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SLIP CASTING OF ZIRCONIUM DIBORIDE

C. E. Holcombe, Jr

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the **ATOMIC ENERGY COMMISSION** *under* **U. S. GOVERNMENT** **Contract W-7405 eng 26**

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ABSTRACT

The slip casting of zirconium diboride (ZrB_2) shapes was studied. The best slip casting properties were obtained with three percent sodium carboxymethylcellulose (CMC) solution as the liquid phase along with powder that had been ball milled for one week. The stability of the slip, casting rates, and flow properties were investigated.

Various shapes were slip cast, indicating the capability of the method to produce complex shapes, both large and small. Both drain casting and solid casting were employed.

A brief investigation established the feasibility of slip casting (with a 3% CMC solution as the liquid phase) hafnium diboride, pure boron, boron carbide, chromium diboride, and a zirconium diboride-10 percent tungsten cermet.

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SUMMARY

The Oak Ridge Y-12 Plant^(a) has used slip casting to form regular and irregularly shaped objects of ZrB_2 . A three percent aqueous solution of sodium carboxymethylcellulose (CMC) proved to be the optimum liquid phase of the slip.

Excellent casting properties were obtained with solid-liquid ratios of 78:22 and 82:18, which gave a faster casting rate. The use of powder that had been ball milled for one week was necessary to achieve maximum stability of the suspension and to increase the casting rate. Preliminary blending of the dissolved CMC solution and the forcing of the solution through a 50-micron sieve before preparing the slip improved the casting properties and stability of the slip.

A change in pH by the addition of HCl or KOH did not improve the casting properties of the slip. This fact is advantageous since regulation of the slip pH is troublesome.

Methods were investigated for controlling the casting rate for producing thick and thin-walled shapes. The dependence of the capillary properties of the plaster molds on the grade of plaster and on the water/plaster ratio used in preparing the molds was studied, and the effect of the percentage of liquid phase of the slip on the casting rate was determined.

Increasing the temperature of the slip and mold to 50° C to increase the casting rate impaired the left-over slip for reuse.

Application of two films (one of talc and one of sodium alginate) was necessary to achieve mold release. Crucibles were produced by sintering at 1,700 - 1,950° C for one to two hours. Talc seems to have acted as a sintering aid and then disappeared through volatilization.

Various shapes of zirconium diboride were slip cast, including large (6" H x 6" D) crucibles, cones, Knudsen cells, trays, and a coffee cup. These shapes illustrated the capability of the method to produce complex objects.

Slips were prepared for producing shapes of hafnium diboride, pure boron, boron carbide, chromium diboride, and a zirconium diboride-ten percent tungsten cermet; CMC was used as the suspension agent for these slips.

The uniform packing of the particles over the entire cross section of the casting, as well as the uniform wall thicknesses produced, gave some advantages to this method of forming articles.

(a) Operated by the Union Carbide Corporation for the US Atomic Energy Commission.

INTRODUCTION

Since an alternative forming process to cold pressing and sintering for very hard, refractory materials was needed for the fabrication of zirconium diboride (ZrB_2) crucibles, the method of slip casting was considered. This method offers the advantages of yielding products of uniform porosity and high density, while being very economical. Parts of uniform wall thicknesses (whether thick or thin-walled) can be readily produced. Slip casting has only recently become an important forming process for nonclay systems.

There are many parameters to consider in preparing a usable slip (or a stable suspension): type and amount of deflocculant (or dispersant), type of liquid, solid-to-liquid ratio, viscosity of the slip, and pH of the slip. The properties of the slip which are of interest are casting rate, stability, and flow properties. The properties of importance of the cast parts are density, strength, release rate, and sintering properties (whether warpage or interaction with the deflocculant occurs). The casting rate depends on: (1) the plaster-to-water ratio in initially making the mold, since this determines the porosity of the mold; (2) the type of plaster, since each type has different properties depending on degree of refinement and additives; (3) the moisture content of the mold, which affects its suction; (4) the density of the slip or the solid-to-liquid ratio; (5) the particle size of the powder used in preparing the slip—both (4) and (5) affect the mobility of the particles in suspension; and (6) the type and thickness of the release agent, such as the sodium alginate film technique.^(b) Once the parameters of a slip are determined, the slip can be used routinely for producing complicated shapes and large parts without difficulty.

