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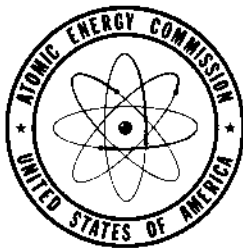
CRUCIBLE HANDBOOK

A Compilation of Data on Crucibles Used for
Calcining, Sintering, Melting, and Casting

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CRUCIBLE HANDBOOK

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INTRODUCTION

Personnel in the atomic energy program are confronted at times with an immediate need for information concerning the properties of commercially available nonmetallic crucibles. Some of the information is unavailable to the casual worker, and the published portion is widely scattered throughout the literature.

Since nonmetallic crucibles are usually ceramic,

the ORNL Ceramic group felt that a valuable contribution could be made by compiling information from both published and unpublished sources in a form that would enable the casual worker to ascertain readily the type of crucible best suited to his needs and to find a source of supply on the market for each type. In addition, forming methods are presented to aid those who may wish to fabricate their own crucibles.

FABRICATION OF CERAMIC CRUCIBLES

Ceramic raw materials are obtained mostly as powders or grains from which crucibles are produced generally by a forming procedure at room temperature followed by a high-temperature treatment to produce strength. Principal forming methods requiring this procedure are jiggering, extruding, ramming, dry-pressing, and slip-casting. Another procedure combines forming and heating in one operation and is called "hot-pressing."

JIGGERING

Jiggering is an adaptation of the potter's-wheel method of forming and consists in forcing the moist ceramic composition against the inside of a rotating mold by means of a stationary jigger tool. The mold is usually made of plaster of paris, although steel or wooden molds are employed in some cases. Jiggering is useful in forming circular products in which a high degree of uniformity in structure and low porosity are not essential. It permits the use of coarse-grained raw materials, which, in some cases, add to the resistance of the crucible to cracking during rapid temperature changes. A certain degree of plasticity in the composition is desirable, and the process lends itself more readily to the forming of ware containing plastic clay than to ware containing only nonplastic ceramic materials.

EXTRUDING

Extruding consists in forcing a column of the moistened material through a die. It is especially adapted to the production of rods and tubes, rather

than to the making of crucibles, although extruded rods are sometimes cut into sections and machined into crucibles in the moist, dry, or fired state. The need for a special steel die for each different shape makes this process rather inflexible. A plastic mixture is desirable, and some degree of plasticity can be given to nonplastic materials by fine grinding, by deairing, and by adding plasticizers and lubricants. The extruded product usually has medium-to-high porosity and rather uniform texture.

RAMMING

Ramming is a method in which a moistened composition is tamped by hand or with an air hammer between the wall of a mold and a core. The mold and core may be made of plaster, wood, or steel; steel is preferable since coarse grains in the ceramic mixture tend to embed themselves in softer mold materials and make removal of the crucible difficult. Ramming is particularly adapted to the forming of tubes or crucibles of round or irregular shapes and for compositions of low plasticity and coarse grain sizing. Binders such as starch or resins from paper wastes (such as Goulac) are usually added to give dry strength to the crucible. Coarse grain sizing generally increases the resistance of the fired crucible to rapid temperature changes; consequently, ramming is probably the method best suited for forming heat- and shock-resistant crucibles of nonplastic materials. However, it requires a separate mold for each shape and therefore is rather inflexible. Also, uniform

density and low porosity cannot be expected in rammed crucibles because of the nature of the procedure and the compositions used.

DRY-PRESSING

Dry-pressing is a procedure in which a powdered mixture of the desired composition is dampened with a suitable liquid and formed in a mold, usually of steel, under mechanical or hydraulic pressure. This method is suitable for forming compositions of low-to-medium plasticity and fine-to-medium grain sizing. It would be used more often for producing high-temperature crucibles, except that a carefully machined and therefore costly steel mold for each size and shape is required. Uniform density is difficult to attain by dry-pressing, since a higher density is produced nearer the moving portions of the mold. Furthermore, lamination cracks from entrapped air are often encountered.

SLIP-CASTING

Slip-casting is probably the most readily adaptable method for the casual forming of nonplastic crucibles. This method of fabrication depends upon the ability of plaster of paris molds to extract the liquid from a suspension, leaving the solid particles as a coating on the mold. The general procedure consists in pouring a slip of about the consistency of gravy into the plaster mold, which immediately begins to absorb water and to build up a coating of the solid particles. As soon as the coating has attained the desired thickness, the remaining slip is poured from the mold, leaving the center hollow. A solid casting can be made by continually adding the slip as the water is absorbed until the entire cavity in the mold is filled with the dewatered composition. If the original slip was in the proper state of deflocculation, the casting will shrink away from the mold in a short time and can then be removed. To be successful, slip-casting

requires a mold of the proper shape and character and a properly deflocculated slip.

Mold

The proper method of mold making is described in books on pottery making and in literature available from the manufacturers of plaster of paris (Table 1). Figure 1 shows the properties obtained by various plaster-water mixtures.

Deflocculation

A fundamental requirement for good slip-casting behavior is a proper degree of deflocculation, a term that denotes a rather stable suspension of solid particles in a liquid medium. Deflocculation is frequently accompanied by a slowing down of the rate of absorption of the liquid by the mold and by a thinning (lowered viscosity) of the slip. These effects favor easier casting by prolonging the casting time (which is rather short in the case of most nonplastic materials) and by permitting efficient draining of the excess slip from the mold to form smooth inner surfaces in the case piece.

Deflocculation is attained by the presence (usually in fractions of a per cent) of a soluble, ionizable dispersing agent that may be either a base, an acid, or a salt. Dispersing action is ascribed to the adsorption upon the surfaces of the solid particles of a layer of oriented molecules of the electrolyte to form a charged sheath. The solid particles being thus similarly charged repel each other, and any tendency toward coalescing and settling is inhibited. In addition, the charged surfaces attract a layer of liquid about each particle, which provides lubrication and free flowing of the suspension.

Characteristics of a well-deflocculated suspension are a slow settling rate, low viscosity, slow rate of absorption of liquid from the slip by the mold, good green strength, high density, minimum shrinkage and less cracking of the piece

TABLE 1. SUPPLIERS OF PLASTER OF PARIS

B. F. Drakenfeld, Inc., 45-47 Park Place, New York 7, N. Y.
Certain-Teed Products Co., 120 South La Salle Street, Chicago, Ill.
Harrop Ceramic Service, Inc., Pearl Street at Gay, Columbus 15, Ohio
National Gypsum Co., Buffalo, N. Y.
The O. Hammel Co., Pittsburgh 30, Pa.
United States Gypsum Co., 300 West Adams Street, Chicago 6, Ill.

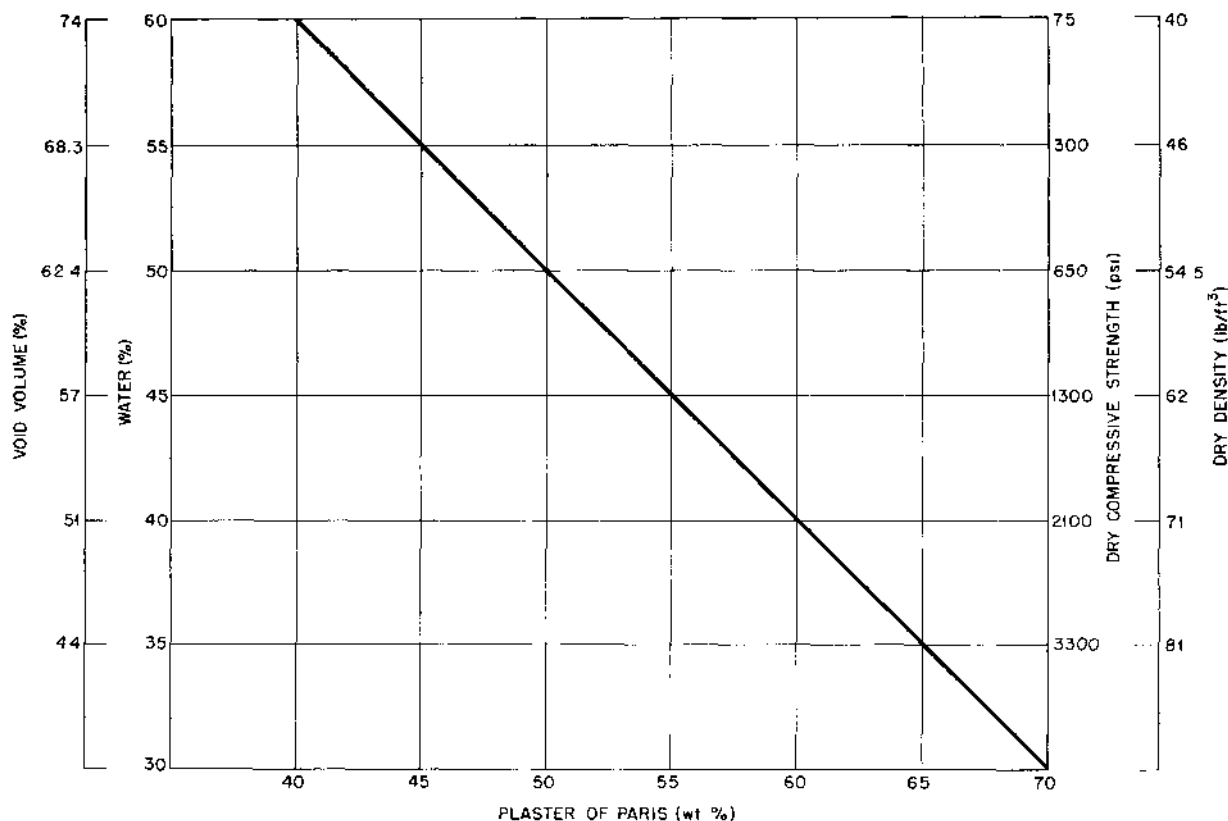


Fig. 1. Effect of Varying Plaster of Paris-Water Mixtures on Properties of the Mold.

in drying, and less tendency of the piece to stick to the mold. Underdeflocculation or overdeflocculation usually have the opposite effects.

Adsorption of the dispersing agent by the solid phase is a surface phenomenon, and proper deflocculation requires that the proportion of surface to volume of the solid shall be extremely high. Plastic clays usually break down readily to fine particles that are plate-shaped and thus are easily deflocculated. In the case of nonplastic materials, the particles are normally not plate-shaped, and fine sizing must be obtained by milling. An average particle size of 3 to 5 μ is usually sufficient for good deflocculation; finer sizing may be desirable in certain cases but is usually attained at the risk of undue contamination from the milling apparatus.

The principal acidic deflocculating agents are the common inorganic acids, which have these valuable properties: (1) they are effective over a rather wide range of concentration compared with basic deflocculants in general, and (2) they volatilize during the firing of the refractory and

leave no deleterious substance in the crucible. Their unfavorable characteristics are: (1) a long period of soaking the nonmetallic material in the acid is usually required; (2) the smooth surfaces of the plaster mold are attacked by the acid, which makes them rough and unusable after three or four castings; and (3) the acid fumes are rather unpleasant to work with.

