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PREPARATION OF MAGNESIUM OXIDE REFRACTORIES

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ABSTRACT

Magnesium oxide was fabricated by hand tamping, mechanical vibration, dry pressing, extrusion, hot pressing and slip casting. The dry forming was done with and without a binder. Slip casting was accomplished from both alcohol and water slurries.

Magnesia ware was fired under a reducing atmosphere in an induction furnace and under an oxidizing atmosphere in an electric furnace and a gas-fired kiln. Pieces fired in the induction furnace in contact with the graphite susceptor showed deep surface pitting.

The melting point of magnesium oxide was determined. Phase studies were performed on the MgO-UO_2 system and on the $\text{MgO-U}_3\text{O}_8$ system.

INTRODUCTION

The Ceramics Group at ANL has extensively investigated the fabrication of magnesium oxide for use as a container material for the melting and purification of uranium. Magnesia meets the requirements of thermal shock, high melting point and inertness to the molten metal.

Difficulty in obtaining various shapes of high-purity magnesia from commercial sources at the time they were needed for these studies necessitated their fabrication at ANL. The purpose of this report is to present a compilation of the investigations upon MgO carried on at ANL along with a brief survey of pertinent work of other investigators.

RAW MATERIALS

Magnesium oxides used in the investigations at ANL were two grades of fused magnesium oxide obtained from Norton Company, commercial MgO (Magnorite) and "Product Dew," and CP Reagent MgO . The commercial grade and "Product Dew" magnesias were ground eight hours in a porcelain-lined pebble mill. The CP MgO was used as received. The grain-size

distribution of the ground commercial grade and "Product Dew," based upon screening for 30 minutes with a standard screen series in a Ro-tap sieve shaker, is shown in Table 1. The CP MgO agglomerated so readily that the openings in the screens became clogged; thus an accurate particle size distribution of the dry material was not possible. It was found however, that with alcohol washing 98 w/o passed through a 200 mesh screen.

Table 1

SCREEN ANALYSES

Mesh	Commercial MgO	"Product Dew"
+ 60	0.0%	0.1%
- 60 + 100	0.1%	10.2%
-100 + 140	17.1%	34.5%
-140 + 200	9.9%	24.3%
-200 + 325	21.6%	20.7%
-325	51.3%	10.2%

FABRICATION

Magnesia has been fabricated by methods common to other ceramic materials, i.e., dry forming, hydrostatic pressing, hot pressing, extrusion and slip casting.

Dry Forming

Dry-forming procedures used in magnesia fabrication vary from hand tamping and mechanical vibration to dry pressing. Hand tamping is accomplished by making small additions of the oxide along with a suitable binder to a mold and tamping firmly after each addition with a chisel-like tool. The greatest difficulty with this method is that the piece is built up of layers of unequal density. Mehl⁽¹⁾ fabricated magnesia crucibles by hand tamping the powdered oxide, using shellac dissolved in alcohol as a binder. It was found that the alcohol-shellac mixture reacted with the magnesia, forming what was termed a magnesia resinate. Firing, even at fairly low temperatures, decomposed this resinate, leaving a magnesia matrix. Investigations of mechanical vibration as a method of fabricating crucibles showed that dry magnesia without a binder was more satisfactory than the oxide with a binder.⁽²⁾ After being formed around a mandrel, the crucible, still on the mandrel, was removed from the mold and sprayed with water or other suitable material to give sufficient green strength to facilitate handling. Among the bonding materials used with dry pressing were hydrated magnesia in water,⁽³⁾ beeswax in carbon tetrachloride,⁽⁴⁾

and MgCl_2 in water.⁽⁵⁾ At ANL, crucible stopper rods were made by jolt packing or mechanically vibrating dry commercial-grade magnesia into graphite molds. Jolting was continued until no appreciable packing occurred over a 3-minute period. No binder was necessary because the rods were not removed from the molds prior to firing. Crucibles and stopper rods were fabricated from commercial MgO and "Product Dew" by tamping and pressing the material along with 7-1/2 w/o water as a binder. The water apparently partially hydrated the magnesia, producing sufficient bond so that the unfired ware could be easily handled. Magnesium stearate was also used as a binder for pressing MgO spacers to fit between the uranium billet and the crucible used for uranium melting. For density and shrinkage studies, right cylinders were dry pressed from commercial MgO , "Product Dew," and CP MgO without a binder; a pressure of 15,000 psi was applied. The pressed pieces were strong enough to be handled without any special precautions.

