BNWL-386

2-

AEC RESEARCH and DEVELOPMENT REPORT

COLD PRESSING AND SINTERING OF RARE EARTH OXIDES

H. T. FULLAM and L. J. KIRBY

APRIL, 1967

BATTELLE-NORTHWEST
BATTELLE MEMORIAL INSTITUTE / PACIFIC NORTHWEST LABORATORY

LEGAL NOTICE

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

PRINTED BY/FOR THE U. S. ATOMIC ENERGY COMMISSION

ARC 6100 RICHLAND, WASH.

BNWL-386
UC-25, Metals, Ceramics,
and Materials

COLD PRESSING AND SINTERING OF RARE EARTH OXIDES

By

H. T. Fullam and L. J. Kirby

Chemical Research Section
Chemistry Department

April, 1967

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy $3.00; Microfiche $0.65

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

COLD PRESSING AND SINTERING OF RARE EARTH OXIDES

H. T. Fullam and L. J. Kirby

INTRODUCTION

As part of the over-all promethium program, methods for fabricating promethium compounds into useable shapes are being evaluated. This report covers work carried out on the cold pressing and sintering techniques. Other techniques being studied are

- Pneumatic impaction
- Hot pressing
- Slip casting
- Fusion casting.

When this work was initiated, the availability of promethium was limited; therefore, most of the compaction studies were made by using samarium and neodymium compounds as standins for promethium. Because neodymium and samarium are adjacent to promethium on the periodic table and the chemical and physical properties of adjacent rare earths are very similar, the results to be obtained with the standins were considered applicable to promethium.

From the compatibility phase of the promethium program[1] it was apparent that promethium sesquioxide would be the fuel form of greatest interest, therefore, the compaction studies were limited to samarium and neodymium sesquioxides. The compatibility work showed also that the method by which the oxides were prepared profoundly influenced the results, so oxides prepared in several ways were used in the compaction studies.

SUMMARY

Samarium and neodymium sesquioxides have been cold pressed to densities greater than 80% of theoretical. Sinter densities in excess of 95% of theoretical have been obtained by sintering at temperatures up to 1500 °C. Cold press densities obtainable were found to depend on:

- The method of preparing the sesquioxide
- The temperature at which the oxide is calcined prior to cold pressing
- The applied pressure.

Sinter densities were found to depend on:

- Sintering temperature
- Sintering time
- Cold press density
- Oxide source
- The temperature at which the oxide is calcined prior to cold pressing.

The variations in cold press and sinter densities with oxide source and calcination temperature probably reflect the effects of particle size, particle size distribution, and surface area variations in different oxide batches.

EXPERIMENTAL PROCEDURES

The samarium and neodymium sesquioxides used in this work were obtained from the Lindsay Chemical Division of American Potash and Chemical Company. Purity of the "as received" material was 99.0%. For most of this work the "as received" oxides received an additional purification treatment,* consisting of dissolving the oxide in nitric acid,

* *This is the purification process used in preparing* Pm_2O_3.

precipitating the rare earth oxalate, and calcining the oxalate at elevated temperatures to convert it to the oxide.

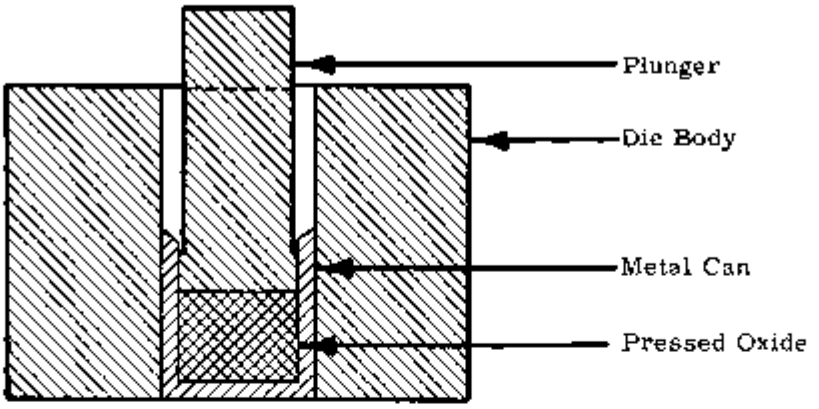
Cold pressing of the sesquioxides was carried out in two ways:

- The oxide was step pressed into a metal can (Figure 1-A).
- Pellets of the oxide were pressed in a single ended solid die (Figure 1-B) or in a single ended split die (Figure 1-C).

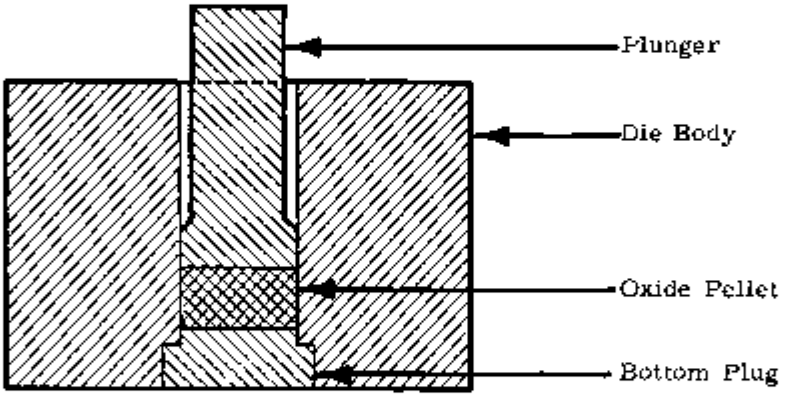
When step pressing into the metal can, the loading operation was carried out incrementally. A small volume of oxide was placed in the can, the plunger inserted, and the desired pressure applied. The plunger was then removed, more oxide added to the can, and the operation repeated. Additional oxide increments were added until the can was filled. The cold press density was determined by taking the physical dimensions and weight of the can before and after loading.

When pressing oxide pellets, a single volume of oxide was placed in the die, the plunger inserted, and the load applied. The pellet was then pressed from the die. It was difficult to prepare a single pellet when two or more increments were used because the pellet tended to laminate and split apart upon removal from the die or during the sintering operation.* Cold press densities of the pellets were determined from the weight and physical dimensions of the pressed pellet.