Basic deflocculants have not been so widely used in the casting of nonmetallic substances, although they have these advantages over the acids: (1) their deflocculating effect takes place almost immediately without prolonged soaking; (2) they do not attack gypsum molds; and (3) they are not unpleasant to work with in most cases. Disadvantages of basic deflocculants are: (1) a rather critical range of concentrations for good deflocculation, and (2) the possibility of contributing to the fired ware a nonvolatile element such as sodium or potassium that may be deleterious, although only 0.1% of dry weight or less is normally present. The basic deflocculants most used are the hydroxides, carbonates, phosphates,

silicates, and organic salts of sodium, potassium, and ammonia. Sometimes mixtures of these are recommended.

The choice of a deflocculant for a given casting application depends, in part, upon the nature of the solid material. Thus, sodium carbonate, which is effective in the case of clay slips, will seldom deflocculate nonplastic materials. Tetrasodium pyrophosphate is effective when used with zircon but is less so with zirconia. Alumina is usually deflocculated with acid, although tetrasodium pyrophosphate has been used successfully with alumina, also.

A water suspension is sometimes inadvisable, as in the casting of CaO crucibles, in which case other liquids such as absolute alcohol, kerosene, or carbon tetrachloride may be used. However, most dispersing agents are not ionized in these liquids, and choice of an effective deflocculant is somewhat of a problem.

HOT-PRESSING

Hot-pressing consists in compressing a ceramic material while it is at a temperature high enough

to permit it to sinter. Very dense and accurately shaped products can be produced by this procedure; it is especially suited to induction heating and to the production of shapes from carbides, nitrides, sulfides, and other easily oxidizable materials, as well as to oxides.

The maximum size of test piece obtainable is limited to about 4 in. in diameter and the maximum pressure to 3000 to 4000 psi; the limitation is due to the low strength of the graphite molds employed. Graphite is used because it is practically the only mold material that is abundant and stable at the high temperatures required (1400 to 2200°C), and it has an advantage in being electrically conductive so that the mold can act as susceptor in induction heating or as resistor. Unfavorable properties are a short mold life of 1 to 3 cycles and a tendency to reduce oxides and to form carbides.

Hot-pressing equipment is costly by reason of the expensive, electrical apparatus required; the hot-pressing procedure is therefore limited to work with expensive raw materials and to those that cannot be fabricated by other methods.

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COMPOSITION OF CRUCIBLES USED FOR MELTING METALS

METAL	CRUCIBLE MATERIALS	REMARKS	REFERENCES	METAL	CRUCIBLE MATERIALS	REMARKS	REFERENCES	METAL	CRUCIBLE MATERIALS	REMARKS	REFERENCES
Alkali metals	Refractory sulfides* Single crystal MgO		1	Iron	Magnesium oxide Beryllium oxide Aluminum oxide Zircon Fire clay Thorium oxide Refractory sulfides	For extremely pure iron, beryllia or thorina is best	1, 10, 11, 12	Steel	Magnesium oxide Silica	Basic steels are melted in magnesium, and acidic steels are melted in silica	9
Alkaline earth metals	Refractory sulfides		1					Thorium	Cerium sulfide Thorium sulfide Titanium nitride Thorium oxide Zirconium nitride	The metal sticks to the sulfide crucibles	6, 10
Aluminum	Zircon Zirconia Graphite Clay-graphite Refractory sulfides Fire clay (dense)	There is least contamination with zircon	1, 2	Lead	Iron Chromite Magnesium oxide Fire clay (dense)		5, 13	Tin	Magnesium oxide Iron Cerium sulfide Thorium sulfide Fire clay		1
Beryllium	Beryllium oxide Graphite Refractory sulfides	Melting must be conducted in a vacuum	3	Magnesium	Steel plate coated with aluminum Heat-treated mixture of 10 to 60% ZnO ₂ 7 to 25% MgO 30 to 80% Al ₂ O ₃ Cerium sulfide Thorium sulfide	The steel plate should be sand-blasted before spraying and heat-treated after spraying	6, 9, 14	Titanium	Cerium sulfide Thorium oxide Barium sulfide Thorium sulfide	Titanium sticks to the sulfide crucibles. There is slight attack of the thorina; melting is accomplished in either a vacuum or an argon atmosphere	1, 6, 18, 19
Bismuth	Cerium sulfide Thorium sulfide		1					Uranium	Magnesium oxide Calcium oxide Cerium sulfide Titanium nitride Zirconium nitride Thorium oxide Thorium sulfide Graphite Nickel		6, 10
Boron	Boron nitride		4	Manganese	Aluminum oxide Magnesium oxide Thorium oxide	The metal should be pure, since a manganese-rich alloy will pick up silica	7				
Brass	Magnesium oxide Graphite Clay-graphite High-grade fire clay	Charcoal or fluxing material on surface of melt helps to reduce oxidation	5	Nickel	Zircon Magnesium oxide Mullite Fire clay (dense)	For melting pure nickel, zircon or magnesia in a vacuum is best	15, 16				
Cadmium	Titanium nitride Zirconium nitride Cerium sulfide Barium sulfide	Cerium sulfide crucibles resist attack better if the porosity is from 10 to 15%**	1, 6	Platinum	Thorium oxide Zirconium oxide Magnesium oxide Zircon	Also for platinum-rich alloys	9, 17				
Chromium	Aluminum oxide		7					Vanadium	Beryllium oxide Magnesium oxide Calcium oxide Aluminum oxide Titanium nitride	These materials were calculated to be suitable for containing molten vanadium	
Copper	Silica Magnesium oxide Aluminum oxide Clay-graphite		5, 8	Rare-earth metals	Refractory sulfides		1	Zinc	Iron Flint fire clay Cerium sulfide Thorium sulfide Clay-graphite		1
Gold	Magnesium oxide Aluminum oxide		9	Rhodium	Zirconium oxide		9				
Halide metals	Refractory sulfides		1	Silicon	Silica		7				
Iridium	Thorium oxide		9	Silver	Graphite Magnesium oxide Aluminum oxide		9	Zirconium	Zirconium oxide Thorium oxide		10

*The refractory sulfides include BaS, CaS, ThS, Ce₂S₃, Ca₂S₃, Th₂S₃, Th₄S₇, and ThS₂.

**Porosity is defined as the volume of air space expressed as percentage of the total volume of the piece.

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ALUMINA CRUCIBLES

TYPES

Clay-bonded

When neutral chemical conditions are required in the melting of metals, alumina crucibles are usually used. Acidity is increased and refractoriness decreased as the proportion of fused alumina is decreased by additions of plastic-bond clay. Clay-bonded alumina crucibles in standard sizes (see Table 2) are especially suited for the melting of steel and ferrous alloys in high-frequency induction furnaces, since they have good thermal shock qualities.

Fused alumina-bonded crucibles that have a silica content of 7 to 11%, such as Norton's* "Alundum" brand, have a pyrometric cone equivalent ranging from C/37 to C/40, 3310°F (1820°C)

to 3425°F (1885°C), and a porosity ranging from 35 to 50%.** Crucibles are available from $1\frac{3}{32}$ in. high by $1\frac{1}{16}$ in. top diameter to 6 in. high by 4 in. top diameter.

Recrystallized Alumina

A 99+% pure alumina powder is formed into crucibles that are heated under conditions that produce a growth of interlocking corundum crystals. A nearly impervious structure (with $0.2\pm\%$ porosity) is obtained that has excellent resistance to both acid and basic attack and is practically inert under varying furnace conditions.

Recrystallized alumina crucibles are suggested for use in high-frequency and vacuum melting of pure metals, including iron, chromium, manganese,

*See "List of Manufacturers."

**Porosity is defined as the volume of air space expressed as percentage of the total volume of the piece.

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TABLE 2. STANDARD SIZES OF INDUCTION FURNACE CRUCIBLES OF CLAY-BONDED ALUMINA, MAGNESIA, AND SILICA

NUMBER	HEIGHT (in.)	OUTSIDE TOP DIAMETER (in.)	OUTSIDE BOTTOM DIAMETER (in.)	CAPACITY (in. ³)
3-P $\frac{1}{2}$	$3\frac{3}{4}$	$1\frac{1}{8}$		2.1
3-P 1	$3\frac{1}{2}$	$1\frac{13}{16}$		5.9
3-P 2	$3\frac{1}{2}$	$2\frac{3}{8}$		10.0
3-L*	$5\frac{1}{2}$	$2\frac{3}{4}$		30.0
3-P 4	$4\frac{1}{8}$	3		20.0
5-L	6	$3\frac{3}{8}$		50.0
10	$7\frac{1}{8}$	$4\frac{3}{4}$	$3\frac{1}{2}$	52.0
12-L	7	$4\frac{1}{4}$		73.0
17-L	8	$4\frac{1}{2}$		87.0
30-L	$9\frac{3}{4}$	$5\frac{3}{4}$	$5\frac{1}{4}$	162.0
170-L	$9\frac{7}{8}$	7		242.0
171	11	$6\frac{1}{2}$		248.0
172-L	11	7		296.0
173	11	$7\frac{1}{2}$		347.0
304	5	$\frac{7}{8}$		1.5
305	$5\frac{3}{4}$	1		2.5
306	$5\frac{5}{8}$	$1\frac{3}{16}$		3.2
307	6	$1\frac{3}{8}$		4.4
308	8	2		13.0
309	8	$2\frac{3}{4}$		23.0
310	$8\frac{1}{2}$	3		39.0
311	10	4		77.0
312	10	5		135.0
313	$12\frac{3}{4}$	6		240.0
410-L	$10\frac{1}{2}$	$5\frac{3}{4}$	$5\frac{1}{4}$	160
509	$12\frac{1}{2}$	$8\frac{3}{4}$	$8\frac{1}{4}$	528

*“L” denotes lip.

TABLE 2 (continued)

NUMBER	HEIGHT (in.)	OUTSIDE TOP DIAMETER (in.)	OUTSIDE BOTTOM DIAMETER (in.)	CAPACITY (in. ³)
510	14½	9		700
512-L	16	9		775
513	13¾	9¾	9	625
515	15⅛	10½		920
529	16¾	12¼	11¾	1,360
H-529	18¾	12¼	11¾	1,480
532	14	12¼	11¾	1,028
545	18¾	14¼		1,945
564	19½	15¼	14	2,600
H-564	23	15¼	14	2,800
572	20½	16¼	14	2,476
576-L	22	16		2,700
580-L	26	19		4,420
601	22½	20	17	4,008
602	22⅛	20		5,570
701	34	25	22	11,250
702	49	34		32,820
703	32	23½		8,280

boron, and germanium; melting special glasses requiring a silica-free crucible; fusing inorganic charges high in alkalis, fluorides, or other halides; and producing fluorescent powders such as phosphates and silicides of zinc, magnesium, or beryllium.

Crucibles are available in standard sizes in three main shapes: A-shape, cylindrical, and conical (see Table 3).

FABRICATION OF ALUMINA CRUCIBLES

Slip-Casting

Raw Materials. Alundum No. 38 (-220 mesh) or any other good grade of fused powdered alumina is satisfactory in slip-casting.

