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INVESTMENT SHELL MOLDS FOR THE HIGH INTEGRITY PRECISION CASTING OF REACTIVE AND REFRACTORY METALS, AND METHODS FOR THEIR MANUFACTURE

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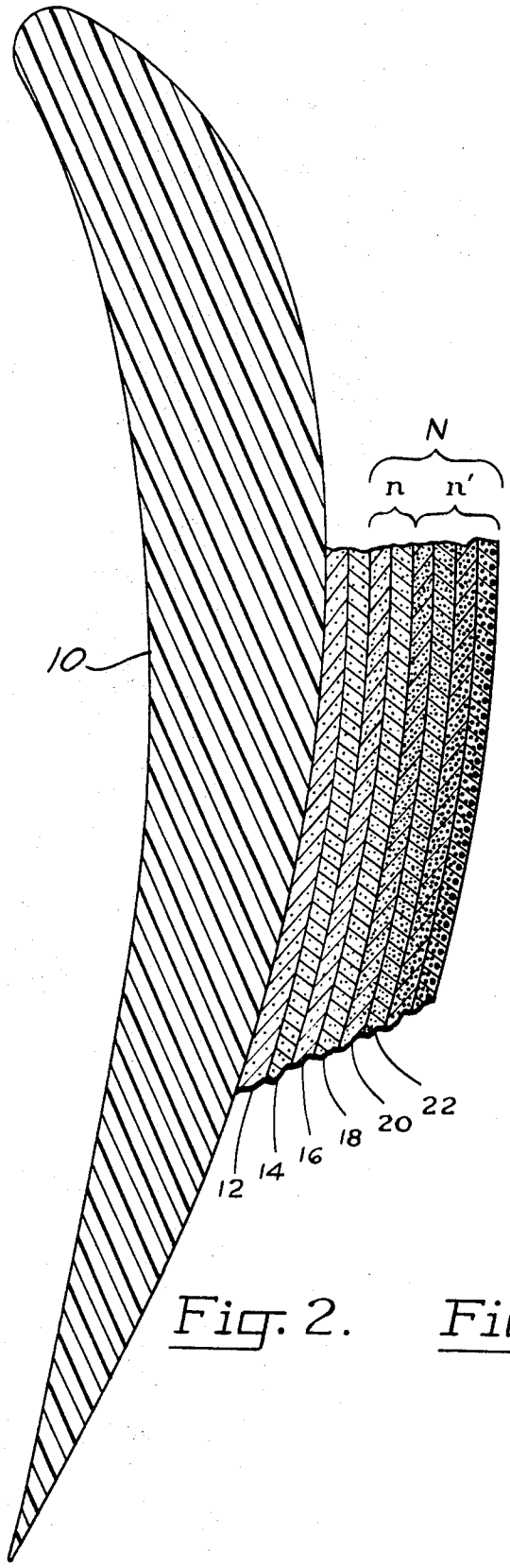


Fig. 2.