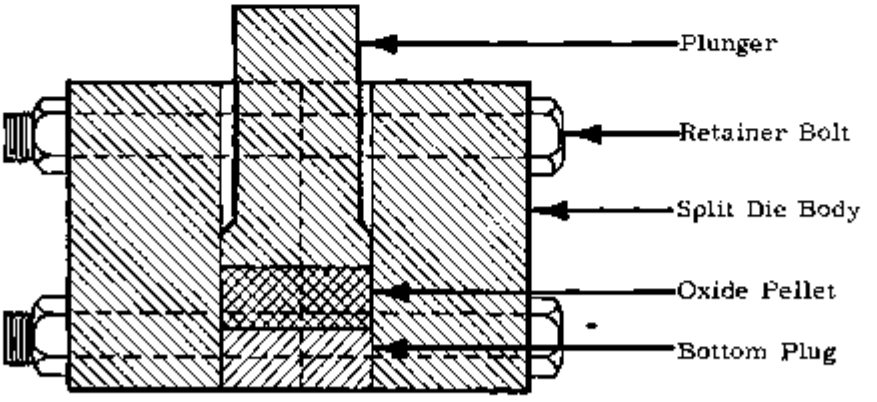
* *However, it was found that a pellet could be made from multiple increments if the upper surface of the pressed pellet was broken up before the next oxide increment was added.*



A - Can Loading Die



B - Solid Body Die



C - Split Die

FIGURE 1. Cold Pressing Dies

Cold pressing was conducted both with and without the use of a lubricant. When a lubricant (stearic acid dissolved in trichloroethylene) was used in pressing pellets, the pellets were easier to remove from the die, and the entire pressing operation was simplified. When step pressing into cans, no lubricants were used because the loaded cans were to be used in compatibility testing.

EXPERIMENTAL RESULTS

COLD PRESSING

When cold pressing the rare earth sesquioxides, the basic objectives are: (1) to obtain a maximum cold press density, and (2) to produce an oxide body with good structural strength and integrity.

Variables Affecting Cold Press Density

The oxide densities obtainable by cold pressing were found to depend on a number of variables such as:

- The applied pressure
- The incremental volume of oxide pressed
- The source of the oxide
- The temperature at which the oxide is calcined prior to cold pressing
- The can material.

The effect of each variable is discussed in detail in the following paragraphs.

Applied Pressure

As one would expect, the most critical variable affecting cold press density is the applied pressure. This effect is shown (Figure 2) for two different cases: (1) oxide step pressed into metal cans, and (2) pressed pellets. In Figure 2,

the density increases very rapidly with increasing pressure up to a value of about 5 g/cm^3, but above this value the rate of increase is much less and is almost linear with pressure. For this work the theoretical density of samarium sesquioxide was taken as 7.74 g/cm^3[2] and the theoretical density of neodymium sesquioxide as 7.31 g/cm^3.[3]

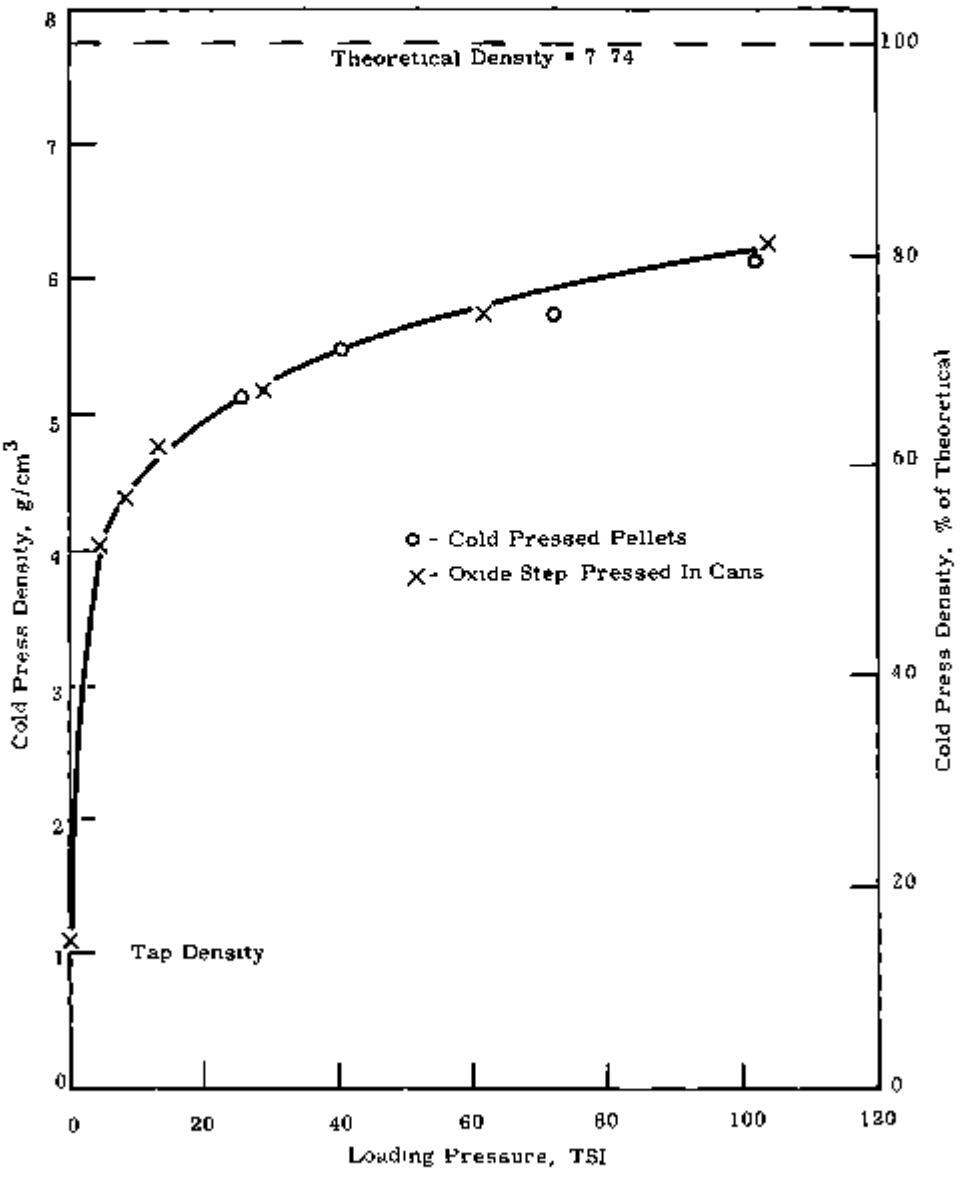


FIGURE 2. Cold Press Density Versus Load Pressure for Sm_2O_3 Calcined at 1100 °C, 24 hr

Loading Increments

When step pressing oxide into a metal can, the final obtainable density will depend on the number of loading increments used to fill the can (Figure 3). It can be seen that the greater the number of increments used, the higher the density for a given applied pressure. This is to be expected due to the friction and uneven pressure distribution encountered in pressing dry solids. The same problem was encountered in cold pressing pellets. Although the pellets were pressed from a single oxide loading, the density obtained depended on the volume (assuming constant pellet diameter) of oxide loaded (Table I). The decrease in pellet density with increased length to diameter ratio (L/D) again reflects the effects of frictional drag and uneven pressure distribution.

