

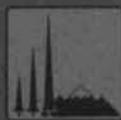
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REPORT

HOT PRESSING OF RARE EARTH OXIDES

H. T. FULLAM  
C. J. MITCHELL

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HOT PRESSING OF RARE EARTH OXIDES

By

H. T. Fullam  
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Chemical Research Section  
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June, 1967

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TABLE OF CONTENTS

	Page Number
INTRODUCTION . . . . .	1
SUMMARY . . . . .	1
PROCESS OBJECTIVES . . . . .	2
PRESSING OPERATION . . . . .	3
HOT PRESSING THE SESQUIOXIDES OF NEODYMIUM AND SAMARIUM . . . . .	4
Density . . . . .	4
Structural Stability and Dimensional Control . . . . .	10
HOT PRESSING PROMETHIUM SESQUIOXIDE . . . . .	12
PROCESS EVALUATION . . . . .	14
REFERENCES . . . . .	16
APPENDIX . . . . .	17



## HOT PRESSING OF RARE EARTH OXIDES

H. T. Fullam, C. J. Mitchell

INTRODUCTION

A program is currently underway at Battelle-Northwest to develop promethium-147 as an isotopic heat source. As part of this program various methods of fabricating promethium sesquioxide into useful shapes are being investigated. Among the compaction techniques being evaluated are cold pressing and sintering,<sup>(1)</sup> slip casting,<sup>(2)</sup> fusion casting, pneumatic impaction, and hot pressing. This report summarizes the results of initial hot pressing studies.

Because of the large volume of oxide required for these studies and since the availability of promethium sesquioxide is limited, the sesquioxides of samarium and neodymium were used as standins for  $Pm_2O_3$  in most of this work. Only enough pressings were made with actual  $Pm_2O_3$  to insure that the results obtained with the standins were applicable to promethium sesquioxide.

SUMMARY

The sesquioxides of samarium and promethium can be compacted to densities in excess of 95% of theoretical by pressing at temperatures of 1590°C and pressures of 5100 psi. Under similar conditions  $Nd_2O_3$  will compress to slightly lower densities.

In addition to the normal operating variables which affect hot press density (time, temperature, and pressure), the temperature at which the oxide is calcined prior to pressing was found to have a pronounced effect on the density obtainable. As a general relationship, the higher the calcination temperature the lower the density which results for a given set of pressing conditions.

For shapes having large length-to-diameter ratios, hot pressing gives a uniform density throughout the shape length. Dimensional control is excellent and shape diameters can easily be controlled to within 0.001 inch. When the pressing characteristics of the oxide are known, shape length can be controlled to within 0.5%.

Hot pressed pellets of the rare earth oxides have excellent physical strength and can be handled readily without physical damage.  $\text{Nd}_2\text{O}_3$  pellets are sensitive to atmospheric moisture, however, and must be handled accordingly to prevent their disintegration.  $\text{Sm}_2\text{O}_3$  and  $\text{Pm}_2\text{O}_3$  pellets, on the other hand, can be left in the open air for many days without suffering any apparent damage.

Based on the experimental results of this program and on qualitative impressions gained during the course of the work, hot pressing appears to be a most practical method of fabricating  $\text{Pm}_2\text{O}_3$  into useful shapes. If only a few  $\text{Pm}_2\text{O}_3$  shapes are to be made, the work could be done in a glovedbox without excessive operator radiation exposure. A semiproduction operation, however, should be carried out in a remotely operated facility such as a manipulator-equipped "hot" cell.

#### PROCESS OBJECTIVES

In compacting promethium sesquioxide into useful shapes, there are several basic requirements which must generally be met.

- The final compacted shape should have a high density to insure a high power density.
- The density of the shape should be uniform.
- Close dimensional control should be maintained to insure ease of encapsulation.
- The compacted shape should possess good physical integrity so that it can be handled readily prior to encapsulation.

In addition to the above requirements, there are certain operational features which the compaction process should possess.

- The physical operations of the process should be relatively simple so that they can be carried out in a gloved box or remote facility.
- If the work is performed in a gloved box the amount of physical handling required should be small so as to reduce operator exposure.
- Physical containment of the oxide within the equipment should be good so as to keep down the background radiation levels.

The final evaluation of hot pressing as a technique for fabricating promethium sesquioxide into useful shapes will be based on all the requirements outlined above.

### PRESSING OPERATION

Two types of hot presses were used in this work. One was a modified version of the miniature hot press developed at Oak Ridge.<sup>(3)</sup> The second was an induction heated press capable of pressing larger shapes than was possible with the miniature unit. The capabilities of each unit are summarized in Table I and described in detail in the Appendix (A). Shapes prepared in this work were limited to right circular cylinders.

Table I

### Characteristics of Experimental Hot Presses

	<u>Miniature Hot Press</u>	<u>Induction Heated Hot Press</u>
Maximum Pressure	6500 PSI	6500 PSI
Maximum Temperature	1700°C	~1700°C
Maximum Shape Diameter	1.00 inch	2.00 inches
Maximum Shape Length	0.50 inch	4.00 inches
Atmosphere	Vacuum	CO-CO <sub>2</sub> -N <sub>2</sub>
Time Cycle	70-80 minutes	7-8 hours

The pressing technique used was identical for each press and consisted of:

- Loading a weighed volume of oxide into a graphite mold.
- Pre-compacting the oxide in a hydraulic press at 100-200 PSI.
- Inserting the mold in the hot press.
- Heating the mold to the desired temperature.
- Applying pressure.
- Maintaining the temperatures and pressure for required time.
- Cooling press to room temperature.
- Releasing pressure and removing mold from press.

The density of the pressed shape was calculated from the weight and physical dimensions of the pellet. No attempt was made to measure the densities by densitometer techniques. At least three pressings were made at each set of conditions and the results averaged. Normally, the standard deviation in density was less than 0.05 gm/cc.

### HOT PRESSING THE SESQUIOXIDES OF NEODYMIUM AND SAMARIUM

Hot pressing of the sesquioxides of samarium and neodymium was studied in detail. Variables affecting the process were evaluated and the data obtained correlated in terms of the process objectives as set forth above.

#### Density

In the hot pressing operation, three process variables affect the density of the pressed shape - time, temperature, and pressure - each of which can be controlled independently of the others. In addition, the physical characteristics of the material being pressed influence the maximum obtainable density. The effects of these (four) variables on the hot press density of  $\text{Sm}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  were determined and the results are summarized below. One other variable which might affect the density - namely die material - was not evaluated as only graphite dies were used in this work.

The current production process for promethium sesquioxide involves the precipitation of the promethium from a nitric acid solution as the oxalate, and the subsequent calcination of the oxalate to the sesquioxide. A similar process was used to prepare the sesquioxides of samarium and neodymium used in this study (See Appendix (B)). Previous work had shown that the oxalate calcination temperature had a pronounced effect on the cold pressing and sintering characteristics of the oxides.<sup>(1)</sup> This was also found to be true in the case of hot pressing. This is shown in Figure 1 where hot press density is plotted as a function of the oxalate calcination temperature for  $\text{Sm}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$ . For  $\text{Sm}_2\text{O}_3$  the maximum density is obtained with oxide calcined at 800-900°C. At higher calcination temperatures the density decreases slowly up to 1200°C and very rapidly thereafter. Samarium sesquioxide produced from oxalate calcined at 750°C or less has a cubic structure, whereas oxide calcined above 750°C has a monoclinic structure. All of the hot pressed pellets possessed a monoclinic structure. This means that the oxide calcined at 750°C or less undergoes a change in crystal structure during the pressing operation. This probably accounts for the apparent discontinuity in the  $\text{Sm}_2\text{O}_3$  curve in Figure 1.