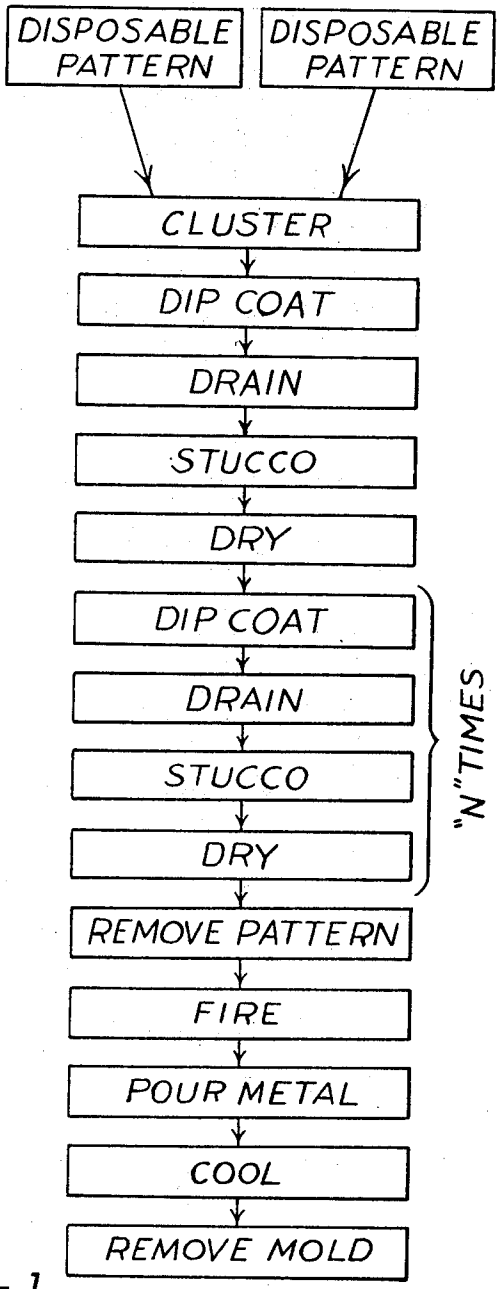


Fig. 1.

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INVESTMENT SHELL MOLDS FOR THE HIGH INTEGRITY PRECISION CASTING OF REACTIVE AND REFRACTORY METALS, AND METHODS FOR THEIR MANUFACTURE

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Original application Oct. 24, 1966, Ser. No. 589,022, now Patent No. 3,422,880, dated Jan. 21, 1969. Divided and this application Aug. 7, 1968, Ser. No. 766,347

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U.S. Cl. 161—225 13 Claims

ABSTRACT OF THE DISCLOSURE

A mold for casting molten reactive and refractory metals comprising a facing portion comprising fine particles of columbium, molybdenum, tantalum or tungsten bound by a refractory oxide and bound to a back-up portion of refractory metallic oxide bound ceramic particles. The metallic oxide may be oxides of zirconium, thorium, hafnium, yttrium or gadolinium.

This is a division of the patent application of Robert A. Brown and Clifford A. Brown, Ser. No. 589,022, filed Oct. 24, 1966, now U.S. Pat. No. 3,422,880, for Method for Making Investment Shell Molds for the High Integrity Precision Casting of Reactive and Refractory Metals.

This invention relates to methods for making investment shell molds for the high integrity precision casting of reactive and refractory metals.

Although there are many types of metal casting molds, none of them is applicable to the high integrity precision casting of such metals as chromium, hafnium, molybdenum, plutonium, niobium, rhenium, thorium, uranium, tantalum, titanium, vanadium, zirconium, and the rare earth metals, all of which are highly reactive chemically in the molten state.

Present day molds for the casting of such metals comprise graphite, carbon, and ceramic material cemented with various binders and prepared by various techniques. Such molds are unsatisfactory for the casting of the refractory and reactive metals for the reason that when they are used one or more of the following undesirable results ensues:

(1) Gross carbonization of the casting surface.

(2) Gross oxygen, hydrogen, or nitrogen contamination in the casting.

(3) Formation of intermetallic inclusions or layers in the casting.

(4) Formation of gas pits, holes, and porosity in the casting.

(5) Embedded non-metallic inclusions or layers in the casting.

(6) Formation of severe cold laps and misrun on the casting surface.

(7) Formation of cracks and tears in the casting.

(8) Formation of a rough casting surface.

(9) Embrittlement or increased hardness of the cast metal.

(10) Production of non-precision castings.

It is the essence of the present invention that the foregoing deficiences of the prior art casting molds and methods may be overcome by the provision of novel investment shell molds having a constitution, and prepared by a method, illustrated in the drawings, wherein:

FIG. 1 is a flow plan illustrating the basic investment shell molding process, a modification of which is the subject matter of the present invention; and

FIG. 2 is a transverse sectional view through a mold of the class prepared by the instant invention.

As is illustrated in the flow plan of FIG. 1, the sequence of operations employed in the manufacture of intricate castings by the investment shell casting technique involves first providing disposable patterns made from waxes, plastics, frozen mercury, or other materials which readily may be removed from the mold. The investment cycle consists of making the patterns by injecting the pattern material into a die, and gating the patterns to a central sprue to form a pattern cluster.