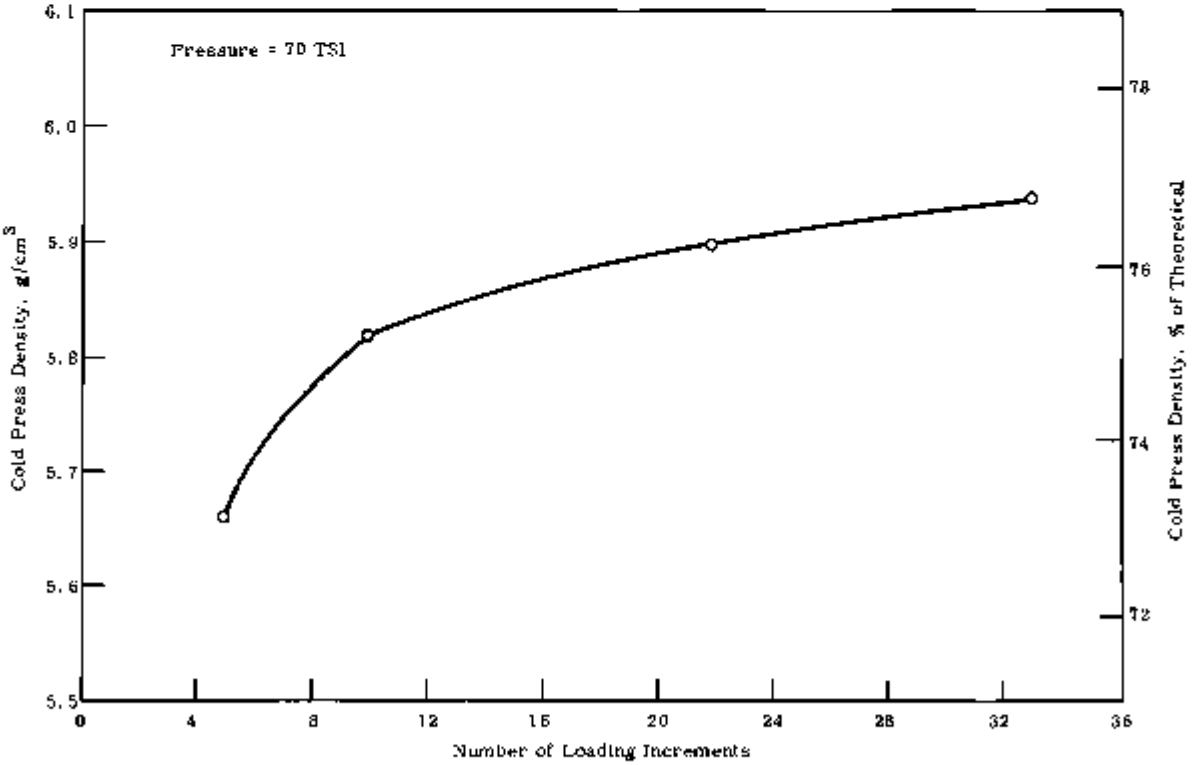


FIGURE 3. Cold Press Density Versus Number of Loading Increments to Fill Can for Samarium Sesquioxide Calcined at 1300 °C

TABLE I. Variation in Cold Press Density with Pellet L/D

Oxide Weight, g	Pressure, TSI	Pellet Dimensions, Diam, in.	Length, in.	L/D	Pellet Volume, cm^3	Pellet Density, g/cm^3
16.03	72	0.501	0.918	1.83	2.96	5.41
8.21	72	0.501	0.443	0.885	1.43	5.75
5.36	72	0.500	0.294	0.589	0.915	5.87

Oxide Source

The variation in cold press density with oxide source is shown in Table II. In each case the oxide was pressed into a 304L SS can, and the pressing operation was identical for each oxide.

TABLE II. Variation in Cold Press Density with Oxide Source

Oxide Source	Applied Pressure, TSI	Cold Press Density % of theor.	g/cm^3
Lindsay Sm_2O_3 - as-received	60	59.4	4.60
Lindsay Sm_2O_3 - Calcined at 1100 °C	60	63.4	4.91
Sm_2O_3 from $Sm(OH)_3$ - Calcined at 1100 °C	60	61.4	4.75
Sm_2O_3 from Oxalate - Calcined at 1100 °C	60	74.3	5.75
Lindsay Nd_2O_3 - as-received	60	63.1	4.61
Lindsay Nd_2O_3 - Calcined at 1100 °C	60	73.2	5.35

As part of the promethium compatibility studies[1] it was necessary to heat some of the samarium oxide (produced by calcining the oxalate at 1100 °C) in 6% H_2–94% Argon at 1000 °C for several hours. This treatment altered the cold pressing characteristics slightly, and increased the cold press density about 1%.

Oxide Calcination Temperature

The temperatures at which the oxalate is calcined affects the cold press density obtainable quite markedly. Figure 4 shows this relationship for samarium sesquioxide cold pressed

