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IMPURITY EFFECTS ON THE CREEP OF POLYCRYSTALLINE
MAGNESIUM AND ALUMINUM OXIDES
AT ELEVATED TEMPERATURES

TECHNICAL PROGRESS REPORT

April 1, 1966 to December 23, 1966

ATOMIC ENERGY COMMISSION

Contract Number

AT(11-1) - 1591

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

Institute of Materials Research
University of Utah
Salt Lake City, Utah 84112

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TECHNICAL PROGRESS REPORT

December 23, 1966

PROJECT TITLE:

Impurity Effects on the Creep
of Polycrystalline Magnesium
and Aluminum Oxides at Elevated
Temperatures

CONTRACT:

AEC AT(11-1) - 1591

CONTRACTOR:

University of Utah
Institute of Materials Research

PERIOD REPORTED:

April 1, 1966 to December 23,
1966

PROJECT PERSONNEL:

Principal Investigator

Dr. Ronald S. Gordon
Assistant Professor
Department of Ceramic Engineering

ABSTRACT

The activities under Contract No. At(11-1) - 1591 during the period 1 April 1966 to 23 December 1966 are described in this report. Most of the work during this period has been concerned with the design and construction of a vacuum hot-press and two high temperature creep testing facilities. A description of these is given in the report.

Initial exploratory experiments have been conducted on (1) the hot-pressing of pure and doped (Fe_2O_3) magnesia and (2) the creep of pure dense (or nearly dense) hot-pressed magnesia. Pure and doped (Fe_2O_3) magnesia specimens have been hot-pressed to theoretical density at pressures between 20,000 and 35,000 psi. and temperatures between 1040 and 1260°C. Preliminary results from the hot-pressing and creep of dense (or nearly dense) hot-pressed magnesia indicate that grain growth can take place in significant amounts below 1300°C. An analysis into the role of a changing microstructure (grain growth) on the creep process in magnesia is being undertaken. In addition, the effect of a small amount of porosity on grain growth during creep is being studied.

INTRODUCTION

The activities under contract No. AT(11-1)-1591 during the period 1 April 1966 to 23 December, 1966 are described in this report.

Most of the work during this period has been concerned with the design and construction of a vacuum hot press and two high temperature creep testing facilities. A description of these will be given in the report. Considerable time and effort also was spent in preparing high purity magnesium oxide powder, the starting material for hot pressing.

Finally, some preliminary experimental results are reported in two areas:

1. Hot pressing of magnesium oxide
2. The creep of dense polycrystalline magnesium oxide.

CONSTRUCTION AND OPERATION OF THE VACUUM HOT-PRESS

A schematic diagram of the hot-press apparatus is shown in Figure 1. The apparatus consists of a sealed water cooled chamber capable of being evacuated. Conax "swagelok" power leads and thermocouple glands are used to supply power to the heating elements and to measure the temperature of the hot-press mold inside the chamber. A bellows assembly, enclosing a stainless steel rod attached to its top, is used to transmit pressure to the sample while still maintain-

Figure 1. Schematic - Vacuum Hot-Press

ing a vacuum in the chamber. In this way, a static seal instead of a dynamic seal is employed. The stainless steel rod rests upon a refractory brick in contact with a TZM* plate. This plate thus transmits pressure to the plungers inside the hot-press mold. At the bottom of the mold is another plate resting on another refractory brick. A piece of 1/8 inch thick asbestos is situated between this brick and the bottom of the vacuum container. The supporting plate, upon which the container rests, is water cooled.

The heating element is 14B and S gauge coiled molybdenum wire. This coil is wound around the inside of a mullite tube with mullite spacers holding apart the segments of the coil. The spacers and coils are held flat against the tube by small thermocouple protection tubes wired in place by molybdenum wire. This arrangement also holds together the mullite tube, which invariably cracks due to thermal shock. The leads to the heating element are protected by layers of silica cloth.

Prior to this construction, Kanthal A-1 wire cast in castable alumina was used as the heat source. However, the lower temperature limit of the Kanthal and the large amount of water given off by the castable required that this method of heating be abandoned.