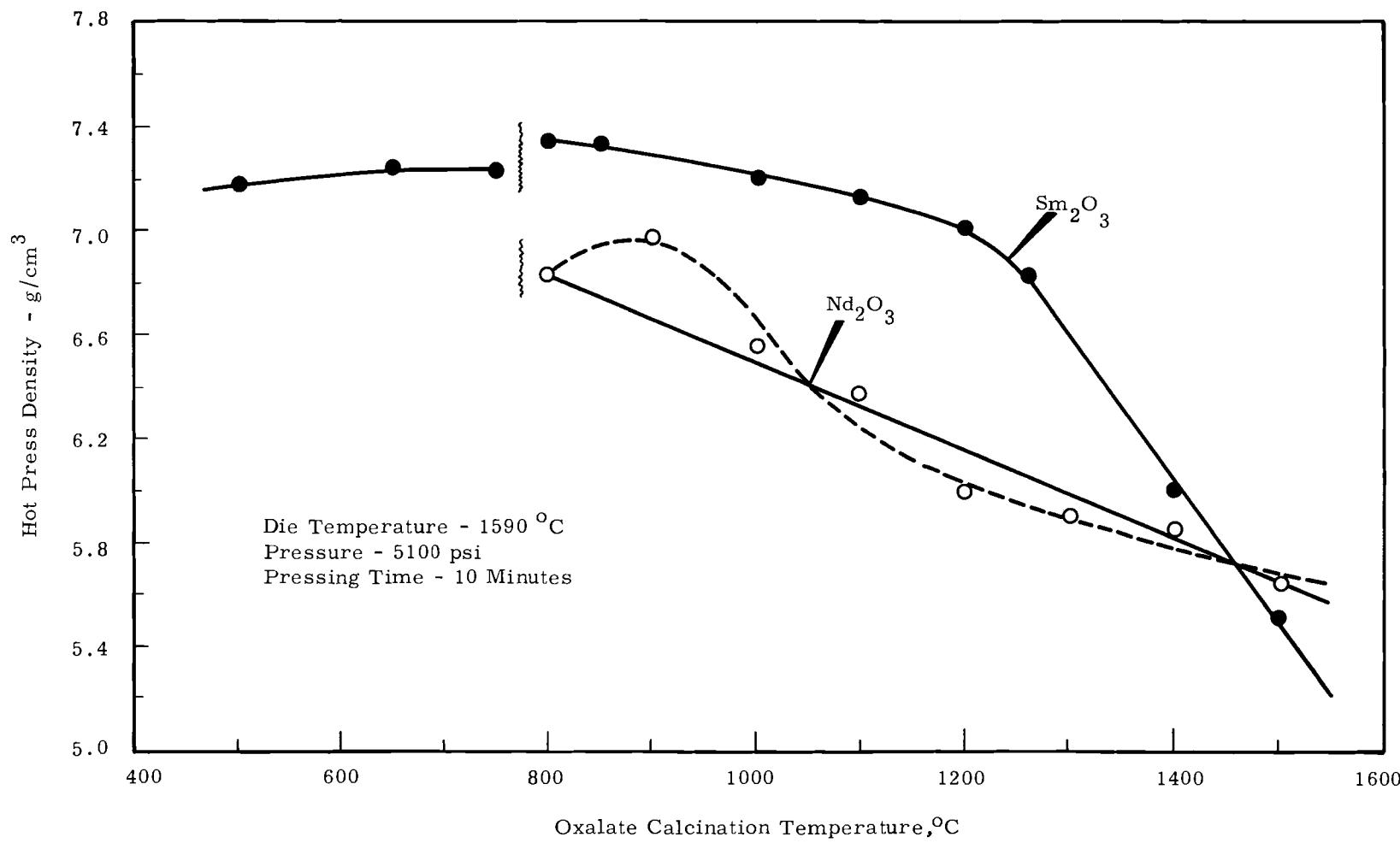


FIGURE 1 - Variation in Hot Press Density of  $\text{Sm}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  with Oxalate Calcination Temperature

The data for  $\text{Nd}_2\text{O}_3$  is very irregular and it is difficult to correlate density with the oxalate calcining temperature. The general trend is the same as for  $\text{Sm}_2\text{O}_3$  with higher calcination temperature giving lower hot press densities.  $\text{Nd}_2\text{O}_3$  calcined at 900°C gave a much higher density, however, than oxide calcined at 800°C. Since the crystal structure of both oxide batches was the same prior to pressing (hexagonal), it is difficult to explain the high density obtained with the oxide calcined at 900°C. If the data for 900°C are ignored, a linear relationship between density and calcining temperature can be approximated (Figure 1 - solid line). If the 900°C data are included, a very irregular relationship results (Figure 1 - dashed line).

An attempt was made to correlate the hot pressing characteristics of  $\text{Nd}_2\text{O}_3$  and  $\text{Sm}_2\text{O}_3$  calcined at various temperatures with oxide surface area and particle size. This attempt, which was only partially successful, is summarized in Section D of the Appendix.

The effect of pressing time\* on the hot press density is shown in Figure 2. From the data, it can be seen that only a slight increase in density results from pressing times in excess of five minutes. This can be observed visually during the pressing operation by the fact that ram travel is negligible after the first 4-5 minutes of pressing. For those pressings in which time was not a variable, ten minutes was taken as the standard pressing period.

The effects of temperature and pressure on the density of  $\text{Sm}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  are summarized in Figures 3-6. The results are not unexpected and show that the higher the temperature and pressure, the higher the density of the pressed oxide. In each of the figures the pronounced effect of oxalate calcination temperature on density is readily apparent.

Since hot pressing is carried out under conditions where plastic deformation of the oxide is possible, one would not expect a variation in oxide density as the L/D of the cylinder is varied. This was borne out by the results as summarized in the following table.

\*Pressing time is herein defined as the time during which the oxide is maintained at temperature and pressure.

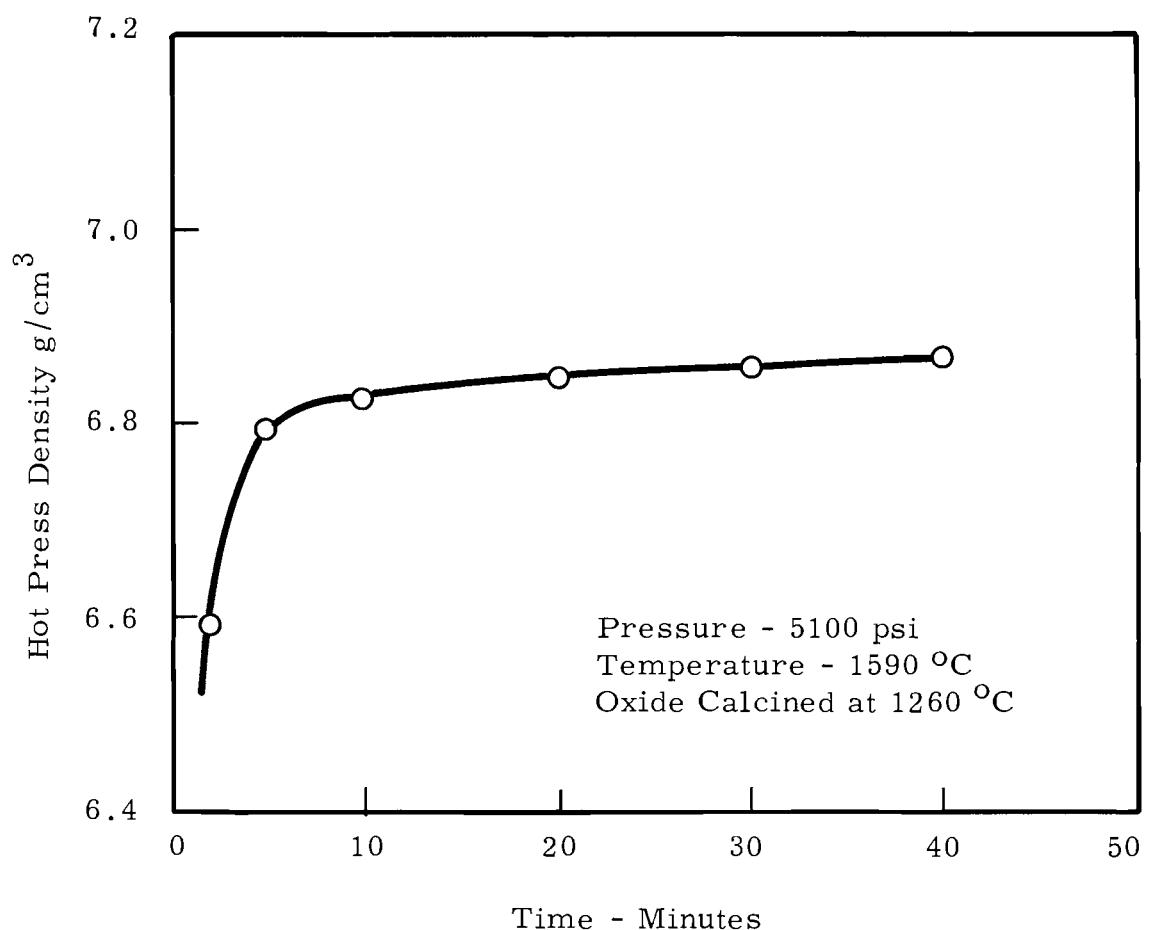


FIGURE 2 - The Variation in Density of  $\text{Sm}_2\text{O}_3$  with Pressing Time

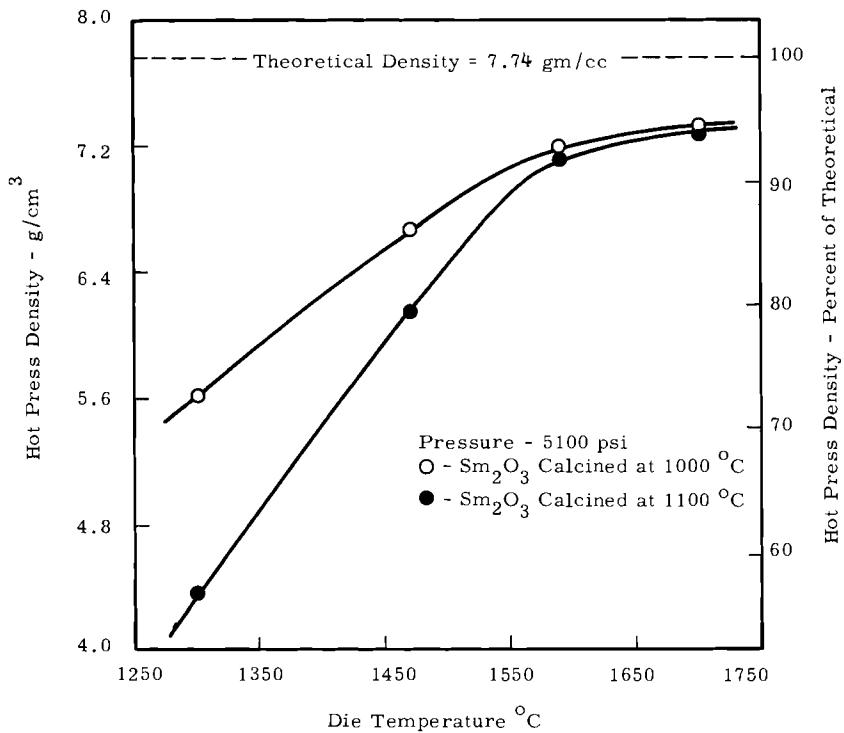


FIGURE 3 - Hot Press Density of  $\text{Sm}_2\text{O}_3$  as a Function of Die Temperature