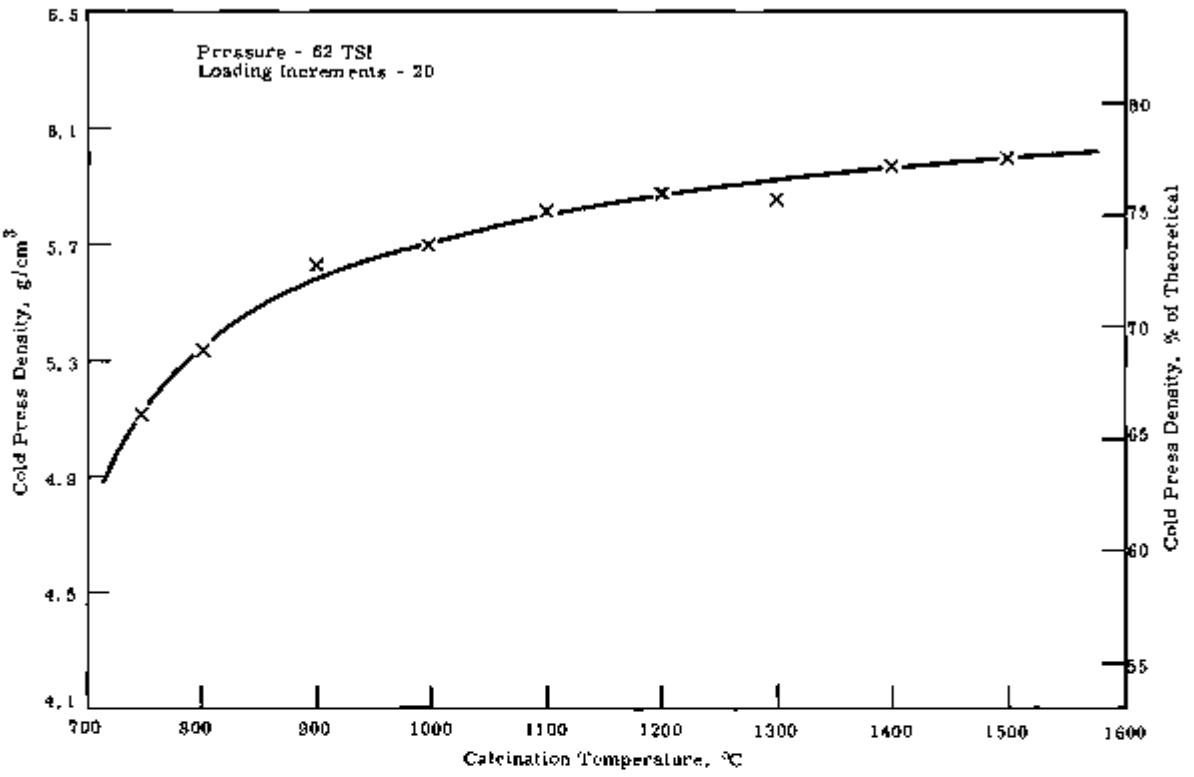


FIGURE 4. Cold Press Density of Sm_2O_3 as a Function of Calcination Temperature

into 304L SS cans. The length of time the oxalate is calcined at temperature does not appear to affect the cold press density appreciably as long as the calcination time is four hours or longer (Figure 5). For those studies in which calcination time was not variable, a period of twenty-four hours at temperature was used as the standard calcination time.

The variation in cold press density, with (1) the source of the oxide and (2) the temperature at which the oxalate is calcined, probably reflects the effects of particle size, particle size distribution, and surface area variations for each batch of oxide.

An attempt was made to screen the various batches of oxide to obtain some idea of particle size and size

distribution. However, for all the oxide calcined at 1100 °C or less, all of the material passed through the 325 mesh screen—the finest screen available. The batches calcined at 1200 °C and above were screened and the results are shown in Table III.

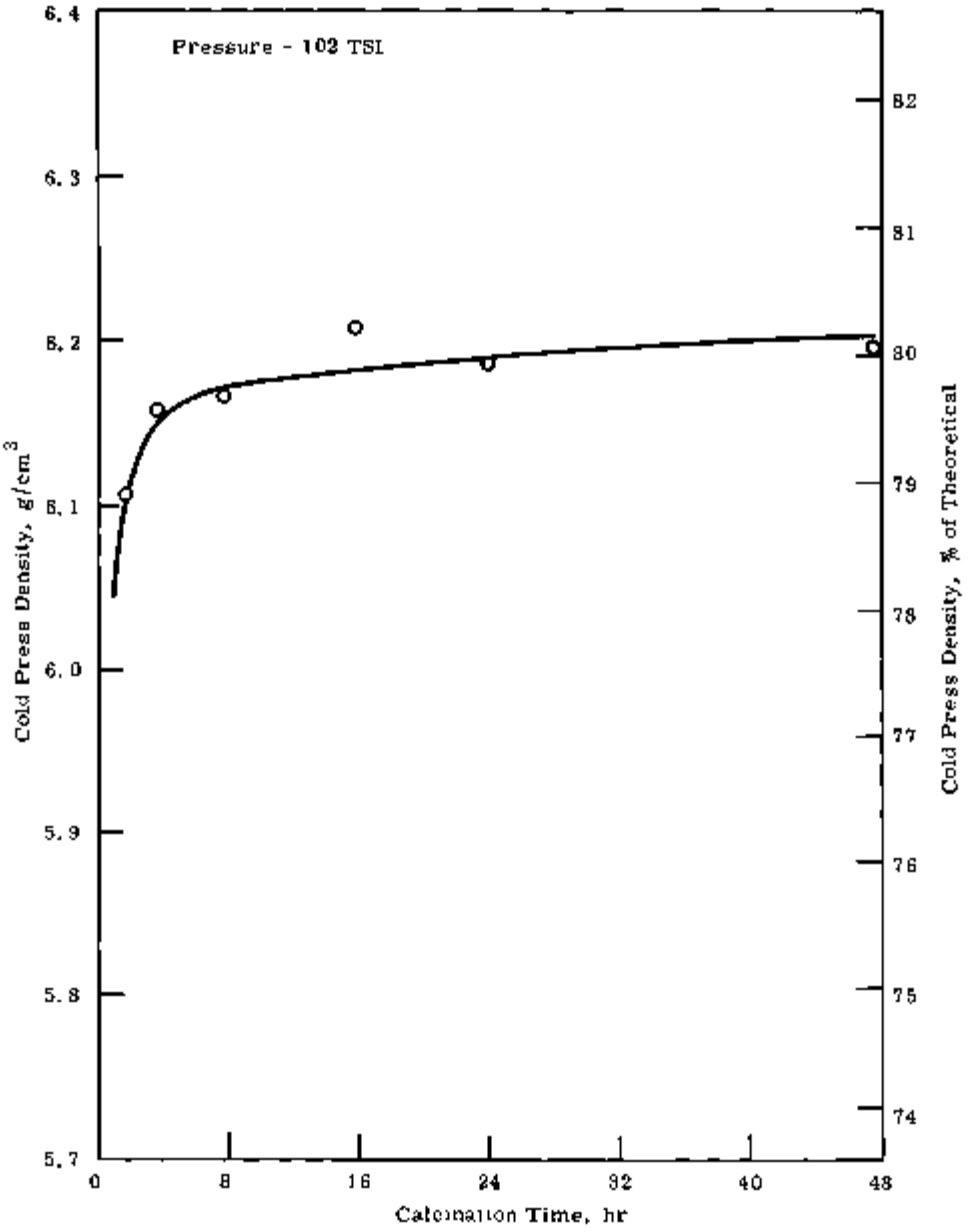


FIGURE 6. Cold Press Density as a Function of Calcination Time for Samarium Sesquioxide Caclined at 1100 °C

TABLE III. Particle Size Distribution of Sm_2O_3 Calcined at Various Temperatures

	Oxide Passing Through Screen, wt%					
	-325	-250	-200	-150	-100	-60
Lindsay "As-Received"	100					
1100 °C	100					
1200 °C	71.5	87.8	97.9	100		
1300 °C	62.5	80.3	99.1	100		
1400 °C	48.2	67.5	81.4	93.5	100	
1500 °C	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 samarium oxide. Some of the settling curves obtained are shown in Figure 6, and, as expected, the results indicate that the higher the calcination temperature, the larger the average particle size and the more rapid the settling rate. Although the particle size distribution for each oxide batch was not obtained from the sedimentation method used, the data indicate that the cold press density obtainable increases as the average oxide particle size increases.

The tap density of samarium sesquioxide was measured and was found to increase as the calcination temperature increased (Figures 7 and 8). Surface area of the oxide was measured by using the standard BET method. The variation in surface area with oxide calcination temperature is not great (Table IV), but it does generally decrease with increasing calcining temperatures up to 1000 °C and then remains essentially constant at about 0.4 to 0.6 m^2/g.