Three molybdenum sheets, spaced at about one half inch intervals, are wrapped around the mullite tube. These sheets serve as radiation shields. Radiation shields are also placed over the top

*The plate, plungers, and mold are constructed of a titanium-zirconium-molybdenum alloy (TZM) obtained from Climax Molybdenum Company.

of these to reflect radiation downward. The whole mold is completely shielded except for the top-plunger which extends above the shields.

A Chromel-Alumel thermocouple is used to measure temperature. An NRC model 201 thermocouple gauge is used to measure pressure within the chamber and a dial guage is used to measure the degree of compaction. A glass cold trap cooled by dry ice and alcohol is situated between the vacuum pumps and the hot-press chamber to keep harmful gases from the pumps.

Removal of the bellows from the hot-press provides easy access to the mold position. To start a hot-pressing experiment, the mold is lowered into the chamber and the bottom plunger is inserted. Then about 30g of magnesium oxide powder in the form of a disc prepressed at 48,000 psi is placed inside the mold, and the top plunger is positioned. A few chips of titanium metal acting as a getter are placed on top of the mold to insure that the mold will be protected from oxygen attack due to any outgassing or leaking. The thermocouple is then placed in the hole provided for it and the top radiation shields are arranged. The top TZM plate and brick are then positioned. After the "O" ring is inserted into place, the bellows and the stainless steel rod combination is lowered and bolted to the chamber. After checking the supply of dry ice in the cold trap, the system is evacuated to about 25 microns (Hg) or less before the power is turned on. Evacuation to this pressure usually requires 20 to 30 minutes.

The temperature is raised by varying the power until a maximum of about 1250°C is reached. It is necessary to remain below 1300°C,

the recrystallization temperature of the TZM alloy. During the heating period, a small amount of pressure, applied by a hydraulic press, is maintained on the sample. When the mold reaches the pressing temperature, the pressure on the sample is raised to the desired level. The pressure is then held there for a few minutes before it is released. At this time the temperature is lowered by gradually reducing the power to the heating element.

In order to prevent the sample from cracking during cooling, it is necessary that the bellows and the attached steel rod be lifted off the sample with mechanical jacks. Atmospheric pressure acting through the bellows-steel rod combination is enough to crack the sample during cooling.

A schematic of the hot-pressing cycle is shown in Figure 2. Preliminary data on the pressing time, temperature, and pressure, as well as the properties of the pressed magnesium oxide will be presented in a later section of this report.

Prior to the purchase of the TZM mold, a series of hot-pressing experiments were conducted using graphite molds. Samples of magnesium oxide containing about 2% LiF were readily pressed to theoretical density at 1000°C and 5000 psi without the aid of a vacuum. These experiments were performed to check the construction of the press and have value only in that capacity, since the objective of this study is the hot-pressing of pure magnesia which requires higher pressures.

It was found that the magnesia adhered to the faces of the plungers and the walls of the die during pressing. This adherence

Figure 2. Schematic - Hot-Pressing Cycle

caused the sample to crack into many pieces during cooling because of the difference in thermal expansion between magnesium oxide and the mold. Following the technique of I. W. Lachman (1) of Corning Glass Works, the faces of the plungers and the sides of the die were coated with an alumina (Alcoa A-14) slurry. This procedure eliminated the adhesion problem and large pieces of pressed magnesium oxide were obtained. Whole samples were not uncommon. Preliminary studies have been started on the hot-pressing of magnesia containing 0.5 and 1.0% Fe_2O_3 . Samples of these were pressed with equal facility as with pure material.

DESIGN AND CONSTRUCTION OF THE HIGH TEMPERATURE CREEP TESTING FACILITIES

One creep apparatus was completely constructed to test the creep of hot-pressed polycrystalline magnesia. A second apparatus is near completion. Except for the heating elements, the two apparatuses are identical. In one, heating is accomplished by a Kanthal A-1 resistance wound furnace and, in the second, for higher temperature work, a molybdenum resistance wound furnace is employed.

Hot-pressed magnesium oxide is cut into test specimens which are creep-tested under four point loading. A schematic of the four point loading arrangement is given in Figure 3. The two alumina support points are cut from a triangular recrystallized impervious alumina rod (Morganite Inc.). These supports rest upon an alumina tube and are situated in the hot zone of the furnace. They are held in place by castable alumina. A 3/8 inch diameter alumina rod, with a 3/16 inch hole drilled through it, is used to apply the load.

