from UDHP-3 graphite clu parting lay
	Identity	ОЛНР1 ^{2 б}	0DHP-2 *6	0.011P-3 ² 6	однр-4 26

28	Sample whole. 2 1/2 x 3 1/4 in. central area translucent, red; remainder grey- white, opaque.	Sample whole. 2 1/4 x 3 1/8 in. central area trans- lucent, red; re- mainder, corners opaque.	Sample whole, but showing healed cracks. Trans- lucent central area smaller, less dark than ODHP-6.
	3.379 g/ст ^э (~94.28%)	3.427 g/cm ² (~55.6%)	3.497 g/cm ³ (~97.5%)
	<pre>% @ Load @ ~5 ton/min to 115 ti; tons (still neating), main- red in tain 115 tons @ 2300°F for 00°C, 30 min.; end run, releasing ated load and heat. % no phite cloth ayers top</pre>	<pre>% Load @ ~5 ton/min to 115 % tons (still heating), main- in tain 115 tons @ 2300°F for % 30 min.; end run, releasing leated load and heat. % no phite cloth ayer top m</pre>	<pre>e @ Start heating again @ ii 1700°F, load @ ~5 ton/min to 1300°F 115 tons; maintain 115 tons @ 2300°F for 30 nin.; end cloth run, releasing load and heat. ayer ottom. 100°F (~1260°C) (in vacuo), cool (in vacuo), cool (in vacuo), cool); for 5 min.</pre>
	Coldpress 20,000 ps presinter air at 11 2 hr. He to 1750°H load; gra parting 1 and botte	Coldpress 26,000 ps sintered air @1100 16 hr. H to 1750°F load; gra parting 1 and botto	Coldpress 20,000 ps Heat to 2 no load; graphite parting 1 top and b Hold @ 23 for 2 hr to 1700°F
	185g (T-2)	185g (T-2, T-3)	185g (T-3)
	орнг-5 ²⁶	орнр-6 ^{2 5}	0DHP-7 ²⁶

i

.

•

.

Identity	Charge	Pretreat	Pressure-Temperature Sequence	<u>Bulk Density</u>	Comments
0DHP-8 ²⁶	185g (T-3)	Coldpress @ 20,000 psi; sintered in air @ 1200°C, 4 hr. Heated to 1700°F, no load; graphite layer top and	Load @ ~5 ton/min to 115 tons (still heating); maintain 115 tons @ 2300°F for 30 min.; end run. cloth bottom	3.523 g/cm ³ (~98.31%)	Sample whole, no open or healed cracks. 1 3/4 x 2 3/4 in. Central area more translu- cent, darker color ation than ODHP-7, Flowed and filled mold better than #7, but not as wel as #6.
27 00HP-9	185 <u>8</u> (T–3)	Coldpress @ 20,000 psi (~37% of $\rho_{\rm th}$); Heat to 2150°F, no 10ad; graphite cloth top and bottom	Load @ ~5 ton/min to 115 tons (still heating); maintain 115 tons @ 2300°F for 1 hr; end run, releasing load and heat.	3.513 g/cm ³ (~98.02%)	Sample whole excep for slight open crack at edge. Central area not as large or trans- lucent as ODHP-5.
0DHP-10 ²⁷	185g (T-4)	Coldpress @ 20,000 psi; sintered in air @ 1260°C, 20 hr. Heat to 2200°F and soak 15 min., no load; graph cloth top and	Lcad @ ~5 ton/min to 115 tons (still heating), maintain 115 tons @ 2300°F for 1 hr; end run, re- leasing load and heat. ite	3.518 g/cm ³ (~98.17%)	Sample whole. Flowed out about same as #9. Trans lucent and less re in central area.

Ĩ.

