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[54] **LEACHABLE CERAMIC CORES**

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[52] **U.S. Cl.** **164/132**

[51] **Int. Cl.** **B22d 29/00**

[58] **Field of Search** 164/132, 369; 249/61, 62, 63, 64

[56] **References Cited**

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[57] **ABSTRACT**

Ceramic cores having at least sufficient zinc oxide to provide essential continuity throughout the structure are provided. Such cores are included in metal castings from which they are leached under acidic or alkaline conditions to provide cavities within the castings.

3 Claims, No Drawings

LEACHABLE CERAMIC CORES

This is a division of application Ser. No. 739,156 filed June 24, 1968.

This invention relates to novel refractory cores and molds for use in ferrous and non-ferrous metallurgy. In particular this invention relates to leachable refractory cores and molds consisting essentially of zinc oxide although including, before calcining and firing, varying amounts of organic and inorganic additives and/or diluents of which inorganic additives are generally retained after calcination and firing.

In the production of complex mechanical parts and pieces it is frequently necessary to provide cavities or internal passages of relatively complex shape and quite accurate dimensions. Some internal passages may be formed by drilling or other conventional metal-working operations, but use of ceramic cores is preferred practice because of the economies of processing possible. Furthermore, precise internal configurations may be required in positions which are either prohibitively difficult or impossible to machine by conventional methods but are readily produced using leachable cores. Illustrations are internal undercuts, flanges, bosses, or threads, complex internal air foil shapes, curving or helical passageways, etc.

In an illustrative process, a preformed leachable ceramic core of the desired configuration and dimensions is positioned in an injection molding die of the external shape etc. desired, and while suitably supported, is surrounded by a wax pattern of the object to be cast together with suitable sprues. A refractory shell, suitably of conventional investment composition, is then formed around the wax and leachable core assembly by positioning in a suitable mold and pouring the investment therearound with conventional debubbling, etc. Alternatively the shape may be dipped repeatedly in the investment composition. After drying the invested mold, wax is melted and partially drained from the mold and residual wax is then burned out. The desired metal is poured into the resultant cavity in the hot mold by gravity, centrifuging or other process. After solidification of the casting, the shell mold is removed from the metal casting. Suitable connections are made to the ceramic core and it is removed by leaching to leave cavities, channels, etc. as desired. The manner of using leachable cores will be apparent to those skilled in the art.

Leachable ceramic compositions used heretofore have usually been soluble only in hydrofluoric acid and/or hot caustic baths (i.e., sodium hydroxide). It will be recognized that not all alloys can survive under such strenuous chemical conditions. In fact, hot fused caustics are known to have deleterious effects on many metals. Less strenuous conditions for leaching would be very desirable to permit more widespread applicability of leachable cores to difficult problems of fabrication.

It is an aim of this invention to provide refractory cores which tolerate conditions for casting metals, for example at mold temperatures 1000°–1200° C., and are dissolvable at relatively rapid rates under conditions of such moderate acidity that there is no attack of metals such as aluminum, lead, iron, copper, nickel, silver, brass, bronze, chrome-nickel alloys, lead-tin alloys, lead-bismuth alloys, or high temperature alloys such as Haynes Stellite Alloy No. 31 of the Union Carbide

Corp. Other aims and objects of the invention will become evident on reading the present disclosure.

It is found that zinc oxide is admirably suited to preparing moldable compositions and thus in achieving aims of this invention, when it is compounded in finely divided or powdered form with binders such as starches, waxes, polyvinyl alcohol, thermoplastic resins, etc. in amounts according to methods of molding to be employed. Optionally, up to 40 percent or more of inert filler or diluent, such as zircon in relatively fine sizes, and/or up to 25 percent of a bulk filler to promote porosity such as powdered organic materials, wood flour, or other cellulosic filler, etc. are included in the composition. The amount of filler must not be so great that it will react completely with zinc oxide under conditions either of firing the core or during casting of metal. For example, zircon reacts at elevated temperatures e.g., 1100° C., with zinc oxide to give zirconia and zinc silicate. Compositions including weight percentages above 40–50 percent of zircon may therefore be so reacted above 1000° C. that no zinc oxide remains and the core is no longer leachable.

