⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 233 478**
A1

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **87100559.1**

㉒ Date of filing: **16.01.87**

(51) Int. Cl.⁴: **B22C 1/00** , B22C 9/06

㉚ Priority: **17.01.86 JP 7658/86**
17.01.86 JP 7659/86
17.01.86 JP 7660/86
17.01.86 JP 7661/86
17.01.86 JP 7662/86
17.01.86 JP 7663/86
17.01.86 JP 7664/86
21.01.86 JP 10916/86

㊸ Date of publication of application:
26.08.87 Bulletin 87/35

(84) Designated Contracting States:
DE FR GB IT SE

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(54) Mold, method of producing mold and casting method.

(57) Disclosed are a porous calcia mold containing not less than 40 wt% CaO, a mold containing 95 to 10 wt% CaO and 5 to 50 wt% graphite, a mold containing not less than 40 wt% CaO, not more than 5 wt% low-eutectic temperature oxide and not more than 40 wt% high-eutectic temperature oxide, and a mold provided with a layer containing not less than 40 wt% CaO on the surface which comes into contact with a molten metal.

A method of producing a porous mold by baking a molded body obtained by a slip casting method or an injection molding method, and a method of producing a mold by baking a molded body (1) while bringing a member for preventing the deformation of a molded body (2) into contact with the molded body (1) are also disclosed.

In addition, a method of casting a highly active metal, a high-melting point metal, or an alloy containing such a metal by using one of the above-described molds, and a casting method comprising the steps of placing a bottomless porous calcia mold on a metal chill plate, pouring a molten metal by top-pouring and gradually solidifying the molten metal from the lower part while insulating the riser are also disclosed.

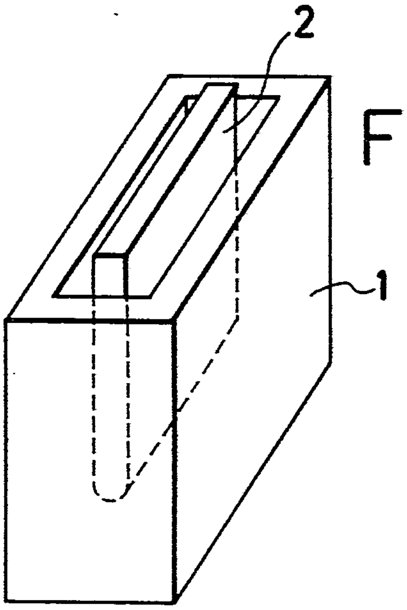


FIG. 1

MOLD, METHOD OF PRODUCING MOLD AND CASTING METHOD

FIELD OF THE INVENTION AND RELATED ART STATEMENT

The present invention relates to a mold containing calcia (CaO) as the main constituent, a method of producing such a mold and a casting method using such a mold. A mold according to the present invention is capable of casting even an active metal and a high-melting point metal.

It is known that a calcia refractory material is thermodynamically stable even at a high temperature, and has a refining effect. Japanese Patent Publication No. 849/1979 discloses a method of deoxidizing and desulfurizing a molten steel by adding aluminum to the molten steel which is accommodated in a container lined with a basic refractory material containing much CaO under vacuum or an argon atmosphere.

In order to obtain a highly purified casting, it is necessary not only to prepare a highly pure molten metal but also to use a mold which does not contaminate the molten metal. As a mold used for casting an active metal (including alloy) such as titanium and zirconium, rammed mold, investment mold, water-cooled copper mold, sand mold (using zirconium sand, olivine sand etc.) etc. are conventionally known. A rammed mold is made by molding a material of graphite powder with a carbon or resin binder, drying and baking the molded body. As an investment mold are known what is called a tungsten powder coated mold which is made of a slurry of tungsten and a metal binder, what is called an oxide mold which is made of a combination of a slurry of an oxide and an oxide binder, and a graphite mold which is made of a graphite slurry and a binder containing carbon.

When an active metal is poured into such a conventional mold, a mold reaction occurs, and in the case of a graphite mold, carbon is produced, while in the case of a magnesium or zirconium mold oxygen contaminates the surface of the casting. Especially, when an investment mold using an oxide binder is used, the ingress of not only oxygen but also nitrogen occurs. Such a contamination on the surface of a casting requires the step of removing the contaminated layer from the surface, thereby making the manufacturing process very complicated. A casting method using a water-cooled copper mold is disadvantages in that the mold is expensive and entails a risk of explosion due to leakage of water.

When a highly active metal or alloy is cast by a casting method using casting sand, there is a fear of unfavorable metal content such as silicon and iron mixing into the casting by reduction. For the above-described reasons, it is difficult to obtain a sound casting of a highly active and fragile metal such as pure chromium, chromium alloy, titanium alloy, e.g., nickel titanium alloy by a conventional casting method.

OBJECT AND SUMMARY OF THE INVENTION

Accordingly, it is a primary object of the present invention to provide a mold which is capable of casting an active metal such as titanium and zirconium, or an alloy containing such an active metal and is capable of producing a highly purified casting free from contamination of C, O, N, etc.

It is a second object of the present invention to provide a mold which is capable of casting a high-melting point metal such as tungsten and vanadium or an alloy containing such a high-melting point metal and is capable of producing a highly purified casting.

It is a third object of the present invention to provide a method of producing such a mold.

It is a fourth object of the present invention to provide a casting method using such a mold.

A first mold of the present invention is a porous calcia mold containing not less than 40 wt% CaO.

A second mold of the present invention is a calcia mold containing not less than 40 wt% CaO and 0.1 to 8 wt% halide.

A third mold of the present invention is a calcia graphite mold containing 95 to 10 wt% CaO and 5 to 50 wt% graphite.

A fourth mold of the present invention is a calcia mold containing not less than 40 wt% CaO, not more than 5 wt% low-eutectic temperature oxide, and nor more than 40 wt% high-eutectic temperature oxide.

A fifth mold of the present invention is provided with a layer of a calcia refractory material containing 40 wt% CaO on the surface of the mold which comes into contact with a molten metal.

A method of producing a mold according to the present invention comprises the steps of pouring a slurry of a non-aqueous solution of calcia powder or particles containing not less than 40 wt% CaO into a liquid-absorbing master mold to make a deposit on the surface of the master mold, removing the master mold, drying the deposit, and baking the deposit at a baking temperature for a baking time which are so determined that a sintered body to be obtained will be porous.

Another method of producing a porous calcia mold according to the present invention comprises the steps of kneading calcia particles with an organic binder, injection molding the kneaded material, removing the binder, and baking the molded body at a baking temperature for a baking time which are so determined that a sintered body to be obtained will be porous.

Still another method of producing a calcia mold according to the present invention comprises the steps of baking a molded body of a calcia particulate molding material while bringing a member for preventing the deformation of a molded body into contact at least with a part of the molded body.

In a casting method according to the present invention, one of the above-described molds is used to cast a highly active and/or high-melting point metal (including an alloy).

A casting method according to the present invention comprises the steps of placing a bottomless calcia mold on a metal chill plate, pouring a molten metal by top-pouring, and gradually solidifying the molten metal from the lower part while insulating the riser of the mold.

BRIEF DESCRIPTION OF THE DRAWINGS AND PREFERRED EMBODIMENTS

Fig. 1 is an explanatory perspective view of an embodiment of a method according to the present invention;

Figs. 2 and 3 are vertical sectional views of the method shown in Fig. 1;

Figs. 4(a) to 4(c) are enlarged sectional views of the inner walls of molds according to the present invention showing the examples of the layers of a calcia refractory material formed thereon;

Figs. 4(d) to 4(f) are graphs showing the content of CaO of the respective layers of a calcia refractory material shown in Figs. 4(a) to 4(c);

Figs. 5 and 6 are explanatory side elevational views of a method according to the present invention;

Fig. 7 shows the configuration and the dimensions of a master mold; and

Figs. 8 and 9 shows the dimensions of a mold.

The above-described first to fifth molds will first be explained in the following.

First Mold:

A first mold according to the present invention is a calcia mold containing not less than 40 wt% CaO. Calcia has a high melting points, as described above, and thermodynamically stable even at a high temperature. Since the stability and the heat resistance of the molds increase with the increase in CaO content, the molds contain at least 40 wt% (herinunder % means wt% unless otherwise specified), preferably at least 50 %, and more preferably at least 60 % CaO.

Since the material of the first mold is calcia, which has a high melting point and is thermodynamically stable even at a high temperature, it is easy to cast a high-melting point and/or highly active metal and it is possible to obtain a casting free from contamination on the surface thereof. Furthermore, since the mold is porous, it is efficient in resistance to thermal shock, and has high heat retaining properties and good durability. In addition, it is possible to reuse the calcia material many times, and since the position of the shrinkage cavity is high, the yield is enhanced.

Since the first mold is cheap, and reusable due to the high resistance to thermal shock, it greatly reduces casting costs.

The first to fifth molds of the present invention are adaptable to an inner mold called a core as well as an outer mold. Since CaO has slaking properties, it is possible to remove these molds by hydrating them by utilizing the slaking properties.

The materials which the molds can contain as well as CaO are exemplified by an oxide, a carbide, a nitride, carbon and a halide. As an oxide, an oxide having a high melting point such as magnesia (MgO) and zirconia (ZrO_2) is preferable. As examples of a carbide and a nitride, silicon carbide, silicon nitride, and aluminum nitride will be cited.