Con ser

	:		I	
Pressing flat (mold component) distorted. Sample opaque. T-4 mate- rial seems to press differently.	New pressing flat distorted. Sev- eral cracks no- ticed; ends and corners opaque, white: Remainder translucent, ex- cept for white specks, agglomerates.		!	
3,406_g/cm ³ (~95.03%)	not determined)
Coldpress @ Load @ ~5 ton/min to 115 20,000 psi; tons (still heating); heat to 1750°F maintain 115 tons @ no load; 2300°F for 1 hr; end run, graphite releasing load and heat bottom	Coldpress (Load $\mathfrak{E} \sim 5 \ ton/min \ to \ 125 \ 20,000 \ psi tons; maintain \ 125 \ tons \ (36% of \rho_{th}); (2300°F for 1 hr; end no preture trun, releasing load and sintering; heat. heat. heat to 2175°F to load, graphite to load, graphite cloth top and bottom.$			· · ·
185g(T-4)	200g Grace spinel, Lot S-5570, as rcceived	١		
ODHP-11 ²⁷	0DHP-12 ²⁹			

.



Fig. 11. Relative translucency of five plano-plano polished 2 x 4 x 1/4 in. spinel pieces: (a) ODHP-7, (b) ODHP-8, (c) ODHP-9, (d) ODHP-10, and (e) blank cut from 4.6 in.dia hot pressing, NB-2-197. Specimens backlighted. Top four produced from sulphete-derived spinel from Phase I, reddish in color; bottom specimen produced from Grace spinel S-5570, translucent, greyish in color.

completed the set of five such specimens called for in the contract. These specimens are illustrated in Fig. 11.

Microstructures_____

Microstructural studies (not illustrated) have confirmed the very gassy nature of the sulphur-laden Phase I spinel powders and the resultant deleterious effects upon the densification process undertaken by Kodak. Those process variations (e.g., presintering, heating to relatively high temperatures in vacuo under no-load conditions, etc.) which facilitated substantial outgassing within the open porosity regime tended to favor densification; failure to provide for such outgassing resulted in opacity, associated with many microstructural evidences of trapped branching pores, presumably ges-filled. Both kinds of spinel, whether hot pressed or hot molded, yielded at ~2300°F (1260°C) the rather uniform and equiaxed fine grained (~0.2µm) structure obtained in earlier studies.^{6,8,10} Specimens which were cut down and hot pressed a second time (press-forged) retained the uniformity of microstructure, but had somewhat larger grain size (~0.3-0.5µm). In this case, grain growth is thought to be related to strain-anneal processes (additional straining, longer time at temperature), and is





associated with some improvements in translucency. The latter effect may be related to pressure- and strain-induced reductions in pore size (below optical wave lengths) as well as to time-temperature dependent (diffusional) reductions in total pore volume.

Infrared Transmission

Figure 12 shows that process-related improvements in densification and translucency are possible, even if the quality of the starting powder is not optimized. Figure 13 gives comparative data for two specimens fabricated from the Grace S-5570 spinel. Comparisons of Figs. 12 and 13 suggest that absorption bands in the infrared may be characteristic of the anions of the respective precursors and perhaps other impurities.

Phase IIB: Rate Controlled Sintering of Spinel

The findings of this phase of the study have been reported in detail in a recent dissertation, $^{23\alpha}$ from which the text of this section largely has been taken. This work has now been presented orally, 23b and the material is being readied for submission as two separate papers



Fig. 13. Infrared transmittance curves for thin (#177) and thick (NB-2-197) spinel pieces hot pressed from Grace S-5570 spinel powder.²⁹

intended for <u>Journal</u> publication. Details of the work,^{23a} were forwarded to AMMRC and a summary is given here.

- Finely divided, magnesia-rich magnesium aluminate spinel (Grace S-2 DBM, Table 2), cold pressed to 50 percent density, was sintered under conditions of programmed rates of densification (rate controlled sintering).
- Constant densification rates ranging from 2.85 x 10⁻⁴ min⁻¹ to 6.19 x 10⁻³ min⁻¹ were successfully maintained during these experiments.
- 3. For the sintering of spinel at constant densification rates between 60 and 90 percent of theoretical density a rate independent correspondence of temperature and density was discovered:

$$\ln D = 1.96 + 1.48 \times 10^{-3} T.$$

4. For rate controlled sintering of spinel between 60 and 90 percent of theoretical density, the maintenance of constant densification rates resulted in constant heating rates:

$$\frac{dU}{Ddt} = 1.48 \times 10^{-3} \frac{dT}{dt}$$

- 5. A microstructure consisting of idiomorphic, cubic grains³² was formed in spinel samples that were subjected to the following treatments:
 - a. Heating of powder compacts at 4.0°C/min to temperatures ranging from 1225°C to 1392°C (resulting in densities ranging from 66 to 86 percent of theoretical);
 - b. Rapidly cooling to room temperature;
 - c. Reheating at 4°C/min to 1225°C, followed by 0.162°C/min from 1225°C to 1485°C (resulting in a final density of 94 percent).
- 6. The kinetic data from experiments in which spinel powders were sintered at constant densification rates were observed to be non-Arrhenian, and were interpreted to indicate that the sintering process is not diffusion controlled; rather, they suggest that the principal mass transport mechanism is plastic flow.
- 7. The isothermal densification rates of spinel samples, having been previously sintered at varying constant rates to ~94 percent density and later reheated to 1420°C, decreased with increasing values of prior constant densification rate. Prior densification rates $\geq 17 \times 10^{-4}$ min⁻¹ (equivalent to ~1.1°C/min) resulted in negative isothermal rates (i.e., bloating), as shown in Fig. 14.

For reasons already described, it was not possible within this program to extend this phase of the work experimentally beyond Johnson's controlled linear densification rate range, reaching fractional densities of ~94 - 95%. To achieve transparency, ultimately one must go well into final stage densification, >>99%.

The final stage of densification in spinel for fractional densities above 93 - 95% must involve the removal of closed pores by diffusional processes. There is much kinetic and microstructural evidence that closed pores in this material contain gas phases entrapped during earlier stages of densification. The very plastic nature of spinel in this temperature range (> 1400°C) clearly contributes to its very marked tendency to bloat under very modest temperature increases. Although densification during the intermediate stage is essentially independent of densification rates during that stage, the final stages of densification are quite sensitive to rates which obtained during the intermediate stage (see Fig. 14), probably as a consequence of greater quantities of gas which had been trapped in branching pores at the faster densification rates. Intuitively, one reasons that outward diffusion of the gaseous species (under conditions involving very gradual heating to avoid unnecessary bloating of the ductile matrix) will be the key to successful final stage densification in this material. The ductile behavior of spinel at high temperatures involves very mobile dislocations moving on multiple slip systems. This degree of plasticity is not common in most ceramic materials, and hence effects associated with ductility may be relatively unfamiliar to many ceramists concerned with densification. The bloating effects described here are sensitive not only to the increased pressure of the trapped gas phase associated with any incremental

34

يوجي ومرجع محمر والمرو



JAMABHTOSI

S-OF X I-NIW "N

(NORMALIZED

DENSIFICATION

Gine I Des

Isothermal densification rate as a function of prior constant densification rate in initial stage sintering of spinel. (After Ref. 23). Fig. 14.

temperature advance, but in particular, are responsive to the marked influence of an upward change in temperature upon the mobility of previously work hardened dislocations in the surrounding crystalline material. With fast rates at high temperatures, gross bloating not only can but almost certainly will occur. High temperature, long time final stage sintering treatments being employed for spinel by other investigators are likely to have been needed primarily to compensate for gross bloating which almost certainly had been "built-in" during earlier rapid shrinkage occurring at temperatures well into the ductile range.

Rate controlled sintering optimized for final stage densification, not just for linear rates, has not been achieved to date. Though not yet specifically developed for efficient densification of spinel as it now has been for alumina²⁴, this still novel approach continues to be an attractive one. While it may not directly achieve transparency *per se*, rate controlled sintering may prove to be effective in preparing well outgassed, nearly dense compacts (intermediates) well suited for subsequent final stage densification to transparency by controlled atmosphere sintering, hot pressing, or press-forging.