The composition is formed into the desired shapes by methods of the ceramic art such as extrusion, casting, dry pressing, isostatic pressing, injection molding, etc. The composition, as noted, is formulated in detail on the basis of the method of molding which is employed. Thus for dry or isostatic pressing, 2 to 5 percent of starch, wax, polyvinyl alcohol, etc. are incorporated and the composition granulated and dried to less than 1 percent water content. For extrusion, 4 to 7 percent of the above binders are incorporated together with 15 to 22 percent water. For injection molding 17–25 percent thermoplastic binders are included without water. The amounts of the various fillers, binders, etc. are adjusted to alter thermal expansion coefficients, shrinkage on firing and hardness and porosity of the finished core as will be evident to those skilled in ceramic arts.

In sintering ZnO, air is advantageously forced into the kiln to maintain oxidizing conditions. If fired to temperatures of 1050° to 1350° C. zinc oxide cores are quite hard and, when additional finishing is needed, must be shaped and worked using abrasives. They are soft-fired or underfired in a current of air to about 800° to 1100° C., and are then more easily worked, for example, by metal working tools. As noted reactions of fillers may alter properties.

Cores fired at higher temperatures, e.g., 1100° to 1350° C., absorb very little or no water as shown by increase in weight and by failure to be colored by aqueous solutions of suitable dyes. In spite of this density, such hard cores are dissolved at relatively rapid rates in 20 percent aqueous acetic acid at 95° C. They may be dissolved, but somewhat more slowly in more dilute (about 10 percent aqueous) acetic acid.

Other materials which may be used for leaching the zinc oxide cores, i.e., as leachants, are other dilute acids, e.g., sulphuric, nitric, hydrochloric, phosphoric. Dilute alkalis, such as 33 percent potassium hydroxide at 110° C., may also be used but solution is much slower than in acids.

The composition of a fired core may be 100 percent zinc oxide with greater or less porosity and downward to as low as 60 percent of total zinc oxide. In general it is preferred that there be at least 50 percent of uncom-

bined zinc oxide in the fired core to provide essentially continuous paths for dissolution of the core. The lower concentrations of zinc oxide and more porous structures are naturally somewhat cheaper for larger cores. A relatively cheap filler such as zircon may be used and shrinkage may be reduced thereby. As noted above the amount must be sufficiently low so that at no temperature encountered by the core is the zinc oxide phase rendered inaccessible to leachants. It will be evident that amounts of fillers incorporated must be sufficiently low that there is no opportunity for agglomeration into clinker-like masses which will not pass out of the cavities remaining after leaching of cores.

The zinc oxide which is used is of commercially available grades and may be either American Process or French Process. Particle sizes may range from 0.4 to 0.8 microns mean particle size for U.S.P. Grades (normally used in cosmetics, pharmaceuticals, etc.) to ceramic grades having mean particle sizes of up to 2 to 5 microns. Typical purities range from 99.8% ZnO for U.S.P. grades to 99.4% ZnO for ceramic grades. The U.S.P. grades are advantageous from purity and reactivity standpoints but the ceramic grades offer advantages of easier forming and lower shrinkage during sintering. It is sometimes desirable to blend materials of the two grades together in order to benefit from the desirable properties of both. to blend materials of the two grades together in order to benefit from the desirable properties of both.

The composition of zinc oxide and whatever inorganic filler is first ball-milled to effect particle size reduction when desired. It is then mixed with organic binders and any liquids, plasticizers, etc. in suitable equipment such as a muller-type mixer to a desired consistency which is a thick dough for extrusion into rods, tubes, etc. Wood flour or other organic fillers are incorporated in the same equipment or, the composition is mixed with 17 to 25 percent of thermoplastic resins, for example, for the injection molding of cores suitable to provide internal passages for complex air foil shapes for turbine engines.

Unfired green shapes are formed by a selected convenient method, dried and then fired at temperatures in the range of 800° to about 1100° C. when a porous core body is desired or at higher temperatures up to about 1350° C. when a hard body impervious to water absorption is desired. An initial firing to destroy all or part of the organic materials may be employed if desired. Shrinkages of the order of 10 to 20 percent occur and are carefully controlled. Allowance therefor is made in shaping the piece prior to sintering. After cooling the leachable core body of zinc oxide is further finished if necessary by diamond grinding, etc.