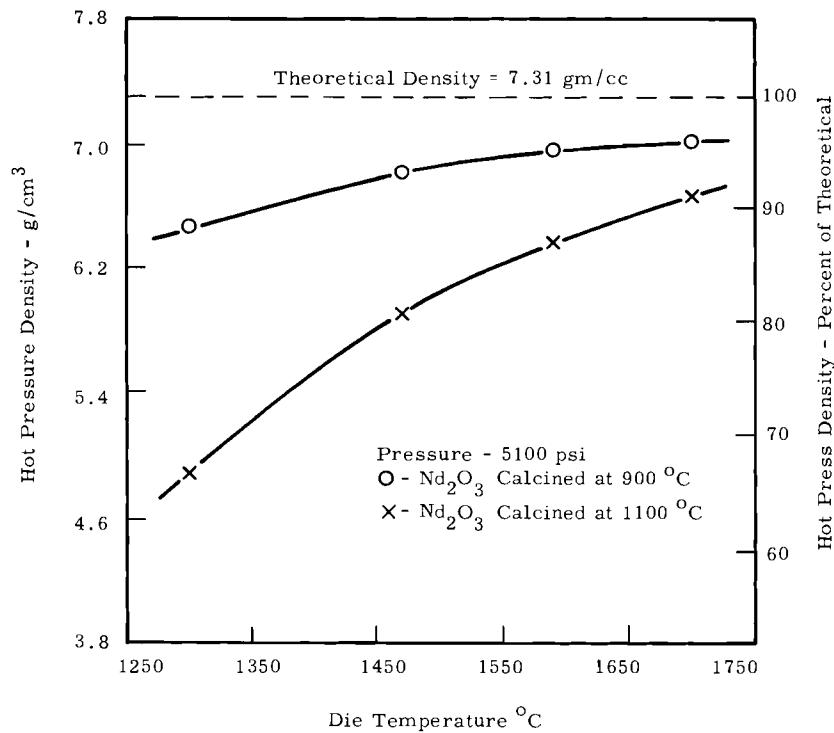


FIGURE 4 - Hot Press Density of  $\text{Nd}_2\text{O}_3$  as a Function of Die Temperature

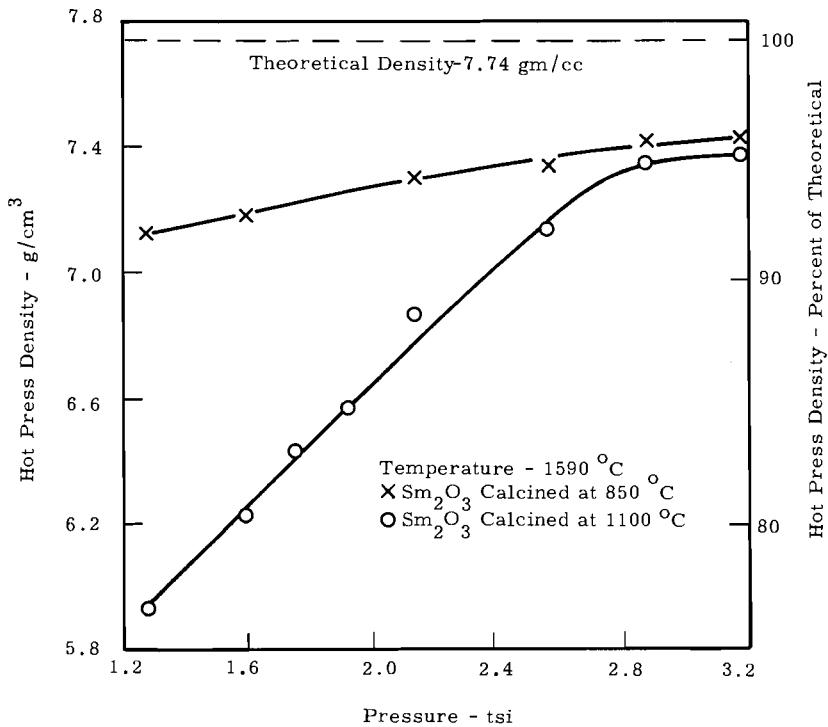


FIGURE 5 - The Effect of Pressure on the Hot Press Density of Sm<sub>2</sub>O<sub>3</sub>

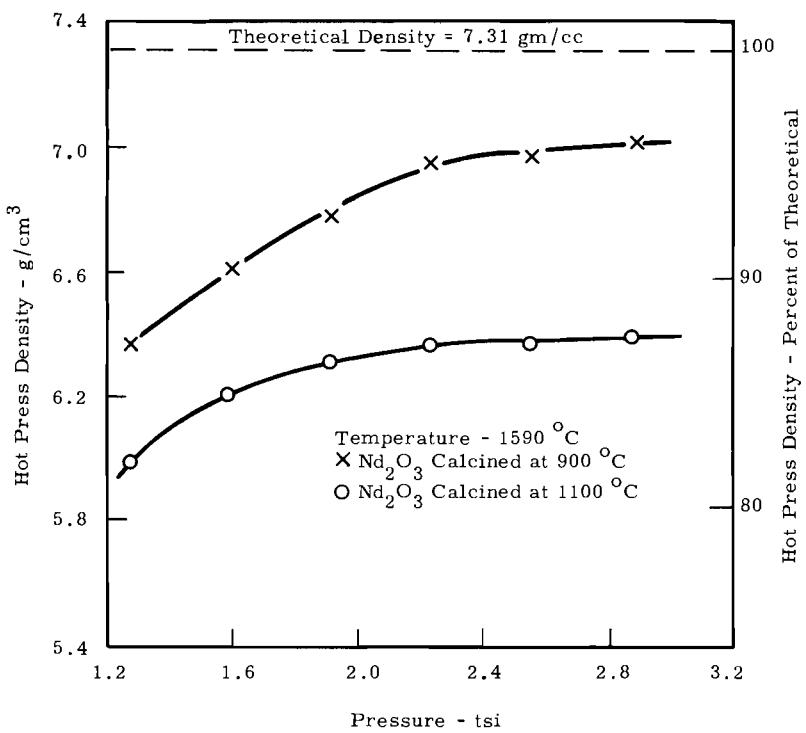


FIGURE 6 - The Effect of Pressure on the Hot Press Density of Nd<sub>2</sub>O<sub>3</sub>

Table IIThe Effect of L/D on Hot Press Density of  $\text{Sm}_2\text{O}_3$ 

<u>Oxide</u>	<u>Calcining Temp. °C</u>	<u>Pressure PSI</u>	<u>Temperature °C</u>	<u>L/D</u>	<u>Density g/cm³</u>
$\text{Sm}_2\text{O}_3$	1260	5100	1590	0.23	6.83
$\text{Sm}_2\text{O}_3$	1260	5100	1590	0.34	6.85
$\text{Sm}_2\text{O}_3$	1260	5100	1590	0.46	6.88
$\text{Sm}_2\text{O}_3$	1260	5100	1590	0.59	6.82
$\text{Sm}_2\text{O}_3$	1260	5100	1590	1.04	6.87
$\text{Sm}_2\text{O}_3$	1260	5100	1590	1.75	6.91

It was also found that the density was uniform throughout a cylinder with a high L/D. This was determined by sectioning a cylinder (4 sections) with an L/D of 4 and measuring the density of each section. Typical hot pressed cylinders of  $\text{Sm}_2\text{O}_3$  are shown in Figure 7.

The maximum densities obtainable with existing equipment were determined and the results were as follows:

Table IIIMaximum Densities Obtained with Available Hot Presses

<u>Oxide</u>	<u>Calcining Temp. °C</u>	<u>Pressure TSI</u>	<u>Temperature °C</u>	<u>Time Minutes</u>	<u>Density</u>	
					<u>g/cm³</u>	<u>% of Theor.</u>
$\text{Sm}_2\text{O}_3$	800	3.18	1700	30	7.47	96.5
$\text{Nd}_2\text{O}_3$	900	3.18	1700	30	7.08	96.8

With stronger dies it should be possible to exceed the 3.18 TSI pressure limit of the existing equipment and thus obtain densities greater than 97% of theoretical.

Structural Stability and Dimensional Control

Samarium sesquioxide shapes which have been pressed at temperatures of 1300°C and above and pressures greater than 1.2 TSI have excellent structural integrity. Pellets pressed at lower temperatures and pressures often crack upon removal from the mold. The oxide shapes produced at high temperatures and pressures have good compressive strength, uniform texture and appearance, very few visible flaws, and are very stable to moisture pickup.