Grinding. When the alumina is coarser than 3 to 5 μ , it will probably need milling to be cast

successfully. An alumina-lined mill with alumina balls is preferable if contamination is to be avoided. Iron balls in an iron mill have been used; the iron contamination is subsequently removed by means of a magnetic separator, after which it is leached by acid. Thus, 1 kg of Alundum No. 38 was milled dry for 32 hr in an iron mill of 1-gal capacity that contained 10 kg of iron balls. Two liters of water was added to the powder, and this suspension was passed 25 times through a magnetic separator. Then 200 ml of concentrated HCl was added, and the slip was stirred for 8 hours. After filtering and washing, the suspension was brought to the proper pH according to Table 4 by adding HCl or tetramethylammonium hydroxide and to the proper specific gravity by siphoning off a portion of the supernatant water.

Casting. The usual casting technique is used (cf. "Fabrication of Ceramic Crucibles," this report).

TABLE 3. STOCK SIZES OF CYLINDRICAL RECRYSTALLIZED ALUMINA CRUCIBLES*

DIAMETER (in.)	HEIGHT (in.)	CAPACITY (cc)
$1\frac{1}{16}$	1	5
$\frac{7}{8}$	$1\frac{5}{16}$	10
1	$1\frac{9}{16}$	20
$1\frac{7}{32}$	$1\frac{7}{32}$	20
$1\frac{3}{8}$	$2\frac{1}{2}$	50
$1\frac{7}{16}$	$1\frac{3}{8}$	65
$1\frac{5}{8}$	$3\frac{1}{2}$	95
$1\frac{1}{2}$	$3\frac{9}{16}$	100
$1\frac{17}{32}$	$3\frac{15}{16}$	100
$2\frac{1}{8}$	$3\frac{9}{16}$	175
$2\frac{5}{16}$	$4\frac{3}{32}$	250

*See 13 and 15, "List of Manufacturers."

Drying. Small crucibles should be air-dried overnight; large crucibles should be dried slowly in a dryer.

Firing. Crucibles should be fired at 1750 to 1800°C for 5 hr, either in an induction furnace or an oxypropane kiln.

Properties. Slip-cast alumina crucibles have a total shrinkage of 15%, with apparent porosities of 1 to 3%.

Dry-Pressing

The procedure outlined for dry-pressing beryllia may be followed (cf. "Fabrication of Beryllia Crucibles," this report).

Manufacturers*

Clay-bonded, Fused Alumina Crucibles. Bartley (3), Dixon (12), Electro (10), Massilon (14), Mullite (16), Norton (19), Remmey (20).

Recrystallized Alumina. Laboratory Equipment (13), Morganite (15), Remmey (20).

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*See "List of Manufacturers" for complete names and addresses.

TABLE 4. RELATIONSHIP OF pH AND SPECIFIC GRAVITY TO CASTING PROPERTIES OF ALUMINA SUSPENSIONS

	DRAIN-CAST PROPERTIES			SOLID-CAST PROPERTIES	
	Rapid Release	Medium Release	Slow Release	Rapid Cast	Slow Cast
High Density					
pH	2.95	5.30 to 12.4	4.40 to 12.0	2.95 to 12.4	
Specific gravity	3.0	2.8	2.8	3.0	
Low Density					
pH	6.05 to 10.4			6.05 to 10.75	4.6
Specific gravity	2.8 to 2.6			2.8 to 2.6	2.6

BERYLLIUM OXIDE CRUCIBLES

TYPES

Beryllia

Beryllia is one of the most stable refractory materials and is used for making crucibles that are employed particularly in the melting of pure metals and alloys. It can be used at temperatures close to its melting point, which is over 4530°F (2500°C); it is especially adaptable for use in high-frequency heating. It is claimed to be somewhat volatile in the presence of water vapor at temperatures above 3270°F (1800°C). Beryllia has excellent thermal shock properties and high thermal conductivity and can be fabricated into crucibles that have almost no porosity.

Beryllia crucibles may be used in either oxidizing, reducing, or neutral atmospheres, but they react readily with such oxides as magnesia, calcia, alumina, and silica to form less refractory compounds.

Beryllium oxide powder is considered to be a toxic material, and specific precautions must be taken in its use.

Table 5 lists the standard-size crucibles available on the market.

FABRICATION OF BERYLLIA CRUCIBLES

Dry-Pressing

Raw Materials. Refractory-grade, finely divided beryllia is required for dry-pressing. When the material is c.p. grade or low-fired material, it can be calcined to above 1500°C to make it acceptable.

Grinding. The beryllia is ball-milled to pass a 200-mesh screen, with 14% by weight of phenol-formaldehyde resin and 1% of hexamethylenetetramine added to accelerate curing and act as a lubricant. (Resinox 615, available from Monsanto Chemicals Co., and Bakelite BR-2428 are equivalent resins.) A typical mill charge is: 700 g of beryllia, 104 g of powdered resin, 9.8 g of hexamethylenetetramine, and 4000 g of 1.5-in. Porox balls. After grinding, 21% water that contains a small amount of wetting agent is added and mixed in by hand; this is followed by granulation through a 14-mesh screen. The batch is then dried at 60°C.

Paraffin also makes an effective binder and lubricant. It is added by means of a 20% solution in CCl_4 to the dry-ground beryllia and worked in by hand. Enough solution is added so that the

paraffin is 5 to 10% of the weight of the beryllia. After the CCl_4 has been thoroughly evaporated, the batch is pelletized by forcing it through a 14-mesh screen.

Pressing. The beryllia containing the binder is pressed at 30,000 to 40,000 psi. During the pressing of the resin-lubricated material, the die is uniformly heated to 150 to 155°C. When this heating is not uniform, the pressed material sticks to the die on removal.

Firing. The crucibles are fired to 1950°C by induction-heating in air. A recrystallization appears to take place that causes the ware heated to 1950°C to be much more resistant to attack at higher temperatures than that heated only to 1900°C or less.

Properties. Crucibles with a total shrinkage of 14.5 to 16.5% and densities of about 2.7 are obtained by this procedure.

Slip-Casting

Raw Materials. A refractory-grade, -325 mesh beryllia is preferable for the preparation of crucibles. When a commercial c.p. grade or low-fired material is used, it must be calcined to above 1500°C before milling.

Grinding. When the refractory-grade material is used, the milling is merely to prevent lump formation; about 2 hr is sufficient. However, the calcined material is too coarse to pass a 325-mesh screen, and it must be ground in a steel-ball mill until it can pass such a screen. About 25 hr of grinding, either wet or dry, is usually required to reduce the calcined material to the necessary particle size.

Preparation of Slip. The metal picked up during the grinding operation can be removed with a 10% solution of HCl in two or three leachings, or until the supernatant liquid no longer shows the iron color. The acid is then washed out with distilled water; two or three washings are usually sufficient. On the final wash, the pH should be adjusted to between 4.5 and 5.0, the slip should be allowed to settle, and the supernatant liquid decanted until the specific gravity is about 2.0.

Casting. The usual drain-casting technique is employed, and care is taken that no air is entrapped when the slip is being poured into the plaster mold.

Drying. The green pieces are air-dried overnight.

Firing. The crucibles are fired to 1800°C in either an oxypropane kiln or an induction furnace.

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TABLE 5. STOCK SIZES OF BERYLLIA CRUCIBLES*

NUMBER	OUTSIDE DIAMETER (in.)	INSIDE DIAMETER (in.)	OUTSIDE HEIGHT (in.)	INSIDE HEIGHT (in.)
X-1A	$1\frac{3}{8}$	1	$1\frac{3}{4}$	$1\frac{1}{2}$
X-1B	$1\frac{1}{2}$	$1\frac{1}{8}$	$1\frac{3}{4}$	$1\frac{1}{2}$
X-2A	$1\frac{1}{2}$	$1\frac{1}{8}$	$2\frac{3}{4}$	$2\frac{1}{2}$
X-8A	$2\frac{3}{8}$	$1\frac{3}{4}$	$3\frac{13}{16}$	$3\frac{1}{2}$
X-8B	$1\frac{7}{8}$	$1\frac{5}{8}$	5	$4\frac{5}{8}$
X-12A	$2\frac{9}{16}$	2	$4\frac{1}{4}$	4
X-13A	2	$1\frac{3}{4}$	6	$5\frac{13}{16}$
X-14A	2	$1\frac{5}{8}$	7	$6\frac{11}{16}$
X-17A	$2\frac{9}{16}$	$2\frac{3}{32}$	$5\frac{1}{2}$	$5\frac{1}{8}$
X-28A	$2\frac{1}{2}$	2	$8\frac{1}{4}$	$7\frac{3}{4}$
X-33A	$3\frac{3}{8}$	$2\frac{3}{4}$	6	$5\frac{11}{16}$
X-39A	$2\frac{15}{16}$	$2\frac{9}{16}$	8	$7\frac{3}{4}$
X-44A	$4\frac{1}{2}$	$3\frac{3}{4}$	$4\frac{3}{8}$	4
X-47A	$2\frac{15}{16}$	$2\frac{9}{16}$	10	$9\frac{3}{4}$
X-49A	$3\frac{7}{8}$	$3\frac{5}{16}$	$5\frac{15}{16}$	$5\frac{1}{2}$
X-89A	4	$3\frac{7}{16}$	9	$8\frac{1}{4}$
X-130A	5	$4\frac{1}{8}$ to $4\frac{1}{4}$	$10\frac{1}{4}$	$9\frac{1}{2}$
X-157A	$5\frac{3}{8}$	$4\frac{7}{8}$	$8\frac{7}{8}$	$8\frac{3}{8}$
X-250A	7	6	12	11
X-405A	$7\frac{3}{4}$	$7\frac{1}{8}$	12	11
X-425A	$7\frac{1}{2}$	$6\frac{7}{8}$ to 7	12	$11\frac{1}{4}$
X-590A	$9\frac{3}{4}$	$8\frac{1}{2}$	$11\frac{1}{2}$	$10\frac{1}{2}$
X-670A	$8\frac{1}{2}$	$7\frac{1}{4}$ to $7\frac{1}{2}$	16	$15\frac{1}{4}$
X-1000A	10	9	16	15
X-1500A	$11\frac{1}{2}$	$10\frac{3}{8}$	$19\frac{1}{2}$	$18\frac{1}{2}$
X-2000A	12	11	23	22
X-2700A	$14\frac{1}{4}$	$13\frac{1}{4}$	21	20

*Brush (4).

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Properties. Beryllia crucibles prepared by this method can be expected to have a total shrinkage of 14% and an apparent porosity of about 1%. Generally they are white, hard, and emit a bell-like tone when struck.

Manufacturers

Beryllia Crucibles. Brush (4), Massilon (14), Norton (19).

References

J. G. Thompson and M. W. Mallett, "Preparation of Crucibles from Special Refractories by Slip

Casting," RP1236, *J. Research Natl. Bur. Standards* 23, 319 (1939).

