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CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

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ABSTRACT

A technique has been developed for the chemical production of very pure magnesium oxide powder. This powder is then fabricated by specialized hot-pressing techniques into theoretically dense polycrystalline specimens. Details of the process, including starting reagents, are given. Chemical analysis of the MgO produced by this technique indicates that the material contains approximately one tenth as much impurity as a pure MgO from a commercial source, although the analytical techniques are subject to some question.

Initial studies of this pure MgO demonstrate grain growth approximately 100 times that found in MgO of conventionally good purity. Moreover, in the pure material there is no evidence of the reheat porosity at very high temperatures that is found in dense pieces of less pure material.

Author

I. INTRODUCTION

Modern research in the field of materials and their properties has faced a continual problem in the procurement and characterization of high-purity specimens for study. Investigators are often unable to relate results to the fundamental characteristics of the material and may report different results for what is supposedly the same material. These difficulties can often be ascribed to the presence of small but significant amounts of impurity. A fundamental study of the mechanical behavior of non-metals, now being conducted at this Laboratory, very quickly revealed this same problem and indicated the necessity for a program to produce highly pure, chemically characterized magnesium oxide. The choice of magnesium oxide was made because of its simple, easily

understood structure and the availability of pure reagents for its production.

The selection of the general technique of chemical solution purification was made on the basis of practicality and cost. Solid-state purification alternatives, such as zone-refining, seem beyond the present state of the art because of incompatibility with atmosphere, extreme temperatures, etc. The technique used here involves the formation of a magnesium nitrate solution from pure reagents, additional purification by a selective chelating agent, precipitation of magnesium carbonate, and calcination to form magnesium oxide.

Preparation of this material was carried out under controlled conditions in a laboratory employing filtered air and maintained at a positive pressure with respect to its surroundings.

This area was restricted to required personnel who wore special garments, head coverings, shoes, and plastic gloves. The utmost care was taken during the preparation to prevent contamination of the material.

II. CHEMICAL PURIFICATION PROCEDURE

The materials and solvents used in making high-purity magnesium oxide are listed in Table 1. The procedure, patterned after that developed at the Oak Ridge National Laboratory (Ref. 1), was used to produce small quantities (approximately 100 g) of high-purity MgO. All handling was accomplished with the aid of glass, plastic, or plastic-coated metal implements. Glass equipment was used with acid solutions, and plastic (polypropylene or polyethylene) with basic solutions.

Chunks of sublimed magnesium about a cubic inch in size were acid-washed in dilute nitric acid (1 part HNO₃ to 25 parts H₂O) until all surface contamination from prior handling was removed. After acid washing, the metal chunks were dissolved in nitric acid to make a 3 M solution of magnesium nitrate. Owing to the violent exothermic reaction between the magnesium metal and the nitric acid, it was necessary to place the magnesium chunks in a 1:25 dilute nitric acid solution and add the remaining acid dropwise for a period of hours. A 5 to 10%

excess of nitric acid was added to dissolve the magnesium completely.

Upon complete solution of the magnesium, the pH of the magnesium nitrate solution was adjusted to about 5.5 by the addition of concentrated ammonium hydroxide. The ammonium hydroxide must be added slowly while the nitrate solution is stirred; otherwise, magnesium hydroxide will be precipitated. The pH was checked without introducing foreign matter, by putting a drop of the solution on pH-indicator paper.

The magnesium nitrate solution was then placed in a cylindrically shaped separatory funnel. An equal volume of 0.5 M thenoyltrifluoroacetone (TTA) in 4-methyl-2-pentanone was added to the funnel. The chelate extraction was brought to equilibrium by repeated gentle inversions of the separatory funnel for approximately 3 min. Violent mixing may emulsify the two immiscible solutions, a condition that is detrimental to the kinetics of extraction (Ref. 2). The chelate extraction step was repeated, since extractability of a metal depends equally heavily on the pH of the aqueous phase and on the reagent concentration in the solvent and is independent of the metal concentration in the solution (Ref. 2). Thus, for a given amount of solvent, the best results are obtained by a large number of extractions with small amounts of the solvent (Ref. 2). The technique used here was to employ three extractions. The first extraction was made with a solution used twice previously and subsequently discarded, the second with a solution used once previously, and the third with a fresh solution. The last two solutions were saved for future use. Upon completion of the extraction, the aqueous phase was filtered into a 2-gal polypropylene digestion chamber, shown in Fig. 1. The construction of this chamber is entirely of plastic (polyethylene, polypropylene, or nylon) to protect the alkaline solutions from contamination.