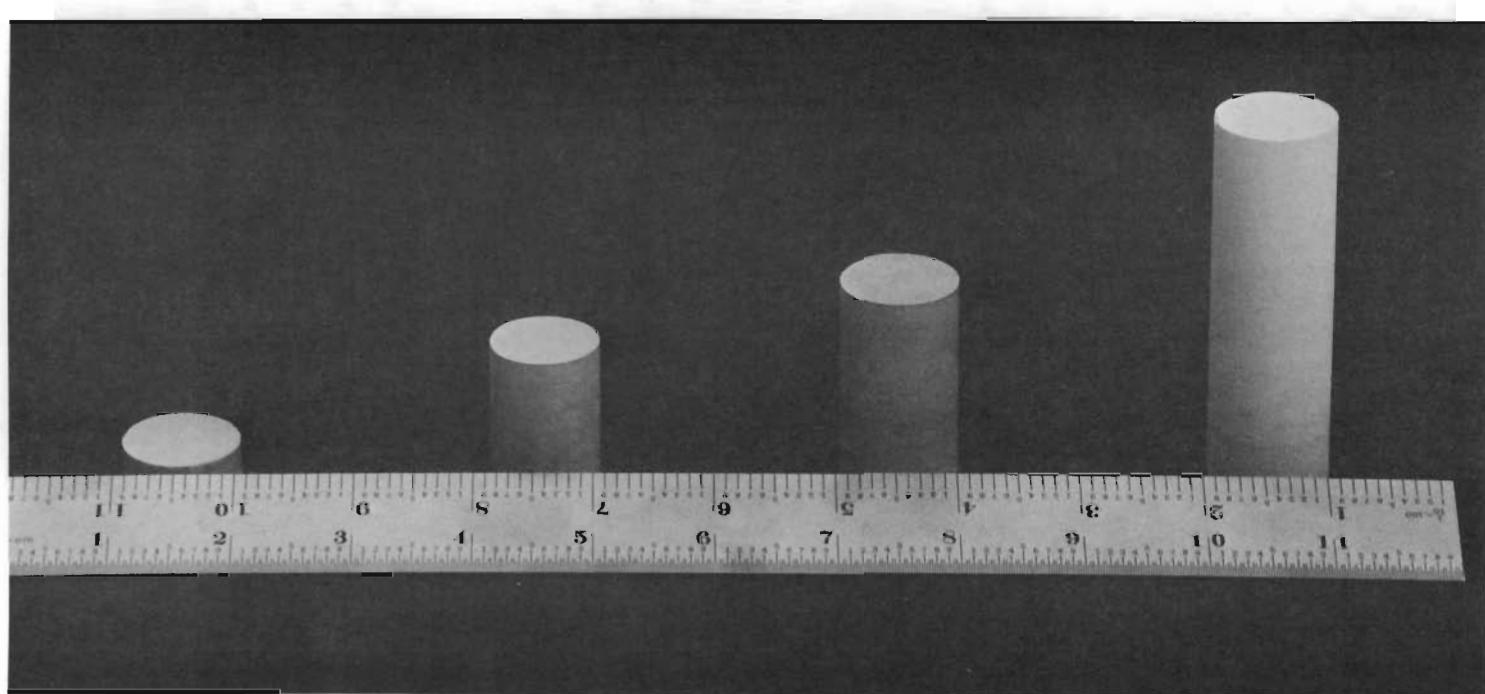


FIGURE 7 - Typical Hot Pressed  $\text{Sm}_2\text{O}_3$  Cylinders

Neodymium sesquioxide behaves quite similarly to  $\text{Sm}_2\text{O}_3$  except for its poor resistance to moisture pickup. Hot pressed pellets of  $\text{Nd}_2\text{O}_3$  which have good structural integrity will, when exposed to the atmosphere, fall apart quite rapidly due to moisture pickup. A pellet pressed at  $1700^\circ\text{C}$  will begin to crack after one-two days exposure and will be a pile of powder after three-four days (see Figure 8). As a point of comparison, a samarium sesquioxide pellet pressed at  $1700^\circ\text{C}$  is stable for many months before cracks develop.

At the pressing temperatures that were used ( $1300$ - $1700^\circ\text{C}$ ) some reaction occurs between the oxide and the graphite die. This results in the formation of a very thin carbide film on the surface of the oxide body. In addition, there is always some free graphite contamination on the surface of the oxide. Both the free graphite and the carbide can be removed by heating the oxide in air at  $600$ - $800^\circ\text{C}$  for a few hours.

Hot pressing is a versatile process which can be used to produce a variety of shapes. This work was limited to right circular cylinders, but many other shapes could have been produced with the proper dies. Dimensional control is excellent and if the thermal expansion coefficient of the material to be pressed is known, the diameter of the pressed cylinder can be controlled within 0.001 inch. Even if the thermal expansion coefficient is not known, the die size to give a specific cylinder is easily determined by trial and error. In using graphite dies some wear of the die occurs, and if close dimensional tolerances are required the die has to be replaced quite frequently. For this work, where close dimensional control was not a prerequisite, as many as thirty pressings were made from a single graphite die.

#### HOT PRESSING PROMETHIUM SESQUIOXIDE

To check the validity of the assumption that the results obtained with  $\text{Sm}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  were applicable to  $\text{Pm}_2\text{O}_3$ , several pressings were made with actual promethium sesquioxide. At the time of pressing the oxide contained approximately 6%  $\text{Sm}_2\text{O}_3$  due to radioactive decay. The  $\text{Pm}_2\text{O}_3$  was prepared by precipitating the oxalate and then calcining at three different temperatures ( $800$ - $950$ - $1100^\circ\text{C}$ ) to

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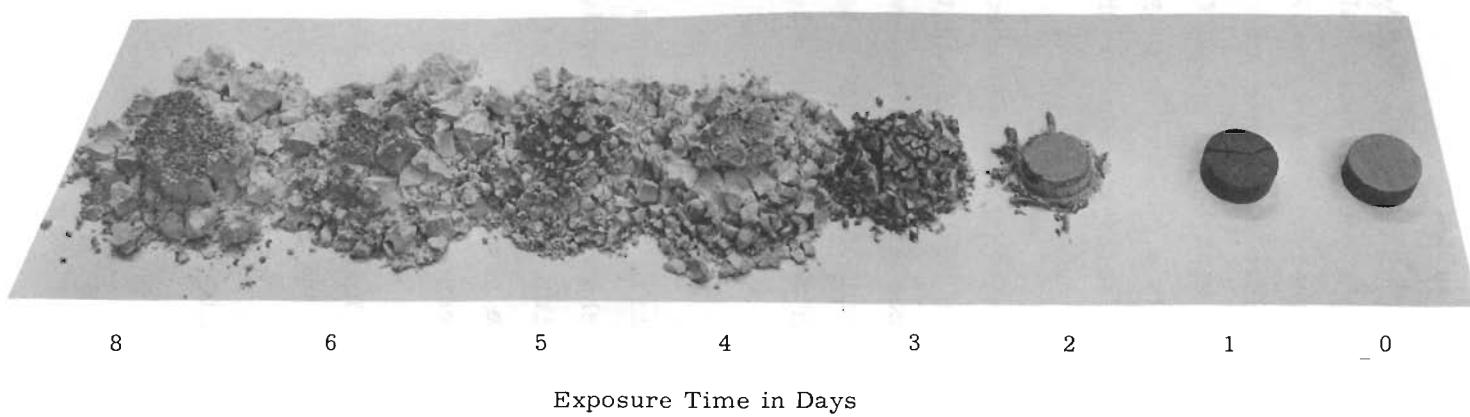


FIGURE 8 - Breakup of Hot Pressed  $\text{Nd}_2\text{O}_3$  Pellets Upon Exposure to the Atmosphere

convert the oxalate to the oxide. Two pellets were pressed from each batch and the averaged results are shown in Figure 9. The theoretical density of the  $\text{Pm}_2\text{O}_3$ -6%  $\text{Sm}_2\text{O}_3$  mixture was taken as the weighted average of the individual values ( $0.94 \times 7.43 + 0.06 \times 7.74 = 7.45 \text{ g/cm}^3$ ).

From the results, it can be seen that the pressing characteristics of  $\text{Pm}_2\text{O}_3$  are slightly improved over those of  $\text{Sm}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  (as far as density is concerned). The variation in  $\text{Pm}_2\text{O}_3$  density with calcining temperature is less and the density is higher at the higher oxalate calcining temperature than is the case with  $\text{Sm}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$ .  $\text{Pm}_2\text{O}_3$  shows a maximum density for a calcining temperature of 950°C and lower densities with 800°C and 1100°C oxide. This is similar to the data for  $\text{Nd}_2\text{O}_3$  which shows a maximum density with 900°C oxide. It appears, therefore, that the pressing results obtained with  $\text{Sm}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  are generally applicable to  $\text{Pm}_2\text{O}_3$ .

The only major difference encountered in pressing  $\text{Pm}_2\text{O}_3$  was that it appeared to be more sensitive to thermal shock than either  $\text{Sm}_2\text{O}_3$  or  $\text{Nd}_2\text{O}_3$ . This means that the press must be cooled at a slower rate to prevent the  $\text{Pm}_2\text{O}_3$  pellets from cracking. As a point of comparison, approximately 30 minutes were required to cool the press with  $\text{Sm}_2\text{O}_3$ , whereas twice this time was taken to cool the press with  $\text{Pm}_2\text{O}_3$ .

#### PROCESS EVALUATION

In evaluating hot pressing as a process for fabricating promethium sesquioxide into useful shapes, the evaluation was based on the requirements set forth in an earlier section. While most of the process variables have been studied in detail, some of the evaluations which follow are based on qualitative impressions gained during the course of the work and in some cases have not been verified by experimental work.

- Density. Promethium sesquioxide can be hot pressed to densities in excess of 95% of theoretical quite readily. Based on the results obtained with  $\text{Sm}_2\text{O}_3$ , the density of large shapes is very uniform and one would expect  $\text{Pm}_2\text{O}_3$  shapes to show the same uniformity of density.

