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PREPARATION OF ALUMINUM TITANATE
CRUCIBLES BY SLIP CASTING FOR
HIGH-TEMPERATURE
APPLICATIONS

M. K. Morrow
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**PREPARATION OF ALUMINUM TITANATE CRUCIBLES BY
SLIP CASTING FOR HIGH-TEMPERATURE APPLICATIONS**

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ABSTRACT

An alumina-titania mixture ($\text{Al}_2\text{O}_3\text{-TiO}_2$) was synthesized by the hydrolysis of a refluxed benzene solution of the respective metal isopropylates. This powder, after calcining, was mixed with a 0.5 percent solution of sodium alginate in a 43 gm/57 ml ratio to form a suspension suitable for slip casting. Several thick-walled crucibles were cast and later sintered to produce aluminum titanate (Al_2TiO_5) crucibles as the end product. This material is of special interest because of its applicability for containing molten uranium without contaminating the metal.

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SUMMARY

Pure-phase aluminum titanate was successfully slip cast and sintered in order to prepare crucibles that are suitable for melting uranium metal.

A large quantity of the mixed oxides of aluminum and titanium ($\text{Al}_2\text{O}_3\text{-TiO}_2$) was prepared from the respective organometallic precursors: aluminum isopropylate, $\text{Al}(\text{OC}_3\text{H}_7)_3$, and titanium isopropylate, $\text{Ti}(\text{OC}_3\text{H}_7)_4$.

The mixed oxide powder was calcined at 800°C in air to prepare aluminum titanate (Al_2TiO_5).

Using molds prepared from a 1:2 weight ratio of water and dental plaster, the aluminum titanate was slip cast into a variety of shapes and successfully sintered.

A marked improvement in viscosity of the slip was noted with an adjustment of the pH to a level between 11.6 and 11.9.

The optimum solid-to-liquid ratio for aluminum titanate slips was found to be 43 grams of the titanate to 57 milliliters of a 0.5 weight percent solution of sodium alginate.

INTRODUCTION

Preliminary experiments, at the Oak Ridge Y-12 Plant,^(a) have indicated that uranium metal can be successfully melted at 1,200° C in an aluminum titanate (Al_2TiO_5) crucible prepared by isostatic pressing and sintering techniques. The uranium did not appear to wet the aluminum titanate crucible (about 80% dense) or react with it. Emission spectrographic analysis showed no contamination resulting from the crucible. Therefore, a method was sought for the production of aluminum titanate crucibles of uniform porosities and wall thicknesses by a rapid, economical method. The slip-casting process was chosen in order to meet these objectives, since simple and complicated shapes and large parts could be produced without difficulty.

According to the literature,^(b) aluminum titanate has several interesting properties that include: (1) its high refractoriness, (2) its near-zero coefficient of thermal expansion which results in a high thermal shock resistance, and (3) its high resistivity with a high negative temperature coefficient of resistivity. The main arguments against its use as a ceramic material were: (1) its low strength, and (2) its incapability of forming a hard mass by sintering at ordinary temperatures.^(b) When numerous sintering aids were added to help correct these faults, the advantageous properties of the pure substance began to disappear.

(a) Operated for the US Atomic Energy Commission by the Union Carbide Corporation's Nuclear Division.

(b) Bhattacharyya, B. N. and Sen, Sudhir; "Aluminum Titanate Formation and Properties", *Cent Glass Ceram Res Inst Bull*, 12 (3), pp 91-103 (1965).

PREPARING ALUMINUM TITANATE CRUCIBLES

SYNTHESIS OF THE COMPOUND

The method previously used by Bhattacharyya and Sen to synthesize aluminum titanate (Al_2TiO_5 or $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$) was by mixing and calcining the two finely-ground oxides which had been produced commercially; however, this aluminum titanate powder could not be sintered into shapes without a sintering aid. It was decided that one of the problems which prevented sintering the titanate powders by other investigators may have been that the two oxides were not really mixed intimately, partially because of their large particle size. Sinterable aluminum titanate powders were prepared by the synthesis of the 50:50 mole percent aluminum oxide-titanium oxide mix. The hydrolysis of the metal isopropylates in benzene was according to the reaction:

In actual preparations under an argon atmosphere, one kilogram of aluminum isopropylate, $\text{Al}(\text{OC}_3\text{H}_7)_3$, was dissolved in two liters of benzene. To this solution was added 736 milliliters of titanium isopropylate, $\text{Ti}(\text{OC}_3\text{H}_7)_4$. The solution was refluxed for three hours and then allowed to cool. While stirring vigorously, demineralized water was added dropwise to hydrolyze the organometallics. An excess of water was added to increase the speed of the filtration process.