SUMMARY AND CONCLUSIONS

In terms of direct results, that part of this effort aimed at producing transparent polycrystalline spinel shapes did not turn out as well as one might have expected from prior (small-batch) work. The technical problems encountered are common ones in scale-up campaigns; individually, they tend to be amenable to relatively straightforward identification and correction, but collectively and in conjunction with other operational factors, they can and do result in cascade effects of considerable magnitude. In this case, the process for powder production in Phase I was not brought under adequate chemical control for a variety of reasons, none of which were really apparent at the time the material was being produced. Thereafter, lack of good material created unexpected difficulties for the hot molding effort in Phase IIA, effectively preventing meaningful optimizations of optical properties. Similarly, "critical experiments" capable of demonstrating final stage densification by rate controlled sintering, based on valuable nonisothermal kinetic information which had been gained in Phase IIB, were adversely affected. Yet many important and positive things have been learned, and described herein, which ultimately should be of value in scaling up production of high quality spinel materials from any precursor, and in subsequent densification processes suited to production of large transparent shapes.

In retrospect, it would have been most desirable (and in the future should be considered mandatory in programs of this nature) to assure that timely, local access to reliable analytical services be routinely available for on-line process control as well as for post facto quality assurance. This viewpoint certainly implies no disparagement of the analytical services provided most cooperatively by the vendor involved. Rather, it acknowledges that the process-analysis-control linkage is so intimate and so demanding of promptness that it cannot be managed effectively at a distance.

More emphasis should have been placed upon dynamic processing of the prepursor salt, in the interests of developing a very uniform and reproducible feed material for the dynamic calcining furnace. For example, continuous casting of a relatively thin sheet (~1/16 in. thick) would have permitted more rapid cocrystallization, better drying, easier comminution, and a more uniformly sized feed material for the furnace, as well as more efficient handling and consequent minimization of exposure to contamination.

Though optimization of sulphur removal was not achieved in these experiments, the dynamic calcining furnace worked quite well, and is considered to offer considerable promise for efficient and reproducible processing of reactive ceramic powders. [This view has been confirmed by more recent work, done elsewhere³⁴]. It is, however, very dependent upon close control of feed material (constitution, size, and size distribution) if a uniformly fired product is to be produced.

It is probable that sulphur is "a bad actor" where spinel is concerned, and that, hereafter, spinel derived from precursors other than sulphates should be emphasized. There are a number of unresolved scientific questions about the

physiochemical form of sulphur residues in spinel powders, and about the characteristic reddish color developed when such powders are densified at high pressures by hot pressing and/or hot molding. When reheated at temperatures above that at which they were densified, many ceramics hot pressed to transparency tend to bloat and become opaque. Sulphur-derived spinel follows this pattern⁸. Recent unpublished research, comparing direct transmission electron microscope images obtained from ion beam thinned foils of unbloated and bloated spinel, indicates that the bloating begins on an almost molecular scale in otherwise homogeneous grains tending to cluster in very tiny bubbles rather reminiscent of fission fragment gases clustering in irradiated nuclear fuel materials. The implication is that the sulphur residue, S0,, may have been accomodated directly within the spinel structure itself. If so, this may explain the tenacity with which spinel powders retain sulphur during calcination, even at temperatures well above the dissociation points of its precursor salts.