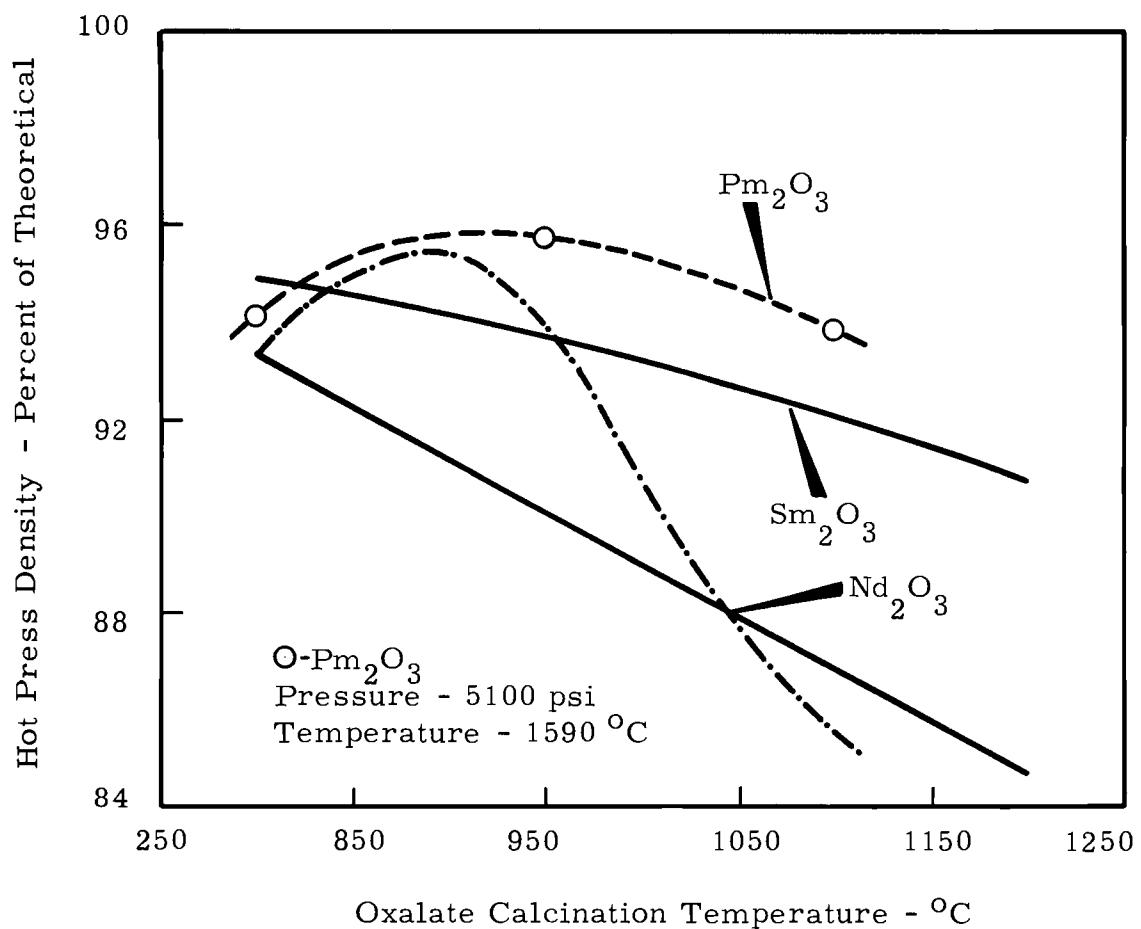


FIGURE 9 - Variation in  $\text{Pm}_2\text{O}_3$  Density with Oxalate Calcination Temperature

- Dimensional Control. The hot pressing process gives excellent dimensional control, and shape diameters can be maintained within 0.001 inch quite easily. Once the pressing characteristics of the oxide have been determined, body lengths can be controlled within 0.5%. When graphite dies are used, however, close dimensional control requires that the dies be replaced after 5-6 pressings.
- Physical Strength. Hot pressed rare earth oxide pellets have excellent physical strength and can be handled very readily without fear of physical damage.  $\text{Nd}_2\text{O}_3$  pellets, however, are extremely sensitive to moisture pickup and subsequent loss of physical strength. Neither  $\text{Pm}_2\text{O}_3$  nor  $\text{Sm}_2\text{O}_3$  pellets exhibit such a tendency and can be left in the open for many days without any apparent harm.  $\text{Pm}_2\text{O}_3$  pellets appear to be more sensitive to thermal shock than  $\text{Sm}_2\text{O}_3$  or  $\text{Nd}_2\text{O}_3$  and must be heated and cooled more slowly to prevent cracking.
- Physical Operation. With a properly designed press, hot pressing can be carried out quite easily in either a gloved box or remote facility. Some physical handling of oxide is required, so that operator radiation exposure can become a problem in a gloved box operation if a large number of shapes are to be fabricated. Operation in a remotely operated facility would appear to be more practical for any semi-production operation.
- Physical Containment. Although the hot pressing of  $\text{Pm}_2\text{O}_3$  requires the handling of dry oxide powder, the physical containment of the oxide within the pressing equipment or storage facilities does not appear to be a problem (assuming reasonably careful "housekeeping"), and hot pressing can be carried out in a gloved box without excessive cleanup or buildup in the background radiation level.

Based upon the above considerations, hot pressing appears to be a practical method of fabricating  $\text{Pm}_2\text{O}_3$  into useable shapes. A limited number of shapes could be fabricated in a gloved box, but a semi-production operation should be handled in a remotely operated facility.

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2. H. T. Fullam, Slip Casting of Rare Earth Oxides, BNWL-437, June 1967.
3. T. E. Quimby, E. E. Pierce and R. E. McHenry, Hot Presses for Glove Box and Manipulator Cells, Undocumented, Isotopes Development Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

APPENDIXA. Equipment

As stated previously, two hot presses were used during the course of this work, each being designed for a specific application. The miniature hot press as developed at Oak Ridge<sup>(3)</sup> was intended for gloved box operation. The induction heated unit was designed for fabrication of relatively large shapes and was not intended for use with radioactive materials.

A.1. Miniature Hot Press

The miniature hot press is shown in Figures 10 and 11. The press utilized a spiralled graphite heating element which was powered by a high amperage-variable output DC welder. TZM multilayer heat shields were placed around the heating element. The single-ended graphite die was located inside the heating element and supported by a graphite block. In operation, the temperature of the die was measured with an optical pyrometer by sighting through a slot in the heating element.

The press was normally operated under vacuum (~50 microns), the absolute pressure being measured with a McLeod gage. Pressure was applied to the plunger of the die through a piston and double bellows arrangement. The piston was actuated by a hand operated hydraulic jack with a maximum pressure capability of 5000 PSI.

Typical heating and cooling curves for the press are shown in Figure 12. Normally it required about twelve minutes for the press to reach the desired operating temperature. After the power was turned off, it usually required a cooling period of about 20 minutes before the press could be disassembled. Figure 13 shows the die temperature as a function of power input. With the welder available, die temperature was limited to a maximum of about 1700°C. Temperature distribution in the hot zone was not at all uniform, and it was necessary, therefore, to arrange the plug and piston within the graphite die so that the oxide was positioned in the die at the exact level viewed by the optical pyrometer.