As a halide, an alkaline metal, an alkaline earth metal, a fluoride and a chloride of lead, and a double salt containing these elements will be mentioned. To state them more concretely, they are, for example, CaF_2, MgF_2, BaF_2, SrF_2, NaF, LiF, KF, PbF_2, CsF, Na_3AlF_6, $CaCl_2$, $MgCl_2$, NaCl, and KCl. It is preferable to add 0.1 to 8 % of at least one halide selected from the above-described group. Addition of such a halide makes the surface of a casting smooth and facilitates the baking of a calcia mold.

The molds can contain carbon (C) as a material except CaO. Graphite is preferable as a carbon material. Both natural graphite and artificial graphite are usable. Since graphite is scaly, the molding properties are poor, and since it is inherently poor in reactivity, it is difficult to form graphite into a ceramic bond and the strength of the sintered body is therefore apt to be lowered. Therefore, when graphite is used as a material for a calcia mold, it is effective to add a small amount of metallic aluminum. When aluminum is baked in a non-oxidizing atmosphere, a highly corrosion-resistant reaction product such as aluminum carbide and aluminum nitride is produced, which enhances the corrosion resistance of the mold and the bonding strength between graphite and the surrounding structure, thereby improving the strength of the mold.

When the calcia mold is produced, calcium hydroxide as well as limestone, calcinated limestone, namely, quick lime, and electrofused calcia which is melted in an arc furnace is usable as a material. A mineral containing CaO such as larnite, merwinite, anorthosite and dolomite is also usable.

In order to produce the mold, at least one selected from the group consisting of the above-described oxide, carbide, nitride, carbon and halide is added to such a calcia material, as desired, and a slurry is made by mixing them into a non-aqueous solution. When the slurry is made, if the particle diameter of the particulate molding material is too small, it is often the case that the shrinkage at a later step of baking becomes excessively large or the sintered body becomes pressure tight. Therefore, it is preferable to classify the particulate molding material so that the fine particles having a particle diameter of not more than 0.1 mm is at least 40 % and at most 50 %. On the other hand, if the particle diameter of the particles is too large, the surface of the mold becomes rough, so that the largest particle diameter is at most 1 mm, preferably at most 0.5 mm.

A liquid used for preparing the slurry is a non-aqueous solution, namely, a liquid containing no water, because calcia has slaking properties.

As a non-aqueous solution, a solution having an appropriate viscosity is used. For example, alcohol - (monovalent or polyvalent alcohol) with mastic gum dispersed therein, toluene with oleic acid dissolved therein, alcohol with oleic acid dissolved therein, oil with oleic acid dissolved therein, carbon tetrachloride with beeswax dissolved therein, and isobutyl acetate are preferable, but the present invention is not limited thereto and any non-aqueous liquid which does not slake calcia is usable.

It is preferable to adjust the viscosity of such a non-aqueous solution so that when in is made into a slurry, it has an appropriate viscosity to be poured into a master mold at ordinary temperature. Other additives used in a slip casting method such as deflocculant, antifoamer, germicide, and cheleating agent for inactivating unnecessary ions may be added to the slurry.

In order to produce the first mold, such a slurry is poured into a liquid-absorbing master mold. As the master mold, a mold having properties of absorbing the above-described non-aqueous solution is used, and a gypsum mold is most preferable. The configuration of the master mold is not specified so long as it has a configuration of a female mold of a mold to be obtained.

When the slurry is poured into the master mold, the non-aqueous solution of the slurry is absorbed by the master mold, and the solid content of the slurry adheres to the inner surface of the master mold, in other words, what is called deposition progresses. After a predetermined amount of solid content has deposited to the inner surface of the master mold, the slurry in the master mold is discharged, if necessary, and thereafter the liquid of the deposit on the inner surface of the master mold is left to be further absorbed by the master mold. This step of liquid absorption reduces the liquid of the deposit, and therefore facilitates the release of the deposit. Thereafter, the mother mold is removed. In the present invention, it is preferable to apply a mold release agent to the inner surface of the mother mold in advance in order to facilitate the removal of the mold.

After the completion of the removal of the mold, the molded body obtained is dried. The molded body is preferably dried gradually at a temperature lower than the boiling point of the non-aqueous solution. In the latter period of the step of drying, the molded body may be dried at a temperature higher than the boiling point.

The dried molded body is next baked. Preferably, the molded body is first calcinated at a temperature at which the organic material which has been dissolved in the non-aqueous solution is oxidized away, and thereafter the molded body is baked to be sintered. In a method of producing a mold according to the present invention, the temperature and the time for baking are selected so that the sintered body to be obtained will be porous. These baking conditions are different depending upon the components in the mold other than CaO. For example, if a comparatively large amount of halide or oxide which constitutes a compound having a low melting point together with CaO is contained, the baking temperature is low and the baking time is short. Needless to say, if the baking temperature is high, the baking time is short, while a low baking temperature requires a long baking time. To state this concretely, if the molded body contains 40 to 80 % CaO, it is ordinarily baked at about 850 to 1,350°C for about 1 to 10 hours. If the CaO content exceeds 80 %, the molded body is preferably baked at a comparatively high temperature of 1,200 to 1,700°C for about 1 to 5 hours.

The sintered body obtained is ground, if necessary, to finish a mold.

The mold of the present invention is porous. The porosity is preferably 10 to 40 vol%, more preferably 15 to 30 vol%. If the porosity is less than 10 vol%, the resistance to thermal shock and the insulating effect of the mold are lowered.

Another method of producing the porous calcia mold is as follows.

At least one selected from the group consisting of the above-described oxide, carbide, nitride, carbon and halide is added to the above-described calcia material, as desired, to make a particulate molding material. If the particle diameter of the particulate molding material is too small, it is often the case that the shrinkage at a later step of baking becomes excessively large or the sintered body becomes pressure tight. Therefore, it is preferable to classify the particulate molding material so that the fine particles having a particle diameter of not more than 0.1 mm is at most 20 %, preferably at most 10 %. On the other hand, if the particle diameter of the particles is too large, injection is difficult and the surface of the mold becomes rough, so that the largest particle diameter is at most 1 mm, preferably at most 0.5 mm, and more preferably at most 0.3 mm.

An organic binder is added to the particulate molding material and they are kneaded. The kneaded material is injection molded.

As the organic binder, a non-aqueous binder which does not slake calcia is used. For example, not only a thermoplastic resin such as polystyrene, polyethylene, cellulose acetate, polyvinyl alcohol, acryl and polypropylene but also a thermosetting resin such as novolak is usable. A plasticizer, a lubricant and an auxiliary may be used together with the organic agent.

As a plasticizer, diethyl phthalate, paraffin, dibutyl phthalate, wax, dioctyl phthalate, fatty ester, etc. are preferable. As a lubricant, zinc stearate, aluminum stearate, magnesium stearate, diglycol stearate, bread crumb, mineral oil, etc. are preferable. As an auxiliary, atactic polypropylene, a group of a plurality of resins having different decomposition temperatures, a sablimating material such as naphthalene, natural vegetable oil such as peanut oil and soybean oil, natural animal oil, etc. are preferable. The amount of organic binder to be added is preferably about 0.1 to 20 wt% with respect to 100 wt% of particulate molding material. A plasticizer, a lubricant and an auxiliary are preferably added at most 10 wt% in total amount.

After the addition of an organic binder etc., the material is heated to, for example, about 80 to 150°C, if necessary, stirred and kneaded, and thereafter it is cooled to be solidified. The solidified material is then crushed and dressed into particles of a diameter of not more than 0.5 mm, preferably not more than 0.3 mm. In place of crushing, the material may be granulated by extrusion or the like.

The thus-obtained injection molding material is supplied to an injection molding machine, injected into the die to obtain a molded body. As an injection molding machine, various kinds of molding machines such as a screw in-line type injection molding machine and a plunger injection molding machine are usable. In such an injection molding machine, the injection molding material is heated in a heating cylinder, kneaded to be plasticized, and injected into a die by the advancement of a screw or a plunger. The die has a configuration of a female mold of a mold to be obtained.

The obtained molded body is cut or ground, as occasion demands, to finish it into a predetermined configuration, and the binder is removed. In order to remove the binder, for example, the temperature is gradually raised to about 350 to 500°C in the air atmosphere, and the resin content is removed by decomposition, sublimation or oxidation.

Thereafter the molded body is baked to obtain a sintered body. The baking conditions are the same as those described above. To state this concretely, if the molded body contains 40 to 80 % CaO, it is ordinarily baked at about 850 to 1,350°C for about 1 to 10 hours. If the CaO content exceeds 80 %, the molded body is preferably baked at a comparatively high temperature of 1,000 to 1,500°C for about 1 to 5 hours.

The sintered body obtained is ground, if necessary, to finish a mold.

In the above-described method of producing a calcia mold, a member for preventing the deformation of a molded body may be brought into contact with at least a part of the molded body while it is being baked. This member greatly lessens the deformation of the body to be sintered in the step of baking, and enhances the dimensional accuracy of the mold. Since the member for preventing the deformation of a molded body is reusable many times, it is possible to produce a multiplicity of molds of the same inner dimension with accuracy.

The member for preventing the deformation of a molded body is made of a material which does not react with the calcia particulate molding material during baking the molded body. A ceramic material such as alumina is preferable.

The member for preventing the deformation of a molded body has an outer surface having the configuration in conformity with that of the inner surface of a mold to be obtained. This member may have a configuration which makes the member in close contact with either the entire part of the inner surface of the mold, or only a part thereof. The member for preventing the deformation of a molded body may also consist of a combination of a plurality of parts. If the configuration of the inner surface of the mold is a rectangular parallelopiped, a plate-like or box-shaped member for preventing the deformation of a molded body is used. If the configuration of the inner surface of the mold is a column, a columnar or cylindrical member is used.

