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GRAPHITE SHELL MOLDS AND METHOD OF MAKING

Original Filed March 15, 1961

FIG. 1

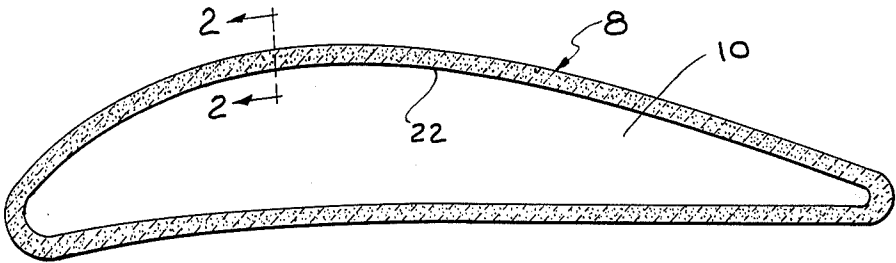


FIG. 2

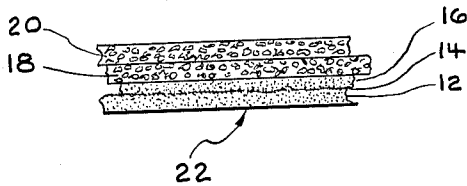
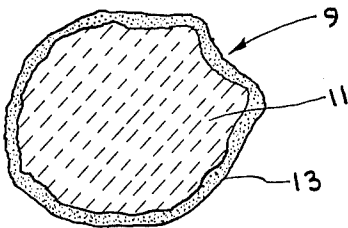


FIG. 3



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**GRAPHITE SHELL MOLDS AND METHOD
OF MAKING**
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Continuation of application Ser. No. 96,050, Mar. 15,
1961. This application Oct. 28, 1964, Ser. No. 407,256
10 Claims. (Cl. 22-129)

This application is a continuation of my copending ap-
plication Serial No. 96,050, filed March 15, 1961, and
entitled "Metal Molding and Molds Therefor," now aban-
doned.

This invention relates to metal casting molds useful
in producing metal castings from high melting point met-
als such as those found in Group IV-B of the Periodic
Table. The invention also relates to a method of produc-
ing such molds and their use in forming cast metal ob-
jects of the type described above. More specifically, this
invention relates to new type ceramic shell metals cast-
ing molds useful in producing metal objects from high
melting point metals and alloys thereof.

One of the more difficult groups of metals to cast is
Group IV-B of the Periodic Table, which includes such
metals as titanium, zirconium and hafnium, and alloys
containing substantial quantities of these metals.

The most commonly used metal found in Group IV-B
is titanium. Since its melting point is extremely high and
it tends to react with certain elements, such as oxygen,
hydrogen, nitrogen and compounds containing these ele-
ments, special casting techniques must be employed to
insure that satisfactory finished objects will be produced.
While titanium and other Group IV-B metals may be cast
using any number of well-known casting processes, it
has been found that the best results are achieved when
lost wax type casting processes are employed.

While there are many modifications of the lost wax
casting processes, the two most commonly used methods
are either those of investment casting or ceramic shell
mold metal casting. This latter process is being favor-
ably received by the lost wax casting industry, since it
overcomes several of the disadvantages inherent in con-
ventional investment type casting processes.

In its simplest form, the ceramic shell process consists
in the formation of a plurality of built-up ceramic coats
about an expendable pattern. The coats are built up using
a stuccoing procedure to form a thin shell of ceramic
about the expendable pattern. The expendable pattern,
which is usually wax or similar type substance, is re-
moved from the mold by the application of heat or sol-
vents and the remaining shell is then used as a mold for
producing the part sought to be formed.

When either investment casting or ceramic shell metal
mold processes are employed in casting parts of the
Group IV-B metals, it has been the experience of the art
to find that the metal, upon pouring, tends to react with
the surface of the mold causing the finished casting to be
unsatisfactory for commercial utilization. One method of
overcoming mold surface reactions with metals, such as
titanium, is to provide a thin film of metal to be cast
against the inner face surface of the mold, whereby a pro-
tective barrier is formed. This particular technique for
producing Group IV-B metal objects is described in de-
tail in U.S. Patent No. 2,806,271, issued in the name of
applicant. While the disclosure of this patent presents a
satisfactory solution to casting Group IV-B metal ob-
jects by the expediency of investment or ceramic shell
molding techniques, it would be beneficial if a simpler
method were available for producing such types of cast-
ing without resorting to the expediency of coating the
mold with metals.