J. L. Utter, *Slip-Casting of Non-Plastic Refractory Materials*, CT-3371.

A. R. Kaufmann and E. Gordon, "Vacuum Melting and Casting of Beryllium," *Metal Progress* 52, 387 (1947).

H. B. Barlett, *Note on the Preparation of Small Dense Beryllia Crucibles*, AECD-2170 (July 28, 1948).

GRAPHITE CRUCIBLES

TYPES

Carbon-bonded

Graphite crucibles are not often obtainable in the carbon-bonded form, but they can be readily machined from graphite stock or electrodes that are pure carbon. As an example of the electrode-forming process, a mixture of coke flour and pitch or tar to serve as a binder is extruded or molded into form and is then baked in gas- or oil-fired furnaces at 1500 to 2000°F. At this stage, the crucibles are designated as "carbon" electrodes. Graphitization is accomplished by direct-resistance furnace heating to 4000°F for several days, which is followed by slow cooling. The two furnace operations require a total of 12 to 16 weeks for completion.

Outstanding among the properties of graphite electrode stock are its high purity, high heat conductivity, ability to withstand rapid heating and cooling without shattering, electrical conductivity, and inertness to most molten materials. The electrode material normally has 29 to 30% porosity and a density of 1.5 to 1.7 (true density of graphite is 2.21 to 2.25). The chief defects are the affinity of carbon for oxygen and the tendency to reduce oxides and form carbides, the tendency of carbon to enter molten materials to form either mechanical mixtures or solid solutions, and the low resistance of the material to erosion and abrasion. Graphite begins to oxidize at about 500°C.

Clay-bonded

Clay-bonded graphite crucibles are formed by jiggering a composition of about 40% by weight of Madagascar flake graphite with a bonding mixture

that consists of plastic fire clay, silica, silicon carbide, and feldspar. The flake graphite imparts exceptional resistance to stresses from temperature and mechanical handling, increases the thermal conductivity of the body, and contributes to the resistance to molten metals. The graphite is protected from oxidation in firing and in use by a silicate glaze that is formed on the outside surface of the crucible as it is fired. In this operation, a temperature of 1200°C and a reducing atmosphere are employed. These crucibles are available in various shapes and capacities ranging from a few ounces to several hundred pounds of molten metal (see Table 6).

The following limitations in the use of clay-bonded graphite crucibles should be observed: (1) In oxidizing furnace atmospheres the graphite tends to burn out, particularly on the unglazed edges, which results in crucible failure. (2) The graphite imparts a certain degree of electrical conductance. (3) The clay bond is rather soft and porous and is attacked by strong alkalies and fluorides. (4) The clay bond tends to rehydrate and crumble in the presence of moisture. (5) Carbon and silicates may be contributed to the charge. (6) Maximum temperature is limited to 1200°C.

FABRICATION OF GRAPHITE CRUCIBLES

Dry-Pressing

Powdered graphite, lampblack, or charcoal is mixed with powdered coal-tar pitch in the proportion of 3 parts of carbon to 1 part of pitch, and the mixture is blended with gum tragacanth and water to form a thick paste. Other binders that

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TABLE 6. STANDARD SIZES OF GRAPHITE AND SILICON CARBIDE CRUCIBLES

NUMBER	HEIGHT (in.)	TOP (in.)	BILGE (in.)	BOTTOM (in.)	APPROXIMATE CAPACITY* (lb of water)
0000	$2\frac{15}{16}$	$2\frac{3}{8}$	$2\frac{3}{8}$	$1\frac{3}{4}$	0.25
1	$3\frac{5}{8}$	$3\frac{1}{4}$	$3\frac{1}{8}$	$2\frac{1}{4}$	0.50
2	$4\frac{1}{2}$	$3\frac{3}{4}$	$3\frac{1}{2}$	$2\frac{7}{8}$	0.75
3	$5\frac{3}{8}$	$4\frac{1}{4}$	$4\frac{1}{8}$	3	1.0
4	$5\frac{3}{4}$	$4\frac{5}{8}$	$4\frac{9}{16}$	$3\frac{1}{8}$	1.50
6	$6\frac{1}{2}$	$5\frac{1}{4}$	$5\frac{1}{4}$	$3\frac{7}{8}$	2.25
8	$7\frac{1}{8}$	$5\frac{7}{8}$	$5\frac{7}{8}$	$4\frac{1}{4}$	3.0
10	$8\frac{1}{16}$	$6\frac{1}{16}$	$6\frac{9}{16}$	$4\frac{13}{16}$	4.8
12	$8\frac{1}{2}$	$6\frac{3}{8}$	$6\frac{7}{8}$	$5\frac{1}{16}$	5.6
14	$8\frac{7}{8}$	$6\frac{11}{16}$	$7\frac{3}{16}$	$5\frac{1}{4}$	6.4
16	$9\frac{1}{4}$	$6\frac{15}{16}$	$7\frac{1}{2}$	$5\frac{1}{2}$	7.2
18	$9\frac{13}{16}$	$7\frac{5}{16}$	$7\frac{15}{16}$	$5\frac{13}{16}$	8.6
20	$10\frac{5}{16}$	$7\frac{11}{16}$	$8\frac{3}{8}$	$6\frac{1}{8}$	10
25	$10\frac{15}{16}$	$8\frac{3}{16}$	$8\frac{7}{8}$	$6\frac{1}{2}$	12
30	$11\frac{1}{2}$	$8\frac{5}{8}$	$9\frac{5}{16}$	$6\frac{13}{16}$	14
35	12	9	$9\frac{3}{4}$	$7\frac{1}{8}$	16
40	$12\frac{1}{2}$	$9\frac{3}{8}$	$10\frac{1}{8}$	$7\frac{7}{16}$	18
45	$13\frac{3}{16}$	$9\frac{7}{8}$	$10\frac{11}{16}$	$7\frac{13}{16}$	21
50	$13\frac{3}{4}$	$10\frac{1}{4}$	$11\frac{1}{8}$	$8\frac{1}{8}$	24
60	$14\frac{7}{16}$	$10\frac{13}{16}$	$11\frac{11}{16}$	$8\frac{9}{16}$	28
70	$15\frac{1}{16}$	$11\frac{1}{4}$	$12\frac{3}{16}$	$8\frac{15}{16}$	32
80	$15\frac{5}{8}$	$11\frac{11}{16}$	$12\frac{11}{16}$	$9\frac{1}{4}$	36
90	$16\frac{3}{16}$	$12\frac{1}{8}$	$13\frac{1}{8}$	$9\frac{9}{16}$	40
100	$16\frac{11}{16}$	$12\frac{1}{2}$	$13\frac{1}{2}$	$9\frac{7}{8}$	44
125	$17\frac{3}{8}$	13	$14\frac{1}{16}$	$10\frac{5}{16}$	50
150	$18\frac{3}{8}$	$13\frac{3}{4}$	$14\frac{7}{8}$	$10\frac{7}{8}$	60
175	$19\frac{1}{4}$	$14\frac{3}{8}$	$15\frac{9}{16}$	$11\frac{3}{8}$	70
200	20	15	$16\frac{1}{4}$	$11\frac{7}{8}$	80

*1 lb of water = 0.96 pt or 27.7 in.³. Dimensions are outside measurements.

Note: Tilting furnace crucibles are furnished with a long lip.

TABLE 6 (continued)

NUMBER	HEIGHT (in.)	TOP (in.)	BILGE (in.)	BOTTOM (in.)	APPROXIMATE CAPACITY* (lb of water)
225	20 $\frac{3}{4}$	15 $\frac{1}{2}$	16 $\frac{13}{16}$	12 $\frac{5}{16}$	90
250	21 $\frac{3}{8}$	16	17 $\frac{5}{16}$	12 $\frac{11}{16}$	100
275	22	16 $\frac{7}{16}$	17 $\frac{13}{16}$	13	110
300	22 $\frac{1}{2}$	16 $\frac{7}{8}$	18 $\frac{1}{4}$	13 $\frac{3}{8}$	120
400	24 $\frac{5}{16}$	18 $\frac{3}{16}$	19 $\frac{11}{16}$	14 $\frac{7}{16}$	160

*1 lb of water = 0.96 pt or 27.7 in.³. Dimensions are outside measurements.

Note: Tilting furnace crucibles are furnished with a long lip.

soften and become adhesive at 100 to 300°C such as coal tar, asphalt, or rosin may be used. Crucibles are pressed from the paste and these are heated at red heat in a reducing atmosphere, whereupon the binder is fused, the volatiles are driven off, and the pitch is coked.

Manufacturers

Graphite Electrode Stock. National Carbon (17).

Clay-Bonded Graphite Crucibles. American Crucible (1), Bartley (3), Dixon (12), Massilon (14), National Crucible (18), Vesuvius (24).

References

H. A. Wilhelm and P. S. Gerald, *Carbon Crucibles*, U. S. Pat. 2,521,495 (September 1950).

MAGNESIA CRUCIBLES

TYPES

Clay-bonded

Magnesia crucibles are suggested for use where basic conditions exist, such as in the induction-melting of steels. The magnesia content may range from 83 to 97% and the porosity from 15 to 20%. Manufacturers specify that crucibles of lower magnesia content may be used up to 3630°F (2000°C), whereas those of higher magnesia content, containing electrically fused magnesia, may be used up to 4530°F (2500°C), depending upon their application. However, magnesia is sensitive to any type of reducing conditions and requires a strong oxidizing atmosphere above 3090°F (1700°C) to minimize its tendency to volatilize, which is considerable in a vacuum at temperatures above 2000°C. Standard-size crucibles suitable for induction-furnace use are listed in Table 2.

FABRICATION OF MAGNESIA CRUCIBLES

Dry-Pressing of Fine-grained Magnesia

Raw Materials. Fused magnesia from General Electric Co., c.p. grade, heavy-calcined magnesia supplied by Mallinckrodt Chemical Works, and White Seal Periclase, -200 mesh, from the Vitre-frax Corp. are suitable materials for dry-pressing. When a crucible with a silica content of less than 2% is desired, the G-E product is "diluted" with the c.p. grade material and calcined to 1300°C; a 1:1 mixture lowers the silica content sufficiently and also makes a satisfactory working body.

Grinding. It is not necessary for the -200 mesh magnesia to be ground. The 1:1 mixture of fused and c.p. material is ground for 15 hr in a mill with Porox balls and 95% ethyl alcohol. The silica pickup in this operation is about 1%.

Preparation for Pressing. After grinding, the material is dried during constant stirring at 105 to 110°C. It is important that all alcohol be evaporated. The material is forced through a 65-mesh screen after it is dried. Either Carbowax 4000 or paraffin can be used as a binder.

Carbowax is added in an aqueous solution (1 g of wax for each 2 ml of solution) until the batch contains 12% by weight of Carbowax. The material is dried at less than 80°C to granulating consistency and then forced through a 14-mesh screen. After further drying at less than 80°C to drive off the remaining water, the material is allowed to cool for pressing.

The paraffin is added in a CCl_4 solution. Sufficient solution is added to the magnesia to form a paste containing paraffin to the extent of 5 to 10% of the weight of magnesia. The CCl_4 is fully evaporated and the material is forced through a 14-mesh screen.

Pressing. The Carbowax-lubricated batches are pressed at 30,000 to 50,000 psi in steel dies heated to 30 to 40°C with jacket heaters. The paraffin-lubricated material is pressed cold at the same pressures.

Drying. The crucibles containing Carbowax are heated in porous saggars (made from insulating brick) to 500 or 600°C in 25 hours. The pieces containing paraffin can be fired directly if the temperature is raised slowly up to 600°C (200 deg/hr).