The member for preventing deformation may be charged into the master mold before molding the particulate molding material, or may be charged into the cavity of the molded body after the particulate molding material has been molded.

The member for preventing the deformation of a molded body maintains the state in which it is in close contact with at least a part of the molded body during the step of baking. The close contact of the member securely prevents the deformation of the molded body during the step of baking.

The method of molding is not limited to the above-described methods, and the methods of die casting, slip casting, rubber press, injection molding, hot press, stamping and so forth are usable.

It is to be understood that the sintering method adopting the member for preventing deformation is adaptable to a method of sintering molds other than the above-described porous mold. It is possible to provide a pressure tight calcia mold by the sintering method adopting the above-described step of preventing deformation. If the step of baking is carried out at a higher temperature than the above-described baking temperature and/or for a longer timer than the above-described baking time, the molded body will be sintered adequately and produce a sintered body having high density. If a particulate molding material has a wide range of particle size, the sintered body will also become pressure tight.

As an experiment, 5 % parts by weight of calcium chloride was added to 100 % parts by weight of calcia particulate molding material, and after they were kneaded, they were molded into a configuration shown in Fig. 1 to obtain a molded body 1. Before molding, a member 2 for preventing the deformation of a molded body had been charged into a master mold, and the calcia particulate molding material was charged into the space between the inner surface of the master mold and the outer peripheral surface of the member 2 for preventing the deformation of a molded body in such a manner as to be rammed.

The calcia particulate molding material used was reagent CaO particles having a CaO purity of 98 %. The dimensions of the mold at the time of molding was 5 cm in length, 15 cm in width, 13 cm in height and 12 cm in depth. The member for preventing the deformation of a molded body is an alumina plate 0.5 cm in length, 10 cm in width and 15 cm in height. The molded body 1 integral with the member 2 for preventing the deformation of a molded body, as shown in Figs. 1 and 2, was baked at 950°C for 3 hours in electric furnace, and after slow cooling the member 2 for preventing the deformation of a molded body was drawn. Thus, a mold of a high dimensional accuracy was obtained.

Second Mold:

A second mold of the present invention is composed of a calcia refractory material which contains not less than 40 wt% CaO and 0.1 to 8 wt% halide. The second mold, which is a calcia mold, is also capable of casting a high-melting point metal, a highly active metal and an alloy containing such a metal with high purity. Since the second mold contains a halide, the surface of the mold is smooth, which produces a casting having a smooth casting surface.

The halide in the mold facilitates the baking and enables a molded body of a mold of a predetermined dimension to be provided even under a low pressure. Halides suitable for the mold have been exemplified above. The halides have a low melting point and many of them have much higher resistance to slaking than CaO. Therefore, the existence of a halide itself improves the resistance to hydration and accelerates the sintering of the material during the step of baking, thereby enhancing the density of the structure of the sintered body. These effects provide in cooperation the mold with high resistance to hydration. The action of accelerating sintering also greatly increases the strength of the mold to be obtained. The halide often exists in grain boundaries, and a layer containing much halide surrounds a CaO particle. It is considered that this fact also improves the resistance to hydration of the mold. Since addition of too much halide reduces the refractoriness of the mold, the content is not more than 8 %, preferably not more than 5 %. Needless to say, since addition of too small amount of halide does not bring about the above-described effects and actions, the content is not less than 0.1 %, preferably not less than 0.3 %. Since the stability and the heat resistance of the mold increases with the increase in CaO content, the mold of the present invention contains at least 40 wt%, preferably at least 70 wt%, and more preferably at least 80 wt% CaO.

The mold may contain an oxide, a carbide, a nitride, carbon as well as CaO. These compounds suitable for the mold have already been exemplified. The mold may either be porous or pressure tight.

In order to produce the second mold, at least one selected from the group consisting of the above-described oxide, carbide, nitride and carbon is added to the above-described calcia material and halide, as desired, to make the main raw material. The main raw material with an appropriate binder added thereto, if necessary, is molded and baked to make a mold.

As the binder, a non-aqueous binder is used. It may be either a liquid or a solid binder. As a liquid binder, alcohol, toluene, alcohol (monovalent or polyvalent alcohol) with anhydrous calcium chloride, mastic gum, acacia gum or the like dispersed therein, toluene with oleic acid dissolved therein, alcohol with oleic acid dissolved therein, oil with oleic acid dissolved therein, carbon tetrachloride with beeswax dissolved therein, and isobutyl acetate are preferable, but any non-aqueous liquid which does not slake calcia such as, for example, various mineral oils such as asphalt, tar and pitch and the residue thereof, animal oil and vegetable oil is usable.

The amount of binder to be used is preferably 1 to 5 wt% of a particulate molding material.

As a solid binder, a thermoplastic resin such as polyethylene, polypropylene, cellulose acetate, acrylic resin and polyvinyl alcohol, a thermosetting resin such as novolak and paraffin are preferable, but other materials which provide molding properties for the raw material are also usable.

Various methods, for example, die casting, slip casting, rubber press, injection molding, hot press and stamping are used for molding the raw material.

The material may be hot pressed with no or a small amount of binder.

The molded or the stamped mold is dried, if necessary, and after it is calcinated at a temperature, preferably lower than the baking temperature, it is baked to be sintered. The baking temperature is not lower than 800°C, preferably 1,200 to 1,800°C. The step of baking is carried out in the air atmosphere, but another atmosphere is possible.

The material for the mold is cheap and is capable of being collected after casting and molded for reuse, so that it is possible to greatly reduce casting costs.

The second mold facilitates the casting of a high-melting point and/or highly active metal. A mold containing a large amount of, for example, not less than 80 wt% CaO is suitable for casting a high-melting pure metal such as chromium and vanadium and an alloy containing a large amount of such metal. A mold containing a large amount of CaO is also suitable for casting a highly active pure metal such as titanium and zirconium and an alloy containing a large amount of such metal.

Third Mold:

A third mold is composed of a calcia graphite refractory material containing 95 to 10 wt% CaO and 5 to 50 wt% graphite. Since the main material of the mold is CaO and graphite having high heat resistance, it facilitates the casting of a high-melting point and/or highly active metal and is capable of producing a casting free from contamination on the surface. Since the third mold contains a comparatively large amount of graphite, the inner surface of the mold is smooth and is therefore capable of producing a casting having a smooth surface. In addition, since the mixing ratio of CaO and graphite is appropriate, the heat retaining properties and the fluidity are better than those of a graphite mold.

In the third mold of the present invention, the heat resistance of the mold is improved by adding not less than 5 % graphite to the material, thereby facilitating the casting of a high-melting point metal. If the graphite content exceeds 50 %, carbon is likely to mix into the molten metal and contaminate it, so that the content of graphite is not more than 50 %. The content of graphite is preferably 10 to 40 %, more preferably 15 to 30 %. Any of natural graphite and artificial graphite such as crushed electrode graphite, pyrolytic graphite and kish graphite is usable in the present invention. Since graphite is scaly, it has poor molding properties, and since it is inherently poor in reactivity, it is difficult to form graphite into a ceramic bond and the strength of the sintered body is therefore apt to be lowered. Therefore, when graphite is used as a material for a calcia mold, it is effective to add a small amount of metallic aluminum. When aluminum is baked in a non-oxidizing atmosphere, a highly corrosion-resistant reaction product such as aluminum carbide and aluminum nitride is produced, which enhances the corrosion resistance of the mold and the bonding strength between graphite and the surrounding structure, thereby improving the strength of the mold.

The third mold may contain various kinds of halides described above as well as CaO and graphite. Since addition of too much halide lowers the refractoriness, the content is not more than 5 %, preferably not more than 3 %.

The third mold may also contain an oxide, a carbide and a nitride. These compounds have been exemplified above. Since the stability and the heat resistance of the third mold in an oxidizing atmosphere increases with the increase in CaO content, the third mold contains at least 10 wt%, preferably at least 30 wt %, and more preferably at least 50 wt% CaO.

It is possible to produce the third mold in the same way as explained in the first and second molds.

Fourth Mold:

A fourth mold is composed of a calcia refractory material containing not less than 40 wt% CaO, not more than 5 wt% low-eutectic temperature oxide and not more than 40 wt% high-eutectic temperature oxide. Since the mold contains an appropriate amount of metal oxide, sintering is easy and has high strength and resistance to slaking. The low-eutectic temperature oxide is at least one selected from the group consisting of metal and semi-metal oxides which have a eutectic temperature below 1,450°C, and the high-eutectic temperature oxide is at least one selected from the group consisting of metal oxides which have a eutectic temperature of not lower than 1,450°C.

Typical examples of low-eutectic temperature oxides and the eutectic temperature with respect to CaO will be shown in the following.

(1) P_2O_5 480°C
(2) V_2O_5 618°C
(3) B_2O_3 970°C
(4) FeO 1,100°C
(5) Fe_2O_3 1,205°C
(6) Al_2O_3 1,400°C
(7) SiO_2 1,436°C

Although such a low-eutectic temperature oxide has an effect of enhancing the sintering ability, it produces a low-melting point composition in a calcia mold, thereby lowering the heat resistance of the mold. Therefore, the content of a low-eutectic temperature oxide is not more than 5 %, preferably not more than 3 %, and more preferably not more than 2 %. Above all, the content of P_2O_5, B_2O_3 and FeO, which greatly lower the heat resistance of the mold, is preferably not more than 1 %.