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It is, therefore, an object of this invention to provide
a casting mold and method peculiarly adaptable for the
casting of high melting point and highly reactive metals,
particularly the metals contained in Group IV-B of the
Periodic Table.

It is a further object of this invention to provide cast-
ing molds and methods for their use which represent im-
provements over the present molds and methods employed
for casting the above-noted metals, including the present
lost wax molds and methods.

It is an additional object of this invention to provide
casting molds and methods employed in their use which
are simpler and more efficient than techniques presently
providing metal castings through the use of ceramic shell
mold processing.

These and other objects of this invention will appear
hereinafter and for purposes of illustration, but not of
limitation, specific embodiments of this invention are
shown in the accompanying drawings in which:

FIGURE 1 represents a cross-section of a ceramic shell
mold having the inner surfaces formed in accordance with
this invention;

FIGURE 2 is an enlarged section of FIGURE 1
through the line 2-2; and

FIGURE 3 represents a cross-section of ceramic par-
ticles employed in accordance with this invention.

In accordance with the invention, it has been found
that it is possible to produce metal objects from Group
IV-B metals and alloys thereof by using the expediency
of coating or otherwise providing the inner face surfaces
of a ceramic metal casting mold with graphite. Such
molds which have their interior face surfaces coated or
formed with graphite are capable of being used in the
production of parts of such metals as titanium without
mold surface reaction occurring. The ceramic molds are
desirably composed of materials having melting points in
excess of 3,000° F.

Since the investment casting or ceramic shell molds
are most commonly used to produce Group IV-B metal
objects, the following general description of the specific
features of the invention will be primarily directed to such
molding processes although it will be understood that the
invention is capable of adaptation to many conventional
type molding operations such as, for instance, cope and
drag or resin shell molding.

FIGURE 1 illustrates a sectional view of a mold 8 for
producing a turbine blade, which is an example of the type
of component cast from metals such as titanium. The
mold consists of a hollow interior 10 into which the metal
is poured. The interior face 22 of the mold is comprised
of a plurality of coatings 12-20, as shown in detail in
FIGURE 2. Coatings 12 and 14 are composed predomi-
nantly of graphite which also has contained therewith
minute quantities of a suitable binder composed of a
ceramic substance. In some instances, the coating 12
forming the inner face surface of the mold may be com-
posed of fine ceramic particles which have been surface
coated with graphite. A typical particle of this type is
shown enlarged in FIGURE 3. In this figure, the numeral
9 refers to a coated particle which comprises a ceramic
particle 11 having an exterior surface coating of graphite
13. It will be apparent that, even where the inner coating
is composed of coated particles of this type, there is still
presented an inner mold face entirely of graphite. It
must be further noted, however, that in the case of casting
highly reactive metals such as titanium, it is essential that
there be no contact with ceramic materials since oxidation
of the titanium would result. Therefore, the invention
contemplates that an essentially pure graphite inner face,
up to a thickness of about .030 inch, be presented to
molten metals of this type.

A large number of the particles shown in FIGURE 3 represent the coating layer 12 of FIGURE 2 when coated particles are used. Although not shown, there also may be admixed with this surface coating minor amounts of free graphite or ceramic particles. This coating is most frequently applied in the form of a liquid dip which will be more fully explained hereinafter. The second coating 14 of FIGURE 1, in a preferred embodiment of the invention, is composed of graphite which is used as the stuccoing agent for coating the dip coat which was initially applied to the expendable pattern used to form the mold. The built-up layers 16-20 are most frequently made from ceramic particles having increasing particle diameters so that the outer coating 20 provides a relatively rough, irregular surface. The inner face coatings of the graphite and ceramic should be formed of small size diameter particles to provide a smooth surface which gives the finished casting a relatively textured, fine surface.

