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COLD PRESSING
OF ALUMINUM-RARE EARTH
OXIDE COMPOSITES

May 1969

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COLD PRESSING OF ALUMINUM-RARE EARTH OXIDE COMPOSITES

By

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H. T. Fullan

ABSTRACT

This report summarizes the results of a brief study of the cold pressing of oxide-aluminum composites. The study originated because of a need to fabricate aluminum- Pm_2O_3 targets for the ^{146}Pm burnout program and was extended to a more general study because of the apparent advantages of the procedure. Rare earth oxide-aluminum composites can be readily compacted into mechanically stable adherent pellets by cold pressing techniques. The densities obtained are dependent on the applied pressure, length-to-diameter ratio of the pellet, and composition of the composite. If oxide density is not a controlling factor, then cold pressing of aluminum composites has many attractive features to recommend it and should be considered as a potential method for fabricating Pm_2O_3 into useful shapes.

TABLE OF CONTENTS

INTRODUCTION.	1
SUMMARY .	2
EXPERIMENTAL.	3
RESULTS AND DISCUSSION	6
CONCLUSIONS .	19
REFERENCES .	21

LIST OF FIGURES

1	Split Sleeve Dies for Pellet Pressing	4
2	Hardness of Pressed Composite Pellets	7
3	Sm_2O_3 -Al Pellets - 20 Grams of Composite at 60 tons/in. ²	8
4	Pellet Density as a Function of Applied Pressure	10
5	Cold Press Density as a Function of Composite Composition	11
6	Variation in Density with Composite Composition	13
7	Density-Composition Relationship for Sm_2O_3 -Al Composites Pressed at Different Pressures	14
8	Pellet Density as a Function of L/D	15
9	Microstructures of Sm_2O_3 -Al Pellets Pressed at 60 tons/in. ²	17
10	Data for Pr_2O_3 -Al Composites	18

COLD PRESSING OF ALUMINUM-RARE EARTH OXIDE COMPOSITES

H. T. Fullam

INTRODUCTION

As part of the Division of Isotopes Development promethium technology program at the Pacific Northwest Laboratory, various methods for fabricating promethium sesquioxide into useful shapes for heat source use are being evaluated by Battelle-Northwest. Fabrication techniques studied to date include cold pressing and sintering,⁽¹⁾ pneumatic impaction,⁽²⁾ slip casting⁽³⁾ and hot pressing.⁽⁴⁾ One other method of potential interest is the cold pressing of aluminum- Pm_2O_3 composites. This procedure, while giving lower promethium densities due to aluminum dilution, possesses certain advantages which make it attractive as a fabrication method. This report summarizes the results of a brief study of the cold pressing of oxide-aluminum composites. The study originated because of a need to fabricate aluminum- Pm_2O_3 targets for the ^{146}Pm burnout program^(5,6) and was extended to a more general study because of the apparent advantages of the procedure.

For most of the work, the sesquioxides of samarium and neodymium were used as stand-ins for promethium sesquioxide. Since the chemical and physical properties of the adjacent rare earths are very similar, and since all promethium sources contain some amount of samarium due to decay, it is felt that the results obtained with the stand-ins would be applicable to Pm_2O_3 .

SUMMARY

Rare earth oxide-aluminum composites can be readily compacted into mechanically stable adherent pellets by cold pressing techniques. The densities obtained are dependent on the applied pressure, length-to-diameter ratio of the pellet, and composition of the composite.

When composite density is plotted as a function of composite composition, a change in slope of the plot occurs at an oxide content of 65 to 75% depending on the applied pressure. This corresponds to the same oxide content at which the continuous phase changes from aluminum to the oxide. Pellet hardness is also a minimum at this same approximate composition.

If oxide density is not a controlling factor, then cold pressing of aluminum composites has many attractive features to recommend it and should be considered as a potential method for fabricating Pm_2O_3 into useful shapes.