Typical examples of high-eutectic temperature oxides and the eutectic temperature with respect to CaO will be shown in the following.

(1) TiO_2 1,475°C
(2) Cr_2O_3 1,930°C
(3) MgO 2,370°C
(4) ZrO_2 2,250°C
(5) ThO_2 2,000°C or higher
(6) Y_2O_3 2,000°C or higher
(7) oxide of rare earth element 1,600 to 2,500 C

Even if a considerably large amount of high-eutectic temperature oxide is contained in a calcia mold, it hardly lowers the heat resistance of the mold. In addition, since the sintering ability of a mold containing a high-eutectic temperature oxide is better than that of a mold containing CaO alone, addition of such an oxide facilitates the baking of the mold and enhances the strength thereof. Increase in the content of a high-eutectic temperature oxide relatively reduces the CaO content and increases the resistance to slaking of the mold. However, too large an amount of high-eutectic temperature oxide lowers the heat resistance of the mold and the stability with respect to a molten metal. Therefore, the fourth mold contains not more than 40 % high-eutectic temperature oxide.

In the fourth mold, the smaller amount of high-eutectic temperature oxide is contained, the better are the properties of the mold such as the heat resistance and the stability. Therefore, the content of a high-eutectic oxide is preferably as small amount as possible in the above-described range. However, when it is necessary to enhance the resistance to slaking and the sintering ability, the content of a high-eutectic temperature oxide is at least 5 %, preferably at least 10 %.

Among the above-described high-eutectic temperature oxides, TiO_2 and Cr_2O_3 have comparatively low eutectic temperatures. Therefore, the content of oxides such as TiO_2 and Cr_2O_3 is preferably not more than 20 %, more preferably not more than 15 %.

The fourth mold may contain various kinds of halides described above as well as CaO. Since addition of too much halide lowers the refractoriness, the content is not more than 5 %, preferably not more than 2 %.

The fourth mold may also contain an oxide, a carbide, a nitride exemplified above and carbon (C).

Since the stability and the heat resistance of the fourth mold increases with the increase in CaO content, the fourth mold contains at least 40 wt%, preferably at least 70 wt %, and more preferably at least 80 wt% CaO.

It is possible to produce the fourth mold in the same way as explained in the first and second molds.

Fifth Mold:

A fifth mold is a mold provided with a layer of a calcia refractory material containing not less than 40 wt% CaO on the surface which comes into contact with a molten metal.

Since the surface of the fifth mold which comes into contact with molten metal is made of calcia which has a high melting point and is thermodynamically stable even at a high temperature, the mold facilitates the casting of a high-melting point and/or highly active metal. A casting to be obtained is a highly purified casting free from contamination of C, O, N etc., and dispenses with any after-treatment such as the removal of the contaminated layer on the surface of the casting. The fifth mold is cheap and since it has high resistance to hydration and strength, it is reusable many times, thereby enabling much reduction in casting costs.

Furthermore, since the fifth mold can be composed of a conventional mold material except for the surface which comes into contact with molten metal, it is possible to utilize an existing equipment and to compensate for the defects in the strength and the hydrating properties of a calcia refractory material.

Examples of providing a layer of a calcia refractory material are shown in Figs. 4(a) to 4 (c).

In Fig. 4(a), a layer 22 of a calcia refractory material is formed on the surface of a mold body 21 which comes into contact with a molten metal. The mold is a non-calcia mold such as a graphite mold or a low-calcia mold.

In Fig. 4(b), the layer 22 of a calcia refractory material is formed on the surface of the mold body 21 with an intermediate layer 23 containing a comparatively small amount of CaO interposed therebetween. In this case, the composition of the intermediate layer 23 is preferably intermediate between that of the material of the mold body 21 and that of the material of the refractory layer 22.

In Fig. 4(c), the layer 22 of a calcia refractory material is formed on the surface of the mold body 21 so that the CaO content of the refractory layer 22 gradually increases toward the surface which comes into contact with a molten metal. In this case, the material of the refractory layer on the side of the mold body 21 is preferably approximate to the material of the mold body 21.

Figs. 4(d), 4(e) and 4(f) show the distribution of the CaO contents in Fig. 4(a), 4(b) and 4(c), respectively.

In the cases shown in Figs. 4(a) and 4 (b), the mold body 21 and the layer 22 of a calcia refractory material fit well with each other, and there is no danger of the refractory layer separating from the mold body.

The thickness of the layer of a calcia refractory material is not specified, and may be determined appropriately in accordance with the size of the mold, and the activity and the melting point of a metal to be cast. Preferably, it is about 0.3 to 2 cm.

Calcia of the refractory layer formed on the fifth mold has a high melting point and is thermodynamically stable even at a high temperature, as described above. Since the stability and the heat resistance of the mold increases with the increase in CaO content in the layer of a calcia refractory material, the layer of a calcia refractory material of the fifth mold contains at least 40 wt%, preferably at least 50 wt %, and more preferably at least 60 wt% CaO.

The layer of a calcia refractory material may contain a halide, an oxide other than CaO, a carbide, a nitride exemplified above and carbon (C) as well as CaO. Since addition of too much halide lowers the refractoriness of the mold, the content is not more than 8 %, preferably not more than 5 %. Needless to say, since addition of too small amount of halide does not bring about the above-described effects and actions, the content is not less than 0.1 %, preferably not less than 0.3 %.

The mold body on which the layer of a calcia refractory material is formed may be composed of graphite or a heat-resistant oxide except calcia such as alumina, which is ordinarily adopted as a mold material. It may also be a low calcia mold containing less than 40 % CaO.

In order to form the layer of a calcia refractory material on the surface of such a mold body which comes into contact with a molten metal, for example, on the entire surface of the inner wall of the mold body, the above-described calcia material and at least one selected from the group consisting of the above-described halide, oxide, carbide, nitride and carbon are prepared as the main raw material, and an appropriate binder is added thereto to constitute a molding material. After adhering the layer of a calcia refractory material to the surface of the mold body by

(a) Pouring the molding material into the mold body when the molding material is a slurry, (slip casting method),

(b) applying the molding material to the surface of the mold body, or

(c) pressing the molding material against the inner wall of the mold body with no or a small amount of binder, the molded body is baked.

When the molded body is baked, it is preferable that it is dried, if necessary, calcinated at a temperature lower than the baking temperature, and is thereafter baked to be sintered. The baking temperature is not lower than 900°C, preferably 1,100 to 1,700°C. The step of baking may be carried out in the air atmosphere if the body to be sintered contains no carbon, but another atmosphere is possible.

In order to form the refractory layer such as that shown in Fig. 4(c), the CaO content of the slurry in the slip cast is increased with time in the method (a), thereby facilitating the formation of the refractory layer containing CaO which gradually increases toward the surface.

The fifth mold may be composed by a hot pressing method or using the calcia refractory material as a stamp material. The mold may be also formed by using the layer of a calcia refractory material as ordinary casting sand.

As the binder used for molding the refractory layer, the above-described non-aqueous binders are ordinarily used.

By using one of these first to fifth molds, a high-melting point metal, a highly active metal and an alloy containing such a metal are cast.

High-melting point metals and highly active metals suitable for casting in the present invention are, for example, lanthanoid elements such as Sc, Y, La, Ce of atomic numbers 58 to 71, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Ru, Os, Co, Ni, Rh, Pd, Ir and Pt. An alloy containing at least one of these elements is also suitable for casting in the present invention.

In the present invention, casting is preferably carried out in an inert gas atmosphere, for example, under vacuum or in an argon atmosphere.

In the case of casting a high-melting point metal such as a pure metal of chromium or vanadium, and an alloy containing a large amount of such metal, a mold containing a large amount of CaO, for example, not less than 80 wt% CaO is preferably used. In the case of casting a highly active pure metal such as titanium and zirconium, or an alloy containing a large amount of such metal, a mold containing a large amount of CaO is also preferably used.

In a casting method of the present invention in which a calcia mold having a porosity of 30 to 70 vol% is placed on a metal chill plate, a molten metal is poured by top-pouring, and the molten metal is gradually solidified from the lower part while insulating the riser of the mold, the metal chill plate increases the cooling speed appropriately, so that it is possible to refine the crystal grain and restrict the position of the shrinkage cavity to the top portion of the casting, thereby improving the yield. Since a calcia mold is used, it is possible to cast a fragile metal without producing a crack.

Furthermore, it is possible to cast highly active metal and alloy such as chromium, chromium alloy, titanium and titanium alloy while preventing an impure metal ingredient from mixing thereinto.

Figs. 5 and 6 are respectively side elevational views of preferred embodiments of the casting method. In the embodiment shown in Fig. 5, a bottomless calcia mold 31 (having a cylindrical configuration and the cavity has a slightly tapered configuration toward the lower side in this embodiment) is placed on a metal chill plate 32, and a riser sleeve 33 of the same calcia is placed on the upper side of the mold 31. The metal chill plate 32 in Fig. 5 is a single-sheet plate, and the central part of the upper surface is recessed in this embodiment for receiving the calcia mold 31 (the recessed portion is not essential).

The embodiment shown in Fig. 6 has the same structure as that of the embodiment in Fig. 5 except that an insulating member 34 is used in place of the calcia riser sleeve 33.