To remove the alcohol and water which still remained on the powder after its synthesis, the hydrated aluminum titanium hydroxide was placed in a vacuum oven at 50°C for 48 hours. Surface-area measurements by nitrogen absorption indicated a surface area of $330 \text{ m}^2/\text{gm}$, which corresponds to an average particle size of 50 Å. Next, the powder was calcined at 800°C in air for 40 hours. After this treatment, surface-area measurements indicated a particle size of 650 Å. When the powder was removed from the furnace while hot, a yellow coloration was noted, indicating a slight oxygen deficiency. However, upon cooling in air, the powder returned to a white color.

SLIP CASTING OF THE COMPOUND

Slip casting is a method that is suitable for nonclay systems, and merits some discussion. Slip casting may be used for producing ceramic goods of both large and small dimensions, and of any shape. A fluid suspension of the powder in a liquid, which is known as a "slip" or slurry, is poured into a mold (a negative of the desired shape) made from plaster.

By capillary action of the pores in the plaster, the liquid is drawn into the mold, leaving the ceramic powder adhering to the walls of the mold. This action forms a "green" casting. The green casting will shrink on drying and pull away from the walls of the mold, making it easy to remove. After it is taken out of the mold, the green casting is allowed to dry and is then sintered.

In actual practice, however, many variables had to be evaluated before a successful slip was obtained. Among these parameters were the suspending agent, the molds, and the properties of the slip.

EVALUATION OF THE SUSPENDING AGENTS

In order to find a suitable medium to keep the powder in suspension, several compounds were tried, as reported in Table 1. As noted, a 0.5 percent aqueous solution of sodium alginate proved to be the most stable.

To test for the best suspending agent, the solutions listed in Table 1 were prepared and allowed to roll on ball-mill rollers overnight. The solutions were then placed in a high-speed blender for one minute immediately before each was tested.

Using an electric mixer, the aluminum titanate powder was slowly added to 50 milliliters of the solution. When the slip appeared to thicken, the addition of powder was discontinued. A determination was then made of the percentage of solid added. Next, the slip was mixed for one hour then poured into a graduated cylinder. Measurements of the amount of clear supernatant above the suspension were taken at regular time intervals (ie, every five minutes) for two hours. This study was used as a measure of the stability of the slip.

PREPARATION OF THE MOLDS

All the molds used were prepared from dental plaster and water mixed in a ratio of 100 grams of plaster to 50 milliliters of water. This mixture was stirred for ten minutes at which time it began to thicken. Before the plaster was poured around the mold form or mandrel to produce a negative of the desired shape, it was sprayed with a fluorocarbon release agent. Two-piece molds were also made for more complicated shapes. The plaster was permitted to harden (20 minutes), then the mold form was removed. The molds were placed in an oven at 50° C until completely dry. Some molds and their titanate shapes may be seen in Figures 1 and 2.

SLIP-CASTING PROCESS

The following steps were used in slip casting aluminum titanate:

1. Calcined aluminum titanate powder was ground with a mortar and pestle and sieved to -200 mesh to remove the larger agglomerates and thus make the particle size more uniform.
2. A 0.5 weight percent sodium alginate solution was prepared, then the aluminum titanate powder and liquid were combined using an electric mixer. A small amount of the powder was added at a time and the batch was allowed to mix for at least two hours (longer time for larger batches) before casting.
3. A 0.2 percent aqueous solution of ammonium alginate was poured into the mold and immediately poured out again. This solution was used as a release agent.