Figure 3. Schematic - Four-Point Loading

Inserted into the hole is a machined crescent shaped alumina key. The key is flat on the bottom side and round on the top. It is this key that rests upon the sample; the rod rests upon the key.

In its unloaded state, the sample is not in true four-point loading. However, upon loading, elastic deformation insures that the sample is under a four-point load (2). This design reduces any thermal expansion effects which might manifest themselves as creep.

Attached to the alumina rod is a brass rod which is connected to the transformer core of a linear variable differential transformer (LVDT Sanborn-Linearsyn 585DT used in conjunction with a Sanborn demodulator convertor, 595-300). The vertical movement of the core changes the output of the LVDT which is received on a strip chart recorder. The LVDT is mounted on a Boeckler non-rotating spindle micrometer head (accurate to two parts in 100,000) which is used to calibrate the LVDT. On the other end of the transformer core is another brass rod with a hook on which weights may be attached to vary the load on the sample. A schematic diagram of the entire creep apparatus is given in Figure 4.

When the sample is in place, the furnace is lowered over it. No weights are added until the sample attains the desired temperature. At this point, subsequent addition of weights results in the complete capture of both the transient and steady-state creep regions.

Exploratory creep experiments were conducted on both sintered magnesia (porous) and hot-pressed magnesia (LiF doped) in order to check the operation of the creep apparatus. In one case, the total creep measured experimentally, checked very well with the total deflection measured by a cathetometer.

Figure 4. Schematic - Creep Apparatus

PREPARATION OF PURE MAGNESIUM OXIDE

Pure magnesium oxide was prepared in a method outlined by Brown (3). The starting material was Gallard Schlesinger 99.99% pure magnesium metal. The metal was dissolved in HNO_3 . NH_4OH was added to this solution forming a precipitate which was filtered off. The remaining solution was then added to a prepared $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution to form MgC_2O_4 by precipitation. The MgC_2O_4 was decomposed to magnesia in an alumina crucible at approximately 900°C for various times. The calcined powder consisted of aggregated particles which were partially broken up by rolling the powder in nalgene bottles containing an alumina ball. Magnesium oxide prepared in this manner was the starting material for the hot-pressing experiments.

The total surface area of two samples of magnesium oxide prepared by the decomposition of MgC_2O_4 at 980°C for 2 3/4 and 23 hours was determined by nitrogen adsorption. The surface area for both samples was $35 \frac{\text{meter}^2}{\text{gm}}$ which agrees well with data in the literature (4,5) for magnesia prepared in a similar manner. If the magnesia crystallites are assumed to be in the form of cubes, a particle size (cube edge) of approximately 0.05μ (or $500 \text{ \AA}$) is calculated.

Optical micrographs of the calcined powder reveal the presence of agglomerates $5\text{-}10 \mu$ in size. A representative micrograph is given in Figure 5. Thus it is concluded that the magnesia prepared from the oxalate consists of agglomerates $5\text{-}10 \mu$ in size, each containing numerous $500 \text{ \AA}$ magnesia crystallites. During the prepressing, it is

Figure 5. Calcined Magnesia (750x)

likely that these agglomerates partially break down but probably not down to the 500 Å level.

HOT-PRESSING RESULTS

The pressing times, temperatures, pressures and final densities of a variety of magnesium oxide samples, which have been hot-pressed, are presented in Table 1. Photomicrographs of samples P20T, P9T and P16T are given in Figures 6 through 8.

It is readily apparent that exaggerated grain growth occurred in some samples. This behavior is striking in the micrograph of sample P16T (Figure 8), in which 20 micron particles are found isolated in a submicron matrix. Samples which were not pressed to end-point density especially showed this phenomenon near the top of the sample (i.e., where the pressure was applied), but often showed only the submicron matrix near the bottom of the sample. This behavior indicates that the more dense regions of the sample exhibit grain growth.