Table 1. Materials and solvents for production of high-purity MgO

Material	Supplier	Grade
Magnesium metal (high purity, sublimed)	Dow Chemical Co.	99.9945% pure Mg (mass spectroscopy data)
Thenoyltrifluoroacetone (TTA)	Columbia Organic Chemical Co., Inc.	99+ % pure (vendor analysis)
4-methyl-2-pentanone (Hexone)	Eastman Organic Chemicals	No purity specified, except that it was not to be used for drugs
Nitric acid	Baker & Adamson of Allied Chemical Corp.	Reagent grade, C.P.
Ammonium hydroxide	Baker & Adamson of Allied Chemical Corp.	C.P.
Ammonium carbonate	Mallinckrodt Chemical Works	4-mesh analytical reagent grade
Distilled water	Sparkletts Drinking Water Corp.	Triple distilled

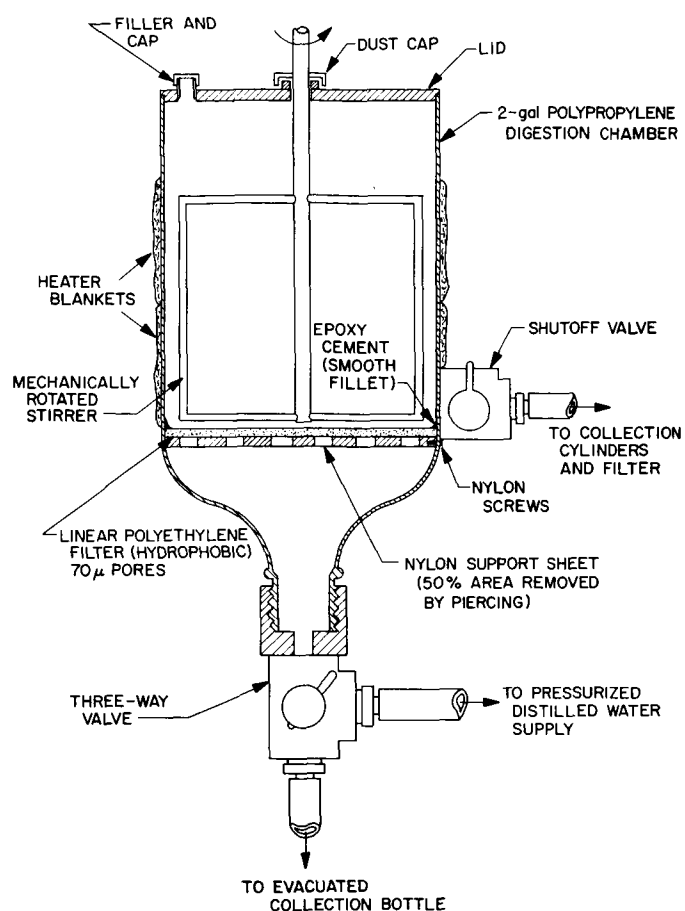


Fig. 1. Schematic cross section of digestion and washing chamber for use in production of high-purity MgO

The pH of the purified magnesium nitrate solution was adjusted to 7.5 by the slow addition of ammonium hydroxide while the solution was stirred. At this point, the nitrate solution was diluted with an equal volume of distilled water.