EXPERIMENTAL

The samarium and neodymium sesquioxides used in this study were obtained from the Lindsey Chemical Division of American Potash and Chemical Company. Purity of the "as received" material was 99.0%. The oxides were given a special purification treatment prior to use. This consisted of dissolving the oxide in nitric acid, precipitating as the rare earth oxalate by the addition of oxalic acid, filtering, washing, and calcining the oxalate at elevated temperatures to convert it to the oxide. Previous work⁽¹⁾ had shown that the temperature at which the oxalate is calcined would affect the density that could be obtained when the oxide was cold pressed. Therefore, for this work a standard calcining operation of 24 hr at 1100 °C in air was used in preparing the Nd_2O_3 and Sm_2O_3 . The Sm_2O_3 produced in this way had a monoclinic structure and a theoretical density of 7.74 g/cm³. The Nd_2O_3 had a hexagonal structure and a density of 7.31 g/cm³. Both oxides were fine powders (-325 mesh) and had surface areas of about 0.5 m²/g.

The aluminum used was a fine dust (-325 mesh) obtained from Baker and Adamson; its purity was 99.9+%.

The aluminum dust and oxide powder were intimately mixed by ball-milling for 1 hr in a porcelain mill, using aluminum balls, to obtain uniform composites.

The pressing studies were carried out using the split sleeve dies shown in Figure 1. The tapered split sleeve was pressed into the tapered die block and an end plug inserted at the base

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FIGURE 1. Split Sleeve Dies for Pellet Pressing

of the sleeve. A weighed amount of aluminum-oxide charge was placed in the sleeve on top of the plug, and the plunger was inserted in the sleeve. A pressure applied with a hydraulic ram was maintained for about 1 min and then released. The die block was inverted and the sleeve ejected with the hydraulic ram. The plunger and plug were removed from the sleeve and the composite pellet removed. The pellet was weighed and its physical dimensions determined with a micrometer so that the bulk density of the pellet could be calculated. At least two pressings were made for each set of conditions and the densities reported are the arithmetic average of the individual values.

The pressing characteristics of the aluminum-oxide composites are good enough that a physically stable pellet can be obtained, even at low pressures, without the use of a die lubricant. Use of a lubricant does improve the visual appearance of the pellets but does not affect the density obtained. Therefore, all the data reported are for pellets pressed without a lubricant.

Two different size dies were used: one having a bore diameter of 0.75 in., and one a bore diameter of 1.00 in. Both were of the split sleeve type, which greatly facilitated pellet removal from the die. Pressures up to 100 tons/in.² could be obtained using either die assembly. Since no pellet density differences were detected between the two dies, they were used interchangeably.

RESULTS AND DISCUSSION

Composites of aluminum and rare earth oxides can be cold pressed very readily to give mechanically stable, dense, adherent pellets that are free from dusting. Pellets containing 20 wt% or more aluminum have the visual appearance of aluminum rod. The hardness of composite pellets of varying composition, which had been pressed at 60 tons/in.², was measured using a modified Rockwell B hardness tester. The results obtained are shown in Figure 2, and the hardness of 1100 Aluminum rod is indicated as a point of comparison. (Since the equipment was modified, the hardness values given are not standard Rockwell B values, but they do serve as a comparison for the different compositions.) The two composites studied, Nd₂O₃-Al and Sm₂O₃-Al, show substantially different hardness values. Each, however, shows a minimum hardness at a composition of about 60 wt% oxide-40 wt% aluminum. The significance of this will be discussed later.

Typical Sm₂O₃-Al pellets are shown in Figure 3. In each case, 20g of material were compacted at 60 tons/in.² in the 1 in. die. Bulk density variations as a function of composition are readily apparent.

The density that can be obtained by cold pressing will depend on several factors:

- The applied pressure
- The composition of the composite
- The pellet length-to-diameter ratio (L/D)
- The physical characteristics of the oxide and aluminum.