The pattern cluster then is dipped into an agitated slurry of the molding material, drained, stuccoed while still wet with particulate mold material in a fluidized bed or by sprinkling, and dried, preferably to a solvent content of less than 20% by volume. The dipping, draining, stuccoing and drying sequence is repeated a desired number of times, indicated by "N" times in the flow diagram, to produce a laminated investment shell mold of the desired thickness and strength.

Thereafter the disposable pattern is removed by methods such as melting or solvent treatment. The mold is cured by being fired at a temperature sufficiently elevated to remove volatiles and provide adequate bonding. The molds then are heated, and filled with molten metal by gravity, pressure, vacuum, or centrifugal force. After cooling, the castings are removed from the sprue and finished in the usual manner.

We have discovered that the foregoing procedure may be modified and adapted to the production of molds suitable for use in the precision casting of reactive and refractory metals by including as an essential component of at least the face coating of the molds, a single one or a mixture of finely divided, metallic, columbium, molybdenum, tantalum or tungsten. By the simple expedient of using these metals, the above noted deficiences of the prior art molds and mold making methods are overcome with the result that there are provided for the first time practical efficient molds for the high integrity, precision casting of reactive and refractory metals.

The investment shell molds of the present invention comprise a facing portion including a major proportion, at least 50% by weight, of finely divided particles of metallic columbium, molybdenum, tantalum or tungsten, all bonded together with a suitable refractory metallic oxide binder, and a back-up reinforcing portion comprising finely divided particles of shell mold back-up material including ceramic mold materials and refractory metal oxide binders, all the mold components being integrally bonded together to form a strong structure having an inner face portion comprised predominantly of one of the indicated metals.

Generally stated, the method of making the herein described investment shell molds for the high integrity precision casting of reactive and refractory metals comprises dip-coating a disposable pattern in a liquid suspension of columbium, molybdenum, tantalum and/or tungsten and a binder therefor comprising a refractory metal oxide and/or a refractory metal compound pyrolyzable to a refractory metal oxide. The dip coated pat-

tern is stuccoed with at least one of the same finely divided metals, after which it is dried.

The foregoing sequence of dip coating, stuccoing and drying is repeated until a shell mold of the desired thickness has been built up about the disposable pattern. The pattern then is removed from the mold, after which the mold is fired at a temperature which is below the sintering temperature of any of its constituents. The firing temperature is predetermined to convert the content of any refractory metal compounds which may be present to refractory metal oxides and also, through the agency of the refractory metal oxides present initially or thus generated, to bond together the finely divided metal particles and mold back-up material particles to form the finished mold.

Considering the foregoing general statements of the invention in greater detail:

As indicated above, the herein described investment shell mold is made by repeatedly dip coating, stuccoing and drying a disposable pattern, indicated symbolically at **10** in FIG. 2, to invest the pattern with mold-forming coatings sufficient in number to build up a finished mold of the desired strength. The coatings thus supplied are in general of three categories and are so illustrated in FIG. 2. The first coatings are termed herein the "facing" coatings and comprise the dip coating and stucco coating **12, 14** making up the inner face of the mold, in direct contact with the molten metal poured therein. A single dip coat-stucco coat combination normally comprise the face coating.

The second category of coatings, termed herein the "adjacent facing coatings, comprise alternate dip coats **16** and stucco coats **18** applied in sequence on top of the face coat. There may be any desired or necessary numbers of such coats, indicated by "n" in FIG. 2.

The third class of coatings applied in making the herein described molds are those which during the use of the molds do not normally come in direct contact with the molten casting metal or with the vapor produced therefrom. These are termed herein "back-up" coatings and comprise alternate dip coats and stucco coats **20, 22** respectively applied in a sufficient number, "*n*" of FIG. 2, to lend the required strength to the mold. Thus there may normally be a total of from 4 to 12 or more adjacent facing and back-up coatings applied to the pattern in building up the mold, the total number being indicated at "N" in FIG. 2.

Each of these coatings has a characteristic composition as required to fulfill the general purpose of the invention, i.e. the provision of an investment shell mold for the high integrity precision casting of reactive and refractory metals.