In the present invention, a molten metal is poured into the bottomless calcia mold 31 by top-pouring. The poured molten metal is cooled by the metal chill plate 32 and gradually solidified from the lower part. The cooling speed is higher than that of a calcia mold having no metal chill plate, so that the position of the shrinkage cavity becomes higher. Further, the riser of the mold is insulated by the calcia riser sleeve 33 or the insulating member 34, whereby the position of the shrinkage cavity become even higher. In the present invention, the calcia riser sleeve 33 and the insulating member 34 may incorporate a heating medium, or the calcia riser sleeve 33 and the insulating member 34 may have a structure which is capable of heating so as to retain the heat of the riser of the mold by providing heat therefor. It will be possible to make the position of the shrinkage cavity still higher by heating in this way.

In the method of the present invention, a calcia mold which is made by molding a calcia particulate molding material together with an appropriate non-aqueous binder, and baking the molded body is preferably used. The calcia particulate molding material preferably contains not less than 60 %, more preferably not less than 80 % calcia. Especially in the case of pouring highly active molten metal such as pure chromium, chromium alloy, pure titanium and titanium alloy (especially high titanium alloy), a high-purity calcia mold containing not less than 90 % calcia is preferably used. As the metal chill plate 32, ordinary steel plate, cast iron plate, copper plate and the like are preferable. In the case of using a metal chill plate of a water-cooling system, a copper plate is preferable.

As the material of the riser sleeve 33, calcia, graphite, and a refractory material containing an exothermic ingredient are preferable. A graphite insulating member facilitates the heating and the heat retaining of the riser of the mold by electrically heating or induction heating. When a calcia insulating member is used, if the member is made of metal powder which is mixed, molded and baked, heat retaining is also possible by induction heating.

It is preferable that the calcia mold has a porosity of 30 to 70 vol%, more preferably about 40 to 50 vol%.

As an experiment, a chromium alloy was poured in accordance with the embodiments shown in Figs. 5 and 6. The dimensions of the mold 31, the metal chill plate 32 and the insulating member 34 are described in Figs. 5 and 6.

The riser sleeve 33 was an insulating sleeve made of calcia which was the same material as that of the mold. The metal chill plates 32 in Figs 5 and 6 were made of copper.

As a result of pouring the chromium alloy, the shrinkage cavity in Fig. 5 was produced at a position 1.4 cm deep from the top surface of the mold, and the shrinkage cavity in Fig. 6 at a position 0 cm deep from the top surface of the mold 31.

The next experiment was carried out for comparison.

A chromium alloy was poured in the same way as in the method shown in Fig. 6 except that the bottom part of the mold 31 was closed by a calcia refractory material in place of the metal chill plate 32. As a result, the shrinkage cavity was produced at a position of 2.8 cm deep from the top surface of the mold.

Hereinunder examples will be explained, but it is to be understood that the present invention is not limited thereto and may be practiced otherwise within the scope of the spirit and scope of the invention.

Example 1 (on the first mold)

80 parts by weight of electrofused calcia (having a CaO purity of 98 %) which had been crushed into particles of 0.5 to 0.1 mm in diameter and classified, 10 parts by weight of $Ca(OH)_2$ of a commercially available class first reagent and 10 parts by weight of magnesia clinker which had been crushed into particles of not more than 0.5 mm in diameter were mixed to prepare 100 parts by weight of particulate molding material. 50 parts by weight of ethyl alcohol with mastic gum dispersed therein so as to have a concentration of 5 % was prepared, and this was mixed with the particulate molding material to make a slurry.

A gypsum mold having a configuration and dimensions shown in Fig. 7 was prepared. The slurry was poured into the gypsum mold, and after 30 minutes had passed the excess slurry was discharged. After this state was maintained for 1 hour more, the gypsum mold was removed. The molded body was dried at 70°C for 1 hour, and thereafter calcinated at 850°C for 3 hours. The molded body was then baked at 1,100°C for

3 hours to be sintered. These steps of calcinating and baking were carried out in the air atmosphere. The thus-obtained sintered body 40 had a configuration and dimensions shown in Fig. 8. The porosity was 25 vol%. In Fig. 7, the reference numeral 41 denotes a cover, 42 a gypsum mold, 43 a vent hole, and 44 a hole for pouring and discharging a slurry.

By using this mold, an alloy having a composition of Ti -6 % Aℓ -4 % V was cast at 1 atm in an argon atmosphere. The temperature of the molten metal at the time of casting was 1,650°C. The molten metal was poured into the mold, and after solidification chemical analysis of O and N on the surface of the casting was carried out. The casting was cut and the height of the shrinkage cavity was measured. The results are shown in Table 1.

Example 2 (on the first mold)

A mold was produced and casting was carried out in the same way as in Example 1 except for the following conditions (a) to (g).

(a) The composition of the material was as follows:

90 parts by weight of dolomite clinker (64.5 % CaO, 30.9 % MgO, 2.3 % Fe_2O_3, 1.8 % SiO_2, 0.4 % $A\ell_2O_3$) which had been crushed into particles of not more than 0.5 mm in diameter and classified, 10 parts by weight of $Ca(OH)_2$ and 10 parts by weight of lime stone which had been crushed into particles of not more than 1 mm in diameter.

(b) As the non-aqueous solvent, toluene with oleic acid dissolved therein so as to have a concentration of 5 % was used.

(c) The mixing ratio of the solid material and the non-aqueous solution was 100 : 50.

(d) The molded body was baked at 1,000°C for 3 hours.

(e) An alloy of 60 % Zr and 40 % Co was cast.

(f) The temperature of the molten metal at the time of casting was 1,500°C.

The results of the chemical analysis of the surface of the casting obtained and the measurement of the height of the shrinkage cavity are shown in Table 1. The porosity of the mold was 28 vol%.

Example 3 (on the first mold)

A mold was produced and casting was carried out in the same way as in Example 1 except for the following conditions (a) to (g).

(a) The composition of the material was as follows:

90 parts by weight of commercially available quick lime (98.0 % CaO, 0.08 % SiO_2) which had been crushed into particles of not more than 0.5 mm in diameter, 10 parts by weight of dolomite clinker (same as in Example 2) which had been crushed into particles of not more than 0.5 mm in diameter.

(b) As the non-aqueous solvent, isopropyl alcohol with oleic acid dissolved therein so as to have a concentration of 5 % was used.

(c) The mixing ratio of the solid material and the non-aqueous solution was 100 : 50.

(d) The molded body was baked at 1,100°C for 3 hours.

(e) An alloy of 54 % Ni and 46 % Ti was cast.

(f) The temperature of the molten metal at the time of casting was 1,400°C.

The results of the chemical analysis of the surface of the casting obtained and the measurement of the height of the shrinkage cavity are shown in Table 1. The porosity of the mold was 29 vol%.

Example 4 (on the first mold)

A mold was produced and casting was carried out in the same way as in Example 1 except for the following conditions (a) to (g).

(a) The composition of the material was as follows:

3 parts by weight of electrofused calcia in Example 1 was replaced by anhydrous calcium chloride of a class first reagent. Other components were the same as in Example 1.

(b) As the non-aqueous solvent, kerosine with oleic acid dissolved therein so as to have a concentration of 5 % was used.

(c) The mixing ratio of the solid material and the non-aqueous solution was 100 : 50.

(d) The molded body was baked at 1,000°C for 3 hours.

(e) Pure chromium was cast.

(f) The temperature of the molten metal at the time of casting was 1,950°C.

The results of the chemical analysis of the surface of the casting obtained and the measurement of the height of the shrinkage cavity are shown in Table 1. The porosity of the mold was 27 vol%.

Example 5 (on the first mold)

A mold was produced and casting was carried out in the same way as in Example 1 except for the following conditions (a) to (g).

(a) The composition of the material was as follows:

5 parts by weight of electrofused calcia in Example 1 was replaced by ZrO_2 (class first reagent), and 1 part by weight of electrofused calcia was replaced by graphite powder. Other components were the same as in Example 1.

(b) As the non-aqueous solvent, carbon tetrachloride with beeswax dissolved therein so as to have a concentration of 5 % was used.

(c) The mixing ratio of the solid material and the non-aqueous solution was 100 : 50.

(d) The molded body was baked at 1,100°C for 3 hours.

(e) An alloy of Mn -3 % Aℓ was cast.

(f) The temperature of the molten metal at the time of casting was 1,350°C.

The results of the chemical analysis of the surface of the casting obtained and the measurement of the height of the shrinkage cavity are shown in Table 1. The porosity of the mold was 24 vol%.

Table 1

Example No.	Results of Analysis (ppm) O	N	Height of Shrinkage Cavity (cm)
1	1,200	68	17.5
2	580	50	18.0
3	580	32	19.1
4	140	168	14.0
5	169	155	15.0

As is clear from Table 1, according to the present invention, it is easy to cast a highly active metal, a high-melting point metal, and an alloy containing such a metal. The casting obtained is a highly purified casting free from contamination of C, O, N, etc., and dispenses with any after-treatment such as the removal of a contaminated layer on the casting surface. Furthermore, according to the present invention, it is possible to elevate the position of the shrinkage cavity, thereby preventing the shrinkage cavity from being produced at the central part of the casting, so that the yield is enhanced.

Example 6 (on the second mold)

85 parts by weight of electrofused calcia (having a CaO purity of 99 %) which had been crushed into particles of not more than 0.2 mm in diameter and classified, 5 parts by weight of CaF_2 of a class first reagent and 10 parts by weight of magnesia clinker which had been crushed into particles of not more than 0.2 mm in diameter were mixed to prepare 100 parts by weight of particulate molding material. 10 parts by weight of ethyl alcohol with anhydrous calcium chloride dissolved therein so as to have a concentration of 4 % was prepared, and this was mixed with the particulate molding material and was die cast.