(b) Rempes, P. E., Weber, B. C., and Schwartz, M. A.; *Bull Am Ceram Soc*, 37, p 334 (1958).

SLIP CASTING

LIQUID PHASE OF SLIP

Dobrovolskii, et al,^(c) studied the slip casting of small articles of ZrB_2 . Solutions of sodium alginate, polyvinyl alcohol, starch, sodium polymethacrylate, and sodium carboxymethyl-cellulose (CMC) were tested as the liquid phase. The best liquid phase for the slip composition was a three percent solution of CMC. A solid-liquid ratio of 78:22 gave the best casting properties.

Rempes, Weber, and Schwartz presented general unrefined techniques for slip casting a variety of metals, ceramics, and cermets, including zirconium diboride. Their recommendation of the use of a combination of sodium alginate and acrylic acid polymer solutions as a suspension agent proved very difficult because of rapid settling (instability) and a slow casting rate.

To determine the optimum liquid phase for a ZrB_2 slip, several suspension agents were used. Relative stability was determined by casting a small crucible from each slip and observing the uniformity of the wall thickness (thick-bottomed parts resulted from unstable slips). The results are summarized in Table 1, where it is seen that CMC solutions were the best dispersants for ZrB_2 powder.

Table 1

CHARACTERISTICS OF SLIPS OF ZrB_2 PREPARED WITH
DIFFERENT SUSPENSION AGENTS

	Suspension Agent	Characteristics of Suspensions of Powdered ZrB_2
I	1/2 of 3% CMC 1/2 of 3% calcium lignin sulfonate	Adequate stability; casting rate and release rate rapid; surface bumpy.
II	calcium lignin sulfonate	Adequate stability at 1 to 3% solutions; foamed when mixed with ZrB_2 ; casting rate too rapid; release rate rapid.
III	sodium lignin sulfonate	Suspensions were unstable up to 3%; foamed when mixed with ZrB_2 ; settled rapidly.
IV	1/2 of 0.5% sodium alginate 1/2 of 1.0% acrylic acid polymer	Slips unstable with pure ZrB_2 ; however, when used with ZrB_2 containing 10 wt % W, slips with adequate stability resulted, but had a low casting rate.
V	CMC	Slips with excellent stability and a good casting rate at 2 to 3% CMC solutions; unstable below 2% CMC in the solution.

(c) Dobrovolskii, A. G., Dobrovolskii, G. G., Lyduvinskaya, T. A., and Popichenko, E. Ya; *IZV Akad Nauk SSSR, Neorgan Materialy*, 2, (5), pp 864-869 (1966).

PREPARATION OF SLIP

The slip was prepared by mixing ZrB_2 powder with an aqueous solution of CMC in a propeller mixer for two hours. The stability of the slips was influenced mainly by the particle size of the ZrB_2 powder, the CMC content in the liquid phase of the slip, and the method of preparation of the slip. Aqueous solutions with a CMC content greater than two percent formed stable slips when the powder that was ball milled for one week (median size of 10 microns) was used. Coarser powder (median size of 15.5 microns) required a three percent CMC solution to form a stable slip. The two and three percent solutions of CMC formed slips which had equal casting rates. The use of a ball-milled powder (50% < 10 microns; 90% < 23 microns^(d)) resulted in an increased casting rate and stability when compared to slips produced from as-received commercial powder (50% < 16 microns; 90% < 41 microns), and the smaller particle-size powder seemed to eliminate the thixotropic nature of the CMC slips prepared from coarser powder. The method of preparation of the aqueous solution of CMC also influenced the stability of the slip. Solutions of CMC preliminarily mixed in a blender at high speed for two minutes after dissolution of the CMC and then passed through a 50-micron sieve, in comparison with unscreened solutions, formed much more stable slips (when the particle size was constant). The blending and rubbing through a sieve seemed to break up the CMC conglomerates and also caused a small increase in the casting rate.