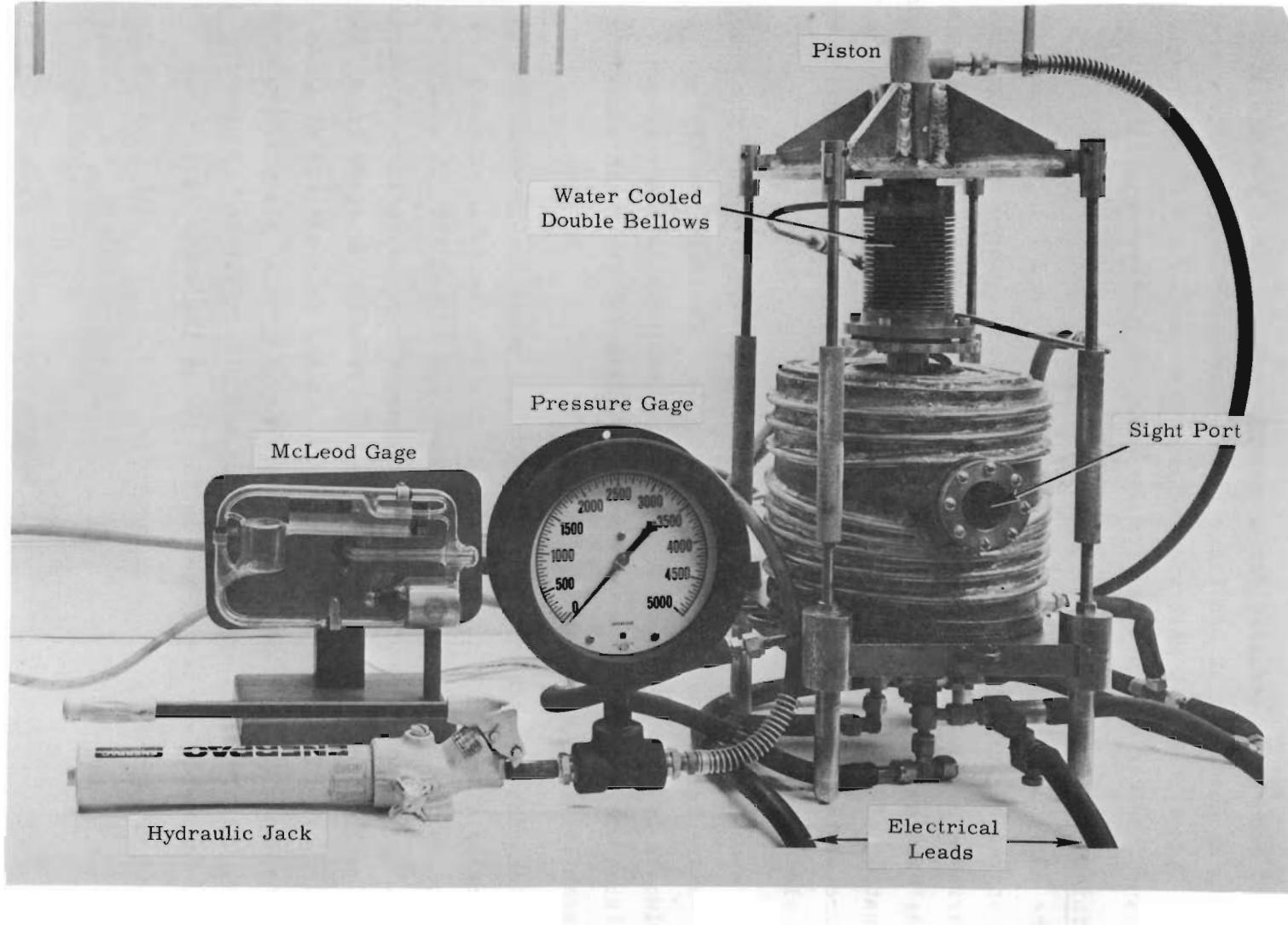


FIGURE 10 - Miniature Hot Press and Accessory Equipment

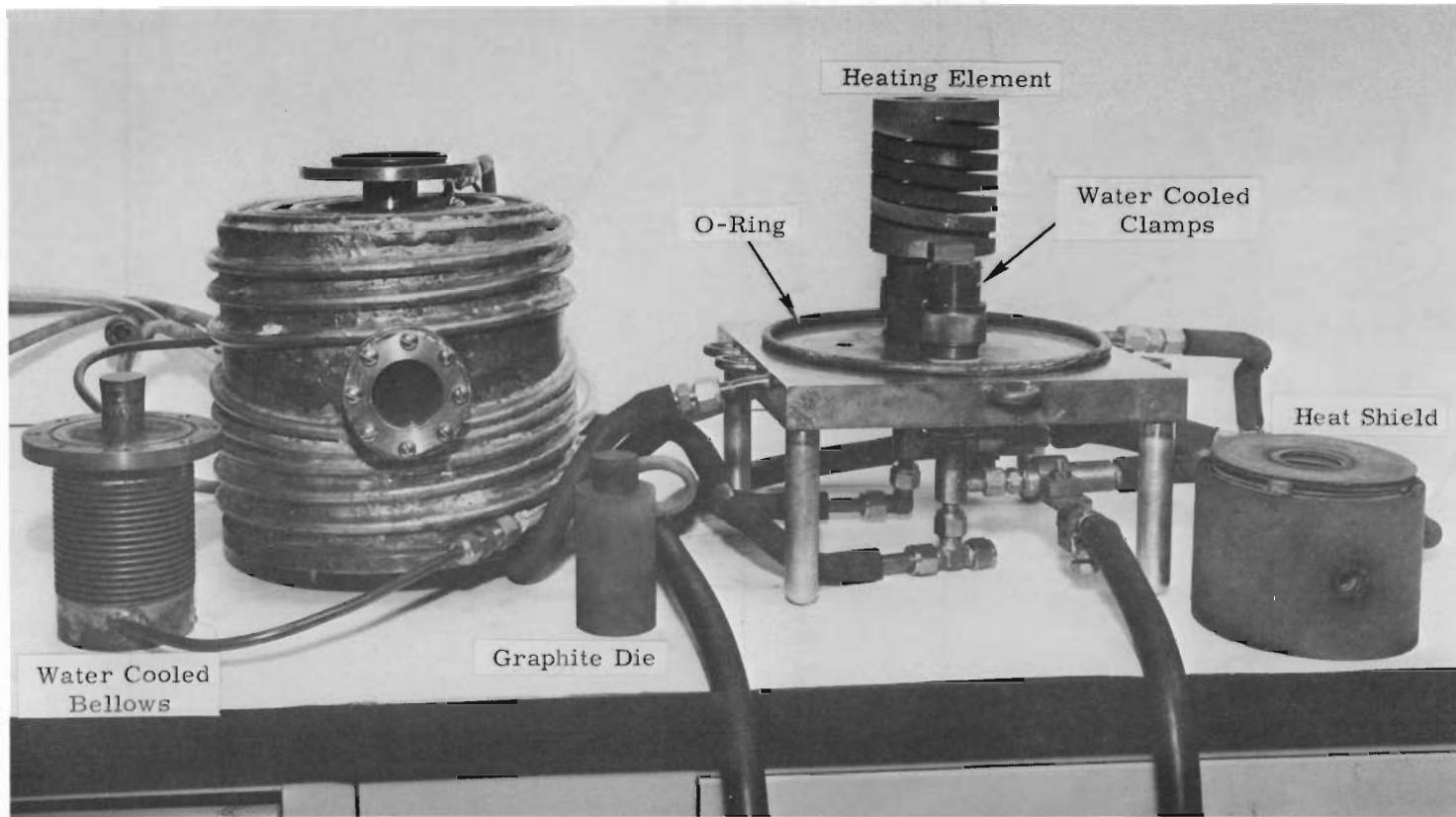


FIGURE 11 - Miniature Hot Press - Disassembled

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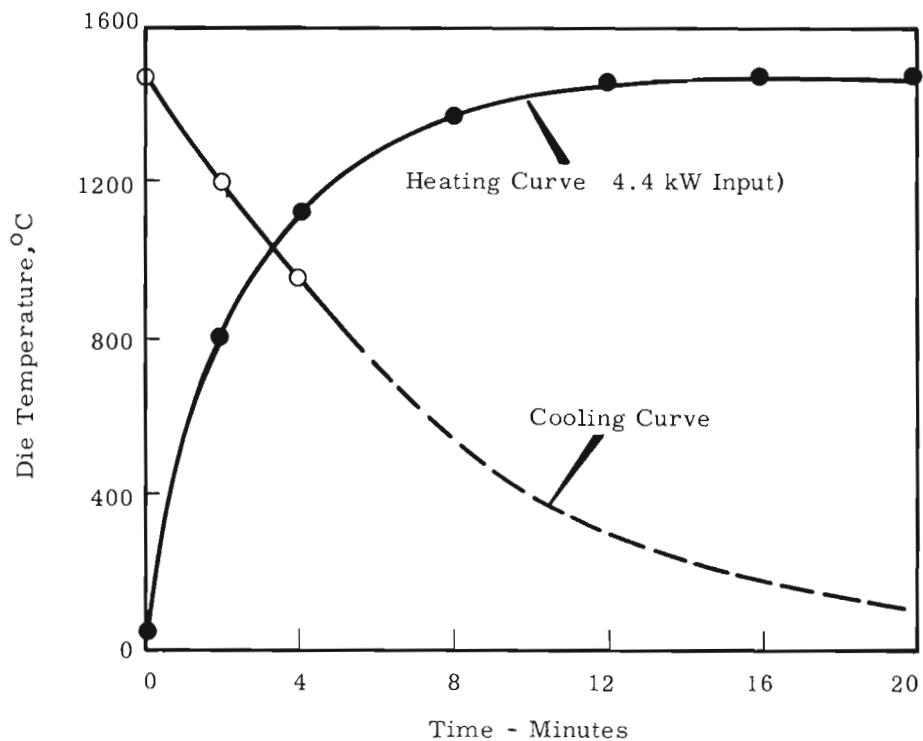