Thus the preferred components of the integral facing, adjacent facing and back-up coating systems may be selected from the following:

INTEGRAL FACING AND ADJACENT FACING COATING SYSTEMS

(A) Metal mold materials and refractory metal oxide binders

Mold materials:
- (1) Columbium
- (3) Tungsten
- (2) Molybdenum
- (4) Tantalum

Binders:
- (1) Colloidal gadolinia
- (2) Colloidal yttria
- (3) Colloidal thoria
- (4) Colloidal zirconia
- (5) Colloidal hafnia

(B) Metal mold materials and refractory metal oxide forming binders

Mold materials:
- (1) Columbium
- (2) Molybdenum
- (3) Tantalum
- (4) Tungsten

Binders:
- (1) Metal-organics:
  - (a) Thorium chloroalkoxides
  - (b) Zirconium chloroalkoxides
  - (c) Hafnium chloroalkoxides
  - (d) Zirconium alkoxides
  - (e) Thorium alkoxides
  - (f) Hafnium alkoxides
- (2) Basic oxyhalogenides:
  - (a) Hafnium
  - (b) Zirconium
- (3) Polymeric carboxylates:
  - (a) Hafnium
  - (b) Zirconium

(C) Metal-refractory metal oxide mold materials and refractory metal oxide binders

Mold materials:
- (1) Columbium
- (2) Molybdenum
- (3) Tantalum
- (4) Tungsten with
- (5) Gadolinia
- (6) Hafnia
- (7) Thoria
- (8) Yttria
- (9) Zirconia

Binders:
- (1) Colloidal gadolinia
- (2) Colloidal yttria
- (3) Colloidal thoria
- (4) Colloidal zirconia
- (5) Colloidal hafnia

(D) Metal refractory metal oxide mold materials and refractory metal oxide forming binders

Mold materials:
- (1) Columbium
- (2) Molybdenum
- (3) Tantalum
- (4) Tungsten with
- (5) Gadolinia
- (6) Hafnia
- (7) Thoria
- (8) Yttria
- (9) Zirconia

Binders:
- (1) Metal-organics:
  - (a) Thorium chloroalkoxides
  - (b) Zirconium chloroalkoxides
  - (c) Hafnium chloroalkoxides
  - (d) Thorium alkoxides
  - (e) Zirconium alkoxides
  - (f) Hafnium alkoxides
- (2) Basic oxyhalogenides
  - (a) Hafnium
  - (b) Zirconium
- (3) Polymeric carboxylates
  - (a) Hafnium
  - (b) Zirconium

BACK-UP COATING SYSTEMS

(1) The systems listed under Integral Facing and Adjacent Facing Coating Systems.

(2) Ceramic-Ceramic Systems.

(A) Ceramic mold materials and refractory metal oxide binders

Mold materials:
(1) Alumina
(2) Aluminum silicates
(3) Forsterite
(4) Olivine
(5) Silica
(6) Thoria
(7) Zircon
(8) Zirconia
(9) Gadolinia
(10) Hafnia
(11) Yttria

Binders:
(1) Colloidal alumina
(2) Colloidal silica
(3) Colloidal gadolinia
(4) Colloidal yttria
(5) Colloidal thoria
(6) Colloidal zirconia
(7) Colloidal hafnia

(B) Ceramic mold materials and refractory metal oxide forming binders

Mold materials:
(1) Alumina
(2) Aluminum silicates
(3) Forsterite
(4) Olivine
(5) Silica
(6) Thoria
(7) Zircon
(8) Zirconia
(9) Gadolinia
(10) Yttria
(11) Hafnia

Binders:
(1) Metal-organics:
(a) Hafnium chloroalkoxides
(b) Titanium chloroalkoxides
(c) Thorium chloroalkoxides
(d) Zirconium chloroalkoxides
(e) Hafnium alkoxides
(f) Silicon alkoxides
(g) Thorium alkoxides
(h) Titanium alkoxides
(i) Zirconium alkoxides
(2) Basic oxyhalogenides:
(a) Hafnium
(b) Zirconium
(3) Polymeric carboxylates:
(a) Hafnium
(b) Zirconium
(4) Ammonium silicate

The foregoing materials may be employed singly or in combination with each other and with other materials falling within the scope of the invention.