To precipitate the hydrated magnesium carbonate, saturated ammonium carbonate solution (approximately 30 g per 100 ml of distilled water at 20°C) was added dropwise. The ammonium carbonate solution is added in excess of the stoichiometric amount in order to precipitate the hydrated magnesium carbonate completely. The precipitate and the carrier solution were heated to 90°C and mechanically stirred for 8 hr to complete precipitation. (Magnetic stirrers used in preliminary investigations were unsatisfactory because of abrasion between the stirring bar and the reaction chamber.) Proper digestion helps to eliminate nitrates carried down during the precipitation.

The precipitate in the digestion chamber was then vacuum-filtered and washed with distilled water by resuspending and stirring. This process was carried out entirely within the digestion chamber by alternately vacuum-extracting and back-filling through the three-way valve at the bottom. The washing continued until the filtrant showed less than 2.5 $\mu\text{g/g}$ of nitrate (Ref. 3). The digestion and the washing were important since the presence of nitrates makes subsequent calcining and fabricating more difficult. The washed precipitate was then drawn off through the side shutoff valve (Fig. 1) and into polypropylene cylinders where a porous filter was used to extract water. The moist cakes were dried at 90°C for 24 hr in covered polypropylene cylinders. The dried precipitate was shown to be hydromagnesite (a hydrated magnesium carbonate, $4 \text{MgO} \cdot 3 \text{CO}_2 \cdot 4 \text{H}_2\text{O}$) by means of X-ray diffraction and thermogravimetric studies.

The final decomposition of the hydromagnesite into MgO was accomplished by vacuum calcining. The dried cakes were slid into porous alumina crucibles with porous covers (1- to 2- μ pores) and placed inside a stainless steel vacuum can. A liquid nitrogen-trapped mechanical pump was used to evacuate the system. The cold trap was necessary to prevent the large volumes of carbon dioxide and water from entering the pump and to prevent oil from back-streaming into the material. Chemical analysis showed that such back-streaming introduced impurities of low atomic number (e.g., Na, F, Cl, K, S) into the material. Such contamination was also noted during vacuum hot-pressing operations if pumps on such equipment were not cold-trapped.

The hydrated magnesium carbonate decomposes rapidly at 350°C under vacuum. The maximum temperature at which the calcining is performed affects the final chemical and physical properties of the MgO powder. Table 2 shows the changes in particle size observed at various calcining temperatures. A temperature of 650°C was selected as a standard since it offered a reasonable compromise of speed and completeness of reaction coupled with fine particle size. The extremely low calcining temperatures (350-500°C) resulted in difficulty during subsequent fabrication, which was apparently related to surface contamination on the fine reactive particles.

The densification of the high-purity MgO powder is the next step in the production of useful specimens. Attempts to cold-press and sinter the material resulted in a cracked porous specimen because of difficulty in controlling the rate of densification. The most satisfactory

Table 2. Effect of temperature on MgO

Temperature, °C	JPL special grade MgO			Fisher M-300 MgO		
	Grain or particle diameter, μ	Apparent density, g/cm ³	Remarks	Grain or particle diameter, μ	Apparent density, g/cm ³	Remarks
	Vacuum-calcined at listed temperatures from hydromagnesite to complete decomposition.			Method of production unknown. Received as 0.05- μ particles.		
450	0.011	Powder			Powder	
650	0.017	↓			↓	
750	0.018					
850	0.11	↓			↓	
	Hot-pressed in air at listed temperatures for ½ hr in Al ₂ O ₃ dies.					
800	0.1	3.50	Starting material calcined at 650°C. Pressing pressure, 10 kpsi.	0.1	2.56	Pressing pressure, 12 kpsi.
900	4.0	3.57		0.1	3.46	
1100	30.0	3.57		0.3	3.56	
	Theoretically dense specimens reheated to listed temperatures for 1 hr in O ₂ .					
1700	110	3.57	Grain diameter of specimen initially ~ 1 μ .	50	3.58	Grain diameter of specimen initially ~ 1 μ .
2200	300-5000	3.57		138	3.48	

technique was hot pressing, employing oxide dies and punches, thus eliminating the introduction of impurities normally found when conventional graphite die hot-pressing techniques are used (Ref. 4). The pressings were conducted in a resistance-heated furnace that was capable of operating at temperatures up to 1200°C in a mechanically pumped vacuum, or in air, oxygen, or a variety of inert gases.