Hydrostatic Pressing

One method of increasing density beyond the scope of ordinary cold compaction is hydrostatic pressing. In this process, a piece which has been previously formed by dry pressing or some other means is placed in a rubber membrane and subjected to hydrostatic pressure. Wygant⁽⁶⁾ produced pellets of 3.51-g/cc density by pressing reagent-grade calcined MgO hydrostatically to 25,000 psi.

Hot Pressing

Hot pressing, the process by which a ceramic material is sintered at elevated temperature under pressure, has been used to fabricate magnesia to 96% of theoretical density. Murray and co-workers⁽⁷⁾ measured a density of 3.17 g/cc for MgO pressed at 1200°C and found a maximum density of 3.50 g/cc at 1500°C (theoretical density 3.65 g/cc).

Extrusion

For the final application and type ware required at ANL, i.e., small quantities of crucibles, spacers and stopper rods for use in uranium melting, it was considered not practicable to investigate thoroughly the extrusion process. Work has been done on extrusion of easily sinterable fine-grained magnesia powders, such as those used in the Battelle Memorial Institute sintering investigation.⁽⁴⁾ The extrusion of MgO requires the addition of a plasticizing agent in order to develop flow properties without the use of extreme pressures. To give the necessary plasticity to MgO for the extrusion process, organic plasticizers such as cellulose acetate⁽⁸⁾ have been employed.

Slip Casting

Thompson and Mallet⁽⁹⁾ performed the first comprehensive survey on slip casting of magnesia shapes. In their investigation, casting was done in plaster molds, using absolute alcohol as the suspending medium. Greenaway⁽¹⁰⁾ found that the major difficulty involved in slip casting MgO from an alcohol slurry was the removal of the cast piece from the plaster mold. To circumvent this difficulty, he cast in a paper extraction thimble which burned off during firing. At ANL it was found that magnesium oxide could be cast from a water suspension. In this investigation, magnesia boats, $14\frac{1}{2} \times 2\frac{1}{2} \times 2\frac{1}{2}$ in., were fabricated by slip casting from an aqueous slurry into plaster molds. Four kg of -80 mesh MgO grain was milled in a porcelain-lined pebble mill containing 5 kg of porcelain pebbles. After milling approximately 16 hours, the particle size was reduced to 90% -325 mesh. Just before casting, 1 kg of -80 mesh magnesia along with 1.25 liters of 1 N hydrochloric acid was added to the mill, after which milling was continued for an additional hour. A cast wall of $\frac{1}{4}$ -inch thickness, which was found adequate for green strength, was built up on the plaster in less than 15 seconds. As soon as this thickness was reached the remaining slip was poured from the mold.

Stoddard et al.,⁽¹¹⁾ milled -200 mesh magnesia in a porcelain-lined pebble mill with 30 w/o distilled water for 15 hours and obtained a particle size of -325 mesh. After grinding, the slurry was aged in a constant temperature cabinet for 24 hours. After aging the suspension 1:1 HCl and coarse grain MgO were added, the slip was poured into plaster of Paris molds, allowed to come to the desired wall thickness and the surplus drained.

FIRING

Crucibles prepared from commercial MgO and "Product Dew" were fired in both reducing and oxidizing atmospheres. Crucibles to be fired under reducing conditions were put in a graphite susceptor and fired by induction. Stopper rods which were compacted in graphite molds were fired by induction, with the mold as the susceptor. The crucibles to be sintered in an oxidizing atmosphere were fired to 1500°C in a silicon carbide resistor furnace. To increase density, some crucibles were fired to 1800°C in a gas kiln.

At ANL it was found that firing of MgO crucibles in graphite was not satisfactory due to the reduction of the oxide, which caused roughness and some deep pitting of the surface where graphite particles came in contact with the magnesia; therefore suitable sintering could not be achieved by this method. Figure 1 shows, on the left, a crucible fabricated from commercial magnesia and fired by induction in a graphite susceptor. On the edge of the crucible can be seen a pit where apparently the MgO was in direct contact with graphite.