LITERATURE CITED

- W. W. Kriegel, H. Palmour III and D. M. Choi, "The Preparation and Mechanical Properties of Spinel", Chapter 12 (pp. 167-186) in Special Ceramics, 1964. P. Popper, Ed., Academic Fress (London) Ltd., 1965.
- L. D. Barnes, "Rate Controlled Hot Pressing of Magnesium Aluminate Spinel", Unpublished Master of Science Thesis, Department of Mineral Industries, North Carolina State University at Raleigh, 1967.
- H. Palmour III (North Carolina State University), Final Report: Flow and Fracture in Spinel Structured Ceramics. Contract DA31-124-ARO-D-207, U. S. Army Research Office - Durham, 41 pp., January, 1970.
- 4. H. Palmour III and H. Z. Dokuzoguz, "Finely Divided Spinel", U. S. Patent No. 3,544,266, December, 1970.
- 5. H. Palmour III, R. A. Bradley, and D. R. Johnson, "A Reconsideration of Stress and Other Factors in the Kinetics of Densification", Chapter 22 (pp. 392-407) in Kinetics of Reactions in Ionic Systems. T. J. Gray and V. D. Frechette, Eds., Materials Science Research, Vol. 4, Plenum Press, New York, 1969.
- 6. R. A. Bradley, "The Effect of Doping and Heat Treatment on the High Temperature Strength of Polycrystalline Magnesium Aluminate". Unpublished Master of Science Thesis, Department of Mineral Industries, North Carolina State University, 1968.
- 7. H. Palmour III, personal communication, May 15, 1967.
- (a) C. E. Zimmer, "Sapphire Whisker Reinforced Spinel", Unpublished Master of Science Thesis, Department of Materials Engineering, 1970.
 - (b) C. E. Zimmer and H. Palmour III, "Sapphire Whisker Reinforced Spinel", Presented in a Symposium on Advanced Materials: Composites and Carbon, 73rd Annual Meeting of the American Ceramic Society, Chicago, Apr. 1971. To be printed in the Symposium Proceedings (In Press).
- 9. H. Palmour III and C. E. Zimmer, "Ceramic-Ceramic Composites with Whisker Reinforcement", U. S. Patent Application, Serial No. 138,753, April 29, 1971.
- 10. H. Palmour III, personal communication, July 1, 1969.
- S. C. Carniglia, "Grain Boundary and Surface Influence on Mechanical Behavior of Refractory Oxides - Experimental and Deductive Evidence", Chapter 24, (pp. 425-471) in The Role of Grain Boundaries and Surfaces in Ceramics. W. W. Kriegel and H. Palmour III, Eds. Materials Science Research, Vol. 3., Plenum Press, New York, 1966.
- R. W. Rice, "The Compressive Strength of Ceramics", pp. 195-229 in Ceramics in Severe Environments. W. W. Kriegel and H. Palmour III, Eds. Materials Science Research, Vol. 5, Plenum Press, New York. (In Press).
- 13. W. J. Ferguson and R. W. Rice, *ibid*, pp. 261-270.
- 14. N. J. Petch, "Cleavage Structures", J. Iron Steel Inst. <u>174</u> 25 (1953).

- W. H. Rhodes, P. L. Berneburg, and J. E. Niesse (AVCO Corporation), "Development of Transparent Spinel (MgAl₂0₄)", 85 pp. Final Report, Contract DAAG-46-69-C-0113, Army Materials and Mechanics Research Center, Watertown, Massachusetts, October, 1970.
- 16. D. Sellers (Coors Porcelain Company), personal communication, April 1971.
- A. Gatti and M. J. Noone (General Electric Company), "Feasibility Study for Producing Transparent Spinel (MgAl₂0₄)", Final Report, Contract DAAG-46-69-C-0096, Army Materials and Mechanics Research Center, February, 1970.
- (a) R. J. Bratton, "Initial Sintering Kinetics of MgAl₂0₄", J. Am. Ceram. Soc. <u>52</u> (8) 417-419 (1969).
 - (b) R. J. Bratton, "Characterization and Sintering of Reactive MgAl₂0, Spinel", Am. Ceram. Soc. Bull. <u>48</u> (11) 1069-1075 (1969).
 (c) R. J. Bratton, "Sintering and Grain-Growth Kinetics of MgAl₂0,", J. Am. Ceram. Soc. 54 (3) 141-143 (1971).
- A. GatEi⁴ (General Electric Company), "Development of a Process for Producing Transparent Spinel Bodies", Final Report, 35 pp, Contract N 00019-69-C-0133, Naval Air Systems Command, Sectember, 1969.
- 20. F. Stermole (Coors Porcelain Company), personal communication, August, 1970.
- H. Palmour III and D. R. Johnson, "Phenomenological Model for Rate Controlled Sintering", pp. 779-791 in Sintering and Related Phenomena. G. C. Kuczynski, N. A. Hooten and C. F. Gibbon, Eds., Gordon and Breach, Publishers, New York, 1967.
- 22. (a) R. A. Lawhon, "Rate Controlled Sintering of Polyphase Ceramic Bodies by Direct Instrumentation," Unpublished Master's Thesis, Department of Materials Engineering, North Carolina State University at Raleigh, 1970.
 - (b) R. A. Lawhon and H. Palmour III, "Rate Controlled Sintering in Polyphase Whiteware Bodies", pp. 62-70 in (limited circulation) Proceedings of 1970 Fall Meeting, Materials and Equipment and Whitewares Divisions, The American Ceramic Society, Columbus, Ohio, 1970.
- 23. (a) D. R. Johnson, Densification Kinetics of Spinel Sintered Under Rate Control. Unpublished doctoral dissertation, Department of Materials Engineering, North Carolina State University at Raleigh, 1970.
 - (b) D. R. Johnson and H. Palmour III, "Densification kinetics of spinel sintered under rate control", Paper (65-B-71) presented before the Basic Science Division, 73rd Annual Meeting of the American Ceramic Society, Chicago, April 28, 1971.
- 24. M. L. Huckabee and H. Falmour III, "Fine Grained Alumina Sintered Under Rate Control", submitted (August, 1971) to the American Ceramic Society for publication.
- R. J. Weagley (Eastman Kodak Company), letter report, January 19, 1970.
- 26. <u>ibid</u>, April 30, 1970.