The molded body was dried at 100° C for 1 hour, and thereafter baked at 950°C for 3 hours in the air atmosphere to be sintered. The thus-obtained sintered body had a configuration and dimensions shown in Fig. 8.

By using this mold, pure titanium was cast at 1 atm in an argon atmosphere. The temperature of the molten metal at the time of casting was 1,700°C. The molten metal was poured into the mold, and after solidification chemical analysis of O and N on the surface of the casting was carried out. The results are shown in Table 2.

Example 7 (on the second mold)

A mold was produced and casting was carried out in the same way as in Example 6 except for the following conditions (a) to (g).

(a) The composition of the material was as follows:

90 parts by weight of dolomite clinker (64.3 % CaO, 30.9 % MgO, 2.3 % Fe_2O_3, 1.8 % SiO_2, 0.4 % $A\ell_2O_3$) which had been crushed into particles of not more than 0.3 mm in diameter and classified, 3 parts by weight of $CaC\ell_2$ and 10 parts by weight of lime stone which had been crushed into particles of not more than 1 mm in diameter.

(b) As the binder, an alcoholic solution (5 %) of calcium chloride was used.

(c) The mixing ratio of the solid material and the binder was 100 : 10.

(d) The molded body was baked at 1,100°C for 3 hours.

(e) An alloy of 60 % Zr and 40 % Co was cast.

(f) The temperature of the molten metal at the time of casting was 1,550°C.

The results of the chemical analysis of the surface of the casting obtained are shown in Table 2.

Example 8 (on the second mold)

A mold was produced and casting was carried out in the same way as in Example 6 except for the following conditions (a) to (g).

(a) The composition of the material was as follows:

85 parts by weight of quick lime (98.0 % CaO, 0.08 % SiO_2) which had been crushed into particles of not more than 0.1 mm in diameter and classified, 5 parts by weight of $MgC\ell_2$ and 10 parts by weight of dolomite clinker (same as in Example 7) which had been crushed into particles of not more than 0.1 mm in diameter.

(b) As the binder, an alcoholic solution (5 %) of calcium chloride was used.

(c) The mixing ratio of the solid material and the binder was 100 : 10.

(d) The molded body was baked at 1,350°C for 3 hours.

(e) An alloy of 68 % Ni and 32 % La was cast.

(f) The temperature of the molten metal at the time of casting was 1,400°C.

The results of the chemical analysis of the surface of the casting obtained are shown in Table 2.

Comparative Example 1 (on the second mold)

A mold was produced and casting was carried out in the same way as in Example 6 except for the following conditions (a) to (c).

(a) The raw material was commercially available silica sand powder (98 % SiO_2) alone.

(b) As the binder, water-glass was used and was hardened by CO_2 gas.

(c) The mixing ratio of the solid material and the binder was 100 : 5.

Comparative Example 2 (on the second mold)

A mold was produced and casting was carried out in the same way as in Example 7 except that the material for the mold was commercially available silica sand.

Comparative Example 3 (on the second mold)

A mold was produced and casting was carried out in the same way as in Example 8 except that the material for the mold was commercially available silica sand.

The results of the chemical analyses of the surfaces of the castings obtained in Comparative Examples 1 to 3 are shown in Table 2.

Table 2

		Results of Analysis (ppm)	
Example		O	N
	No. 6	880	38
	7	530	50
	8	95	30
Comparative			
Example	No 1	23,000	125
	2	6,200	95
	3	2,800	85

According to the present invention, it was easy to cast a highly active metal, a high-melting point metal, and an alloy containing such a metal. The castings obtained were highly purified castings free from contamination of C, O, N, etc., and dispensed with any after-treatment such as the removal of a contaminated layer on the casting surface.

Example 9 (on the third mold)

80 parts by weight of electrofused calcia (having a CaO purity of 98 %) which had been crushed into particles of not more than 0.2 mm in diameter and classified, 20 parts by weight of pyrolytic graphite were mixed to prepare 100 parts by weight of particulate molding material. 5 parts by weight of the pitch of heavy oil was added thereto and the mixture was heated to 150°C. After the mixture was mixed adequately, it was die cast.

After the molded body was calcinated at 900°C for 1 hour, it was baked at 1,200°C for 3 hours to be sintered. These steps of calcinating and baking were carried out in a nitrogen atmosphere. The thus-obtained sintered body had a configuration and dimensions shown in Fig. 8.

By using this mold, pure titanium was cast at 1 atm in an argon atmosphere. The temperature of the molten metal at the time of casting was 1,700 C. The molten metal was poured into the mold, and after solidification chemical analysis of C, O, N on the surface of the casting was carried out. The results are shown in Table 3.

Example 10 (on the third mold)

A mold was produced and casting was carried out in the same way as in Example 9 except for the following conditions (a) to (g).

(a) The composition of the material was as follows:

83 parts by weight of calcia clinker (98.0 % CaO, 1.0 % MgO, 0.1 % Fe_2O_3, 0.1 % SiO_2, 0.1 % $A\ell_2O_3$) which had been obtained by baking limestone at 1,500°C and crushed into particles of not more than 0.3 mm in diameter and classified, 3 parts by weight of $CaC\ell_2$, and 15 parts by weight of crushed electrode graphite which had been crushed into particles of not more than 0.1 mm in diameter.

(b) As the binder, kerosine -0.5 wt% oleic acid was used.

(c) The mixing ratio of the solid material and the binder was 100 : 5.

(d) The molded body was baked at 1,200°C for 3 hours.

(e) An alloy of 60 % Zr and 40 % Co was cast.

(f) The temperature of the molten metal at the time of casting was 1,550°C.

The results of the chemical analysis of the surface of the casting obtained are shown in Table 3.

Example 11 (on the third mold)

A mold was produced and casting was carried out in the same way as in Example 9 except for the following conditions (a) to (g).

(a) The composition of the material was as follows:

70 parts by weight of electrofused calcia which had been crushed into particles of not more than 0.1 mm in diameter and classified, and 25 parts by weight of crushed electrode graphite which had been crushed into particles of not more than 0.1 mm in diameter.

(b) As the binder, the pitch of petroleum was used.

(c) The mixing ratio of the solid material and the binder was 100 : 5.

(d) The molded body was baked at 1,350°C for 3 hours.

(e) An alloy of 60 % V and 50 % Aℓ was cast.

(f) The temperature of the molten metal at the time of casting was 1,750°C.

The results of the chemical analysis of the surface of the casting obtained are shown in Table 3.

Comparative Example 4 (on the third mold)

A graphite mold having the dimensions shown in Fig. 8 was produced by machining a commercially available graphite electrode, and by using this mold pure titanium was cast in the same way as in Example 9.

Comparative Example 5 (on the third mold)

A mold was produced and casting was carried out in the same way as in Example 10 except for the following conditions (a) to (c).

(a) The raw material was commercially available silica sand powder (98 % SiO_2) alone.

(b) As the binder, water-glass was used and was hardened by CO_2 gas.

(c) The mixing ratio of the solid material and the binder was 100 : 5.

The results of the chemical analyses of the surfaces of the castings obtained in Comparative Examples 4 and 5 are shown in Table 3.

Table 3

Example		Results of Analysis (ppm)		
		C	O	N
	No. 9	80	890	80
	10	60	670	60
	11	790	90	5
Comparative Example	No 4	420	930	220
	5	55	6,200	95

Table 3 shows that according to the present invention, it is easy to cast a highly active metal, a high-melting point metal, and an alloy containing such a metal. The casting obtained is a highly purified casting free from contamination of C, O, N, etc., and dispenses with any after-treatment such as the removal of a contaminated layer on the casting surface. The surfaces of the molds according to the present invention were smooth and the casting surfaces were also smooth.

Example 12 (on the fourth mold)

70 parts by weight of electrofused calcia (having a CaO purity of 98 %) which had been crushed into particles of not more than 0.2 mm in diameter and classified, 20 parts by weight of ZrO_2 of a class first reagent and 10 parts by weight of magnesia clinker which had been crushed into particles of not more than 0.2 mm in diameter were mixed to prepare 100 parts by weight of particulate molding material 10 parts by weight of ethyl alcohol with anhydrous calcium chloride dissolved therein so as to have a concentration of 4 % was prepared, and this was mixed with the particulate molding material and was die cast.

The molded body was dried and calcinated at 100°C for 1 hour, and thereafter baked at 950°C for 3 hours to be sintered. These steps of calcinating and baking were carried out in the air atmosphere. The thus-obtained sintered body had a configuration and dimensions shown in Fig. 8.

By using this mold, an alloy consisting of 64 % Ti and 36 % Al was cast at 1 atm in an argon atmosphere. The temperature of the molten metal at the time of casting was 1,500°C. The molten metal was poured into the mold, and after solidification chemical analysis of O and N on the surface of the casting was carried out. The results are shown in Table 4.

Example 13 (on the fourth mold)

A mold was produced and casting was carried out in the same way as in Example 12 except for the following conditions (a) to (g).

(a) The composition of the material was as follows:

90 parts by weight of calcinated lime which had been crushed into particles of not more than 0.3 mm in diameter and classified, 3 parts by weight of Cr_2O_3 of a class first reagent and 7 parts by weight of Y_2O_3 of a class first reagent.

(b) As the binder, an ethyl alcoholic solution (4 %) of potassium chloride was used.

(c) The mixing ratio of the solid material and the binder was 100 : 10.

(d) The molded body was baked at 1,000°C for 3 hours.

(e) An alloy of 60 % Zr and 40 % Co was cast.