A variety of die materials were employed during this program. Molybdenum alloy dies¹ with and without molybdenum disilicide coatings were used but were plagued with galling. Various commercial grades of aluminum oxide were tried but none were found to be successful at the temperatures and pressures required. Some success was obtained with these commercial aluminum oxides by circumferentially supporting them with a molybdenum ring. The ring was sized so that all of the stress was theoretically supported by the ring at the temperature used. Dense silicon carbide was used but was not superior to other die materials. All of these showed limited success, but the most satisfactory material for the dies was found to be aluminum oxide that had been hot-pressed in a graphite system (Ref. 5).

During the compaction of oxide powders between aluminum oxide rams, welding normally occurs at the

interface. Such welding results in fracture of the specimen upon cooling, owing to differential thermal expansion. Spriggs (Ref. 4) recommends hot ejection, which aids in preventing this fracture, but during this program it was found that such hot ejection was detrimental to die life. The most successful procedure for preventing welding to the rams was the inclusion of a separator between the ram and the powder to be compacted. This separator was of the same nominal composition as the powder and normally took the form of a disc or a thin layer of coarse grains. If MgO rams were used and their ends were carefully cleaned by a warm phosphoric acid etch prior to hot pressing, then complete weld joints could be produced between the rams and the specimen. Improved translucency of the pressed specimen was obtained if the powder loaded in the die case was washed with absolute alcohol just prior to loading into the furnace.

The densification by means of hot pressing for this high-purity MgO occurred at a lower temperature than with conventional MgO (Fisher M-300).² Theoretically dense specimens could be obtained at temperatures as low as 800°C and pressures of 10,000 psi. At temperatures above this, grain growth became extremely rapid (see Table 2). This more rapid densification, as compared with conventional MgO, probably stems from at least two factors. First, the finer particle size results in shorter

¹Climax Molybdenum Co., New York, N. Y., Grade TZM.

²Fisher Scientific Company, Fair Lawn, New Jersey.

diffusion distances required for densification. Second, an increase in the diffusion rate would exist as shown by the considerable difference in grain size at the same temperature (see Table 2).

Numerous chemical analyses were made to obtain details of the purity of the material produced with this technique. However, the present analytical methods are not generally satisfactory for low levels of impurities in such materials as this. A variety of analytical techniques were used, e.g., emission spectroscopy, spark source mass spectroscopy, and wet chemical methods. The results were generally in disagreement, even within a given technique. The results suggest two difficulties, (1) un-

satisfactory analytical techniques and (2) inhomogeneity in the materials. In spite of these difficulties, the typical results in Table 3 give some indication of the purity obtained. Note the presence of generally unreported quantities of impurities of low atomic number even in the high-purity MgO. The effect of these impurities should not be overlooked in studies of such oxides.

Other evidence for a real difference between the material produced by this procedure and commercial magnesium oxides is shown by the differences in pressing behavior shown in Table 2 and Fig. 2 and the difference in behavior during reheating. These reheat data were determined from samples of dense hot-pressed MgO