While any ceramic shell metal casting technique may be used to form the preferred molds of the invention, it is beneficial to use the ceramic shell molding process of a type which may be found in the application of Theodore Operhall et al., entitled "Metal Casting Process and Elements and Compositions Used in Same," Serial No. 708,628, filed January 13, 1958, now Patent No. 2,961,751.

This process has as one of its chief points of novelty the use of an outer ceramic coating which forms a portion of the shell and which contains substantial quantities of a ceramic material which reaches a state of incipient fusion at the temperatures used to melt out the pattern from the mold. The expendable patterns, when used in the process, are frequently mounted in clusters using conventional spruing and gating to produce such a cluster. The clustered pattern is then dipped into a dip coating slip having the following typical composition:

8,000 cc. colloidal silica (30% grade) (specific gravity 1.198);
165 pounds zircon (99% through 325 mesh) (65-67% ZrO_2 , 34-32% SiO_2);
6,150 cc. water;
110 grams sodium fluoride.

After being coated by the above-described slip, the coated pattern is allowed to drain, which operation removes any excess of the coating. An initial stucco coating is then sprinkled or shaken onto the pattern cluster to produce a fine layer of ceramic onto the patterns. A typical stucco coat would have the following compositions:

Stucco combination—Alundum (100% through 50 mesh with less than 3% through 100 mesh—better than 90% between 60 and 80 mesh).

The coating and stuccoing, in accordance with the processes just described, are continued until a plurality of stuccoed coats are built up around the patterns contained in the cluster. It will be understood that each successive coat must be air dried sufficiently to allow adhesion of the subsequently applied coats to the pattern. As the ceramic shell starts to form about the patterns, the particle size of the ceramic is increased to give greater rigidity to the finished coated pattern. It is, of course, necessary that the initial coat or coats be composed of a fine particle size ceramic to produce a smooth coating against the outer face surfaces of the pattern.

When the graphite coatings and molds are utilized with a ceramic shell molding process of the type described in said application, it is, of course, necessary that certain modifications and adaptations be made so that the greatest benefits are derived. The most expedient method for coating the interior face surfaces of the mold with the graphite is to form the coatings during the build-up of the ceramic shell onto the expendable pattern. This is accomplished by utilizing a slip as an initial dip coat which contains the graphite generally in combination with minute amounts of a suitable binder. The binder may be com-

posed of the ceramic materials normally used in Patent No. 2,961,751 to form the mold. It is also contemplated that the graphite may be coated around ceramic particles and the coated particles used to form the dip coat slip although this is not always desirable. Where it is desired to employ graphite coated particles, a simple dip coat formula for forming graphite into the face of the mold would have the following general formula:

Ingredients I:	Percent by weight
(A) A finely divided ceramic having a melting point in excess of 3,000° F. -----	50-70
(B) Graphite -----	30-50
(C) From 2 to 15% by weight, based on the combined weight of A and B, of an aqueous colloidal silica sol which contains at least 3% by weight of silica, expressed as SiO_2 .	

In a preferred embodiment, the following dip coat slip of coated graphite might be used:

Ingredients II:	Percent by weight
(A) Stabilized zircon -----	55-65
(B) Graphite -----	35-45
(C) From 3 to 7.5% by weight, based on the weight of A and B of an aqueous colloidal silica sol which contains from 12 to 35% by weight of silica, expressed as SiO_2 .	

Where the molds are to have a coating of substantially pure graphite of about .030 as an inner face or when the inner portions of the mold are to be formed substantially exclusively of graphite, the following composition may be used as a coating composition or as the dip coat composition. This composition may be employed for the first two to three dip coats followed by the use of a graphite stucco:

Ingredients III:	Percent by weight
(A) Graphite -----	99+
(B) Colloidal silica sol (binder) -----	Trace

Subsequent coats will be selected from the following range of compositions:

Ingredients IV:	Percent by weight
(A) A finely divided ceramic having a melting point in excess of 3000° F. -----	30-60
(B) Graphite -----	40-70
(C) From 2 to 15% by weight, based on the combined weight of A and B, of an aqueous colloidal silica sol which contains at least 3% by weight of silica, expressed as SiO_2 .	