The use of columbium, molybdenum, tantalum and tungsten, which are the primary constituents of the foregoing systems, is directly responsible for the production of precision castings in the molds because of their very high melting points, their very low vapor pressures, their lack of a normal tendency to form casting-damaging intermetallic compounds with the various reactive and refractory casting metals, and their freedom from a tendency to react with the reactive and refractory metals to form gases which might contaminate the castings.

The foregoing metals may be used in the form of the pure metals, their alloys or their unalloyed mixtures, in the dip coat and stuccoing compositions, they are employed in finely divided, graded condition having a particle size, for example, in the range of from below 400 mesh to 5 mesh U.S. Sieve Series, i.e. having a particles size of from 0.1 to 4000 microns.

In addition, zirconia, thoria, hafnia, yttria, and gadolinia may be used along with the columbium, molybdenum, tantalum or tungsten as mold materials in the face coating systems, as long as these oxide mold materials are not used in a quantity sufficient to exceed 25 weight percent of the facing portion. Their use as additives is desirable in some instances to reduces the cost of the molds, to alter the thermal conductivity of the molds and to adjust the expansion characteristics thereof. In addition, in some instances they are beneficial in reducing or eliminating cold shut and/or misrun defects.

The binders for the foregoing facing and integral facing coatings in general comprise the refractory metal oxide binders, or the refractory metal oxide-forming binders used in the liquid state, in the dissolved condition, or as solids suspended or dispersed in aqueous or other liquid media. In general those metal oxide binders are preferred which are oxides of the Groups III and IV metals in the Periodic Chart, which have a free energy of formation at 1000° K. greater than 69 kilocalories per gram atom of oxygen in the oxide, which bond upon pyrollization, and which will provide a high temperature bond for the columbium, molybdenum, tantalum or tungsten mold material contained in the integral facing and adjacent facing systems.

Preferred binders of this class are the oxides, or compounds which forms oxides, of zirconium, thorium, hafnium, yttrium or gadolinium. Illustrative of compounds which form such oxides upon pyrolysis, are the polymeric carboxylates such as diacetato zirconic acid (zirconium acetate), the basic oxyhalogemides the metalorgamic compounds, particularly the alkoxides, the alkoxide alcoholates, the oxide alkoxide alcoholates, the polymeric alkoxides, the oxide alkoxides, hydrolyzed alkoxides, halogenated alkoxides, and hydrolyzed halogenated alkoxides of zirconium, thorium, hafnium, yttrium, and gadolinium. Upon pyrolysis the foregoing are converted to metal oxide binders which mature and cure below the sintering temperature of the metal component of the facing and adjacent facing systems, and thus normally ideally serve the purposes of the invention.

In addition to the mold materials, binders, and slurry suspension or dispersion media of the foregoing dip coat systems, there may be employed in suitable quantity conventional additives such as suspension agents green strength promoters, plasticizers, wetting agents, antifoaming agents, deflocculants and coating driers.

In use, the dipcoat components employed in the facing, adjacent facing and back-up coatings are applied in the form of aqueous or organic solvent slurries having, for best results the following viscosities:

DIPCOAT SLURRY VISCOSITIES (Centistokes)

Dipcoat slurry No.	Preferred	General range
1	375	125-750
2	215	50-450
3	275	75-500
4	375	125-750
5	400	200-750
6 on up	450	375-750

The pattern first is treated with a suitable solvent as required to remove any die release agent which may be on its surface. It then is immersed in the agitated first dip coat slurry and rotated to insure complete coverage. After a dwell period of from 10 to 60 seconds it is withdrawn and drained for 15–60 seconds.

The wet pattern assembly then is stuccoed with the finely divided metal, for example, −100 +200 mesh columbium, molybdenum, tantalum and/or tungsten grain. The dip coated and stuccoed pattern assembly then is air dried until the coating is below, for example, a 20% by volume solvent content.