Leachable core bodies are used, for example, in hollow gas turbine blades and stator vanes, pitot tubes, temperature probes, fuel controls, heat exchangers.

EXAMPLE 1

A green, i.e., unfired, zinc oxide cylindrical tube is formed by extruding a blend mixed in a muller-type mixer of 100 parts of U.S.P. grade zinc oxide (average particle size 0.4 to 0.7 microns), 3 parts corn starch and 2 parts microcrystalline wax emulsion and 12 parts of water. The green tube is 2.0 and 5.3 mm. in internal and external diameters respectively. This provides a tube which is impervious to dye or water penetration, and has respective external and internal diameters of 4.4 and 1.6 mm. after firing in a current of air for six hours at 1100° C. The respective diameters of a tube fired for 6 hours at 1000° C. are 4.4 and 1.6 mm. and the tube absorbs up to about 1 percent of water. Shrinkage is less and the diameters are respectively 4.6 and 1.8 mm. after firing at 900° C. This tube absorbs up to about 4.5 percent of water. Solid rods are extruded at a diameter of 6.3 mm. by the same procedure fired as above with similar shrinkage and absorption being obtained. After firing, at indicated temperatures rod diameters are 5.4 mm. (900° C.), 5.2 mm. (1000° C.), and 5.1 mm. (1100° C.).

Tubes and rods in lengths of 55 to 65 mm. are placed in an aqueous solution (20 percent of acetic acid) at 95°–98 C. with following results:

Firing temp. (°C.)	Sample	Water absorption (%)	Sample weight (grams)	Approximate time required for decomposition (min.)
900	Tube	4.5	4.2	25
900	Rod	4.5	6.7	62
1000	Tube	1.0	4.2	18
1000	Rod	1.0	6.8	63
1100	Tube	< 0.1	4.2	21
1100	Rod	< 0.1	6.6	57

Tubes of these types are molded in a wax block and invested by usual procedures. After normal burnout and casting of bronze, the investment is removed and a bronze block in the shape of the wax block is obtained including the ceramic tubes as cores. These cores are removed by leaching with hot **20%** acetic acid. Rods used as cores are dissolved much more slowly because of the smaller end areas available for solution. The cavities in the casting replicate the cores employed.

Samples of core pieces are also dissolved in a 10 percent aqueous solution of acetic acid over somewhat longer times. Samples of rods are dissolved in less than 20 minutes in an ultrasonic bath of 20 percent aqueous acetic acid at same solution concentration and temperature.

EXAMPLE 2

The procedure of Example 1 is repeated except that a blend of **95** parts U.S.P. ZnO and **5** parts wood flour is extruded into rods and tubes. Data are tabulated below.

Firing temp. (°C.)	Sample	Water absorption (%)	OD (mm.)	ID (mm.)	Sample weight (grams)	Approximate time required for decomposition (min.)
900	Tube	9.0	4.7	1.8	3.4	13
900	Rod	9.0	5.6	—	5.4	30
1000	Tube	4.7	4.5	1.7	3.4	12
1000	Rod	4.7	5.2	—	5.3	20
1100	Tube	2.0	4.4	1.6	3.4	13
1100	Rod	2.0	5.1	—	5.4	17

These tubes are employed as cores as described in Example **1** for silver casting. Leaching by dilute hydrochloric acid yields a silver block having cavities replicating the outer surfaces of tubes.

EXAMPLE 3

The procedure of Example 1 is repeated except that a blend of 90 parts U.S.P. zinc oxide and 10 parts wood

flour is extruded into rods and tubes. The data are tabulated below.

Firing temp. (°C.)	Sample	Water absorption (%)	OD (mm.)	ID (mm.)	Sample weight (grams)	Approximate time required for decomposition (min.)
900	Tube	20	4.7	1.8	2.8	15
900	Rod	20	5.7	—	4.4	25
1000	Tube	10	4.5	1.7	2.8	17
1000	Rod	10	5.2	—	4.3	25
1100	Tube	7	4.3	1.6	2.8	19
1100	Rod	7	5.0	—	4.4	30

These tubes and rods are employed as cores as in Example 1 and are dissolved more readily from the metal block.