The viscosity of a one percent solution of CMC is sometimes used to designate the type used, since different types of CMC have an extremely variable molecular weight. The CMC used in this work had a viscosity of 20 centipoises in a one percent solution. To determine the effects of pH changes on CMC solutions, viscosity changes of a three percent CMC solution (unadjusted pH was 9.6) with pH were measured by adding concentrated HCl to

Figure 1. RELATIONSHIP BETWEEN VISCOSITY OF A THREE PERCENT CMC SOLUTION AND pH.

lower the pH and a 30 percent KOH solution to raise it. The pH values were determined using a pH meter. A viscometer was used for viscosity measurements, after calibration with mineral oil of standard viscosity. Figure 1 shows that the solution was stable and had a viscosity of 52 to 56 centipoises through the pH range from 4 to 12. The viscosity increased rapidly below a pH of 3, forming a gel of insoluble glycolic acid below a pH of 2. The viscosity decreased when the pH was raised above 12 with no apparent instability resulting.

- (d) All particle size measurements were made by an electronic counting technique where a very dilute, well-dispersed suspension is caused to flow through a small aperture, with essentially one particle at a time passing a screening device. Particles passing through the screening device are detected by the change they produce in the electrical conductivities of the medium.

The fluidity of the slips was determined with respect to the solid-liquid ratio and to pH. From Figure 2, it is seen that the viscosity depends on both the particle size of the ZrB_2 powder and on the solid-liquid ratio. Changes in the ZrB_2 slip viscosity with solid-liquid ratio (liquid was 3 wt % sodium carboxymethylcellulose [CMC] solution) were measured for commercial -325 mesh material (median size of 16 microns) and for powder that was ball milled for 24 hours before preparing the slip. A slight change in the curve (viscosity versus solid-liquid ratio) was noted, with the viscosity decreasing slightly, at each particular liquid content for the ball-milled material compared to the as-received material. The relationship between viscosity and the liquid-solid ratio was determined for powder that was ball milled for one week (median size of 10 microns), and a substantial change resulted with much lower viscosities occurring at each particular liquid content compared to the previous results. When the fine powder (ball milled for one week) was used, a flowable slip could be made with only 18 percent liquid.

Figure 3. RELATIONSHIP BETWEEN VISCOSITY AND pH OF A ZrB_2 SLIP CONTAINING 24 PERCENT LIQUID.

Figure 2. DEPENDENCE OF THE VISCOSITY OF THE SLIP ON THE CONTENT OF THE LIQUID PHASE AND ON PARTICLE SIZE OF THE ZIRCONIUM DIBORIDE.

The pH-viscosity relationship of a ZrB_2 slip containing 24 percent liquid (3% CMC solution) is shown in Figure 3, and was similar to that of the three percent CMC solution (Figure 1), with the slip becoming very unstable below a pH of 6. No viscosity minimum was observed, but the viscosity continued to decrease as the pH became basic through a pH of 13. However, use of a slip with the pH adjusted to 13 led to a reduced casting rate, and it was concluded that pH adjustments were not beneficial.

Thus, a slip prepared from a three percent aqueous solution of CMC with a solid-liquid ratio of 78:22 had a viscosity of approximately 400 centipoises and possessed good fluidity and mold-filling qualities when ZrB_2 powder that was ball milled for one week was used. No

thixotropic behavior was noted when fine powder was used, even with two-hour casting times, although pronounced thixotropic behavior was noted after 30 minutes when coarse powder was used. The solid-liquid ratio can be changed to 82:18 (viscosity $\approx$ 1,200 centipoises), resulting in an increased casting rate.