Table 3. Atomic ppm of impurities in MgO

Impurity	JPL special grade MgO			Fisher M-300 MgO		
	Calcined powder		Hot-pressed ^a	Powder as received		Hot-pressed ^a
	MS	ES		ES	VA	
H	190	—	100	—	—	50
Li	ND	—	ND	—	—	1.8
B	4.2	ND	ND	40	10	300
C	— ^b	—	— ^b	—	—	— ^b
N	300	—	70	—	0 ^c (NO ₂)	100
F	1200	120	300	140	—	3000
Na	30	—	7	180	0 ^c	61
Al	160	100	250	150	0 ^c	100
Si	100	130	100	1000	300	1800
P	ND	10	8	7	—	120
S	200	—	56	50	50	420
Cl	18	—	38	180	27	80
K	35	—	1.7	—	—	64
Ca	30	50	7	1000	50	310
Ti	ND	3	ND	50	—	66
Cr	ND	ND	ND	10	—	16
Mn	ND	ND	1.4	70	0 ^c	22
Fe	ND	ND	5	200	100	510
Ni	11	ND	3.5	5	—	10
Cu	23	1	7.3	1	3	12
Zn	ND	ND	ND	ND	0 ^c	ND
Cd	ND	ND	ND	ND	—	15
Ag	ND	—	ND	—	—	ND

NOTE: MS Spark source mass spectroscopy. Impurities not detected or not listed are < 1 ppm.
ES Emission spectroscopy (except F, Cl, P, and S, by wet methods). Impurities not listed are not reported or not detected. Impurities not detected are below varying detection limit.

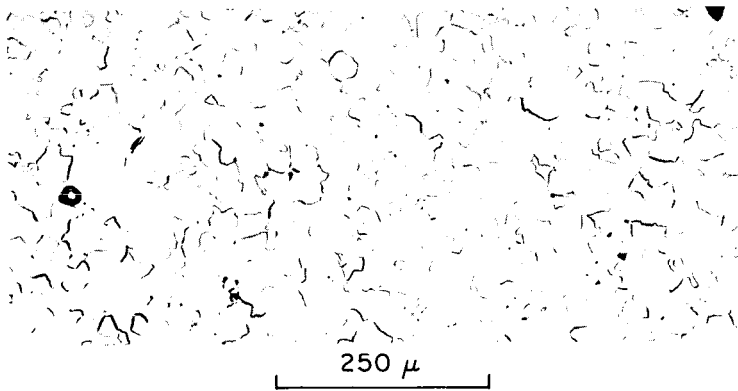
VA Vendor analysis.

ND Not detected.

^a Hot-pressed in Al₂O₃ die cases, 12,000 psi for 1/2 hr at 1100°C.

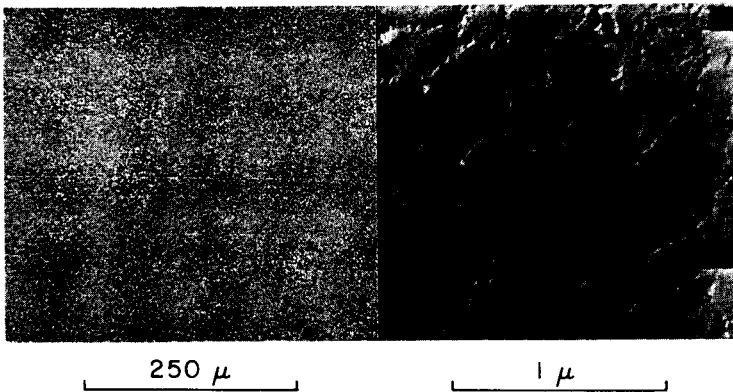
^b Carbon masked by mass of Mg.

^c Detection limit not given.

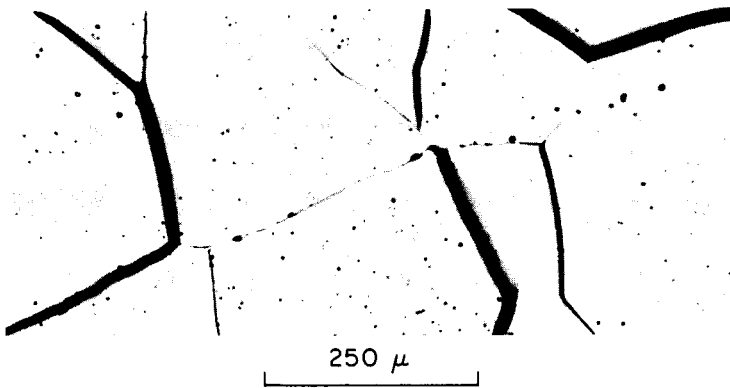


AS-PRESSED SPECIMENS

JPL SPECIAL GRADE MgO
 PRESSED IN AIR FOR 1/2 hr IN Al₂O₃ DIE
 AT 10 kpsi AND 1100°C.
 STARTING MATERIAL, 0.017μ-D GRAINS.
 MECHANICALLY POLISHED, ETCHED WITH
 50% HNO₃.
 OPTICAL MICROGRAPH.