From the formula entitled Ingredients II, it should be noted that stabilized zircon is used. Experience in producing titanium castings wherein stabilized zircon was used as the ceramic in conjunction with the graphite, indicates more beneficial heat transmission rates at the inner face surface of the mold are achieved, thus reducing the likelihood of surface reactions. As previously indicated, many times it is desirable to coat the ceramic with the graphite rather than using the two materials separately to form the face coating of the mold. One of the chief advantages of so coating the ceramic is to provide a relatively homogeneous mass for forming into the face surfaces of the mold. The pre-coating of the ceramic with graphite also has the advantage of providing a means for easily forming graphite into the mold areas where it is most beneficial. Since it is important that the inner face surfaces of the mold are composed of fine particles, relatively fine particle size graphite must be used. Such fine particle size graphites tend to have a low density and are very difficult to formulate into ceramic slips of the type described above. The coating of the ceramic particles with the graphite may be accomplished by any conventional method, such as ball milling, which will permit formation of the finely divided graphite onto the surface of the larger ceramic particles.

After the expendable pattern has been treated with dip coat formulas containing graphite and finely divided ceramic, it is then sprinkled, sprayed or in some manner coated with a solid coating which builds up a layer around the pattern. Since the graphite layer deposited against the pattern in the initial dip coat operation is quite thin, the first stucco layer is most desirably formed from graphite. The particle size of the graphite used in this stucco coating may be of the same size or it may be somewhat larger than the particle size of the graphite used in formulating the ceramic slip. It will be understood that minor amounts; viz, up to 40% by weight of ceramic may be incorporated with the stucco graphite coating without departing from the spirit of the invention.

Generally, graphite layers are built up using successive dip coats III and stucco coats of graphite until the graphite layer is from $\frac{1}{16}$ to $\frac{1}{8}$ of an inch in thickness. In the case of the outer graphite layers, larger amounts of ceramic may be employed in both the dip and stucco coats. The build-up of these subsequent graphite layers is for purposes of insuring that the metal poured into the mold will completely contact a surface which is predominantly graphite. When referring to the surface of the interior face of the mold as being predominantly graphite, it is meant to infer that at least 99 percent of the total exposed surface area which would contact the metal poured into the mold is so composed of graphite.

While forming the graphite around the expendable pattern by using the technique of dip and stucco coats, it will be obvious to those skilled in the art that the interior of the mold may be formed by coating graphite onto the pattern without using a liquid system. Thus, the graphite could be brushed onto the pattern or it could be electrostatically deposited, using such expedients as a high voltage delivering device.

After a sufficient number of coats have been built up around the pattern cluster whereby rigidity and strength have been imparted, it has been found beneficial to coat the pattern, in accordance with said application, with a special eutectic composition which has a lower fusion point than the fusion point of the initial ceramic coats placed around the pattern cluster. The eutectic coating is usually similar in composition to the initial coating but contains additional ingredients which form the eutectic thus described. A typical eutectic composition of this type will have the following composition:

8,000 cc. colloidal silica (30% grade) (specific gravity 1.198);

165 pounds zircon (99% through 325 mesh) (65-67% ZrO_2 , 34-32% SiO_2);

6,250 cc. water;

115 grams sodium fluoride;

18.5 pounds feldspar (K_2O , 8%; CaO , 6%; ZnO , 9%; Al_2O_3 , 16-19%; SiO_2 , 60-63%).

The eutectic coating is formed about the pattern in a manner similar to that in which the prior coats had been applied. After the eutectic coating has been allowed to dry and the entire coated pattern cluster is sufficiently free of excess moisture, the coated pattern cluster is melted out in an oven, the temperature of which is preferably at about 1,800° F. As a general rule, the time required to completely remove the pattern from the ceramic shell will vary with the temperature used and the type of material used in the pattern. At the temperature of 1,800° F., the melt-out time will vary from between 3 to 30 minutes. The melt-out temperature may vary between about 400° F. to as high as 2,200° F., depending on the procedure to be employed.

In a preferred embodiment, after firing, the shell is post-coated with additional amounts of ceramic coatings which are similar in their thermal characteristics to that of the eutectic coating. This additional coating has the advantage of tending to seal any cracks or fissures that

may have occurred in the mold during the melt-out cycle when the mold is heated prior to pouring. Thus, the eutectic mixture tends to form a fused surface over the outer segments of the mold acting as a seal to prevent cracks from causing imperfections in the finished metal product.