Table 1
EVALUATION OF VARIOUS SUSPENDING AGENTS

Suspending Agent	Compound in Solution (wt %)	Solid in Slip (%)	Comments
Sodium alginate	0.25	47	Stable; too fluid; did not cast well.
Sodium alginate	0.5	43	Stable; fluid.
Sodium alginate	1.0	29	Stable; viscous.
Polyvinyl alcohol	1.0	43	Unstable.
Sodium carboxymethylcellulose	0.5	40	Stable; viscous; cast too rapidly.
Sodium carboxymethylcellulose	2.0	43	Stable; viscous.
Sodium carbonate and sodium silicate in a 1:1 mixture	0.5	46	Stable; a solid is formed quickly when cast.
Methylcellulose	0.5	37	Too viscous to flow.
Sodium lignin sulfonate	3.0	51	Sets up.
Calcium lignin sulfonate	3.0	47	Sets up.
Ammonium alginate	0.5	40	Solidifies quickly when cast.
Gantrez resin ⁽¹⁾	1.0	39	Stable; did not cast well.

(1) A copolymer of methyl vinyl ether and maleic anhydride.

4. After the mold had dried, it was filled with slip. The thicker the wall desired, the longer the slip was allowed to remain in the mold. When the desired wall thickness was reached (usually 45 minutes to yield 1/16 to 1/8-inch walls on the green casting), the mold was turned upside down and the excess slip drained off.
5. After the green casting pulled away from the sides of the mold it was removed and permitted to air dry before being placed in an oven at 50° C for 24 hours.

Figure 1. TWO-PIECE MOLD AND SINTERED ALUMINUM TITANATE BOTTLE.

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PROPERTIES OF THE SLIP

Several variables were tested and found to affect the results of slip casting aluminum titanate. Among these variables were: pH, the solid/liquid ratio, density of the slip, and particle size of the starting powder.

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Figure 2. SINTERED ALUMINUM TITANATE PRODUCT, GREEN CASTING, AND ONE-PIECE MOLD.

Viscosity

A slip of low viscosity is desired since the slip must be able to flow. However, as much solid as possible should be in the slip so the casting rate will not be too slow. As shown in Figures 3 and 4, pH has a dramatic influence on the viscosity of the aluminum titanate slip.

The pH was raised by the dropwise addition of a 30 percent aqueous solution of sodium hydroxide to the slip. The ideal viscosity occurred between a pH interval of 11.6 to 11.9 (Figure 3). To obtain this pH, 1.3 milliliters of a 30 percent sodium hydroxide solution were added for every 100 milliliters of liquid.

In order to test the viscosity on the acidic side, concentrated hydrochloric acid was added directly to the slip. However, the slurry gelled immediately due to the nucleating action of the aluminum titanate particles to precipitate out alginic acid. This

Figure 3. VISCOSITY AS A FUNCTION OF pH FOR THE ALUMINUM TITANATE SLIP. (Basic Side)

Figure 4. VISCOSITY AS A FUNCTION OF pH FOR THE ALUMINUM TITANATE SLIP. (Acidic Side)

Particle Size and Density

The aluminum titanate powder appeared to be forming agglomerates which made the slip gritty and caused the cast crucibles to be rough. In order to compensate for this effect, the powder was ground with a mortar and pestle or dry ball milled and passed through a 200-mesh (74-micrometer) sieve. Precautions were also taken to protect the powder from moisture since it appeared to be slightly hygroscopic. The powder prepared in this manner produced a smooth slip that was highly conducive to slip casting.

Since the process just described is somewhat slow and tedious, it was decided to try to ball mill the slip itself. However, this technique has yet to be proved successful since ball milling reduces the particle size of the smaller particles as well as the large ones, and it has been shown that particles which are too small have as much of an adverse effect on slip casting as those that are too large. Cracking of cast articles produced from a fine-grained slip occurred during drying. Therefore, the sieving of material that has been previously ground by mortar and pestle (or dry ball milling) is recommended.

The theoretical density of a slip with the 43 gm/57 ml solid/liquid ratio is 1.46 gms/cc (based on the theoretical density of 3.73 gms/cc for Al_2TiO_5). The measured density was 1.47

problem was circumvented by acidifying the solutions of 0.5 percent sodium alginate before adding the powder. Although the viscosities obtained were low, as indicated in Figure 4, the powder began to settle. When using an acidic slip, the casting rate was much too fast. These data indicate that a pH in the basic range works as a deflocculant in this case.