CONTROL OF THE CASTING RATE

Preparation of Molds

Plaster (chemically, CaSO_4), consisting of fine needlelike crystals which form a porous body upon setting after being mixed with water, was obtained in four different grades. The capillary properties of the plaster molds depend on the properties of the plaster and on the water/plaster ratio used in the preparation. Thus, to determine the capacity of the different grades of plaster to absorb the liquid phase of the slip, blanks (about 4" D x 1 1/2" T) were prepared, and the cumulative water absorption of the blanks was determined by complete submersion. The results are seen in Figure 4, where it is seen that a water/plaster ratio of 0.90 was used for all grades except that from Vendor A. A ratio of 0.50 was used for the

Vendor A plaster since a higher water content resulted in water floating on the cast blank when it was prepared. From Figure 4, it is seen that chemical-grade plaster of Paris would be best for a fast casting slip, since it removes the greatest amount of water. However, since plaster of Paris forms a weak mold, the grade from Vendor B would be optimum for thick-walled parts. For thin-walled parts, the grades from Vendor C or Vendor A might be preferable.

Figure 4. CUMULATIVE WATER ABSORPTION ON COMPLETE SUBMERSION OF DRY PLASTER BLANKS (FOR COMMERCIAL GRADES).

Changes in the water/plaster (W/P) ratio can also be used to vary the water absorption of a particular grade of plaster. A greater W/P ratio increases the porosity of the mold (which increases the absorption of the mold and thus increases the casting rate of the slip). Conversely, a lower W/P ratio decreases the porosity of the mold (thereby decreasing the absorption of the mold and thus decreasing the casting rate of the slip). Using blanks of molding plaster identical to that previously described, the relationship between the cumulative water absorption for molding plaster with time for W/P ratios of 0.60 to 0.90 is presented in Figure 5. The similarity between Figures 4 and 5 is obvious, showing that necessary casting rates can be affected similarly by the grade of plaster and the W/P ratio of the plaster.

Typical molds were prepared by mixing the required amounts of water and plaster for 5 to 8 minutes (until a creamy consistency is reached) and then pouring the plaster over a mandrel (the shape of the part desired) to allow it to harden. After setting, the mandrel was removed and the mold dried. Molds consisted of either one piece or many parts, depending on the complexity of the product. A typical one-piece mold is seen in Figure 6 along with an unfired ZrB_2 crucible prepared in it. A two-piece mold is shown in Figure 7. An aluminum mandrel was used to fabricate this large mold ($\sim 6'' \text{ D} \times 7'' \text{ L}$ in the working cavity) which was needed to prepare crucibles for use in a carbon induction furnace. Multipiece molds are necessary when little shrinkage of the cast piece occurs on drying, and always aid in the removal of the part.

Casts of ZrB_2 stuck tightly to the plaster and were difficult to separate from both one or two-piece molds. To improve the separability of the castings, the working surface of the molds was coated with two films—a film of talc and then a film of sodium alginate. (A film of sodium alginate alone did not insure the necessary separability.) The film of talc was applied by pouring a water suspension of talc into the working cavity of the mold and immediately draining it off. The thin talc film was then treated with a film of sodium alginate (0.2% solution) in the same manner. The molds were considered ready for use after the film had dried from 5 to 30 minutes.

Percentage of Liquid Phase

Casting rate is also affected by the percentage of liquid phase of the slip. Table 2 shows the relationship between the casting rate (sintered wall thickness) and percentage of suspending medium in the slip. It is seen that the fastest casting rates occur at 18 to 22 percent liquid (3% CMC) phase.