Molds produced in accordance with the above are capable of being preheated prior to firing at temperatures between 1,600-2,200° F. and preferably between 1,700-1,900° F. without mold deformation occurring even when the mold is subjected to such temperatures for prolonged periods of time. After the mold is thus preheated, the metal is poured into the mold which is then allowed to cool and the ceramic shell removed from the finished metal object. It is recommended that the molds be either heated in a reducing or neutral atmosphere or packed in a material such as graphite during the heating operation. There is, of course, then avoided any possibility of deterioration of the graphite coatings and subsequent oxidation of the metal being cast.

The types of ceramics useful in producing ceramic shell molds of the type described above are such materials such as alumina, titania, stabilized zircon, fused quartz, thoria, chromite, sillimanite, mullite, and magnesia.

In the eutectic coat, it is desirable to make use of an amount of feldspar capable of imparting the desired strength characteristics described, but it is undesirable to make use of such concentration as will lead to excessive diffusion into the mold or will cause the development of hot tears. Feldspar in amounts less than 0.05 part per one part by weight of zircon or other filler in the dip coat has been found to be insufficient to impart the desired strength characteristics. When the amount of feldspar exceeds 0.25 part per one part by weight of zircon or other filler, the mold becomes so strong that it will lead to hot tears in operation and excessive diffusion into the mold may occur. It is preferred to make use of the feldspar in an amount within the range of 0.08-0.15 part by weight of the feldspar to one part by weight of the zircon or other filler in the dip coat or about 8-15 percent by weight of the ceramic solids of the dip coat.

In operation, the feldspar has a tendency progressively to diffuse inwardly during firing. Since it is undesirable to have the feldspar penetrate into the inner surfaces of the mold, the time and temperature for heating should be balanced with the amount of feldspar to enable eutectic formation without complete penetration. Too much feldspar, that is, above the amount previously indicated, would enable progressive reaction to penetrate farther into the shell mold where undesirable conditions can be developed since the feldspar is capable of reaction with the metal while in the molten state. Further, it can form products which do not have the desired heat-shock resistance and thus, the formation of such products should be limited to outer portions of the shell mold. Thus, it is desirable to limit the addition of feldspar to dip coat compositions forming the outer coatings or the outer coating of the shell mold. While description has been made to the use of the outer coating as the eutectic coating containing the feldspar, it will be apparent that the eutectic coating can constitute one of the intermediate dip coats, which may or may not be stuccoed, on the condition that the eutectic coat is spaced at least two coats and preferably five or more coats from the face of the shell mold.

Practice of the concept described by modification of the dip coat to embody feldspar in an outer coating provides a shell mold having an inner face which is still highly refractory and incapable of reaction with the molten metal and an outer coat which functions as a lower maturing coat which is capable of automatically sealing up pores and cracks that may form while at the same time wetting the particles with the eutectic type of binder markedly to increase the strength and toughness

of the shell mold while, at the same time, reducing its heating time and temperature to maturity.

By varying the composition of the eutectic coating, temperature for maturing can be varied from 1,000–2,300° F. Though not equivalent, use can be made of iron oxide, borax or stannous chloride and the like low temperature vitrifiable inorganic materials instead of feldspar. The eutectic coat composition will generally be used at a lower viscosity than the conventional dip coats for stuccoing. In the composition described, the feldspar acts differently than borax in that it is capable of greater stability in suspension without upsetting the balance as compared to borax.

In the firing operation to mature the ceramic materials and to effect removal of the wax patterns from the shell mold, it is desirable in addition to the obvious need for avoiding oxidation to avoid the use of temperatures much in excess of 2,200° F. because otherwise the materials will tend to form a glassy phase which adversely affects the mold. The minimum temperature is that temperature sufficient to activate the binder and, as previously noted, may be as low as 400° F. Within the temperature range of 1,600–2,200° F., time is not an important factor and very often 3 minutes is sufficient at these temperatures, but it is preferred to heat for about 30 minutes. Heating for more than 30 minutes at the temperatures described is not harmful, provided substantial precautions have been taken to avoid oxidation. Above 2,200° F., the strength properties of the shell mold will be increased, but reactions are possible which might cause excessive shrinkage in the shell mold.