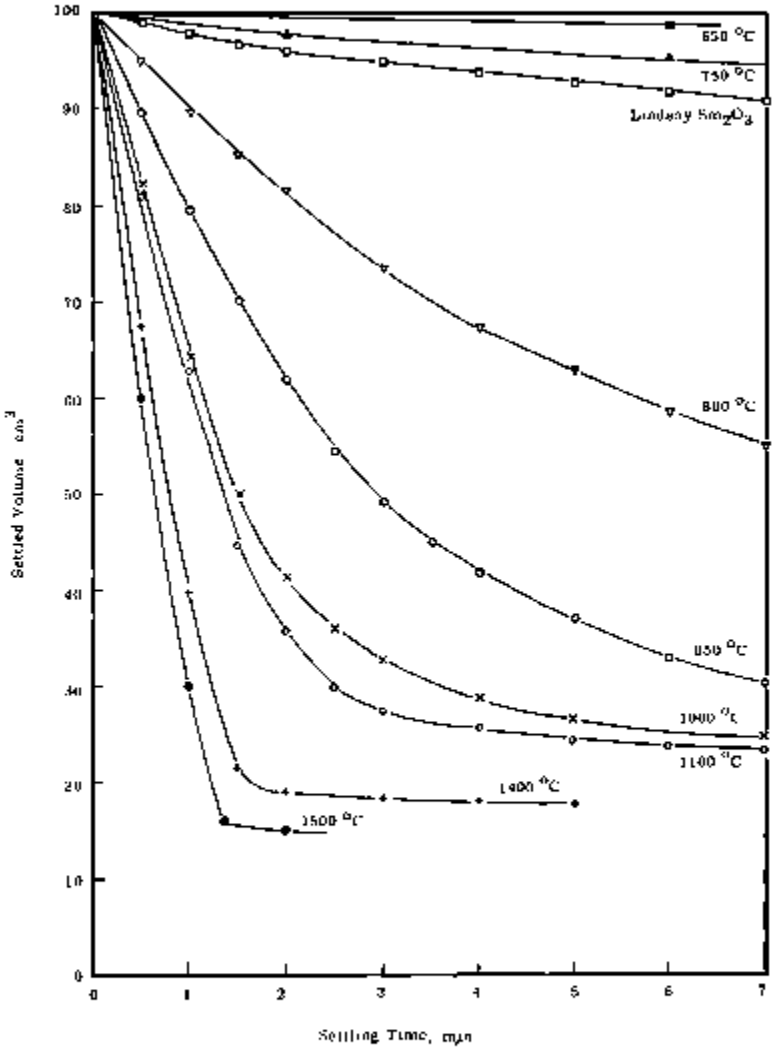


FIGURE 6. Settling Curves for Sm_2O_3 Calcined at Various Temperatures

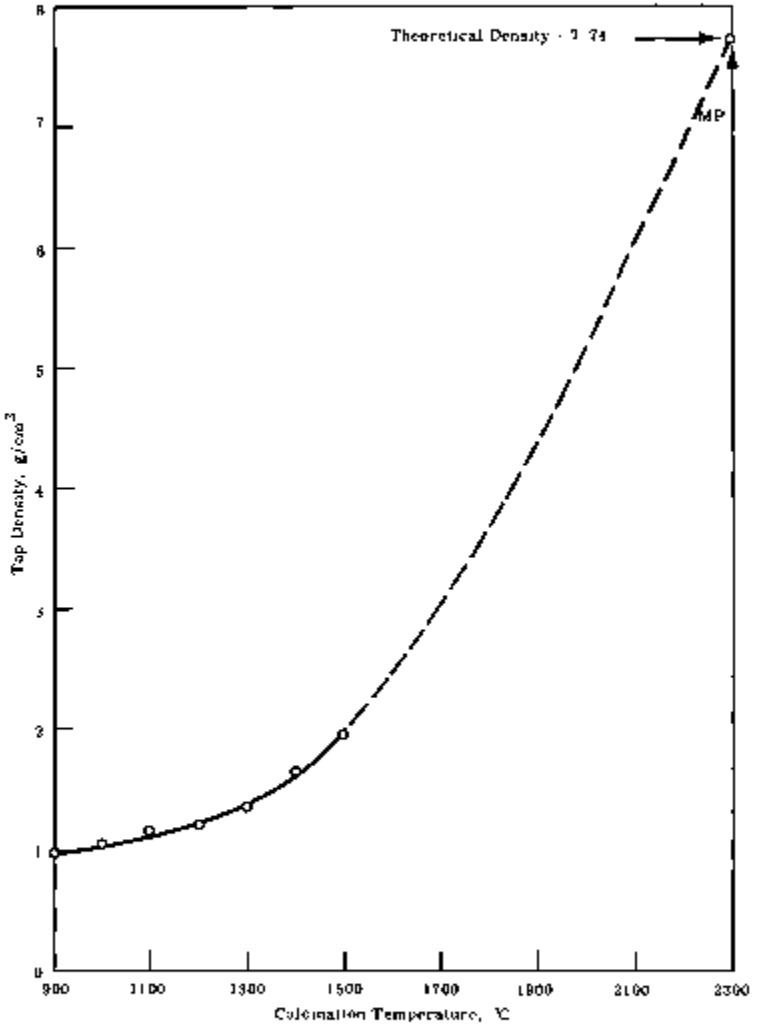
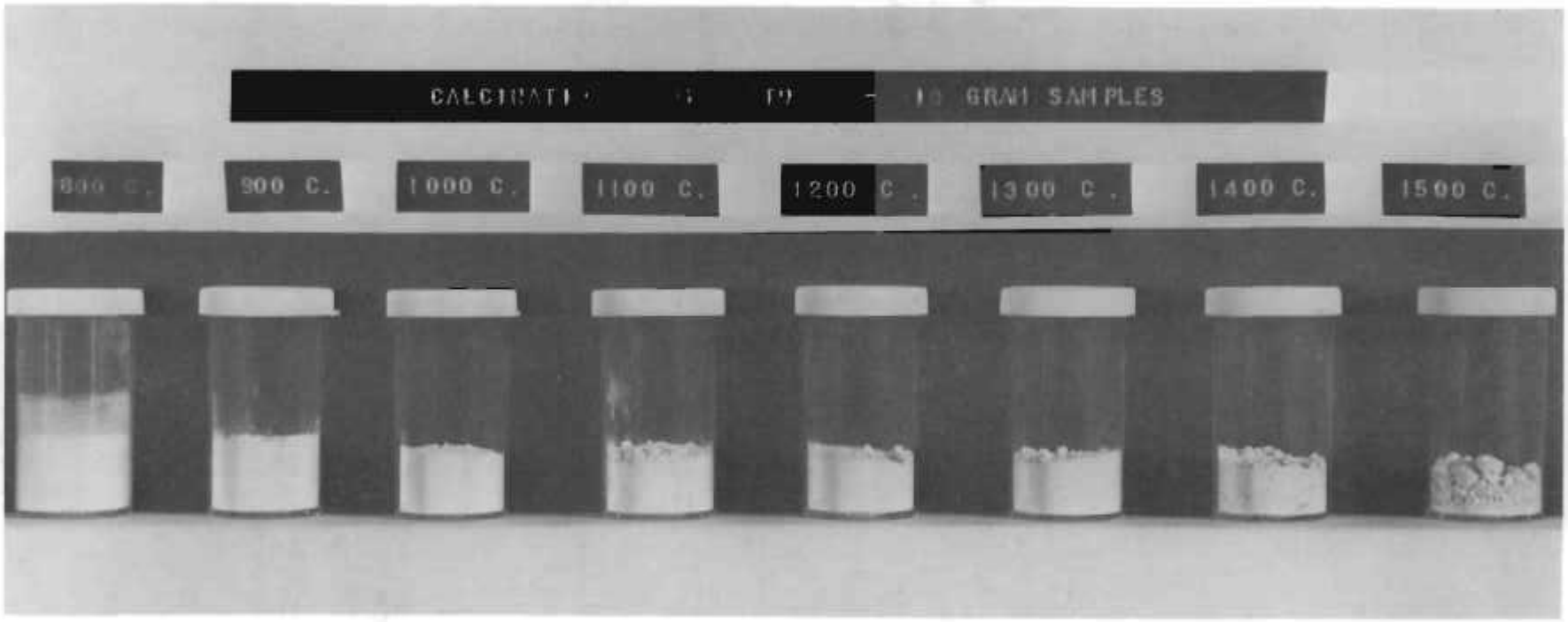