Firing. The crucibles are fired at 1750 to 1800°C from 30 min to 1 hour.

Dry-Pressing of Grain-sized Magnesia Crucibles

Raw Materials. Magnesia supplied by General Electric Co. or Norton Co. is used to fabricate grain-sized crucibles. The Norton product should be -20 +100 mesh.

Grinding. Equal amounts of General Electric and Norton products are ball-milled in naphtha for 24 hours. A 2000-g batch of the magnesia mix requires $\frac{1}{2}$ gal of balls and $\frac{3}{4}$ gal of naphtha in a 1-gal mill. Ninety-eight per cent of the ground material should be less than 200 mesh.

Preparation for Pressing. The grain-sized body is made up of 63% coarse material and 37% fines. About 98% of the coarse fraction should be held on a 100-mesh screen and should have the following grain-size distribution:

Screen Interval	Per Cent
-28 +35	15 ± 8
-35 +48	40 ± 5

-48 +65
-65 +100

35 ± 3
10 ± 3

The two increments are mixed dry in a Simpson mixer; then 5% by weight of distilled water is added and mixed with the increments for not more than 5 minutes. The batch is pelletized by forcing it through a 10-mesh screen and is then bottled. The damp material should not set unpressed for more than 48 hours.

Pressing. The magnesia is pressed in a steel die at 10,000 psi.

Drying. The crucibles are air-dried overnight or for 16 hr; this is followed by 24 hr of drying at 90°C.

Firing. The magnesia crucibles are fired to 1750°C either by induction or in a gas kiln.

Slip-Casting

Raw Materials. Fused magnesia supplied by General Electric Co. is suitable for casting crucibles. When a crucible with a silica content lower than 2% is desired, the fused product is mixed in equal parts with a calcined (1500°C) c.p. grade magnesia. (Mallinckrodt Chemical Works product has a silica content of less than 0.30%.) Shrinkages vary from 7 to 15% according to the firing temperature. Apparent porosities of from 0.5 to 8.5% may be expected.

Grinding. The magnesia is ground dry or with absolute alcohol for 34 hr in a steel-ball mill.

Preparation of Slip. When excess alcohol is used in grinding, the slip should be adjusted to a specific gravity of 2.2 or 2.3. Dry-ground magnesia should be blunged with alcohol and adjusted to the same specific gravity.

Casting. The crucibles are cast in plaster molds in the usual drain-casting manner. The slip and green crucibles should be protected from the air as much as possible to prevent scumming.

Drying. The crucibles are dried in a desiccator overnight.

Firing. The crucibles should be fired at 1850 to 2050°C by induction heating with a 30-min soak.

Manufacturers

Magnesia Crucibles. American Crucible (1), Bartley (3), Dixon (12), Electro (10), Massillon (14), Norton (19).

References

H. B. Barlett, *The Preparation of Small Dense Crucibles of Magnesia*, CT-3372.

NITRIDE CRUCIBLES

Nitride crucibles are not available commercially at present. They are fabricated most readily by dry- or hot-pressing. Any of the refractory nitrides may be used in the fabrication of crucibles. The ones most suitable for the purpose, listed with their melting points, are: Be_3N_2 , 2197°C; ScN , 2650°C; TiN , 2950 \pm 50°C; ZrN , 2980 \pm 50°C; HfN , 3300°C; VN , 2100°C; TaN , 3100°C; and UN , 2500°C.

FABRICATION OF NITRIDE CRUCIBLES

Dry-Pressing

Raw Materials. The dry-pressing technique described here is specifically adaptable for fabricating ZrN and TiN , but it can be used with the other nitrides that are sufficiently stable to stand the grinding and firing.

Grinding. The nitrides are ground with steel balls in a rubber-lined mill for 75 to 90 hr so that 95% of the particles achieve a grain size less than 8 microns. A sample mill charge for TiN in a 1-qt mill would be: 400 g of coarse nitride (-20 mesh), 1.6 kg of alloy steel balls varying in diameter from $\frac{1}{8}$ to $\frac{5}{8}$ in., and either 200 g of alcohol or 250 g of water; a charge for ZrN in a 1-qt mill

would be: the same as for TiN , except that only alcohol is used as a grinding medium and the charge is increased to 600 grams.

Preparation for Pressing. After grinding, the batch is mixed with a solution of Carbowax compound 4000 in hot benzene. The Carbowax should be from 6 to 10% of the weight of the nitride used. The slurry is stirred and ground in a mortar until all the benzene has evaporated; after that, the material is pelletized by forcing it through a 14-mesh screen.

Pressing. The pelletized material is pressed in a steel die at 15,000 to 20,000 psi. Crucibles can also be pressed hydrostatically without the use of a binder.

Drying. The crucibles are held at 250°C for several hours to remove the Carbowax.

Firing. The crucibles are fired in an induction furnace with a tungsten heating element in an ammonia atmosphere, ZrN at 2050°C for 30 min and TiN at 1600°C for 30 minutes.

References

G. R. Finlay and G. Fetterly, "Boron Nitride - An Unusual Refractory," *J. Am. Ceram. Soc.* 31, 141 (1952).

ALUMINUM SILICATE CRUCIBLES

TYPES

Fire Clay

Fire-clay crucibles are prepared from a mixture of carefully selected raw and calcined fire clays, die-pressed or jigged in steel or plaster of paris molds, and fired to about pyrometric cone 12. Their range of chemical analyses is as follows:

SiO_2	50.0 to 69.0%
Al_2O_3	25.0 to 45.0%
Fe_2O_3	1.0 to 2.0%
CaO	0.1 to 0.40%
MgO	0.10 to 0.5%
TiO_2 and alkalis (Na_2O and K_2O) ...	about 1% each

These crucibles are inexpensive and are useful to a maximum temperature of 2750°F (1510°C). Their porosity ranges from 15 to 25%. In use, they

may contaminate the melt with silica and with iron from the clay.

Fire-clay crucibles are used extensively in mining for fire assay work and for melting non-ferrous metals, enamels, chemicals, and glasses. Table 7 lists the standard sizes commercially available. They are also available with or without pouring lips and in a form with a triangular cross section.

Sillimanite or Mullite

Sillimanite or mullite crucibles are usually used when a more refractory aluminum silicate than fire clay is required. They are suggested for use in induction furnaces for melting glass and metals. These crucibles contain mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, as principal ingredient, together with excess silica. The material is often clay-bonded and in most cases suggested for safe use up to 3100°F

TABLE 7. STANDARD SIZES OF FIRE-CLAY CRUCIBLES

JOSEPH DIXON CRUCIBLE CO. (12)			THE DENVER FIRE CLAY CO. (9)	
Size	Height (in.)	Top Diameter (in.)	Height (in.)	Top Diameter (in.)
A	2 $\frac{5}{8}$	1 $\frac{5}{8}$		
B	3	1 $\frac{7}{8}$		
C	3 $\frac{1}{2}$	2 $\frac{1}{4}$		
D	4	2 $\frac{3}{8}$	4	2 $\frac{3}{8}$
E	4 $\frac{1}{2}$	2 $\frac{7}{8}$		
F	5	3	5	3 $\frac{1}{8}$
G	5 $\frac{1}{2}$	3 $\frac{5}{8}$	5 $\frac{5}{8}$	3 $\frac{5}{8}$
H	5 $\frac{3}{4}$	4	5 $\frac{3}{4}$	3
I			6	4
J	6 $\frac{1}{2}$	4 $\frac{1}{2}$	6 $\frac{3}{8}$	4 $\frac{1}{2}$
K	7 $\frac{1}{8}$	5	7 $\frac{1}{4}$	4 $\frac{3}{4}$
L	7 $\frac{3}{4}$	5 $\frac{1}{4}$	8	5 $\frac{1}{4}$
M	8 $\frac{1}{4}$	5 $\frac{7}{8}$		
N	9 $\frac{1}{2}$	6 $\frac{1}{2}$	9 $\frac{1}{8}$	6 $\frac{1}{2}$
O	10	7	9 $\frac{7}{8}$	7
P	10 $\frac{3}{4}$	7 $\frac{3}{4}$	11	7 $\frac{3}{4}$
Q	12	8 $\frac{3}{4}$	12 $\frac{1}{2}$	9
S	14 $\frac{1}{4}$	9 $\frac{3}{4}$		

(1700°C). Two typical chemical compositions are as follows:

Pyrometric cone equivalent C/38 (3335°F) C/38 to 39

	Taylor Sillimanite (%)	Taylor Sillimanite, Fortified (%)
Al ₂ O ₃	61.20	68.72
SiO ₂	35.35	28.48
Fe ₂ O ₃	0.84	0.70
TiO ₂	1.96	1.40
CaO	0.11	0.15
MgO	0.05	0.08
Alkalies	0.48	0.46
Porosity (%)	20.0 to 22.5	20.0 to 23.0

A list of standard sizes is shown in Table 2.

Two types of mullite crucibles are produced by the Richard C. Remmey Sons Co.: crystalline mullite, a low-fired (2786°F, 1530°C) material that has a comparatively high percentage of mullite crystals and a firing range of 3390°F (1865°C); and recrystallized mullite, a high-fired (3200°F, 1760°C) material, of nearly 100% crystalline structure that has less than 0.5% porosity, an alumina content of over 70%, and a firing range of 3425°F (1885°C) (see Table 8).

Chemical porcelain, such as that produced by the Coors Porcelain Co., is essentially a mullite body that may or may not be glazed. Its limit of

TABLE 8. STOCK SIZES OF SILLIMANITE-MULLITE CRUCIBLES

MANUFACTURERS NUMBER	INSIDE DIAMETER (in.)	WALL THICKNESS* (in.)	HEIGHT (in.)
With Pouring Lip			
CS-2 (6)	$3\frac{5}{8}$	$\frac{1}{2}$	8
CS-3 (6)	$2\frac{1}{4}$	$\frac{1}{4}$	$5\frac{1}{4}$
CS-5 (6)	$2\frac{3}{4}$	$\frac{5}{16}$	$6\frac{3}{8}$
CS-7 (6)	$6\frac{1}{4}$ (bilge) 4 (bottom)	$\frac{5}{8}$	$9\frac{1}{4}$
CS-8 (6)	5	$\frac{1}{2}$	$9\frac{1}{2}$
CS-8A (6)	5	$\frac{3}{8}$	$11\frac{3}{8}$
01 (20)	$1\frac{1}{2}$ (top) $\frac{5}{8}$ (bottom)	$\frac{3}{16}$ *	3
1 (20)	$2\frac{1}{2}$ (top) $1\frac{1}{4}$ (bottom)	$\frac{1}{4}$ *	$3\frac{1}{2}$ to 4
2 (20)	3 (top) $2\frac{1}{8}$ (bottom)	$\frac{1}{4}$ *	$3\frac{3}{4}$
4 (20)	$4\frac{1}{4}$ (top) 3 (bottom)	$\frac{5}{16}$ *	$5\frac{1}{2}$
10 (20)	$5\frac{1}{2}$ (top) $3\frac{3}{4}$ (bottom)	$\frac{3}{8}$ *	$7\frac{1}{2}$
11 (20)	$6\frac{5}{8}$ (top) $4\frac{5}{8}$ (bottom)	$\frac{7}{16}$ *	10
12 (20)	$10\frac{7}{8}$ (top) $8\frac{7}{8}$ (bottom)	$\frac{9}{16}$ *	12
S1 (20)	$1\frac{1}{2}$	$\frac{1}{4}$ *	$3\frac{3}{4}$
S3 (20)	$2\frac{1}{8}$	$\frac{1}{4}$ *	$3\frac{1}{2}$
S6 (20)	$2\frac{3}{8}$	$\frac{1}{4}$ *	$5\frac{1}{4}$
S8 (20)	3	$\frac{1}{4}$ *	$6\frac{1}{4}$
Without Pouring Lip			
CS-6 (6)	$5\frac{1}{4}$ (top) 4 (bottom)	$\frac{1}{2}$	$6\frac{1}{2}$
2099A (9)	$\frac{1}{2}$	$\frac{3}{16}$	$3\frac{5}{8}$

*Wall thickness for recrystallized mullite is 25 to 50% less than that shown above for crystalline mullite.

use unglazed is 2550°F (1400°C), and glazed is 2280°F (1250°C). The capacities of these cruci-

bles range from 0.75 to 250 cc (glazed) and from 15 to 1900 cc (unglazed).