(f) The temperature of the molten metal at the time of casting was 1,550°C.

The results of the chemical analysis of the surface of the casting obtained are shown in Table 4.

Reference Example 1

A mold was produced and casting was carried out in the same way as in Example 12 except for the following conditions (a) and (b).

(a) The material was electrofused calcia alone having a particle diameter of not more than 0.2 mm.

(b) The molded body was calcinated at 900°C and thereafter baked at 1,100°C for 3 hours.

The results of the chemical analysis of the surface of the casting obtained are shown in Table 4.

Reference Example 2

A mold was produced and casting was carried out in the same way as in Example 13 except for the conditions (a) and (b) in Reference Example 1.

The results of the chemical analysis of the surface of the casting obtained are shown in Table 4.

Table 4

		Results of Analysis (ppm)	
Example		O	N
	No. 12	630	56
	13	580	55
Reference Example	No 1	570	110
	2	540	104

Table 4 shows that according to Examples 12 and 13, it is possible to cast a highly purified alloy of approximately the same level as those of Reference Examples 1 and 2. In Examples 12 and 13, the baking temperature of the molds are considerably low and the baking time is short in comparison with those of Reference Examples 1 and 2.

When the molds of Examples 12 and 13 and Reference Examples I and 2 were left in the air, considerable slaking was produced on the surfaces of those of Reference Examples 1 and 2 in about 2 days, while almost no slaking was produced on the surfaces of the molds of Examples 12 and 13. Thus, it was confirmed that the molds of Examples 12 and 13 were efficient in resistance to slaking.

Examples 14 (on the fifth mold)

A CaO material was prepared by crushing sintered calcia (having a CaO purity of 98 %) into particles of not more than 0.5 mm in diameter and classifying them, and other components were added thereto to prepare molding materials having the compositions shown in 1 to 3 of Table 5. A calcia layer was formed of each of the molding materials on the entire inner surface of a graphite mold body by a slip casting method. The mold was dried at 250°C for 30 hours and thereafter baked at 1,200°C for 2 hours in vacuo to be sintered, whereby a layer of a calcia refractory material was formed. The step of baking was carried out in the air atmosphere. The thus-obtained mold had a configuration and dimensions shown in Fig. 9. In Fig. 9, the reference numeral 51 denotes a mold body, and 52 a layer of a calcia refractory material.

By using each of these molds, an alloy consisting of 80 % Ti and 20% Ni was cast at 0.2 atm in an argon atmosphere. The temperature of the molten metal at the time of casting was 1,600°C. The molten metal was poured into the mold, and after solidification chemical analysis of O, N and C on the surface of the casting was carried out. The results are shown in Table 6.

Table 5

(wt%)

Mold No.	1	2	3
CaO Material	99.8	68.9	89.8
$CaCl_2$ Material	0.2	0.1	0.2
CaF_2 Material	-	1	-
MgO Material	-	-	10
ZrO_2 Material	-	30	-

Comparative Example 6 (on the fifth mold)

Casting was carried out in the same way as in Example 14 by using an Al_2O_3 mold and a graphite mold.

The results of the chemical analyses of the surfaces of the castings obtained are shown in Table 6.

Table 6

		Results of Analysis (ppm)		
	Mold	O	N	C
Example 14	No. 1	650	45	30
	No. 2	710	48	32
	No. 3	760	40	28
Comparative Example 6	Al_2O_3 Mold	1,200	51	33
	Graphite Mold	980	60	120

As is clear from Table 6, according to the present invention, it is easy to cast a highly active metal, a high-melting point metal, and an alloy containing such a metal. The casting obtained is a highly purified casting free from contamination of C, O, N, etc., and dispenses with any after-treatment such as the removal of a contaminated layer on the casting surface. The sintering ability and the resistance to hydration of the molds were very high.

Examples 15 to 17 (production of a porous mold by utilizing an injection molding process and casting by using the mold)

Example 15

80 parts by weight of electrofused calcia (having a CaO purity of 98 %) which had been crushed into particles of 0.3 to 0.1 mm in diameter and classified, 10 parts by weight of $CaCO_3$ of a commercially available class first reagent and 10 parts by weight of magnesia clinker which had been crushed into particles of not more than 0.5 mm in diameter were mixed to prepare 100 parts by weight of particulate molding material. 5 parts by weight of polyethylene powder was also prepared.

The particulate molding material and polyethylene powder were charged into a sand mill provided with a heater. After the temperature was raised to 150°C to knead the materials adequately, the mixture was cooled. The mixture was crushed by an attrition mill and thereafter sieved so that the particle diameter was not more than 0.3 mm. The sieved material was charged into a screw in-line type injection molding machine and was injected into the die.

After burring the molded body, it was heated to 500°C in the air. After it was held for 3 hours in this state, the binder was removed. The temperature was raised to 1,200°C and the molded body was baked for 3 hours to make a cylindrical mold having a porosity of 53 vol%. Fig. 8 shows the dimensions of this mold.

By using this mold, pure titanium was cast at 1 atm in an argon atmosphere. The temperature of the molten metal at the time of casting was 1,700°C. The molten metal was poured into the mold, and after solidification chemical analysis of O and N on the surface of the casting was carried out. The casting was cut to measure the height of the shrinkage cavity. The results are shown in Table 7.

Example 16

A mold was produced and casting was carried out in the same way as in Example 15 except for the following conditions (a) to (g).

(a) The composition of the material was as follows:

90 parts by weight of dolomite clinker (64.5 % CaO, 30.9 % MgO, 2.3 % Fe_2O_3, 1.8 % SiO_2, 0.4 % Al_2O_3) which had been crushed into particles of 0.3 to 0.1 mm in diameter and classified, and 10 parts by weight of lime stone which had been crushed into particles of not more than 0.3 mm in diameter.

(b) As the binder, polyethylene powder was used.

(c) The mixing ratio of the solid material and the binder was 100 : 5.

(d) The molded body was baked at 1,100°C for 3 hours.

(e) An alloy of 60 % Zr and 40 % Co was cast.

(f) The temperature of the molten metal at the time of casting was 1,500°C.

The results of the chemical analysis of the surface of the casting obtained and the measurement of the shrinkage cavity are shown in Table 7. The porosity of the mold was 55 vol %.

Example 17

A mold having a porosity of 56 vol% was produced and casting was carried out in the same way as in Example 15 except for the following conditions (a) to (g).

(a) The composition of the material was as follows:

60 parts by weight of commercially available quick lime (98.0 % CaO, 0.08 % SiO_2) which had been crushed into particles of 0.5 to 0.1 mm in diameter and classified, 10 parts by weight of $Ca(OH)_2$ and 30 parts by weight of dolomite clinker (same as in Example 16) which had been crushed into particles of not more than 0.3 mm in diameter.

(b) As the binder, polypropylene was used.

(c) The mixing ratio of the solid material and the binder was 100 : 5.
(d) The molded body was baked at 1,100°C for 3 hours.
(e) Pure chromium was cast.
(f) The temperature of the molten metal at the time of casting was 1,950°C.

Comparative Example 7

Casting was carried out under the same conditions as in Example 17 except that the mold was a metal (steel) mold. The results of the chemical analysis of the surface of the casting obtained and the measurement of the shrinkage cavity are shown in Table 7.

Table 7

	Results of Analysis (ppm)		Height of Shrinkage Cavity (cm)
Example	O	N	
15	890	41	18
16	590	48	17.5
17	150	180	16
Comparative Example 7	138	182	3.4

Claims

1. A porous mold comprising a calcia refractory material containing not less than 40 wt% CaO.

2. A mold according to Claim 1, wherein a component other than CaO is at least one selected from the group consisting of an oxide, a carbide, a nitride, carbon and a halide.

3. A mold according to Claim 2, wherein said oxide is magnesia and/or zirconia.

4. A mold according to Claim 2, wherein said carbide is silicon carbide.

5. A mold according to Claim 2, wherein said nitride is silicon nitride and/or aluminum nitride.

6. A mold according to Claim 1, wherein said mold has a porosity of 10 to 40 vol%.

7. A mold according to Claim 2, wherein said halide is at least one selected from the group consisting of CaF_2, MgF_2, BaF_2, SrF_2, NaF, LiF, KF, PbF_2, CsF_2, $Na_3A\ell F_6$, $CaC\ell_2$, $MgC\ell_2$, NaCℓ and KCℓ.

8. A mold comprising a calcia refractory material containing not less than 40 wt% CaO and 0.1 to 8 wt% halide.

9. A mold according to Claim 8, wherein said halide is at least one selected from the group consisting of CaF_2, MgF_2, BaF_2, SrF_2, NaF, LiF, KF, PbF_2, CsF_2, $Na_3A\ell F_6$, $CaC\ell_2$, $MgC\ell_2$, NaCℓ and KCℓ.

10. A mold comprising a calcia graphite refractory material containing 95 to 10 wt% CaO and 5 to 50 wt% graphite.

11. A mold according to Claim 10, wherein said calcia graphite refractory material further contains at least one selected from the group consisting of an oxide, a carbide, a nitride, and a halide.

12. A mold comprising a calcia refractory material containing not less than 40 wt% CaO, not more than 5 wt% low-eutectic temperature oxide and not more than 40 wt% high-eutectic temperature oxide, said low-eutectic temperature oxide being a metal or semi-metal oxide having a eutectic temperature below 1,450°C and said high-eutectic temperature oxide being a metal oxide having a eutectic temperature of not lower than 1,450°C.