The grain growth appears to depend on three factors: time, temperature and pressing pressure. These are also the three variables that control densification. It is well known that time and temperature affect grain growth, but not much is known about the effect of pressure. It seems most likely, from a speculative point of view, that the pressure enhances grain growth because it brings the individual grains into more intimate contact so that material transport across the boundaries occurs easier. Pressure may also enhance diffusion.

Figure 6. Hot-Pressed Magnesia doped with 0.67% Fe_2O_3 - P20T (1180x).

Figure 7. Hot-Pressed Magnesia - P9T (1160x).

Figure 8. Hot-Pressed Magnesia - P16T (1180x).

It is interesting to note that Lowrie (6) did not report significant grain growth on hot-pressed magnesium oxide until much higher temperatures and longer times. Spriggs et. al. (7) reported that it required 100 minutes for grains to increase an order of magnitude in size. Their grain growth experiments were conducted at temperatures between 1300°C and 1600°C. In light of the two works cited, the grain growth encountered in this study during hot-pressing is perplexing. To minimize grain growth, temperature and time will be held at a minimum and pressure will be increased in the hot-pressing operation. Further observations will be made in the next section which will point out a need for grain growth studies.

TABLE I

<u>Sample</u>	<u>Ultimate Pressure</u>	<u>Pressing Time</u>	<u>Pressing Temperature</u>	<u>Composition</u>	<u>Density</u>	<u>Percent Theoretical</u>
P9T	20000 psi	26 min.	1259°C	Pure MgO	3.581	100 %
P10T	20000 psi	25 min.	1246°C	Pure MgO	3.570	99.7 %
P12T	30000 psi	43 min.	1040°C	Pure MgO	3.564	99.5 %
P13T	30000 psi	24 min.	1105°C	1.19% Fe ₂ O ₃	3.580	99.9+%
P14T	30000 psi	15 min.	1128°C	0.49% Fe ₂ O ₃	3.610	100.8 %
P15T	35000 psi	60 min.	1095°C	Pure MgO	3.581	100 %
P16T	15000 psi	25 min.	1185°C	Pure MgO	3.544	98.9+%
P17T	10000 psi	48 min.	1195°C	Pure MgO	3.33	93.0 %
P20T	30000 psi	35 min.	1173°C	0.666% Fe ₂ O ₃	3.557	99.6 %

It should be noted that the sample doped with Fe₂O₃ (Fig. 6) gave a microstructure very similar to that reported for LiF doped hot-pressed magnesium oxide (8). The average grain size is less than 10 microns and quite uniform.

It has been found that dense magnesium oxide samples are not difficult to prepare. Control of microstructure has been found to be more difficult than anticipated, but the results seem to indicate that control is not impossible. The impure samples do not seem to be as troublesome as the pure ones. Lower temperatures and shorter pressing times offset by higher pressures seems to be the approach to follow. In fabricating porous samples, it seems most advantageous to remain at low temperatures and control the amount of porosity by the applied pressure.

EXPERIMENTAL CREEP RESULTS

Initial creep experiments were made with hot-pressed samples of pure magnesia containing less than 2% porosity. Specimens were cut from the hot-pressed discs and polished on a diamond wheel. Each sample was a small rectangular beam of about 25mm length and 1.5 and 4.0mm height and width respectively. Creep temperatures ranged between 950°C and 1290°C.

Stresses were calculated according to the method of Timoshenko (9). The stress (σ) is calculated from the equation

$$\sigma = \frac{Mh}{2I} \cdot \frac{2n+1}{3n} \left(\frac{2y}{h} \right)^{1/n} \quad (1)$$

which is derived assuming a steady state creep equation of the type

$$\epsilon = k \sigma^n t \quad (2)$$

The definitions of the terms in equations (1) and (2) are as follows:

σ = stress in any fiber a distance y from the neutral axis
(center of beam)

h = height of the beam

n = exponent in the creep equation

k = constant in the creep equation

ϵ = strain in any fiber a distance y from the neutral axis

t = time

I = moment of inertia of the beam about its neutral axis

$$= \frac{bh^3}{12}$$

b = base of the beam

M = bending moment of the beam in four point loading

$$[= \frac{P}{4} (L-l)]$$

L = length of large span (= 0.760")

l = length of small span (= 0.329")