SILICA CRUCIBLES

TYPES

Clay-bonded

Clay-bonded silica crucibles contain about 95 to 98% silica in the form of quartzite and have porosities ranging from 20 to 30%. The possibility of silica, alumina, or iron contamination from the crucible should not be overlooked.

These clay-bonded crucibles are suggested for use where acid conditions exist, such as in the melting of steels, ferrous metals, and siliceous glasses. They are particularly suited for induction heating, with a useful temperature range up to 2800°F (1540°C), depending on the application.

High-Silica

Imported Hessian sand crucibles are used primarily for the melting of precious metals. They are produced either with a circular cross section (ranging in size from $3\frac{3}{4}$ in. in height by $2\frac{1}{2}$ in. in diameter to 11 in. in height by $7\frac{5}{8}$ in. in diameter) or with a triangular cross section (ranging from $2\frac{1}{8}$ in. in height by $1\frac{1}{2}$ in. in diameter to 4 in. in height by 3 in. in diameter).

Another material used for precious-metal melting is produced by the Western Gold and Platinum Works under the trade-mark "Wesgo." Its composition is not given in the company's literature, but according to its physical properties, it is probably a siliceous material. Its recommended continuous service temperature is 2190°F (1200°C), and it can be used for short intervals up to 2640°F (1450°C). This material is produced in a large variety of shapes ranging in size up to 6 in. in height by $2\frac{3}{4}$ in. in inside diameter.

Vitreous Silica

Vitreous silica crucibles consist of 99 to 100% pure silica fused into a glass. They have a low thermal expansion, are resistant to heat shock, are strongly resistant to acid slags, and may be used for continuous operation up to 2012°F (1100°C) or for short periods up to 2460°F (1350°C). They are readily attacked by basic materials and fluorides and may contribute silica to molten metals. Water absorption is less than 1%.

Vitreous silica is obtainable in either opaque or transparent form; the opaque form is glazed or unglazed in standard sizes (see Table 9).

Vycor Glass

Vycor crucibles are made from a soft glass that separates into two phases, one high in silica and the other high in borates. The borates are leached out and the resulting siliceous framework is shrunk into a homogenous structure by heating. Normally, 2.9% of B_2O_3 and 0.4% of Al_2O_3 are present. Vycor crucibles are less expensive than fused silica and have the same advantages and disadvantages.

Manufacturers

Clay-bonded Silica Crucibles. Dixon (12), Massilon (14).

Fire Clay and High-Silica Crucibles. American Cuttlefish (2), Denver (9), Dixon (12), Massilon (14), Western (25).

Sillimanite or Mullite Crucibles. Bartley (3), Taylor (6), Coors (7), Denver (9), Electro (10), Massilon (14), Mullite (16), Remmey (20).

Vitreous Silica Crucibles. Thermal (22).

Vycor Silica Crucibles. Corning (8).

TABLE 9. STOCK SIZES OF VITREOUS SILICA CRUCIBLES (22)

NUMBER	TOP OUTSIDE DIAMETER (in.)	OUTSIDE HEIGHT (in.)	INSIDE DIAMETER (in.)	INSIDE HEIGHT (in.)	CAPACITY (cc)
Crucibles with Lip					
3	$3\frac{7}{8}$	$4\frac{3}{8}$			350
4	4	$4\frac{1}{2}$			500
6	$4\frac{1}{2}$	$6\frac{1}{8}$			925
7	5	$7\frac{1}{2}$			1,500
14	$5\frac{7}{8}$	$7\frac{3}{4}$			1,875
16	$6\frac{1}{4}$	$8\frac{3}{8}$			2,500
30	$7\frac{3}{4}$	$10\frac{1}{4}$			5,000
60	$10\frac{1}{8}$	$12\frac{3}{4}$			8,000
62	12	$12\frac{1}{2}$			10,000
70	12	20			21,500
Pots					
	16	$21\frac{1}{2}$			12 gal
	19	$21\frac{1}{2}$			17 gal
	19	23			18 gal
	19	$28\frac{1}{2}$			24 gal
	$25\frac{3}{8}$	$37\frac{3}{4}$			50 gal
Cylindrical Crucibles					
			3	$4\frac{7}{8}$	525
			4	$5\frac{1}{2}$	1,000
			$4\frac{1}{2}$	$6\frac{1}{4}$	1,500
			$5\frac{3}{8}$	$7\frac{5}{8}$	2,500

SILICON CARBIDE CRUCIBLES

Silicon carbide (SiC) is produced by a process discovered by Acheson, in which a mixture of coke, sand, and sawdust is heated by electrical resistance to 3000°C. The flat, six-sided silicon carbide crystals that are formed in a crumbly mass inside the furnace are, individually, nearly as hard as diamonds and are stable to about 1800°C. Pure silicon carbide is white, but, ordinarily, the

crystals are an iridescent blue or green from carbon, iron, or other impurities that are present in small amounts on the surfaces. Crucibles made from silicon carbide may be used in a mildly reducing atmosphere up to 1500°C. They are strong and possess high heat conductivity and good resistance to thermal stresses. Also, they are rather heavy and may contribute carbon, silica, sodium,

or boron to the melt. Dissociation of silicon carbide takes place with volatilization of the silica between 1600 and 1800°C. Silicon carbide crucibles are available in a variety of shapes and in sizes varying from a few ounces to several hundred pounds of capacity (see Table 6).

TYPES

Carbon-bonded

Silicon carbide crystals are not readily bonded together to form ware; hence, bonding materials such as carbon, clay, or silica are commonly used. Carbon-bonded silicon carbide crucibles are made from a plastic mixture of silicon carbide, pitch, and tar, which is jiggered in a steel mold of the desired shape, buried in sand, and fired to develop the carbon bond. This carbon bond is protected from oxidation in use by an additional borax bond

that is obtained by dipping the ware in a borax solution and reheating to fuse the borax.

Silicon-bonded

Silicon-bonded silicon carbide crucibles are produced by oxidation of powdered silicon metal that is intimately mixed with the silicon carbide before the jiggering operation. The silicon oxidizes in firing to form a silica bond that does not need protection from oxidation.

Manufacturers

Pure (Recrystallized). Carborundum (5), Electro (10), Norton (19). (A special order will probably be required.)

Carbon-bonded Crucibles. American Crucible (1), Electro (10), Dixon (12), Ross-Tacony (21).

Silica-bonded Crucibles. Ross-Tacony (21).

Silicon Carbide Grain. Carborundum (5), Electro (10), Exolon (11), Norton (19).

SULFIDE CRUCIBLES

Barium sulfide, cerium sulfide ("cerium brass"), Ce_3S_4 - Ce_2S_3 ("cerium black"), thorium sulfide ("thorium silver"), and Th_2S_3 - Th_4S_7 ("thorium brown" and "thorium black") are used to make refractory sulfide crucibles. Large cerium-black crucibles are sensitive to thermal shock, the sensitivity being greater at the Ce_2S_3 end of the solid-solution series. Small crucibles (1 by $1\frac{1}{2}$ in.) show no signs of damage from thermal shock.

FABRICATION OF SULFIDE CRUCIBLES

Dry-Pressing

Raw Materials. Cerium black can be made by mixing correct proportions of CeS and Ce_2S_3 . The resulting crucibles show no traces of the CeS phase by x-ray analysis. Thorium brown and thorium black are prepared by blending and pressing ThS and ThS_2 .

Grinding. Although sulfides do not react with air below 200°C, enough heat is developed in grinding to oxidize them so that they must be ground in an inert atmosphere. This grinding is accomplished by the use of a dry box. The box is first subjected to a partial vacuum and soap and water are used to test the most likely places for leaks. A volume of propane equal to $1\frac{1}{2}$ times the volume of the dry box is passed through without the aid of the fan; then 5 times the volume is

passed through with the fan operating. A steel-ball mill is placed inside the dry box.

Sulfide crushed to 4 mesh in air (since oxidation is negligible in this operation) is screened in the inert atmosphere to remove air. It is then charged into the steel-ball mill that is kept in the dry box during the screening operation. After the ball mill is sealed, it is removed from the dry box and rotated for several hours. The sulfide should be emptied from the mill while it is in the dry box, since a slight oxidation occurs when the sulfide is removed in air.

Another method of grinding sulfides without the use of a dry box is to cover the material in the mill with a solution of 2% cetyl alcohol in ether. After the grinding and emptying processes are completed, the ether is allowed to evaporate into the air during constant stirring of the mix. The cetyl alcohol thus remains as a coating on the sulfide grains. The sulfides should be ground to pass 325 mesh for pressing.

Preparation for Pressing. The sulfides that are ground in a gas atmosphere are mixed with 5% naphthalene by volume and made into a slurry with ether. After the ether has evaporated completely, the batch is pelletized through a 14-mesh screen.

The sulfides that are milled with cetyl alcohol and ether are pelletized through a 14-mesh screen after all the ether has been evaporated.

Pressing. Pressures of 50,000 to 100,000 psi are used in pressing in a steel die.

Drying. The binders can be driven off by heating in a vacuum at 100°C.

Firing. The crucibles are sintered by induction heating for 10 to 30 min in a vacuum (10^{-3} to 10^{-5} mm Hg) at a temperature appropriate to the sulfide. The crucibles are placed on molybdenum during firing.

Barium sulfide should be fired at 1400 to 1600°C. Below 1400°C, the product is powdery; above 1600°C, the sulfide vaporizes.

Cerium sulfide is fired at 1800 to 1900°C, depending on its purity. If both Ce_3S_4 and Ce_2O_2S are present in amounts up to 10% combined, the sintering temperature will be lowered considerably (1600 to 1700°C) and porosities of less than 5% will be attained because of the eutectic between the two compounds. However, the presence of either compound alone has little effect on the sintering temperature.