After the mold has been formed with the interior face surface being composed predominantly of graphite, it is essential as alluded to above, that precautions be taken throughout the molding cycle to insure that the graphite is not removed by oxidation or physical means. The subsequent molding steps which tend to affect the removal of the graphite from the interior of the mold are the removal of the expendable pattern, the curing of the mold, where such step is employed, or the metal pouring operation.

Since it is quite common to remove the expendable patterns from ceramic shell molds at elevated temperatures; viz, in excess of 1,000° F. or more, such expedients are not desirable in using the mold of this invention unless the melt-out procedures are conducted under conditions to prevent oxidation of the graphite. Thus, for instance, blankets of inert gas could be used if high temperature pattern removal processes are used.

One simple method of removing the expendable pattern from the mold without oxidizing the graphite coating is to employ a solvent extraction technique. In such a process, the coated expendable pattern, after drying, is subjected to the action of a suitable solvent which preferentially acts on the pattern but does not affect the mold or its interior graphite face surfaces. It has been found that such solvents as halogenated hydrocarbons of low molecular weights are admirably suited for removal of both wax and plastic patterns. Thus, the chlorinated hydrocarbons, such as chloroform, carbon tetrachloride, ethylene dichloride, perchlorethylene and chlorinated propanes are eminently satisfactory. These solvents may be used either at ambient temperatures or they may be elevated to about their boiling point whereby advantage can be taken of their vapors which tend to solubilize patterns made of waxes or plastics. The above description of the pattern solvents points out that the preferred solvent materials are halogenated lower hydrocarbons which contain three carbon atoms or less in an aliphatic grouping.

Another method of removing the expendable pattern from the mold without disturbing the graphite coating is to employ either hot water or steam.

When it is desirable to mature or set the mold prior to pouring, oxidation of the graphite may be overcome

by surrounding the shell with packed graphite which forms a protective barrier against the inner face of the graphite coating the mold, thus preventing oxidation. In addition to using graphite, other substances such as ceramic, metal powder and the like may be used so long as they do not volatilize or react with the ceramic and/or graphite in the mold.

An extremely critical phase in the production of titanium and similar metal castings in using the graphite coated molds of the invention occurs during the pouring operation. If the metal is allowed to contact the graphite coated molds under oxidizing conditions, the graphite will be quickly oxidized to either carbon monoxide or carbon dioxide, thus allowing the metal to react with the ceramic ingredients of the mold. One method of preventing such reactions from occurring is to conduct the pouring in the presence of an inert gas that does not react with the mold components or the metal under the temperatures used in pouring. A more desirable method, however, is to utilize vacuum techniques during the pouring step. A suitable apparatus for vacuum pouring of lost wax molds is shown in applicant's Patent No. 2,806,271. Suitable adaptations of this device may be made to provide for pouring into the ceramic shell molds of this invention. In order to eliminate traces of air contained in the mold and its surrounding environment, the vacuum utilized in such vacuum pouring operations should be nearly complete, such as 50 microns or less with 10 microns of vacuum giving satisfactory results when titanium is the metal being processed.

After the metal has been poured into the mold, it is necessary to continue the use of either a vacuum or an atmosphere of inert gas until a certain critical temperature, which in the case of titanium is about 900° C., has been obtained. At this point, there is no longer danger of oxidation of the graphite contained within the mold.

It is believed the above presents a new type of casting mold for producing cast metal objects of Group IV-B metals and alloys thereof. These molds and their method of utilization are particularly suited to produce titanium castings which have close tolerance, high quality finishes and suitably grained surfaces. Thus, a very simple solution to a complex and troublesome problem has been presented which now makes the casting of Group IV-B metal within the reach of most casting houses which heretofore have been unable to produce such castings due to the difficulty in working with such high melting point metals.