The dried assembly then is immersed in the agitated second dip coat slurry for 10–60 seconds, drained for 15–60 seconds, stuccoed with −100 +200 mesh metallic columbium, molybdenum, tantalum, or tungsten grain, and air dried to a solvent content below about 20% by volume.

This assembly then is treated with the third and subsequent dip coat slurries, drained, stuccoed and dried in similar manner until a mold of the desired thickness has been built up. In all coatings the previous coating should dry preferably to a solvent content of from 2 to 20% by volume before the subsequent coating is applied in order to prevent the previous coating from dissolving in the subsequent dip coating slurry. This may be required from 30 minutes to 6 hours drying time, depending on atmospheric temperature and humidity and pattern complexity. Vacuum drying may be employed to accelerate the drying procedure if desired, in particular instances.

Although it is desirable that each coating be dried below a 20% by volume solvent content before the subsequent coating is applied, for the reason specified above, it also is desirable that the drying be discontinued before the solvent content goes below a level of about 2% by volume. This results in the production of a resilient coating which expands and contracts with thermal changes and avoids significant cracking or spalling. If the solvent content falls below 2% the coating may become brittle and crack.

As the number of dip coats increases there is an increase in proportion of coarser particles of mold material in each dip coat slurry up to a predetermined number of dip coat slurries, for example, five. Thus the first dip coat slurry may contain only mold material which is minus 325 mesh while the 5th dip coat slurry may contain appreciable amounts of −100 +200 mesh and −20 +50 mesh mold materials. This particle size increase toward the outer coating is also reflected in the stuccoing material, which may be −100 +200 mesh for the first two coatings and −20 +50 mesh for the remaining coatings. The increase in mold material and stucco material particle sizes from the mold face to the outer coatings of the mold produces a very stable investment shell mold capable of producing very smooth surfaced castings, yet permits the venting of any generated gases during casting. It also reduces the possibility of the formation of hot tears in the casting due to the excellent collapsibility of the mold.

Coatings are applied until a mold of the desired strength and permeability is fabricated.

Next the assembly is heated to fluidize and remove the disposable pattern from the shell mold with which the pattern has been invested. The resulting mold then must be cured.

To effectuate the curing operation and to remove most of the volatiles, the molds first are dried in either air or in non-oxidizing atmospheres at from 150–650° F. for an additional 1 to 6 hours, and then at 250–650° F. for 1–6 hours. After the drying cycle, the molds are placed in a furnace provided with a non-oxidizing atmosphere of a selected gas which is non-reactive toward the metal present in the face coating or adjacent face coating of the molds. Such gases are, for example, hydrogen, the inert gases, and dissociated ammonia. A vacuum furnace also may be used. The molds are heated in the furnace to a predetermined peak temperature of from 1500° to 5000° F. at a rate of 50–200° F. per hour. They are maintained at peak temperature for from 1–12 hours.

As a general rule, the molds should be heated during the curing cycle to a temperature which is from 60–75% of the temperature at which the metal to be cast will melt. This converts the metal oxide-forming binder to a metal oxide binder and removes the final vestiges of volatiles from the molds, and provides the molds with a high temperature bond without destroying or distorting the mold.

It is to be emphasized in conjunction with the above that the purpose of using a high temperature binder, i.e. a refractory metallic oxide binder, in the molds of the invention is to bond the mold material without the necessity of sintering it, thereby preserving the precise dimensions of the mold.

The mold then is cooled and filled with the molten casting metal by the usual techniques. The casting metal is poured, allowed to solidify and cool, the mold removed, and the resulting casting finished in the usual manner.

A great variety of refractory and reactive metals economically may be precision cast in the foregoing manner. Such metals include chromium, columbium, hafnium, molybdenum, plutonium, tantalum, thorium, titanium, uranium, vanadium, zirconium, the platinum group metals, the rare earth group metals and yttrium. In casting these various metals, the face coating of the mold material comprises an appropriate facing metal. Illustrative are the following:

Casting metal:	Mold material
Chromium	Molybdenum or tungsten
Columbium	Tungsten or tantalum
Hafnium	Tantalum or tungsten
Molybdenum	Tungsten or tantalum
Plutonium	Columbium, molybdenum, tantalum, or tungsten
Tantalum	Tungsten
Thorium	Columbium or tungsten
Titanium	Columbium, tantalum or tungsten
Uranium	Tantalum, or tungsten
Vanadium	Columbium, molybdenum, or tungsten
Zirconium	Columbium or tungsten

The molds of the present invention and their method of manufacture are further illustrated in the following examples:

EXAMPLE 1

The example illustrates a tungsten integrally faced investment shell mold, bonded with zirconium dioxide and backed up with tungsten bonded with zirconium dioxide.