FIGURE 7. Tap Density Versus Calcination Temperature for Sm_2O_3



Neg 0662320

FIGURE 8. Variation in Samarium Sesquioxide Tap Density with Calcination Temperature

TABLE IV. Surface Area of Sm_2O_3 Calcined at Various Temperatures

Calcination Temperature, °C	Surface Area, m^2/g
800	3.2
900	1.5
1000	0.4
1100	0.5
1200	0.6
1300	0.6
1400	0.4
1500	0.6

Can Material

When cold pressing oxide into cans, the density obtainable depended to some extent on the metal that made up the inner surface of the can (Table V). There was some variation from can to can for each metal, and the given values represent the arithmetic averages for a number of cans. The variation in density for the various metals probably reflect differences in the frictional drag between the metal surface and the oxide.

TABLE V. Variation in Cold Press Density with Can Material

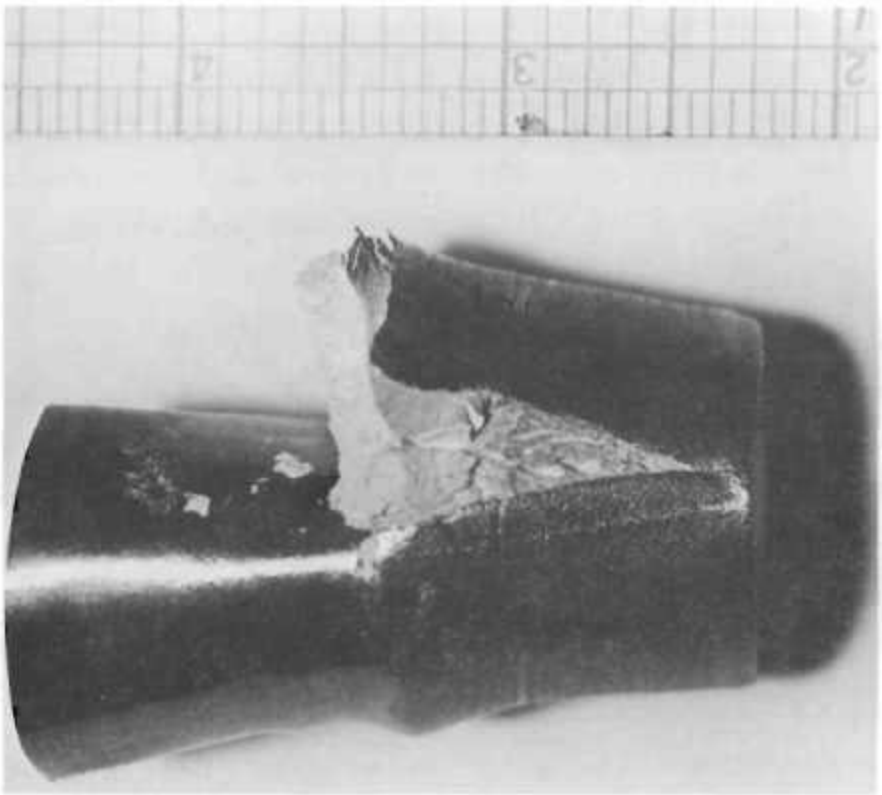
Can Material	No. Cans Loaded	Pressure TSI	Average Cold Press Density	
			g/cm^3	% of Theoretical
304L SS	17	60	5.75	74.3
Rhenium	12	60	5.98	77.3
W–25% Re	5	60	6.05	78.2
Mo–50% Re	5	60	6.04	78.0

Structural Stability

The structural strength of cold pressed rare earth oxide shapes depends primarily on the applied pressure. Pellets pressed at pressures above 10 TSI have good green strength, while those pressed at lower pressures crumble rather easily.

Samarium and neodymium sesquioxides pick up moisture from the air quite readily (Nd_2O_3 is especially bad), which can cause cold pressed shapes to crack and swell. A cold pressed Sm_2O_3 pellet will break up in a few weeks or months when left in the open air, while Nd_2O_3 pellet will crumble in a day or two.

When the oxide is cold pressed into a can and the can is left in the open air, the swelling or flowering of the oxide, due to moisture pickup, can actually split the can. Figure 9 shows a 304L SS can (20 mil wall) that was partially packed with Sm_2O_3 and then left in the open air. The can was split throughout its packed length. In some instances, cans with welded bottoms have swelled enough to blow out the bottom of the can, even with the can top open.



Neg 0662104-1

FIGURE 9. 304L SS Can (20 Mil Wall) Packed with Sm_2O_3 and Left in Open Air

SINTERING

The objectives of the sintering operation are to increase oxide density and to increase the structural strength and physical integrity of the oxide body. While only a limited amount of work has been done on the sintering of rare earth oxides, most of the variables affecting density and structural integrity have been evaluated. All of the sintering studies were carried out by using cold pressed pellets.

Variables Affecting Sinter Density

The results obtained in this work show that a number of factors affect the sinter densities obtainable with rare earth oxides. They are:

- The cold press density
- The temperature at which the oxide is calcined prior to cold pressing
- The time and temperature of sintering.

Each of these variables is discussed in detail below. The method used in preparing the oxide probably affects the sinter density also, but this variable was not evaluated.