The relationship between the casting rate and time for zirconium diboride slips with 18 to 22 percent liquid phase is shown in Table 3. The casting rates for the slip with 18 percent liquid is nearly double that for the 22 percent slip at all times. Thus, for thick-walled parts, a zirconium diboride slip with 18 percent liquid would be optimum.

Figure 5. CUMULATIVE WATER ABSORPTION FOR MOLDING PLASTER WITH TIME FOR DIFFERENT WATER-TO-PLASTER RATIOS.

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Figure 6. ONE-PIECE PLASTER MOLD (USED TO CAST ZrB_2 CRUCIBLES) AND AN UNSINTERED, DRIED CRUCIBLE.

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Figure 7. TWO-PIECE PLASTER MOLD USED TO CAST LARGE CRUCIBLES OF ZrB_2 .

Table 2

RELATIONSHIP BETWEEN THE CASTING RATE
AND THE PERCENTAGE OF
THE SUSPENDING MEDIUM
(3% CMC Solution)

Percent Liquid	Sintered Thickness ⁽¹⁾ (mm)
18	4.45
20	2.80
22	2.98
24	1.73

(1) Average of four measurements; casting time was one hour.

SLIP CASTING OF DIFFERENT SHAPES OF ZIRCONIUM DIBORIDE

The slip was poured into the prepared molds and kept there for a certain time, after which the excess slip was poured off (drain casting). Various shapes were drain cast from zirconium diboride slips with an 18 percent liquid (3% CMC) phase. The shape that proved the most difficult to cast was the large crucible (6" H x 6" D) shown in Figure 8. Because of the density of zirconium diboride (6.09 gms/cc), when the slip was drained from the mold by inversion of the mold, the cast piece released from the mold and collapsed. This action was prevented by tilting the mold at a low angle (about 30 degrees) and slowly rotating the mold (to ensure even draining). This formed a thin film of slip on the top surface of the mold which helped to prevent the cast piece from shrinking away from the walls of the mold too soon (before the strength had increased enough by drying to support the walls of the crucible). However, the piece shrank from the mold walls after about two hours, released, and collapsed. This problem was overcome by cutting a groove all the way around the interior of the mold about one inch from the top of the two-piece mold (the cavity of which was about 7" H). After the slip was drained, the cast piece was held up during drying by the grooved portion of the mold. Cracking usually occurred at the groove after the crucible dried for three to four hours. The crucibles were further air dried for about 20 hours, then dried at 50° C for 24 hours. Finally, the crucibles were leveled by using a coarse saw blade, and the talc layer (used for the mold release) was removed by rubbing with abrasive paper. The dried crucibles at first warped on sintering, which proved to be caused by lack of temperature uniformity within the hot zone of the carbon induction furnace. However, the problem was overcome by using a 1/4-inch-thick carbon crucible with the large zirconium diboride crucible placed inside of it, with a clearance of about 1/4 inch around the sides. The outer carbon crucible equalized the hot-zone temperature, resulting in a large crucible with no warpage when a sintering temperature of 1,700° C for one to two hours was used.

Heating the Mold and Slip

Preheating the slip and mold to 50° C increased the casting rate, but caused the formation of a "skin" on the surface of the slip, impairing the drained slip from further use.

Table 3

RELATIONSHIP BETWEEN THE CASTING RATE
AND TIME FOR ZIRCONIUM DIBORIDE
SLIPS WITH 18 AND 22 PERCENT
LIQUID (3% CMC) PHASE

Time (min)	Sintered Thickness (mm) ⁽¹⁾	
	18 Percent Liquid Phase	22 Percent Liquid Phase
15	2.03	1.25
30	2.93	1.50
45	3.68	1.88
60	4.00	2.25
75	4.40	2.80
90	4.80	2.35
105	3.78	2.70
120	4.68	2.18

(1) Average of four measurements.

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Figure 8. CRUCIBLES SLIP CAST FROM ZIRCONIUM DIBORIDE IN SIZES VARYING FROM MEDIUM TO LARGE.