The dip coat slurry formulations were as follows:

DIPCOAT SLURRY FORMULATION (WEIGHT PERCENT)

	Facing slurry	Adjacent facing slurries		Back-up slurries	
Material	1	2	3	4	5–9
Diacetatozironic acid (22% ZrO_2 in solution) (in water)	15.7	16.1	14.2	13.1	11.83
Tungsten powder (minus 325 mesh)	84.3	72.4	61.58	55.0	47.79
Tungsten grain (minus 100 plus 200 mesh)	0	11.5	24.22	21.7	19.0
Tungsten grain (minus 20 plus 50 mesh)	0	0	0	10.2	21.33
2-ethyl hexyl alcohol	Trace	Trace	Trace	Trace	Trace

In making the mold, a disposable pattern assembly was dipped into the numbered dip coat slurry and alternately stuccoed with graded tungsten having a particle size of from minus 100 to plus 200 mesh for the first two castings and from minus 20 to plus 50 mesh for the remaining coatings.

The mold then was dried at 250° F. for 6 hours and cured at 2300° F. for 3 hours. After cooling it was ready for use.

EXAMPLE 2

This example illustrates a molybdenum integrally faced investment shell mold bonded with zirconium dioxide and backed up with molybdenum and tungsten bonded with zirconium dioxide.

DIPCOAT SLURRY FORMULATION (WEIGHT PERCENT)

Material	Facing slurry 1	Adjacent facing slurries 2	3	Back-up slurries 4	5-9
Colloidal zirconia (22-23% ZrO_2 in solution) (in water)	26.7	25.5	23.0	17.2	13.8
Molybdenum powder (minus 325 mesh)	73.3	66.1	59.5	44.5	33.2
Molybdenum grain (minus 100 plus 200 mesh)	0	8.4	17.5	13.1	9.8
Tungsten grain (minus 20 plus 50 mesh)	0	0	0	25.2	44.2

The mold was prepared in the manner described above, alternately dipping the pattern in the dip coats and stuccoing with finely divided molybdenum with or without the addition of finely divided tungsten in the various dip coats.

After all of the dip coats and stucco coats had been applied, the pattern was removed. The resulting shell mold was dried at 250–400° F. for 3 hours and then cured by heating in a hydrogen atmosphere at the rate of 300° per hour increase up to 2300° F. at which temperatures it was held for 3 hours. It then was cooled, whereupon it was ready for use.

EXAMPLE 3

This example illustrates a columbium (niobium) integrally faced investment shell mould bonded with zirconium dioxide, and backed up with columbium, molybdenum and zirconium dioxide bonded with zirconium dioxide. The dip coat formulations were as follows:

DIPCOAT SLURRY FORMULATION (WEIGHT PERCENT)

Material	Facing slurry 1	Adjacent facing slurries 2	3	Back-up slurries 4	5-13
Trioxodi zirconium hydroxychloride (20% ZrO_2 in solution), in water	23.7	27.5	18.3	16.1	0
Diacetatozironic acid (22% ZrO_2 in solution), in water	0	0	0	0	12.2
Columbium powder (minus 325 mesh)	76.3	72.5	48.2	32.6	0
Molybdenum grain (minus 100 plus 200 mesh)	0	0	33.5	32.4	0
Zirconia grain (minus 10 plus 30 mesh)	0	0	0	8.9	32.1
Zirconia flour (minus 325 mesh)	0	0	0	0	29.5
Zirconia grain (minus 80 mesh)	0	0	0	0	26.2

In the manner heretofore described, the pattern was successively dip coated, drained, stuccoed, dried to form the final mold. Thirteen coatings in all were applied. The stuccoing material employed to the first three dip coats was −60 +200 mesh tantalum grain while that applied to the third and successive dip coats was −10 +50 mesh zircon agregate. In all instances, the coatings were dried below a moisture content of 20% by volume before the next coating was applied.