Cold Press Density

The variation in sinter density with cold press density is shown in Figure 10. The oxide used for this study was samarium oxide, which had been calcined at 1100 °C for 24 hours prior to cold pressing. Although one might expect the same sinter density for a given set of sintering conditions regardless of cold press density, sinter density instead appears to vary linearly with cold press density.

Oxide Calcination Temperature

The sinter density also varied with the temperature at which the oxide was calcined prior to cold pressing. When

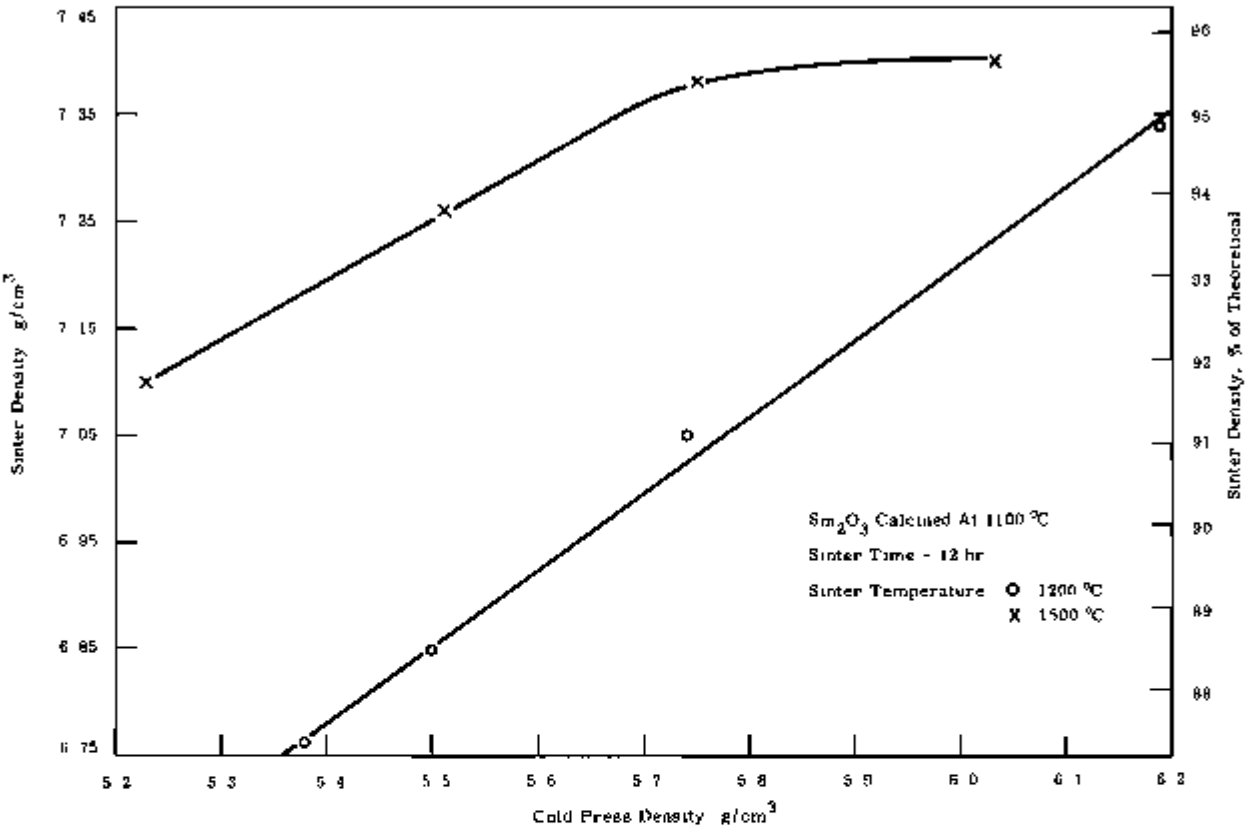


FIGURE 10. Sinter Density as a Function of Cold Press Density

oxide calcined at various temperatures was cold pressed to the same density and then sintered under identical conditions, the sinter density varied (Table VI). This shows that for a given cold press density an increased calcination temperature gives a lower sinter density. This leads to an anomalous situation since increased calcination temperature also gives an increased cold press density. Additional work will be necessary to determine what calcination temperature will give the maximum sinter density.

TABLE VI. Variation in Sinter Density with Sm_2O_3 Calcination Temperature

Calcination Temperature °C	Cold Press Density g/cm^3	Sinter Temperature, °C	Sinter Time, hr	Sinter Density, g/cm3
900	5.77	1200	12	7.12
1100	5.75	1200	12	7.05
1300	5.74	1200	12	6.89
1500	5.78	1200	12	6.81

Sintering Time and Temperature

Sinter density also depends on the sintering time and temperature although the effect of temperature was not as great as expected over the temperature range studied. An increase in sintering temperature from 1200 °C to 1500 °C resulted in an increase in maximum sinter density from 7.34 to only 7.40 g/cm^3 (Table VII) for a given oxide cold pressed to approximately 6.19 g/cm^3.

TABLE VII. Effect of Sinter Temperature on Sinter Density of Sm_2O_3

Cold Press Density, g/cm^3	Oxide Calcination Temperature, °C	Sinter Temperature, °C	Sinter Time, hr	Sinter Density, g/cm^3
6.19	1100	1200	12	7.34
6.18	1100	1300	12	7.38
6.20	1100	1400	12	7.38
6.18	1100	1500	12	7.40

The variation in sinter density with time at temperature is shown in Figure 11. The density increased very rapidly up to a time of 4 hr, but only slightly thereafter. A sinter time of 12 hr was taken as the standard for those studies where sinter time was not a variable.