FIGURE 12 - Typical Heating and Cooling Curves for Miniature Hot Press

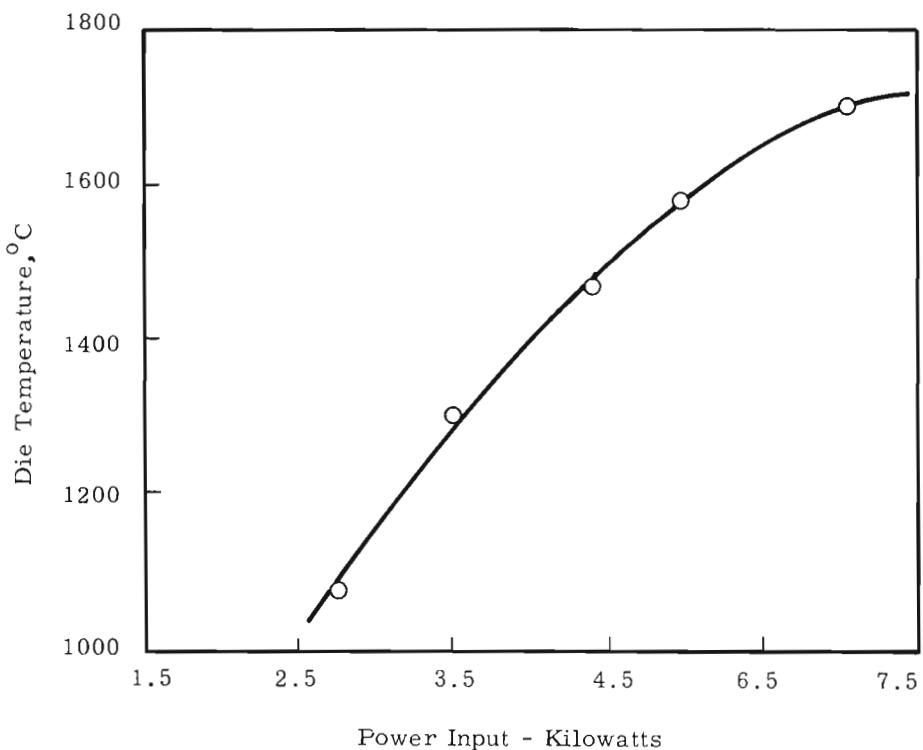


FIGURE 13 - Die Temperature in Miniature Hot Press as a Function of Power Input

#### A.2. Induction Heated Press

The induction heated hot press is indicated schematically in Figure 14. It consisted of a graphite die, which served as the susceptor, located in a quartz tube and insulated with lampblack. A sight port focused on the die (at the same level as the oxide to be pressed) and the temperature was read with an optical pyrometer. The die was protected from atmospheric oxidation by a  $\text{CO}-\text{CO}_2-\text{N}_2$  atmosphere formed by the reaction of the lampblack with oxygen. Pressure was supplied to the plunger by a hydraulic ram with a maximum pressure capability of 5000 PSI. The maximum die temperature obtainable was about  $1700^{\circ}\text{C}$  with the power supply available. Cylinders up to two inches in diameter and four inches long could be pressed in the unit.

#### B. Materials

In the production process currently used for promethium sesquioxide, the promethium is precipitated from a dilute nitric acid solution as the oxalate by the addition of oxalic acid. The oxalate is filtered, washed, dried and then calcined to convert the oxalate to the sesquioxide. Previous work on cold pressing and sintering<sup>(1)</sup> has shown that oxide from different precipitation batches which have been calcined under the same conditions can have different pressing and sintering characteristics. Therefore, the samarium sesquioxide used in this work was prepared by precipitating several oxalate batches and blending these together to give a uniform oxalate feed material. Portions of this feed were then calcined at various temperatures to give the oxide required for testing. All of the work with  $\text{Sm}_2\text{O}_3$  was performed with oxide prepared from the one uniform blend of oxalate. The  $\text{Nd}_2\text{O}_3$  used was prepared in a similar fashion. Because of size limitation with the precipitation equipment, the promethium was processed in approximately sixty-gram batches and each batch was calcined individually. No attempt was made to blend the promethium oxalate batches prior to calcination.

Reasons for the possible differences in pressing characteristics of different batches of oxalate, which were calcined under "identical" conditions, were never defined, but they probably relate to the presence of trace impurities in the oxide.

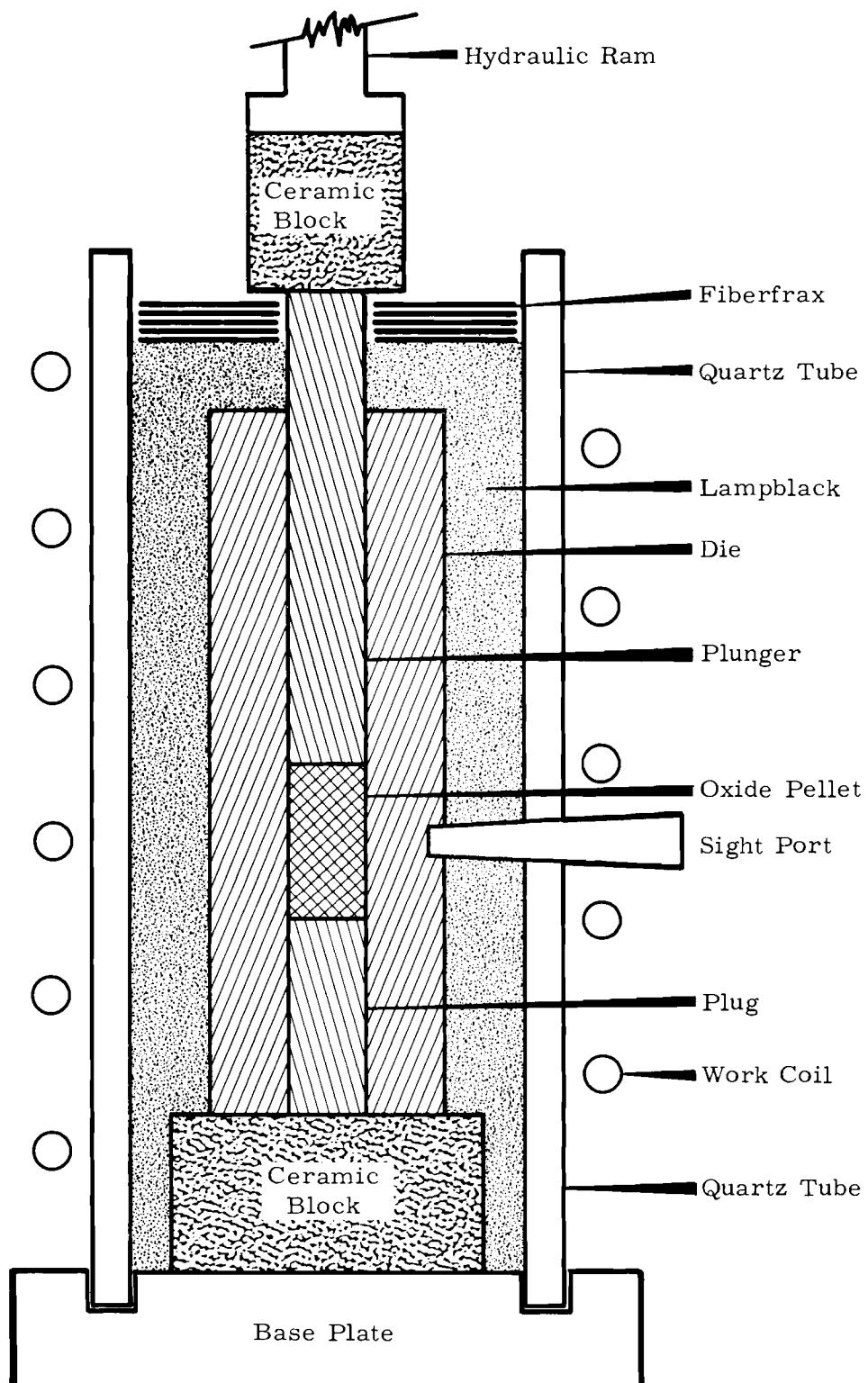


FIGURE 14 - Induction Heated Hot Press

C. Hot Pressing Procedure

To reduce as far as possible, variations in hot press density due to variations in procedure, a uniform pressing method was developed. Several procedures were tried, but the one that was found to be the most effective was as follows (for miniature press operation).

1. The oxide to be pressed was weighed and then loaded into the graphite die in several increments. The oxide was partially compacted in a hydraulic press at 100-200 PSI after each increment was added. This increased the oxide density from its normal bulk density of about one g/cm<sup>3</sup> to about three g/cm<sup>3</sup>, and greatly reduced the amount of ram travel required in the press.
2. The die was then placed in the press and the press assembled.
3. The vacuum pump was turned on and the press evacuated to a pressure of fifty microns. This normally required about 15 minutes pumping time.
4. Power to the press was then turned on and the temperature of the die raised to the required pressing temperature. This normally required about ten minutes with the miniature press. The only temperature control available was through manual adjustment of the power output of the welder. It was found, however, that the temperature could be controlled within  $\pm 10^{\circ}\text{C}$  (as read by the optical pyrometer) by this means.
5. When the die reached the desired temperature, pressure was applied to the piston and maintained at the desired level by hand operation of the hydraulic jack.
6. The press was maintained at temperature and pressure for ten minutes. The welder was then turned off and the press allowed to cool to room temperature while the die was maintained under pressure. (For those studies in which pressing time was a variable the press was maintained at temperature and pressure for whatever time was required.)
7. When the press was cold, the pressure to the die was released and the vacuum broken. The press was then disassembled and the die removed.
8. The pressed oxide pellet was removed from the die, weighed, and its physical dimensions determined.

9. The pellet was heated in a muffle furnace at 600-800°C for a short time to burn off the thin carbide and graphite layer.
10. The pellet was then reweighed and its dimensions measured again.
11. The density of the pellet was calculated from its weight and physical dimensions. The weight change due to graphite and carbide removal normally amounted to less than 0.05% and had little effect on the density value.

When pressing neodymium and samarium sesquioxides, the entire process as outlined above had a time cycle of approximately 70-80 minutes. When pressing promethium sesquioxide in a gloved box, the time required for a complete cycle was about four hours. Most of the additional time was required in the handling of the oxide outside of the hot press (weighing, precompacting, etc.) rather than in the pressing operation itself.

A procedure similar to that outlined above was used with the induction heated press except the time cycle was much longer (7-8 hours) due to the slower heating and cooling rates.

D. Influence of Calcining Temperature on Oxide Surface Area and Particle Size

As discussed in Section 5, the pressing characteristics of rare earth oxides are highly dependent on the temperature at which the oxide is calcined prior to the pressing operation. It was felt that this was due to variations in surface area and particle size for oxides calcined at different temperatures.