For other shapes of zirconium diboride, sintering temperatures up to $1,950^{\circ}\text{C}$ for one hour could be used without warpage. Thus, the optimum sintering temperatures varied from $1,700$ to $1,950^{\circ}\text{C}$, depending on the size of the article to be sintered, with smaller sizes being sintered at the highest temperatures. Densities varied from 60 to 80 percent of theoretical (X ray). Sintering of zirconium diboride crucibles at $2,150^{\circ}\text{C}$ produced warping even with small crucibles. Dobrovolskii, et al, sintered small crucibles of zirconium diboride at $2,200^{\circ}\text{C}$ for 40 minutes. Apparently, these conditions were necessary for producing slip-cast crucibles with densities of 88 percent of theoretical.

A variety of shapes have been slip cast from zirconium diboride. Representative shapes can be seen in Figures 8 through 14. The Knudsen cells in Figure 9 were prepared by solid casting with a brass or aluminum mandrel defining the interior and the plaster mold defining the exterior. The bases were then prepared by abrasive paper.

SLIP CASTING OF OTHER BORON-CONTAINING COMPOUNDS

The method of slip casting was used for producing shapes of pure boron, boron carbide, chromium diboride, and a zirconium diboride-10 percent tungsten cermet. The liquid phase for each material was a three weight percent solution of CMC and varied from 18 to 48 percent liquid content depending on the material (B - 48%; B_4C - 40%; CrB_2 - 23%; ZrB_2 -10% W - 18%). Crucibles from each of these materials were sintered in argon at $1,950^{\circ}\text{C}$ for one hour. All were strong, well-sintered parts, including the pure boron and

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Figure 9. KNUDSEN CELLS OF ZIRCONIUM DIBORIDE FOR VAPORIZATION STUDIES. (Cell on Far Left is a Commercial Carbon Knudsen Cell Used for Comparison)

136225

Figure 10. SLIP-CAST CONES OF ZIRCONIUM DIBORIDE.

136223

Figure 11. ARTICLES SHOWING THE POSSIBILITY OF CASTING COMPLEX SHAPES OF ZIRCONIUM DIBORIDE.

136220

Figure 12. BOATS AND CONTAINERS SLIP CAST FROM ZIRCONIUM DIBORIDE.

136226

Figure 13. TRAYS SLIP CAST FROM ZIRCONIUM DIBORIDE.

136221

Figure 14. SMALL CRUCIBLES AND VARIOUS SHAPES OF ZIRCONIUM DIBORIDE.

boron carbide shapes which were considered very hard to sinter without hot-pressing techniques. The densities varied with the materials (B - 45%; B₄C - 51%; CrB₂ - 75%; ZrB₂-10% W - 60% of theoretical).

Since hafnium diboride (HfB₂) has a higher melting point than zirconium diboride, an investigation of the slip casting of crucibles of HfB₂ was undertaken. Commercial HfB₂ (- 325 mesh) was ground in an argon fluid energy mill until it could be passed through a 500-mesh (25 micron) screen (analysis showed 50% < 4.5 microns; 90% < 12.8 microns). The viscosity relationship with respect to the content of suspending medium (3%-CMC solution) is shown in Figure 15, where it is seen that the shape of the curve is quite similar to that of ZrB₂ (Figure 2). Drain casting small crucibles proved to be very difficult because of slumping. Presumably, this was caused by the increased density of HfB₂ (10.5 gms/cc) compared to ZrB₂ (6.09 gms/cc). However, no settling of the slip occurred, making the viscosity measurements possible. Knudsen cells were successfully prepared (as with ZrB₂) by solid casting a slip with a solid-liquid ratio of 85:15 and were sintered at 2,150° C for one hour.

Figure 15. DEPENDENCE OF THE VISCOSITY OF THE SLIP ON THE CONTENT OF THE LIQUID PHASE FOR HAFNIUM DIBORIDE.