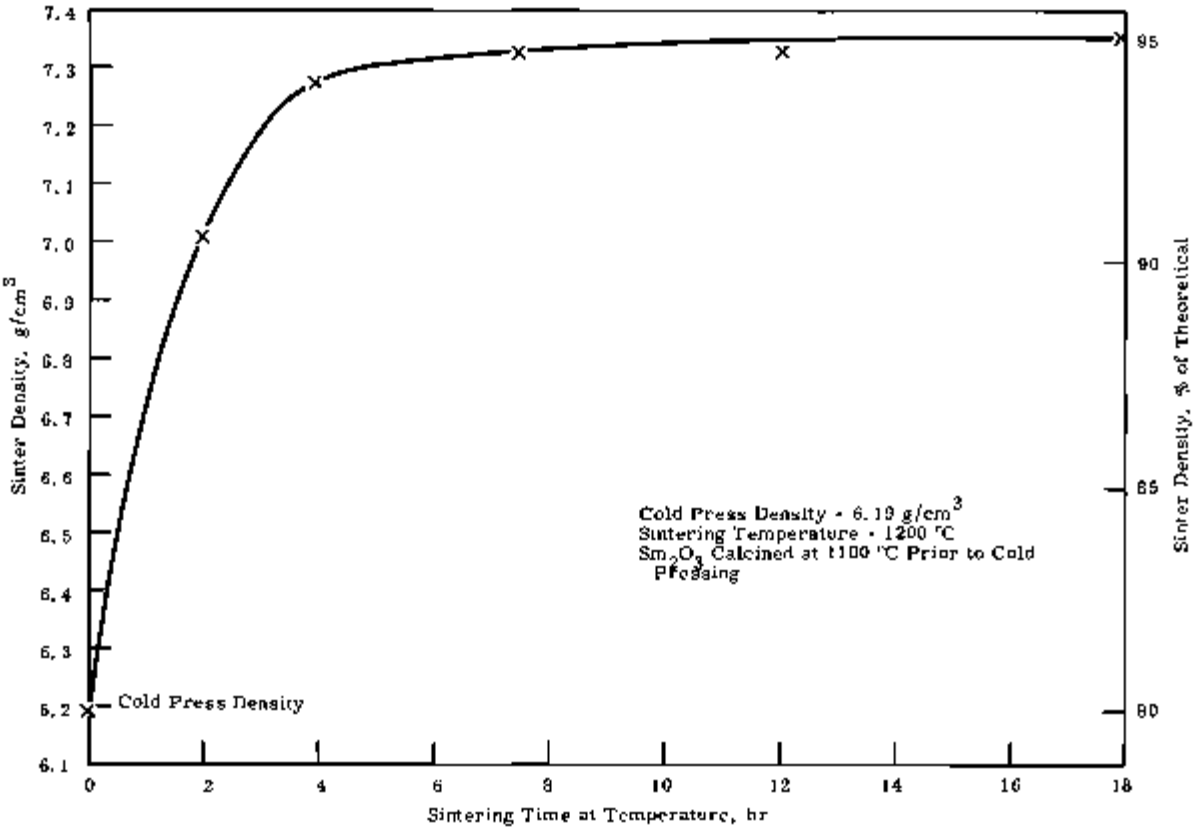


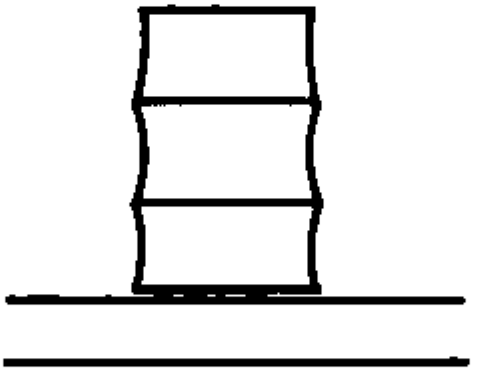
FIGURE 11. The Effect of Sintering Time on the Sinter Density of Samarium Oxide Pellets

With samarium oxide pellets, a "swelling" effect was noted when pellets, heated at one temperature, were reheated to a higher temperature. A total of thirty pellets, whose average density was 7.34 g/cm^3 after being sintered 12 hr at 1200 °C, showed a density of 7.20 g/cm^3 after being reheated for 12 hr at 1400 °C. This swelling may have resulted from entrapped gases that expanded and caused plastic flow of the pellet upon reheating to a higher temperature.

Structural Considerations

When identical cold pressed pellets are sintered under identical conditions, some variation in sinter densities may result. This variation from pellet to pellet may be as much

as 2 to 3%. In addition, the pellets may suffer from uneven shrinkage during sintering, which will give a distorted pellet. Typically, when a green pellet is placed on a refractory surface and then sintered, the upper surface of the pellet will shrink more than the lower surface which is in contact with the refractory. For a cold pressed pellet one inch in diameter, this variation in diameter after sintering may be as much as 10 mils. If green pellets are stacked one on top of another, the sintered pellets will show a "dog bone" effect (see the overemphasized sketch below). For a one inch diameter cold pressed pellet, the variation in diameter can be as much as ten mils between the center and the top and bottom of the pellets after sintering.



A second effect noted was that the distortion of the pellet appeared to depend on the cold press and sinter densities of the pellet. A pellet cold pressed to a low density (resulting in a low sinter density) showed the dog bone distortion sketched below (again overemphasized). A pellet cold pressed to a high density and then sintered to high density

showed a belling effect, with the maximum diameter occurring approximately half way between the upper and lower surfaces.

The L/D for the pellets appeared to affect these variations in diameter, but not enough data were available to substantiate this interpretation.

Sintered pellets are far less susceptable to moisture pickup than cold pressed pellets, but even sintered pellets left in the open air for long periods of time will pick up water. This moisture pickup causes cracking and swelling of the pellets and, eventually, their destruction.

CONCLUSIONS

Samarium oxide can be cold pressed to densities in excess of 80% of theoretical (6.21 g/cm^3) by standard pressing techniques. Strength limitations of the dies and plungers used prevented pressing at pressures above 102 TSI. If better dies were designed so higher pressures could be used, higher cold press densities should be possible. Alternatively, if the samarium oxide was calcined at temperatures above 1500 °C, the cold press density should increase. However, we were unable to verify this because of temperature limitations with the furnaces available.

Sinter densities as high as 95.6% of theoretical (7.40 g/cm^3) were obtained quite easily with Sm_2O_3 which had been cold pressed to maximum density. However, the optimum sintering conditions were not determined, and it should be possible to obtain higher sinter densities if a more thorough study is made of the variables involved. Typical sintered pellets are shown in Figure 12.

Neg 0662802-1

FIGURE 12. Typical Cold Pressed and Sintered Sm_2O_3 Pellets

REFERENCES

1. H. T. Pullam, L. J. Kirby and R. T. Allemann. Promethium Heat Source Compatibility Studies - Part I. 1100 °C Studies, BNWL-327, Pacific Northwest Laboratory, Richland, Washington, 1966. (Classified)

2. R. M. Douglas and E. Staritzky. "Samarium Sesquioxide, Sm_2O_3, Form B," Anal. Chem., vol. 28, p. 552. 1956.

3. K. A. Gschneider. Rare Earth Alloys, D. Van Nostrand Co., New York, 1961.

DISTRIBUTION

Number of Copies	
326	Division of Technical Information Extension
6	Isochem, Inc. S. J. Beard J. S. Cochran O. F. Hill H. H. Hopkins, Jr. P. W. Smith R. E. Tomlinson
4	Richland Operations Office N. T. Karagianes C. L. Robinson R. K. Sharp Technical Information Library
59	Battelle-Northwest F. W. Albaugh J. M. Atwood R. J. Baker E. A. Berreth D. W. Brite L. L. Burger R. E. Burns G. M. Dalen D. R. de Halas K. Drumheller H. T. Fullam (20) K. M. Harmon B. M. Johnson, Jr. L. J. Kirby (10) R. L. Moore A. L. Platt F. P. Roberts R. K. Robinson C. A. Rohrmann R. C. Smith H. H. Van Tuyl E. E. Voiland M. T. Walling E. J. Wheelwright Technical Information Files (5) Technical Publications (2)