Oxygen-free cerium-black materials sinter to low porosities at 1700 to 1900°C; the lowest sintering temperature is for $CeS_{1.5}$, with a rise to 1900°C in the case of $CeS_{1.33}$. With increasing amounts of oxygen present, the sintering temperature drops to as low as 1600°C.

The sintering temperature of thorium sulfide is not much affected by the presence of impurities. When a low-porosity crucible is desired, the sin-

tering temperature should be 1900 to 2000°C. Appreciable amounts of Th_2S_3 limit the sintering temperature to a maximum of 1900°C. Free thorium lowers the sintering temperature; but its presence should be avoided, since it makes the crucible less resistant to attacking metals.

Th_2S_3 - Th_4S_7 crucibles should be sintered at 1700 to 1800°C. The presence of oxygen does not lower the sintering range.

Rough surfaces are caused by sintering at a temperature at which the sulfide has a high vapor pressure. Some defects are caused by the presence of oxygen, which reacts with the sulfides. Recrystallization or discoloration is caused by impurities in the vacuum line. A pure inert gas should be used to break the firing vacuum below 400°C.

References

For procedure in synthesis of sulfides, see E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, "Preparation and Properties of Refractory Cerium Sulfides," *J. Am. Chem. Soc.* **72**, 2248 (1950); and "Preparation and Properties of the Sulfides of Thorium and Uranium," *J. Am. Chem. Soc.* **72**, 4019 (1950). See also, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, *The Preparation and Properties of Refractory Sulfides*, AECD-2242 (Aug. 25, 1948); AECD-2253 (Sept. 7, 1948); and *J. Am. Ceram. Soc.* **34**, 128 (1951).

THORIA CRUCIBLES

Thoria has the highest melting point of any of the available pure oxides—above 5430°F (3000°C). It is stable in both oxidizing and neutral atmospheres, and in carbonaceous atmospheres up to 3990°F (2200°C). With thoria in contact with carbon, formation of the carbide has been observed at 4000°F (2250°C). Thoria has a low vapor pressure at high temperatures, which makes it desirable for vacuum work; however, it has a high density of 9.6 and a high sensitivity to thermal shock. Thoria crucibles are reported to be resistant to chemical attack by acidic and especially by basic fusions and can be used for the fusion of metals of high melting points.

A list of standard-size crucibles is given in Table 10.

FABRICATION OF THORIA CRUCIBLES

Dry-Pressing

Raw Materials. Thoria supplied by Lindsay Chemical Co. is used in making the crucibles. The zirconia flux material can be obtained from Foote Mineral Co. under the trade-mark "Zirconalba."

Grinding. A batch made up of 98% thoria and 2% zirconia (2 to 5% can be used) is ground for 10 hr in a 1-gal porcelain mill loaded with 1-in. Porox balls. A typical mill batch consists of 1680 g of thoria, 34.3 g of zirconia, 4000 g of Porox balls, and 1450 g of water. After grinding, the material should have a particle size finer than about 10 microns.

TABLE 10. STOCK SIZES OF THORIA CRUCIBLES (13)

NUMBER	TOP OUTSIDE DIAMETER (in.)	BOTTOM OUTSIDE DIAMETER (in.)	HEIGHT (in.)	CAPACITY (cc)
T158	$1\frac{7}{32}$	$1\frac{7}{32}$	$1\frac{7}{32}$	20
T160	$1\frac{1}{4}$	$\frac{7}{8}$	$1\frac{1}{4}$	19
T162	$1\frac{5}{8}$	$1\frac{1}{16}$	$1\frac{7}{16}$	28
T164	$2\frac{1}{32}$	$1\frac{13}{16}$	$2\frac{9}{32}$	70
T166	$2\frac{5}{32}$	$1\frac{9}{32}$	$1\frac{25}{32}$	7
T168	$1\frac{5}{8}$	$1\frac{1}{8}$	$2\frac{7}{16}$	50

Preparation for Pressing. After the milled batch is dried, it is passed through a 65-mesh screen by means of a Ro-Tap. A solution of Carbowax compound 4000 in water (0.2 g of wax per milliliter of solution) is added to the dry batch and worked in by hand until 6% by weight is incorporated. The batch is partly dried at 80°C; this is followed by pelletizing through a 14-mesh screen. The material is then dried in shallow trays at 60 to 80°C.

Pressing. The material is pressed in a steel die at 20,000 to 30,000 psi. When less Carbowax binder is used, the die must be heated slightly to achieve the same density as with the 6% binder.

Drying. The Carbowax binder is burned out by placing the crucibles in small saggers (hollowed-out insulating brick) and heating to 500°C in not less than 8 hours. Cracking sometimes occurs as a result of the raw thoria.

Firing. The crucibles are fired at a rate of 8.5°C/min to 1800°C and soaked for 30 minutes. A small oxypropane kiln or an induction furnace can be used for firing.

Properties. Crucibles prepared by this method have densities ranging from 9.55 to 9.70 and are practically nonporous. They are tan in color and have a pearly luster.

Slip-Casting

Raw Materials. Thoria (-300 mesh, code No. 112) supplied by the Lindsay Chemical Co. is suitable for casting.

Grinding. The dry material as received is ground for 4 hr in a steel-ball mill.

Preparation of Slip. The dry-ground thoria is agitated with dilute HCl (10 ml of HCl per 100 ml of water), permitted to settle, and the supernatant acid solution is decanted. Three cycles of leaching should remove the contaminating iron. The decanted acid solution should be tested for dissolved thoria. The leached slip is not washed with water; it should be adjusted to a pH of 3.75 or above and to a specific gravity of 2.0 to 2.5.

Casting. The slip is cast in plaster molds in the usual manner.

Drying. The crucibles should be air-dried overnight. The dry ware is quite fragile.

Firing. Firing of the crucibles should require not less than 30 min to reach 1675°C.

Properties. Shrinkages of 10 to 15% may be expected. Thoria crucibles are quite susceptible to rupture from mechanical or thermal shock.

Manufacturers

Thoria crucibles are not now available as a stock item from Laboratory Equipment (13) or Morganite (15), but some sizes may be available.

References

- O. J. Whittemore, Jr., *The Preparation of Small Dense Thoria Crucibles*, AECD-2187 (July 28, 1948).
- J. G. Thompson and M. W. Mallett, "Preparation of Crucibles from Special Refractories by Slip Casting," RP1236, *J. Research Natl. Bur. Standards* 23, 319 (1939).
- H. K. Richardson, "Small Cast Thorium Oxide Crucibles," *J. Am. Ceram. Soc.* 18, 65 (1935).

TYPES

Zircon

Zircon (ZrSiO_4) is obtained principally from the beach sands of India, Florida, and Australia by washing and flotation operations; it can be purchased either in the naturally occurring grain size ("granular," 100 to 200 mesh) or in milled form. The tetragonal zircon crystals are stable in the range from room temperature to 1500°C , have a rather low coefficient of thermal expansion (approximately 4×10^{-6} in./in./ $^\circ\text{C}$), and a medium thermal conductivity, all of which contribute to thermal shock resistance.

Zircon crucibles are made in standard sizes (see Table 11) mainly by the slip-casting method. Mixtures of 10 to 50% granular and 50 to 90% milled material are self-bonded when fired at 1450 to 1500°C . Porosities up to 5 to 10% are common.

These crucibles can be used at 1700°C , although the silicate tends to dissociate at this temperature and may eventually cause disruption of the ware. Zircon is notable in being unwetted by molten aluminum, and it withstands molten platinum, platinum-rhodium alloys, copper, copper alloys, some enamel frits, and all acid slags. It is also reported to resist the action of metaphosphates, sodium chloride, sodium sulfate, zinc chloride, and potassium chloride at temperatures several hundred degrees above the various melting points. However, zircon crucibles are not recommended for melting strongly basic materials.

Zirconia

Zirconia is produced from the mineral baddeleyite (mainly ZrO_2 plus zircon) or from zircon in an electric arc furnace operation. Electrically fused zirconia does not hydrate readily, has a high melting point of 2700°C , and withstands loads of 25 psi to 2100°C . It is stable chemically in contact with acidic or metal fusions and has been used for containers for melting fused silica. It is not easily reduced except that it may form a carbide when in contact with carbon at 1800 to 1900°C in an inert atmosphere and at 1500°C in a vacuum. Zirconia is a conductor of electricity above 1600°C and should not be used in contact with resistance windings at these temperatures.

The chief defect of electrically fused zirconia is a reversible crystal change at approximately 1100°C from the monoclinic to the tetragonal form, which is accompanied by a considerable volume change.

This behavior may shatter the ware unless the firing procedure is carefully controlled. Severity of the volume change is reduced by additions of 5 to 8% of CaO that has the property of forming cubic solid solutions with the zirconia at 1500 to 1800°C . Zirconia that has been partly changed to the cubic form is termed "stabilized." Its properties are similar to those of electrically fused zirconia, except that the CaO addition imparts resistance to rapid temperature changes, lowers the fusion point by perhaps 100 to 200°C , lowers the temperature of sagging under load to 2050 to 2100°C , and may be detrimental when in contact with certain melts.

Most of the available zirconia ware is made from "stabilized" material and is formed by slip-casting, although the larger sizes are sometimes made by ramming the moistened powder into a mold. Slip-cast crucibles have from 0.7 to 5% porosity, whereas the rammed type have porosities of perhaps 20%. Standard sizes available are given in Tables 12 and 13.

FABRICATION OF ZIRCON AND ZIRCONIA CRUCIBLES

Slip-Casting with Acid Deflocculant

Raw Materials. Electrically fused, -325 mesh zirconia, with beryllia as a fluxing material and with an acid deflocculant, is sometimes used for the casting of crucibles. The zirconia is supplied by the National Lead Corp. and the beryllia flux material by the Brush Beryllium Co.; the refractory grade is preferable.

Grinding. A batch of 99% dry zirconia and 1% beryllia is mixed by grinding in a steel-ball mill for about 4 hours.

Preparation of Slip. Upon removal from the mill, the contaminated mix is leached with a dilute HNO_3 bath (10 ml of HNO_3 per 100 ml of water). To prevent lumping, the acid is first prepared and the powdered zirconia is added. The batch is shaken well and then allowed to settle; the supernatant liquid is removed with an aspirator. This process is repeated until the acid solution is no longer discolored; usually about three washings are required. The acid is removed from the slip by washing two or three times with water. For best casting properties, the slip should have a pH of 0.5 to 1.5 and a specific gravity of 2.8 to 3.2.

Casting. The casting is done in plaster molds by the usual drain method.