It will be understood that changes may be made in the details of materials, their formulations, their applications and in the operations without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. A ceramic slip useful in producing a graphite interior face coated ceramic shell mold for producing Group IV-B metal objects which comprises 50–70% by weight of a finely divided ceramic having a melting point in excess of 3,000° F., 30–50% by weight of graphite, and from 2 to 15% by weight, based on the combined weight of the ceramic and graphite, of an aqueous colloidal silica sol which contains at least 3% by weight of silica, expressed as SiO₂, said graphite comprising a coating on the surfaces of the finely divided ceramic.

2. A ceramic slip useful in producing a graphite interior face coated ceramic shell mold for producing titanium castings which comprises 55–65% by weight of stabilized zircon particles, 35–45% by weight of graphite, and from 3 to 7.5% by weight, based on the weight of the zircon and graphite, of an aqueous colloidal silica sol which contains from 12 to 35% by weight of silica, expressed as SiO₂, said graphite comprising a coat on the surfaces of the stabilized zircon particles.

3. The process of producing a ceramic shell mold suitable for casting Group IV-B metals comprising the steps

of coating finely divided graphite onto the surfaces of a mass of ceramic particles, forming a slip of the coated particles, providing an expendable pattern corresponding to the objects to be cast, forming a primary coating on said pattern with said slip of coated particles, forming a plurality of stuccoed ceramic coats about said primary coat, and removing said expendable pattern from said primary and stuccoed coats whereby said molds have interior face surfaces with substantial quantities of graphite.

4. The process according to claim 3, wherein the ceramic particles consist of zircon.

5. The process according to claim 3, wherein the graphite is substantially uniformly provided in amounts in excess of 99 percent of the interior surface area of said mold.

6. A mold for producing cast metal objects from Group IV-B metals comprising an inner face coat having a thickness in excess of .030 inch composed of greater than 99 percent graphite and a binder, and at least one subsequent coat composed of from 30-60% of a finely divided ceramic having a melting point in excess of 3,000° F., 40-70% graphite, and from 2 to 15% by weight, based on the combined weight of said ceramic and said graphite, of an aqueous colloidal silica sol which contains at least 3% by weight of silica, expressed as SiO₂.

7. A ceramic shell mold for producing cast metal objects from Group IV-B metals which comprises an interior portion made up of a plurality of layers of graphite powder bound with a ceramic binder alternating with layers of graphite stucco, and a plurality of layers of ceramic powder bound with a ceramic binder alternating with layers of ceramic stucco surrounding said interior portion, the material in said ceramic powder and stucco in said outer layers being selected from the group consisting of zircon, stabilized zircon, alumina, titania, fused quartz, thoria, chromite, sillimanite, mullite, and magnesia.

8. A metal casting process for producing Group IV-B metal objects which comprises coating an expendable pattern with a series of alternating dip coats and stucco coats

to build up a shell mold of desired wall thickness about the pattern in which the solids of the first one to three dip coats applied to the pattern consist of at least 99% by weight of graphite and in which the first one to three stucco coats consist of graphite whereby the inner portions of the shell mold disposed about the mold pattern consist essentially of graphite removing the pattern from the mold under non-oxidizing conditions whereby the graphite is maintained to define the inner portion of the mold, pouring the Group IV metals in the mold under non-oxidizing conditions and maintaining the non-oxidizing conditions until the metal has been set in the mold and then removing the metal object from the mold.

9. The process as claimed in claim 8, wherein it includes the step of surrounding the mold with graphite during the drying of the mold and in which the cure is carried out within a temperature range of from 1,600-2,200° F.

10. The process as claimed in claim 8, in which the mold is formed with the inner portions of graphite and with the outer portions of conventional ceramic materials from a ceramic dip coat composition and ceramic stucco.

References Cited by the Examiner

UNITED STATES PATENTS

2,530,853	11/1950	Brennan	22-203
2,548,897	4/1951	Kroll	22-200
2,682,692	7/1954	Kohl	22-193
2,829,060	4/1958	Emblem et al.	22-196
2,886,869	5/1959	Webb et al.	
3,114,948	12/1963	Poe	22-196

FOREIGN PATENTS

752,742 7/1956 Great Britain.

OTHER REFERENCES

"New Breakthrough on Casting Titanium" by Westwood in Modern Casting, March 1960, pages 36-69, copy in 22-193 SM.

MARCUS U. LYONS, *Primary Examiner*.