The surface areas of  $\text{Sm}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  were measured using the standard BET method. The results are shown in Figure 15. It can be seen that the cubic forms of  $\text{Sm}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  have much greater surface areas than the monoclinic  $\text{Sm}_2\text{O}_3$  and hexagonal  $\text{Nd}_2\text{O}_3$ . The variations in surface area of the high temperature forms of the oxides with calcining temperature were not large, and above 1000°C, the areas remained essentially constant. Based on these results, it does not appear that surface area alone could account for the variations in oxide pressing characteristics with calcining temperature.

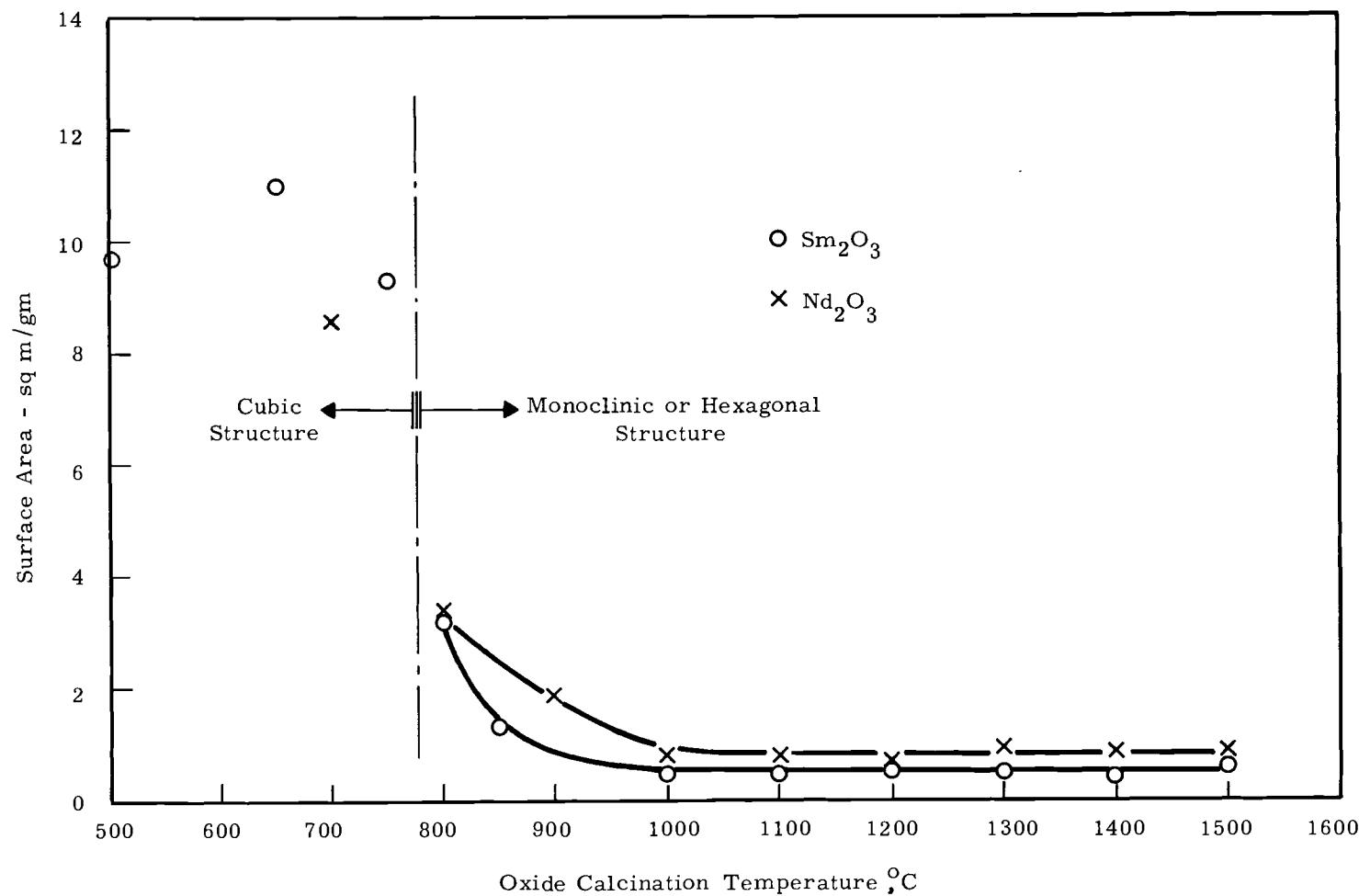


FIGURE 15 - Surface Area of  $\text{Sm}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  as a Function of Oxide Calcination Temperature

An attempt was made to screen the various batches of  $\text{Sm}_2\text{O}_3$  to obtain some idea of particle size and size distribution. It was found, however, that for all the oxide calcined at  $1100^\circ\text{C}$  or less all of the material passed through the 325 mesh screen, which was the finest screen available. Oxide calcined at  $1200^\circ\text{C}$  and above was screened and the results are shown in the following table.

Calcining Temp., $^\circ\text{C}$	Weight % of Oxide Passing through Screen					
	-325	-250	-200	-150	-100	-60
1100	100					
1200	71.5	87.8	97.9	100		
1300	62.5	80.3	99.1	100		
1400	48.2	67.5	81.4	93.5	100	
1500	24.6	48.3	60.9	73.1	79.6	85.0

Since the finely divided oxides could not be adequately sized by screening, a sedimentation technique was used to obtain a comparative measure of the particle size for different batches of oxide. Some of the settling curves are shown in Figure 16. The results indicate, as one would expect, that the higher the calcining temperature the more rapid the settling rate. Although the particle size distribution for each batch of oxide was not obtained from the settling curves, the data indicate that the larger the particle size the poorer the pressing characteristics of the oxide.

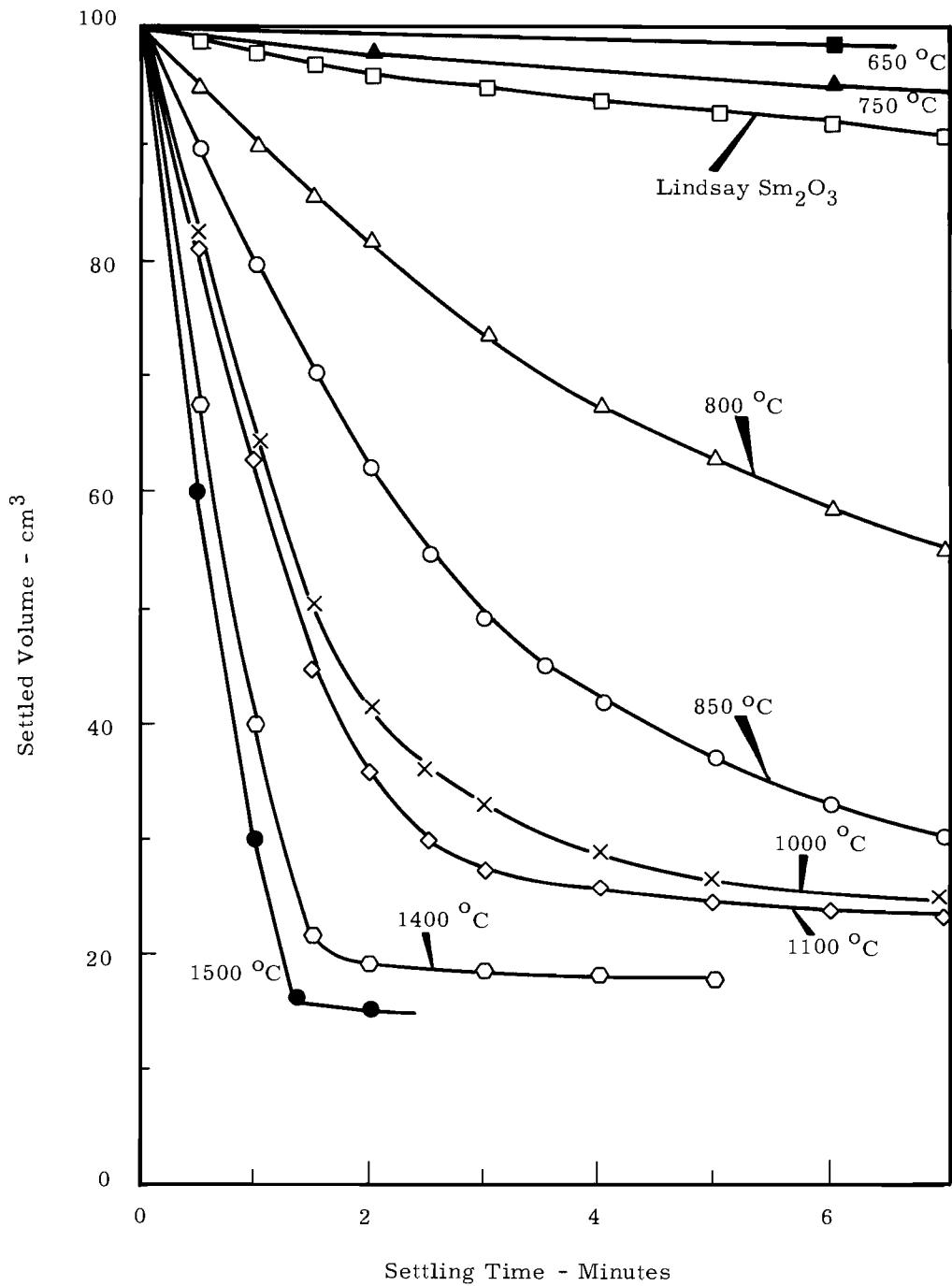


FIGURE 16 - Settling Curves for  $\text{Sm}_2\text{O}_3$  Calcined at Various Temperatures

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