Figure 1. Magnesia Crucibles Fabricated from Commercial Magnesia (left) and "Product Dew" (right)

Macro 27505

On the right is a crucible fabricated from "Product Dew" and fired in a gas kiln. Figure 2 shows a magnesia stopper rod of the type made at ANL.

Figure 2. Magnesia Crucible Stopper Rods

Macro 27504

Figure 3 is a photograph of commercial MgO, "Product Dew" and CP MgO pellets which were dry pressed without binder and fired to 1800°C in a gas kiln. These three materials were fabricated in the same die using the same pressure. Differences in shrinkage during firing can be noted between CP MgO and the other two oxides.

Figure 3. Magnesia Pellets Dry Pressed at 15,000 psi, Fired to 1800°C:
(Left) Commercial MgO (Dens. 2.85 gm/cc);
(Center) "Product Dew" (Dens. 2.35 gm/cc);
and (Right) CP MgO (Dens. 3.14 gm/cc)

Density and Shrinkage

Pellets which were dry pressed from commercial MgO, "Product Dew" and CP MgO were fired in a series of draw trials in order to determine the effect of temperature on shrinkage and density. A group of pellets were removed from the Glo-bar furnace at each 100°C increment from 1200 to 1500°C. Firing was continued above 1500°C in the gas-fired kiln. Again withdrawals were made at 100°C increments up to 1800°C.

The effect of sintering temperature on density and shrinkage are shown in Figures 4 and 5. Commercial MgO showed a gradual increase in density from 2.49 gm/cc at 1200°C to 2.61 gm/cc at 1500°C, a more sharp increase to 2.85 gm/cc at about 1625°C, and then a gradual increase to 2.94 gm/cc at 1800°C, the maximum temperature investigated. "Product Dew" showed a density of approximately 2.22 gm/cc from 1200 to 1500°C. From 1500 to about 1650°C a density increase to 2.35 gm/cc occurred, after which the density appeared to be constant to 1800°C. A very sharp densification from about 1.89 at 1400°C to about 3.11 at 1600°C occurred for CP MgO, which then remained approximately constant to 1800°C. Diametrical shrinkage curves (Figure 5) were in agreement with the density data.

Figure 4. Fired Geometric Density Plotted Against Temperature °C

Figure 5. Fired Shrinkage Plotted Against Temperature °C

MELTING POINT

A review of the literature indicates the melting point of magnesia in air is 2800°C.^(12,13) Lambertson and Mueller⁽¹⁴⁾ investigated the melting point, using a tungsten crucible in an oxygen-free helium atmosphere. By this method they found the melting point to be 2682°C. It was found that at this temperature the tungsten crucible was attacked by the molten MgO. It was decided that the lower melting point, which was some 120°C under that reported in the literature, was due to the inert atmosphere and the fact that the magnesia dissociated slightly.

Phase-equilibrium Studies (MgO- UO_2)

Lambertson and Mueller⁽¹⁴⁾ investigated the MgO- UO_2 system with the aid of a high-temperature quenching furnace which was designed by Eyerly and Lambertson.⁽¹⁵⁾ The samples were heated in a tungsten crucible in an oxygen-free helium atmosphere for about 5 minutes, then quenched. The results of heating these mixtures of MgO- UO_2 are shown

Figure 7. U_3O_8 -MgO Phase Relationships

SUMMARY

1. Magnesia ware fired in contact with graphite showed surface deterioration. No such defect was evident in pieces fired in a gas kiln.
2. Pellets of CP MgO showed very rapid densification beginning at 1400°C . Both commercial MgO and "Product Dew" showed much smaller density increases beginning at about 1500°C .
3. The melting point of magnesia was found to be 2682°C in a He atmosphere, some 120° below the melting point determined in air.
4. No solid solutions were found to exist between MgO and $\text{UO}_{2.0-2.1}$.
5. A solid solution area was shown to exist between MgO and U_3O_8 containing between 50 and 75% MgO.

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