FIGURE 2. Hardness of Pressed Composite Pellets

In this work, an attempt was made to standardize the characteristics of the aluminum and oxide by using aluminum powder of a single type and brand, and by preparing the oxides by the standard procedure described above. The effects of the other variables are discussed in detail below.

In any cold pressing operation, the density obtainable will vary with the applied pressure. Figure 4 shows how the aluminum and individual oxides respond as the pelletizing pressure is increased. As can be seen from the data, aluminum compacts very readily, and densities approaching 100% of theoretical can be obtained at relatively low pressures. Pure Nd_2O_3 and Sm_2O_3 are more difficult to compact and the maximum densities obtainable are about 80% of theoretical.

Intuitively one would expect composite mixtures of oxide and aluminum to exhibit pressing characteristics between those of the individual components. However, when composites of varying composition are cold pressed, the relationship between density and pressure is more complex than one might anticipate. Figure 5 shows the variations in pellet density which are obtained when composites containing 0 to 100% aluminum are pressed at 60 tons/in.² and an L/D of approximately one. Data is presented for both Sm_2O_3 and Nd_2O_3 composites. The abrupt change in slope of the pellet density-composition curves which occurs at oxide contents of 65 to 70 wt% indicates a significant difference in the compaction mechanism of composites containing lesser or greater amounts of oxide. The dashed line shows the actual oxide density as a function of composition.

FIGURE 4. Pellet Density as a Function of Applied Pressure

FIGURE 6. Cold Press Density as a Function of Composite Composition

If one replots the data from Figure 5 as the percent of theoretical density versus composition, the curve shown in Figure 6 is obtained.* Little difference is noted in the data for the two oxide composites when the density is plotted as percent of theoretical.

The data presented in Figures 5 and 6 are for a pressure of 60 tons/in.² Similar experiments were carried out at other pressures from 10 to 80 tons/in.² using Sm_2O_3 -Al composites. The results obtained are shown in Figure 7. In each case, a change in slope is evident, but the point where the change occurs appears to shift slightly with the pressure.

The density obtained for a given composition and pressure will depend to some extent on the length-to-diameter ratio (L/D) of the pellet pressed. The data presented up to this point were obtained with pellets whose L/D was held to approximately one. In Figure 8 is presented data which show how the density will change as the L/D is varied. Aluminum density varies only slightly as the L/D varies from about 0.1 to 2.0. With Sm_2O_3 , however, the density decreases almost linearly with increasing L/D. With composites, the relationships are more complex and depend on the composition.

---

* The theoretical density of a composite is taken as the arithmetic average of the individual components--

$$\text{theoretical density} = \frac{100}{\left(\frac{\text{wt\% oxide}}{\text{oxide density}} \right) + \left(\frac{\text{wt\% Al}}{\text{Al density}} \right)}$$

FIGURE 8. Variation in Density with Composite Composition

FIGURE 7. Density-Composition Relationships for Sm_2O_3 -Al Composites Pressed at Different Pressures

FIGURE 8. Pellet Density as a Function of L/D

The Sm_2O_3 -Al pellets, which were pressed at 60 tons/in.² and whose densities are given in Figure 5 and 6, were sectioned with an abrasive saw and examined by metallographic techniques. Study of the microstructure showed that for oxide concentrations of 60 wt% or less, the aluminum was the continuous phase (see Figure 9). For oxide concentrations of 70 wt% or greater, the oxide is the continuous phase. The transition of the continuous phase from aluminum to oxide occurs, therefore, in the same composition range where minimum hardness and the break in the curve of Figure 5 occurs.

Only a small number of pressings were made with Pm_2O_3 , and these were limited to composites containing 5 to 10 wt% Pm_2O_3 (for use in the ¹⁴⁶Pm burnout studies). The results obtained compare favorably with those obtained with Sm_2O_3 and Nd_2O_3 composites (see Figure 10). It appears from these limited data that the results obtained with the stand-ins are applicable to Pm_2O_3 .