After removal of the pattern, the mold was dried at 250° F. for 4 hours and then heated in vacuo at the rate of 50–200° F. per hour up to 2300° F., at which temperature it was held for 5 hours. After cooling in vacuo, the mold was ready for use.

EXAMPLE 4

This example illustrates tungsten and thorium dioxide integrally faced investment shell molds bonded with zirconium dioxide, and backed up with a silicon dioxide and aluminumsilicate bonded with silicon dioxide. The dip coat slurry formulations were as follows:

DIPCOAT SLURRY FORMULATION (WEIGHT PERCENT)

Material	Facing slurry 1	Adjacent facing slurries 2	3	Back-up slurries 4	5-13
Hydrolyzed zirconium tetraethoxide ethylate (15% ZrO_2), in ethanol	15.3	15.0	14.5	14.0	0
Tungsten powder (minus 325 mesh)	82.9	70.0	80.0	50.0	0
Thorium dioxide powder (minus 325 mesh)	1.8	1.8	1.8	1.8	0
Thorium dioxide grain (minus 20 plus 270 mesh)	0	13.2	23.7	34.2	0
Hydrolyzed tetraethylorthosilicate solution (15% SiO_2), in ethanol	0	0	0	0	21.0
Silicon dioxide grain (minus 100 plus 200 mesh)	0	0	0	0	5.0
Silicon dioxide powder (minus 325 mesh)	0	0	0	0	48.0
Aluminum silicate grain (minus 20 plus 50 mesh)	0	0	0	0	26.0

In this instance the alternate dip coat and stucco coats were built up in the manner above described. The stuccoing material for the first three dip coats was −100 +200 mesh thorium oxide grain, and the material applied to the third and successive dipcoats was −50 +100 mesh calcined aluminum silicate grain. A total of 13 coatings was applied. As before, the pattern was removed from the mold after which the mold was dried and fired, whereupon it was ready for use.

Having thus described our invention in preferred embodiments we claim:

1. A mold for casting molten reactive and refractory metals comprising:
   (a) a facing portion comprising finely divided particles of at least one member of the group consisting of metallic columbium, molybdenum, tantalum and tungsten and a refractory metallic oxide binder therefor, and
   (b) a back up portion comprising finely divided particles of ceramic shell mold back-up material and a refractory metallic oxide binder therefor.

2. The mold of claim 1 wherein the refractory metallic oxide binder comprises the oxide of a metal of the class consisting of the Group III and Group IV metals of the perodic chart, the metallic oxide having a free energy of formation at 1000° K. greater than 69 kilocalories per gram atom of oxygen in the oxide.

3. The mold of claim 1 wherein the binder content of the facing portion and back-up portion comprises from 0.1% to 25.0% by weight of the mold composition.

4. The mold of claim 1 wherein the facing portion includes from 0.1% to 25.0% by weight of refractory metal oxide facing coating material comprising at least one member of the group consisting of zirconia, thoria, hafnium, yttria and gadolinia.

5. The mold of claim 1 wherein the facing portion comprises finely divided particles of metallic columbium.

6. The mold of claim 1 wherein the facing portion comprises finely divided particles of metallic molybdenum.

7. The mold of claim 1 wherein the facing portion comprises finely divided particles of metallic tantalum.

8. The mold of claim 1 wherein the facing portion comprises finely divided particles of metallic tungsten.

9. The mold of claim 1 wherein the refractory metallic oxide binder comprises zirconium oxide.

10. The mold of claim 1 wherein the refractory metallic oxide binder comprises thorium oxide.

11. The mold of claim 1 wherein the refractory metallic oxide binder comprises hafnium oxide.

12. The mold of claim 1 wherein the refractory metallic oxide binder comprises yttrium oxide.

13. The mold of claim 1 wherein the refractory metallic oxide binder comprises gandolinium oxide.

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