P = total load on beam

When $y = \frac{h}{2}$ equation (1) reduces to $\sigma_{\max}$, the maximum stress in the outer fiber

$$\sigma_{\max} = \frac{Mh}{2I} \cdot \frac{2n+1}{3n} \quad (3)$$

The strain ϵ in any fiber a distance y from the neutral axis is given by

$$\epsilon = \frac{y}{R} \quad (4)$$

in which R is the radius of curvature of the beam. For large radii of curvature or small deflections (δ), the radius of curvature is

$$R = \frac{L^2}{8\delta} \quad (5)$$

Thus the strain is given by

$$\epsilon = \frac{8 y \delta}{L^2} \quad (6)$$

For the strain in the outer fiber, equation (6) reduces to

$$\epsilon = \frac{4 h \delta}{L^2} \quad (7)$$

Figure 9 indicates a log-log plot of strain rate and applied stress (σ max) for sample P10T which had a measured density of 3.57. The sample was placed in the creep furnace, allowed to come to equilibrium at 1075°C, and loaded under four point loading with a stress of 113 kg/cm². Thereafter, at intervals of six hours, the stress was increased in four steps to 657 kg/cm². It was observed from the raw data as it came from the strip chart recorder, that the slope continued decreasing slightly for periods up to 100 hours. This indicated that either steady-state had not been reached or multiple creep mechanisms were simultaneously taking place. It is interesting to note that the slope of this curve is significantly less than one. However, it is difficult to compare strain rate data at different stress levels in this experiment since the microstructure (grain size) probably is changing with time.

Figure 9. Strain Rate versus Stress (Plot).

An investigation of the microstructure before (as hot-pressed) and after creep indicated that a thorough investigation of grain growth is necessary to understand the creep mechanism because of the observed change in microstructure. Figure 10 is a photomicrograph (230x) of hot-pressed sample P15T. The grain size distribution is extremely erratic and indicates some exaggerated grain growth. Figure 11 shows the same sample after creep (40 hours at 1286°C). The grain size and distribution have changed. The average grain size is about 35 microns. The micrograph also indicates some residual porosity at three-grain boundary intersections.

Four specimens from this hot-pressed sample (P15T) were crept at 1286°C. Each sample was placed in the furnace for one hour before a stress was applied. Only one load was applied to each sample. Figure 12 indicates the deflection-time curves for the four samples over a 36 hour period. But again, the slope decreases slightly over the entire range. The steady decrease in the slope of the creep curves might actually be related to microstructure changes (i.e. grain growth) taking place during the creep test.

In Figure 13, a log-log plot of the strain-rate (outer fiber) and the applied stress (σ max) are plotted from the data of Figure 12 in three different time periods: 8-16 hours, 20-30 hours and 24-36 hours. Since each sample had the same temperature-time history, it could be assumed that at any given time, the microstructures would be similar. A straight line plot is obtained with the exception that the sample with the least applied stress had a deflection rate larger than the straight line would predict. This deviation most probably was due to

Figure 10. Hot-Pressed Magnesia before creep - P15T (230x)

Figure 11. Hot-Pressed Magnesia after creep - P15T (230x)

Figure 12. Deflection - Time Curves (P15T)

Figure 13. Strain rate versus Stress (P15T)

a small microcrack which was observed to be present in the sample after testing.

It is interesting to note that the slopes of the lines in all three time periods are the same (~ 2.1). It is difficult to make general conclusions from a set of experiments at only one temperature. However, it is significant that other than a linear $\dot{\epsilon}$ versus σ dependence is observed. Vasilos, Passmore, et. al. (10, 11) observed a linear $\dot{\epsilon}$ versus σ behavior in the creep of dense magnesia. However, Wygant (12) observed in his creep studies values of n equal to 2.5 and 3.5 for different types of magnesia.

More work at other temperatures, stresses and grain sizes is needed in order to establish the value of the exponent in the steady state creep equation. In addition, the role of the changing microstructure during the creep process is not clear and needs to be studied extensively. It may not be sufficient to characterize creep data with an average grain size. The actual grain size-time dependence during creep may be required to completely understand the creep process.

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