One other factor, which while not studied in detail, should at least be mentioned. When cold pressed or sintered pellets of Nd_2O_3 , Sm_2O_3 , or Pm_2O_3 are exposed to atmospheric moisture or water, they will react with the water. Given sufficient exposure time, the pellets end up as hydrolyzed powder.^(1,5,6) The rates at which the three oxides react will vary; Nd_2O_3 reacts very rapidly, Pm_2O_3 quite slowly, and Sm_2O_3 at an intermediate rate. After exposure to the atmosphere for many months, Sm_2O_3 -Al and Nd_2O_3 -Al composite pellets (containing 40% or more aluminum), showed almost no indication of reaction with moisture.

FIGURE 10. Data for $\text{Pm}_2\text{O}_3\text{-Al}$ Composites

CONCLUSIONS

From the results presented above, it can be seen that the promethium density in cold pressed composites will be relatively low, especially at high aluminum concentrations. However, several advantages to the process, which in certain cases may outweigh the low density factor, include the following: (1) The composites are easily compacted into mechanically stable pellets. (2) The pellets have the visual appearance and texture of aluminum rod and can be handled without fear of damage. (3) They are non-dusting and easily cleaned of loose particles. (4) The overall process is simple and straight-forward and can easily be carried out in a shielded glove box.

Although it has not been demonstrated experimentally, the results obtained with pellet pressings indicate that aluminum- Pm_2O_3 composites could be pressed into thin sheets or plates which could be handled as such without fear of mechanical damage. Preparation of such sheets may be advantageous in fabricating certain heat or beta sources. Sheet size would only be limited by the size of the press available.

Overall, the process would appear to possess enough advantages that it should be considered for use where promethium density is not an over-riding factor. The use of aluminum would limit the maximum useful temperature of the source, but it would already be temperature limited by the low promethium density.

The procedure would not have to be limited to Pm_2O_3 -aluminum composites. Other isotopes could be used in place of promethium, such as ^{144}Ce , ^{170}Tm , ^{204}Tl , and ^{90}Sr . Other metals such as

silver, gold, platinum, or thorium could be substituted for aluminum. Isotope and metal components could be selected to meet specific heat, X-ray, or beta source requirements.

REFERENCES

1. H. T. Fullam and L. J. Kirby. Cold Pressing and Sintering of Rare Earth Oxides, BNWL-386. Pacific Northwest Laboratory, Richland, Washington, 1967.
2. R. L. Moore (editor). Pacific Northwest Laboratory Radioisotope Technology Programs Quarterly Report: January, February, March, 1967, BNWL-466. Pacific Northwest Laboratory, Richland, Washington, June, 1967. (Confidential)
3. H. T. Fullam. Slip Casting of Rare Earth Oxides, BNWL-437. Pacific Northwest Laboratory, Richland, Washington, 1967.
4. H. T. Fullam and C. J. Mitchell. Hot Pressing of Rare Earth Oxides, BNWL-448. Pacific Northwest Laboratory, Richland, Washington, 1967.
5. R. L. Moore (editor). Pacific Northwest Laboratory Division of Isotope Development Programs Quarterly Report: January-April, 1968, BNWL-781. Pacific Northwest Laboratory, Richland, Washington, May, 1968. (Confidential)
6. K. Drumheller (editor). Pacific Northwest Laboratory Division of Isotope Development Programs Quarterly Report: May-July, 1968, BNWL-877. Pacific Northwest Laboratory, September, 1968. (Confidential)

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80% Al-20% Sm_2O_3
100X

40% Al-60% Sm_2O_3
100X

30% Al-70% Sm_2O_3
100X

10% Al-90% Sm_2O_3
100X

FIGURE 9. Microstructures of Sm_2O_3 -Al Pellets Pressed at 60 tons/in.²