EXAMPLE 4

Sample tubes are produced as described in Example 2 and fired at 1100° C. for 6 hours. Water absorption on the fired tubes is almost 2.0 percent and tubes, 4.4 mm. OD by 1.6 mm. ID by 55 to 65 mm. long and weighing almost 3.4 grams, are placed in heated (90°–98° C.) 20 percent aqueous solutions of hydrochloric acid, nitric acid, sulfuric acid, and phosphoric acid respectively. In all cases, tubes are completely decomposed in less than 25 minutes.

Another tube is placed in a heated (110°–115° C.) 33 percent aqueous solution of sodium hydroxide. Decomposition in this solution requires about 60 minutes.

EXAMPLE 5

The above and other rods and tubes, for example, with blends made before firing, etc. are positioned in cylindrical molds 1.2 to 2.5 cm. in inside diameter to provide coring structure and the metals cast to fill the cavity between the core and mold. No wax is used in this instance. The cores are then leached out and metal cylinders 1.2 to 2.5 cm. in outside diameter are thus obtained having cavities corresponding to the rods and/or tubes. The following metals are used:

1. Solder (2% Au, 60% Sn, 38% Pb)
2. Babbit Metal (Pb-Bi alloy)
3. Aluminum (Type 3003)
4. Bronze (Tin and copper) (Bunting B–54)
5. Brass (Zinc and copper) (Anaconda No. 271)
6. Copper
7. Lead

The ceramic cores are leached out in heated (90°–98° C.) 20 percent aqueous acetic acid solutions. In every case, the cores are completely removed in less than 30 minutes. Tubes are more readily leached than rods. No corrosion or reaction is noticed on any metal and passages of the same diameter as the outer core diameter remain in the metal castings. Using rods or tubes bent to shapes such as pig tails before firing provides openings in the metal castings of shapes substantially impossible to machine.

EXAMPLE 6

Haynes Stellite Alloy No. 31 (cobalt, chromium and tungsten alloy) is representative of high temperature alloys used, for example, in the production of air foil shapes for turbine engines. The alloy is applied in 10 and 20 mil. (0.25 and 0.50 mm.) coatings as a plasma-spray powder on a zinc oxide tube of Example 3 by plasma-spraying. Following application of the high temperature alloy, the core is leached out in a heated (90°–98° C.) solution of 20 percent aqueous acetic acid. The time required for complete decomposition of the core is 50 minutes. No reaction between the alloy and leaching solution is observed. There is thus obtained a Stellite tube of thin wall thickness. It is not believed that a tube of such dimensions could be fabricated by normal techniques.

EXAMPLE 7

A series of compositions are prepared using 75, 50 and 25 parts of finely divided zircon as filler together with 25, 50 and 75 parts of zinc oxide respectively. The zinc oxide and zircon are wet ball-milled for 2 hours and dried and then each mixture is further mixed with 5.0 parts of wood flour to promote porosity and temporary binders are added in the proportions of Example 1. Rods and tubes are extruded and samples of each are fired at 900°, 1000° and 1100° C. for 6 hours. There are thus obtained samples of rods and tubes representing nine combinations of different firing conditions and different compositions.

All samples fired at 900° or 1000° C. dissolve in hot aqueous 20 percent aqueous acetic acid without difficulty. Of the samples fired at 1100° C., only the sample containing 75 percent zinc oxide dissolves under these conditions. In this composition there is more than 50 percent of zinc oxide present after firing and zircon has reacted completely to zirconia (ZrO_2) and zinc silicate. On the other hand, the composition initially including 25 percent of zinc oxide no longer contains zinc oxide after firing as demonstrated by X-ray analysis.

The composition initially containing 50 percent zinc oxide reacts to an extent such that there is less than 50 percent and even less than 40 percent of zinc oxide in the fired ceramic. This is thus insufficient to permit dissolution of the core.

What is claimed is:

1. A process for providing a cavity of predetermined shape and size in a metallic object in which a core consisting essentially of 40 to about 100 percent uncombined zinc oxide refractory essentially continuous therethrough and replicative of the desired cavity is embedded within the selected metal and thereafter the core is removed by leaching zinc oxide therefrom with aqueous solution of acid or alkali.

2. In the process of claim 1 the step of leaching zinc oxide in hot 10 to 20 percent aqueous acid.

3. The process of claim 1 in which leaching is with 33 percent aqueous potassium hydroxide.

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