At a pH between 11.6 to 11.9, the solid-to-liquid ratio was tested. As shown in Figure 5, mixtures containing above 50 percent solid produced an extremely viscous slip. More liquid was added; and, at 43 percent solid, the viscosity was low enough to produce a good slip. Therefore, a solid/liquid ratio of 43 grams of titanate to 57 milliliters of water was used.

Figure 5. RELATIONSHIP BETWEEN PERCENT LIQUID AND THE VISCOSITY OF THE ALUMINUM TITANATE SLIP.

gms/cc. Particle-size distribution of the slip was also determined and it was found that 90 percent of the particles were under 36 micrometers.

SINTERING GREEN CASTINGS

After the green castings were completely dry, they were sintered between 1,450 - 1,650° C for two hours. Most of the crucibles were fired under argon in a carbon induction furnace while the remainder were fired in air in a resistance-heated tube furnace. The crucibles which were sintered under argon turned black, indicating an oxygen deficiency; those sintered in air turned a cream color. However, if the crucibles were removed from the air furnace while they were still hot, they exhibited a yellow color; but, most of the yellow coloration disappeared when the crucibles cooled. This phenomenon was previously noted when the aluminum titanate powder was calcined. Several of the containers fired under argon were reoxidized by heating for four hours at 800° C in air. As can be seen in Figure 6, these crucibles also turned a cream color.

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Figure 6. AN ALUMINUM TITANATE CRUCIBLE THAT WAS SINTERED IN ARGON (LEFT) AND ONE THAT WAS SINTERED IN ARGON AND REOXIDIZED IN AIR (RIGHT).

SLIP CASTING DIFFERENT SHAPES

Crucibles of various shapes were cast from the aluminum titanate slip, as seen in Figures 7 - 11. The shapes that proved most difficult to make were those which possessed sharp angles. The main problem here was that after the piece was cast and the excess slip drained, the powder tended to adhere more at the angles of the mold while it pulled away at the sides, cracking the container.

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Figure 7. ALUMINUM TITANATE SLIP-CAST CRUCIBLES THAT WERE SINTERED IN AIR (LEFT) AND CRUCIBLES THAT WERE SINTERED UNDER ARGON (RIGHT).

Another problem which initiated cracking was the presence of air bubbles that were trapped in the slip. However, if the slip was outgassed before using, this problem was eliminated.

The largest container cast was a 600-milliliter beaker, seen in Figure 2.

SHRINKAGE AND DENSITY CALCULATIONS

Shrinkage calculations were based on the following formulae:

$$\text{Percent Dry Shrinkage} = \left[\frac{V_{\text{mold}} - V_{\text{dry crucible}}}{V_{\text{mold}}} \right] \times 100 ,$$

$$\text{Percent Sintered Shrinkage} = \left[\frac{V_{\text{dry crucible}} - V_{\text{sintered crucible}}}{V_{\text{dry crucible}}} \right] \times 100 , \text{ and}$$

$$\text{Percent Total Shrinkage} = \left[\frac{V_{\text{mold}} - V_{\text{sintered crucible}}}{V_{\text{mold}}} \right] \times 100 ,$$

where V represents the volume of the various items given as subscripts.

From the experimental data it was determined that the average dry shrinkage was 30 volume percent, sintered shrinkage was 50 volume percent, and total shrinkage was 65 volume percent.

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Figure 8. EXTENT OF SHRINKAGE ILLUSTRATED BY COMPARING A SINTERED ALUMINUM TITANATE CRUCIBLE (LEFT) AND A GREEN CASTING FROM THE SAME MOLD (RIGHT).

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Figure 9. SINTERED ALUMINUM TITANATE CONICAL CRUCIBLES.

Figure 10. SINTERED ALUMINUM TITANATE SLIP-CAST CYLINDRICAL CRUCIBLES.

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Figure 11. ADDITIONAL TYPES OF SINTERED ALUMINUM TITANATE CRUCIBLES PREPARED BY SLIP CASTING.

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Densities of the sintered shapes varied from 60 to 80 percent of theoretical, averaging 2.62 gms/cc for five samples.

CONCLUSIONS

This pure-phase aluminum titanate can be successfully slip cast and sintered to prepare refractory containers for molten uranium. Sintered slip-cast crucibles were of acceptable density for this type of application.

X-ray diffraction analysis on a crushed crucible revealed only aluminum titanate to be present.

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