- 27. ibid, May 28, 1970.
- 28. <u>ibid</u>, June 2, 1970.
- 29. ibid, August 19, 1970.
- 30. H. Palmour III, letter of transmittal to AMMRC, March 20, 1970.
- 31. ibid, June 18, 1970.
- 32. H. Palmour III and D. R. Johnson, "Fine Cubic Microstructure Uniquely Achieved by Strain-Induced Recrystallization During Sintering of Spinel". Bull. Am. Ceram. (c. 49 (8) 767 (1970).
- 33. H. Palmour III (Principal Investigator, Contract DAAG 46-69-C-0097), fourth letter report, November 5, 1969.
- 34. S. H. Bomar, Jr., K. V. Logan, and G. P. Rodrigue (Georgia Tech Research Institute), Manufacturing Techniques for Ferrites and Garnets Used in Phased-Array Radar "U". Final Report, 131 pp. Contract DAAH 03-69-C-0334, U. S. Army Missile Command, Redstone Arsenal, Alabama, February, 1971.

South the second second

ARMY MATERIALS AND MECHANICS RESEARCH CENTER WATERTOWN, MASSACHUSETTS 02172

TECHNICAL REPORT DISTRIBUTION FOR MATERIALS TESTING TECHNOLOGY PROGRAM (PEMA - 4931)

Distribution List approved by U. S. Army Materiel Command, AMCQA-E, letter dated 24 December 1970.

No. of Copies То 2 Metals and Ceramics Information Center, Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201 12 Commanding Officer, Defense Documentation Center, Cameron Station, Alexandria, Virginia 22314 Office of Chief of Research and Development, Department of the Army, Washington, D. C. 20310 1 ATTN: CRDPES 1 Commanding Officer, Army Rescarch Office (Durham), Box CM, Duke Station, Durham, North Carolina 27706 Commanding General, U. S. Army Materiel Command, Washington, D. C. 20315 1 ATTN: AMCQA 2 AMCQA-E 2 AMCOA - P 1 AMCRD-TC 1 AMCRL 1 AMCRD-EA 1 AMCRD-T&E 1 AMCRP-OIP Commanding General, U. S. Army Electronics Command, Fort Monmouth, New Jersey 07703 2 ATTN: AMSEL-CB 1 AMSEL-PP-PO 1 AMSEL-WM 1 AMSEL-RD-GT 1 AMSEL-PA-C Commanding General, U. S. Army Missile Command, Redstone Arsenal, Alabama 35809 2 ATTN: AMSMI-RBLD, Redstone Scientific Information Center 1 AMSMI-RKK, Mr. R. Fink 1 AMSMI-RSM, Mr. E. J. Wheelahan 1 AMSMI-RIR, Mr. H. T. Lawson 2 AMSMI-Q 1 AMSMI-M