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TABLE 11. STOCK SIZES OF ZIRCON CRUCIBLES

NUMBER AND MANUFACTURER	OUTSIDE DIAMETER (in.)	HEIGHT (in.)	WALL THICKNESS (in.)	CAPACITY (cc)
15 (23)	$1\frac{5}{8}$	$1\frac{5}{8}$	$\frac{3}{16}$	35
17 (23)	$1\frac{3}{4}$	$3\frac{5}{8}$	$\frac{1}{4}$	75
23 (23)	$2\frac{3}{8}$	$3\frac{1}{4}$	$\frac{1}{4}$	125
25 (23)	$2\frac{1}{2}$	$5\frac{3}{8}$	$\frac{1}{4}$	200
27 (23)	$2\frac{3}{4}$	$4\frac{1}{8}$	$\frac{1}{4}$	275
28 (23)	$2\frac{7}{8}$	$5\frac{1}{2}$	$\frac{1}{4}$	325
33 (23)	$3\frac{3}{8}$	$4\frac{3}{4}$	$\frac{1}{4}$	400
35 (23)	$3\frac{1}{2}$	$6\frac{1}{8}$	$\frac{1}{4}$	550
37 (23)	$3\frac{3}{4}$	$6\frac{1}{4}$	$\frac{1}{4}$	700
40 (23)	4	4	$\frac{1}{4}$	600
45 (23)	$4\frac{1}{2}$	$7\frac{7}{8}$	$\frac{3}{8}$	1300
56 (23)	$5\frac{5}{8}$	$8\frac{1}{4}$	$\frac{3}{8}$	2300
58 (23)	$5\frac{7}{8}$	$6\frac{7}{8}$	$\frac{3}{8}$	2300
60 (23)	6	10	$\frac{3}{8}$	3000
65 (23)	$6\frac{1}{2}$	$8\frac{5}{8}$	$\frac{3}{8}$	3600
MC (13)	$1\frac{3}{8}$	$2\frac{8}{16}$	$\frac{3}{16}$	
MC (13)	$2\frac{3}{8}$	$3\frac{3}{16}$	$\frac{5}{16}$	
MC (13)	$3\frac{9}{16}$	3	$\frac{3}{8}$	
MC (13)	$3\frac{21}{32}$	$3\frac{3}{32}$	$\frac{7}{32}$	
MC (13)	$2\frac{5}{8}$	4	$\frac{3}{16}$	
MC (13)	$2\frac{5}{8}$	$5\frac{5}{8}$	$\frac{5}{32}$	
CZ-1 (6)	2	$3\frac{3}{4}$	$\frac{1}{4}$	
CZ-3 (6)	$2\frac{3}{4}$	$5\frac{1}{4}$	$\frac{1}{4}$	
CZ-4 (6)	$2\frac{7}{8}$	$5\frac{1}{4}$	$\frac{1}{4}$	
CZ-5 (6)	$3\frac{3}{8}$	$6\frac{3}{8}$	$\frac{5}{16}$	
CZ-5 (6)	$3\frac{5}{8}$	$6\frac{3}{8}$	$\frac{5}{16}$	
CZ-6 (6)	$4\frac{1}{4}$	8	$\frac{3}{8}$	
CZ-7 (6)	$7\frac{1}{2}$ (bilge) $5\frac{1}{4}$ (bottom)	$9\frac{1}{4}$	$\frac{5}{8}$	

TABLE 12. STOCK SIZES OF ZIRCONIA CRUCIBLES (UNSTABILIZED) (23)

NUMBER	OUTSIDE DIAMETER (in.)	HEIGHT (in.)	WALL THICKNESS (in.)	CAPACITY (cc)
5	$\frac{9}{16}$	$\frac{1}{2}$	$\frac{1}{16}$	1
7	$1\frac{1}{16}$	$1\frac{1}{16}$	$\frac{3}{32}$	5
10	1	$6\frac{1}{2}$	$\frac{3}{16}$	45
13	$1\frac{1}{2}$	$8\frac{1}{2}$	$\frac{3}{16}$	165
14	$1\frac{1}{2}$	$7\frac{1}{2}$	$\frac{3}{16}$	130
15	$1\frac{1}{2}$	$1\frac{5}{8}$	$\frac{3}{16}$	25
16	$1\frac{5}{8}$	$3\frac{1}{2}$	$\frac{1}{4}$	65
17	$1\frac{3}{4}$	4	$\frac{1}{4}$	85
20	2	$5\frac{1}{4}$	$\frac{1}{4}$	130
21	2	8	$\frac{3}{16}$	250
23	$2\frac{1}{4}$	$3\frac{1}{8}$	$\frac{1}{4}$	125
27	$2\frac{3}{4}$	4	$\frac{5}{16}$	210
28	$2\frac{7}{8}$	$5\frac{3}{4}$	$\frac{5}{16}$	375

Drying. The crucibles should be air-dried overnight.

Firing. The crucibles should be fired to 1800°C by induction or in an oxypropane or oxyacetylene furnace. Slow firing and care in handling dry ware are necessary to prevent cracking.

Slip-Casting with Basic Deflocculant

Raw Materials. Stabilized zirconia is obtainable in both coarse and milled forms. Since the fine material must be depended upon for the deflocculation of the slip, it is essential that its average particle size be from 3 to 5 microns. If it is desirable to produce a less dense ware than that obtained with fine-grained stabilized zirconia, from 10 to 40% of coarse-grained (80 to 100 mesh) material can be stirred into the deflocculated fine material without disturbing the deflocculation appreciably.

Preparation of Slip. When basic deflocculation is to be used, the zirconia must be freed of any acid ions by calcination at red heat. The powder is then dampened by adding 10 to 15 ml of distilled water to 100 g of zirconia. From 1 to 5 ml of a 2% solution of tetrasodium pyrophosphate in water is then stirred into this mix. Proper proportions

to be used in a given case are determined by trial and error. As the optimum deflocculation is approached from neutrality, the mixture usually becomes notably resistant to stirring with a glass rod, but it flows readily under gravity. At the optimum point for good casting, the slip is easily stirred and flows smoothly from a glass rod.

Underdeflocculation of the slip is indicated by a rapid casting rate (5 to 15 sec), thick walls, easy release from the mold, weakness of the dried ware, and rapid settling out of the zirconia from the slip, the settled portion being rather soft and easily returned to suspension. Overdeflocculation is usually attended by a slower casting rate (30 to 45 sec), thin walls, strong ware, and rather slow settling of the zirconia, which forms a dense mass that can be restored to suspension with difficulty. Properties between these extremes should be sought.

Casting. Zirconia usually has a rapid casting rate if dry molds are used. Sufficient wall thickness is often obtained by pouring the slip into the mold and out again in 15 to 30 seconds. Three to four pieces can be cast in a mold before drying of the mold is necessary. A wet mold is likely to cause sticking and to require undue jarring to release the ware.

TABLE 13. STOCK SIZES OF ZIRCONIA CRUCIBLES (STABILIZED) (23)

NUMBER	OUTSIDE DIAMETER (in.)	HEIGHT (in.)	WALL THICKNESS (in.)	CAPACITY (cc)
50-5	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{16}$	0.70
50-2	$\frac{1}{2}$	2	$\frac{1}{16}$	2.35
75-1	$\frac{3}{4}$	1	$\frac{3}{32}$	3.2
75-4	$\frac{3}{4}$	4	$\frac{3}{32}$	12.9
100-1	1	1	$\frac{1}{8}$	6.0
100-6	1	6	$\frac{1}{8}$	38.0
125-2	$1\frac{1}{4}$	2	$\frac{1}{8}$	22.0
125-6	$1\frac{1}{4}$	6	$\frac{1}{8}$	68.0
150-2	$1\frac{1}{2}$	2	$\frac{1}{8}$	34.0
150-8	$1\frac{1}{2}$	8	$\frac{1}{8}$	142.0
175-2	$1\frac{3}{4}$	2	$\frac{3}{16}$	38.0
175-8	$1\frac{3}{4}$	8	$\frac{3}{16}$	169.0
200-2	2	2	$\frac{3}{16}$	55.0
200-8	2	8	$\frac{3}{16}$	237.0
225-2	$2\frac{1}{4}$	2	$\frac{3}{16}$	73.0
225-8	$2\frac{1}{4}$	8	$\frac{3}{16}$	317.0
250-2	$2\frac{1}{2}$	2	$\frac{3}{16}$	94.0
250-8	$2\frac{1}{2}$	8	$\frac{3}{16}$	407.0
275-2	$2\frac{3}{4}$	2	$\frac{1}{4}$	102.0
275-8	$2\frac{3}{4}$	8	$\frac{1}{4}$	543.0
300-2	3	2	$\frac{1}{4}$	126.0
300-10	3	10	$\frac{1}{4}$	704.0

Firing. Stabilized zirconia is usually made rather dense (5 to 10% porosity) by firing to 1730°C in 12 hr and by holding the temperature for 1 hr, allowing the ware to cool with the kiln. Gas firing is usually employed.

Manufacturers

Zircon Crucibles. Bartley (3), Taylor (6), Electro* (10), Laboratory Equipment (13), Massilon (14), Remmey (20), Titanium (23).

*Zirconium oxide lining in silicon carbide crucible.

Zirconia Crucibles. Norton (19), Titanium (23).

References

J. G. Thompson and M. W. Mallett, "Preparation of Crucibles from Special Refractories by Slip Casting," RP1236, *J. Research Natl. Bur. Standards* 23, 319 (1939).

R. W. Knauff, "Zircon Refractories for Aluminum Melting Furnaces," *Metals and Alloys* 18, 1326 (1943).

W. J. Baldwin, "Zircon and Zirconia Refractories," *Chem. Eng. Progress* 44, 875 (1948).

LIST OF MANUFACTURERS

- (1). American Crucible Co., North Haven, Conn.
- (2). American Cuttlefish Bone and Crucible Co., 75 Cliff Street, New York 38, N. Y.
- (3). Bartley Crucible and Abrasive Corp., 15 Muirhead Avenue, Trenton 3, N. J.
- (4). Brush Beryllium Co., 4301 Perkins Avenue, Cleveland 3, Ohio.
- (5). Carborundum Co., Niagara Falls, N. Y.
- (6). The Charles Taylor Sons Co., Cincinnati, Ohio.
- (7). Coors Porcelain Co., Golden, Colo.
- (8). Corning Glass Works, Corning, N. Y.
- (9). The Denver Fire Clay Co., Denver 17, Colo.
- (10). Electro Refractories and Abrasive Corp., 334 Delaware Avenue, Buffalo 2, N. Y.
- (11). Exolon Co., Tonawanda, N. Y.
- (12). Joseph Dixon Crucible Co. Jersey City 3, N. J.
- (13). Laboratory Equipment Corp., St. Joseph, Mich.
- (14). Massilon Refractories Co., Massilon, Ohio.
- (15). Morganite, Inc., 3302 48th Avenue, Long Island City 1, N. Y.
- (16). Mullite Corp., Shelton, Conn.
- (17). National Carbon Co., 30 East 42nd Street, New York 17, N. Y.
- (18). National Crucible Co., Mermain Lane and Queen Streets, Philadelphia 18, Pa.
- (19). Norton Co., Worcester 6, Mass.
- (20). Richard C. Remmey Sons Co., Headley Street and Delaware River, Philadelphia 37, Pa.
- (21). Ross-Tacony Crucible Co., Tacony, Philadelphia 35, Pa.
- (22). Thermal Syndicate, Ltd., 12 East 46th Street, New York 17, N. Y.
- (23). Titanium Alloy Manufacturing Division, National Lead Corp., 111 Broadway, New York 6, N. Y.
- (24). Vesuvius Crucible Co., Swissvale, Pittsburgh 18, Pa.
- (25). Western Gold and Platinum Works, 589 Bryant Street, San Francisco, Calif.