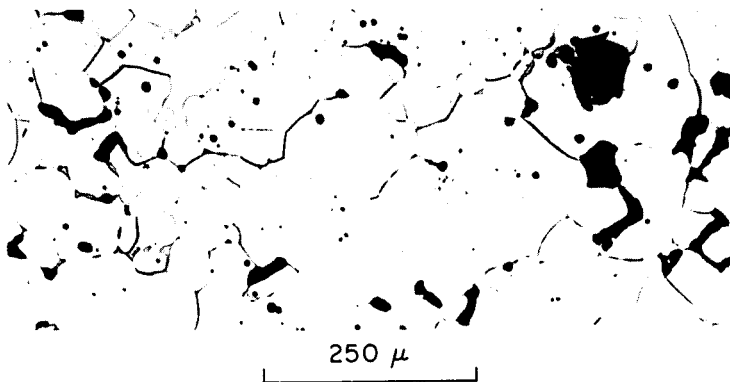


COMMERCIAL MgO
 PRESSED IN AIR FOR 1/2 hr IN Al₂O₃ DIE
 AT 13 kpsi AND 1100° C.
 STARTING MATERIAL, AS-RECEIVED
 FISHER M-300.
 MECHANICALLY POLISHED, ETCHED WITH
 STEAM.
 ELECTRON MICROGRAPH, RIGHT PHOTO.
 OPTICAL MICROGRAPH, LEFT PHOTO.



SPECIMENS REHEATED TO 2200°C

JPL SPECIAL GRADE MgO
 HOT-PRESSED SPECIMEN WITH ~20μ-D
 GRAINS REHEATED IN O₂.
 MECHANICALLY POLISHED, ETCHED WITH
 50% HNO₃.
 OPTICAL MICROGRAPH. (PHOTO SHOWS
 BOUNDARIES OF SMALLER GRAINS; SOME
 GRAINS WERE AS LARGE AS 5 mm IN
 DIAMETER.)



COMMERCIAL MgO
 HOT-PRESSED SPECIMEN WITH ~0.3μ-D
 GRAINS REHEATED IN O₂.
 MECHANICALLY POLISHED, ETCHED WITH
 50% HNO₃.
 OPTICAL MICROGRAPH.

Fig. 2. Microstructure of MgO

placed on setters of the same composition and enclosed in MgO muffles. They were then fired in an ultrahigh-frequency oxide-induction furnace to temperatures up to 2200°C in a 95% oxygen atmosphere. Microstructures are

shown in Fig. 2, while the characteristics of the specimens after this reheat treatment are listed in Table 2. Note the considerably smaller grain size and evidence of second phase in the less pure conventional MgO.

III. SUMMARY

A chemical method for the production of very pure MgO has been developed for routine production of material. This powder may be hot-pressed into theoretically dense polycrystalline specimens without extensive contamination.

Results of chemical analysis studies on this material show that the present methods of determining small amounts of impurities in MgO are generally unsatisfactory. However, analytical results may be interpreted as relative values from one material to another. If this is

done, the high-purity material produced in this study, when compared with a conventional, pure commercial MgO, contains about one tenth as much total impurity.

Initial studies on the behavior of high-purity MgO at high temperatures show lack of reheat porosity (Ref. 5) and more rapid grain growth than conventional good-purity MgO. These findings suggest that studies of polycrystalline MgO at high temperatures must be interpreted in relation to the presence of considerable impurity if conventional material is used.

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