13. A mold according to Claim 12, wherein said calcia refractory material further contains at least one selected from the group consisting of a carbide, a nitride, and a halide.

14. A mold comprising a layer of a calcia refractory material containing not less than 40 wt% CaO provided on the surface of said mold which comes into contact with a molten metal.

15. A mold according to Claim 14, wherein the thickness of said layer is 0.3 to 2 cm.

16. A mold according to Claim 14, wherein said calcia refractory material further contains at least one selected from the group consisting of an oxide, a carbide, a nitride and carbon.

17. A method of producing a mold comprising the steps of:

pouring a slurry of an aqueous solution of CaO powder or particles containing not less than 40 wt% CaO into a liquid-absorbing master mold to form a deposit on the surface of said master mold;

removing said master mold;

drying said deposit; and

baking said deposit at a baking temperature for a baking time which are so determined that a sintered body to be obtained will be porous.

18. A method of producing a mold comprising the steps of:

kneading calcia particles with an organic binder;

inject molding the kneaded material into a configuration of said mold;

removing said binder from the molded body; and

baking said molded body at a baking temperature for a baking time which are so determined that a sintered body to be obtained will be porous.

19. In a method of producing a calcia mold having the steps of molding a particulate molding material and baking the molded body, the improvement comprising the step of baking said molded body while bringing a member for preventing the deformation of said molded body into contact with at least a part of said molded body.

20. A method of casting a highly active metal, a high-melting point metal, or an alloy containing a highly active metal and/or a high-melting point metal characterized in that a porous calcia mold containing not less than 40 wt% CaO is used.

21. A method according to Claim 20, wherein said highly active and high-melting point metal are at least one selected from the group consisting of lanthanoid elements such as Sc, Y, La, Ce of atomic numbers 58 to 71 and Pr, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Ru, Os, Co, Ni, Rh, Pd, Ir and Pt.

22. A method according to Claim 17, wherein said deposit contains 40 to 80 wt% CaO and is baked at 850 to 1,350°C for 1 to 10 hours.

23. A method according to Claim 17, wherein said deposit contains more than 80 wt% CaO and is baked at 1,200 to 1,700°C for 1 to 5 hours.

24. A method according to Claim 18, wherein said molded body contains 40 to 80 wt% CaO and is baked at 850 to 1,350°C for 1 to 10 hours.

25. A method according to Claim 18, wherein said molded body contains more than 80 wt% CaO and is baked at 1,200 to 1,700°C for 1 to 5 hours.

26. A casting method comprising the steps of:

placing a bottomless porous calcia mold having a porosity of 30 to 70 vol% on a metal chill plate;

pouring a molten metal by top-pouring; and

gradually solidifying said molten metal from a lower part while insulating the riser of said mold.

27. A method according to Claim 26, wherein said calcia mold contains not less than 60 wt% CaO.

FIG.1

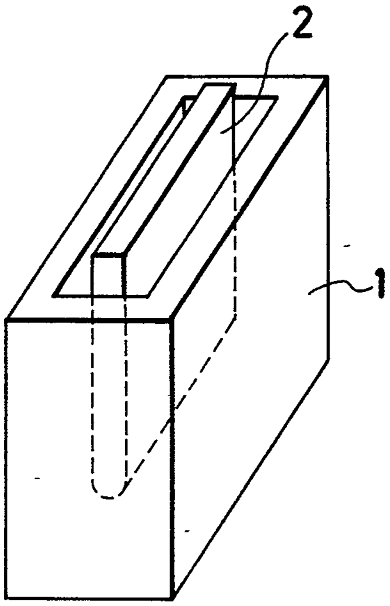


FIG.2

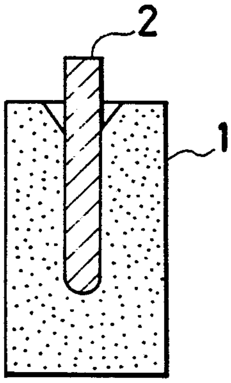


FIG.3

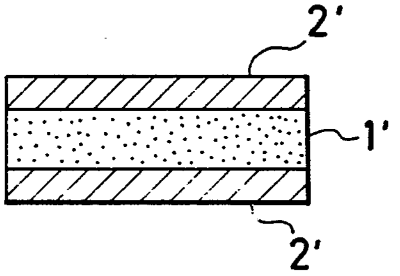


FIG.4

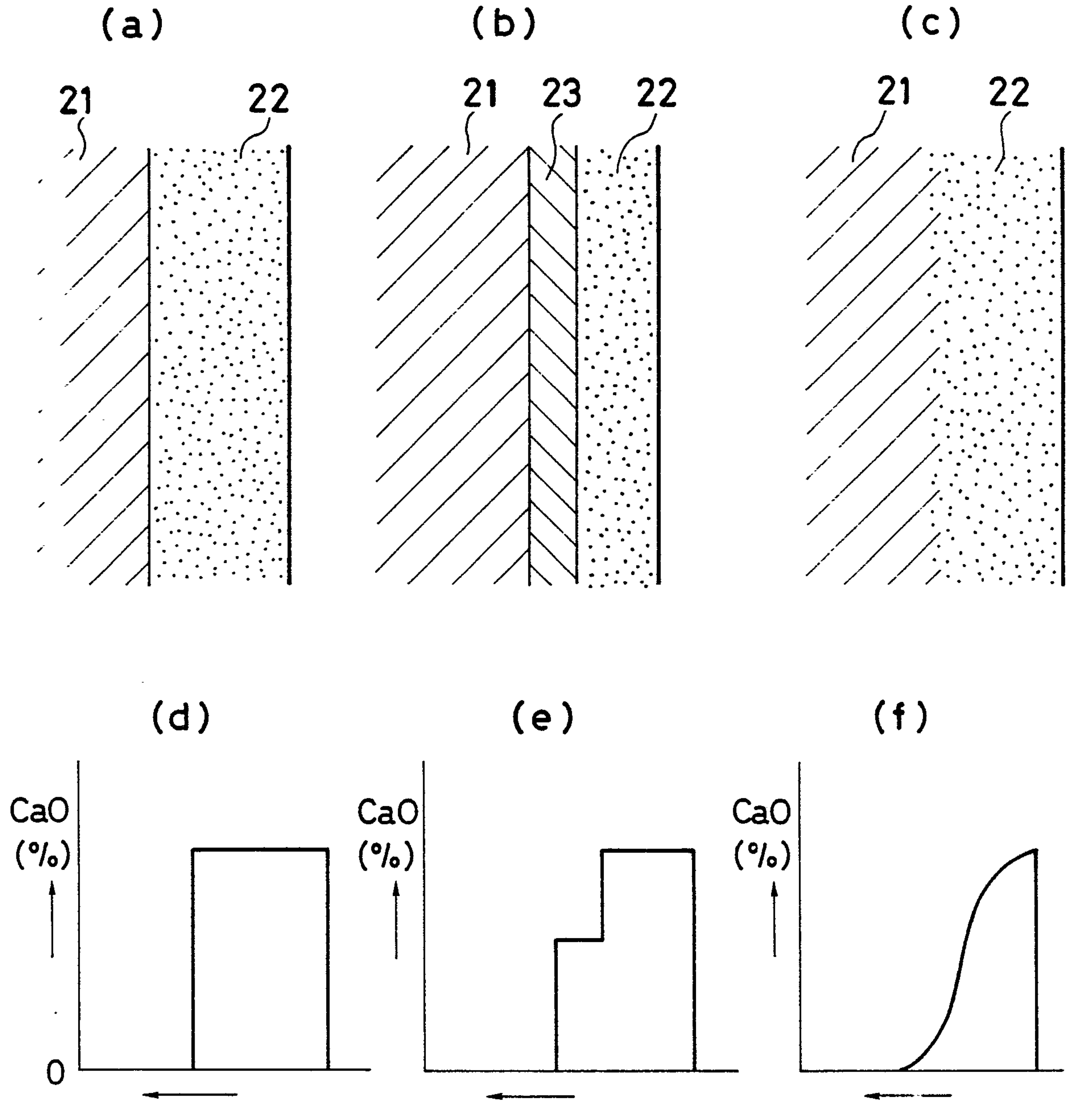


FIG. 5

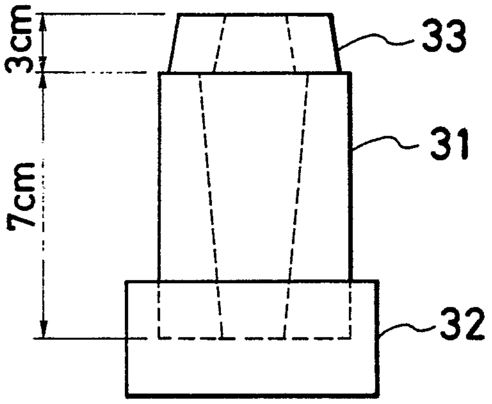


FIG. 6

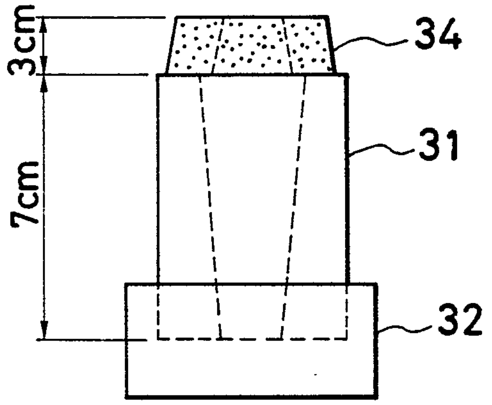


FIG.7

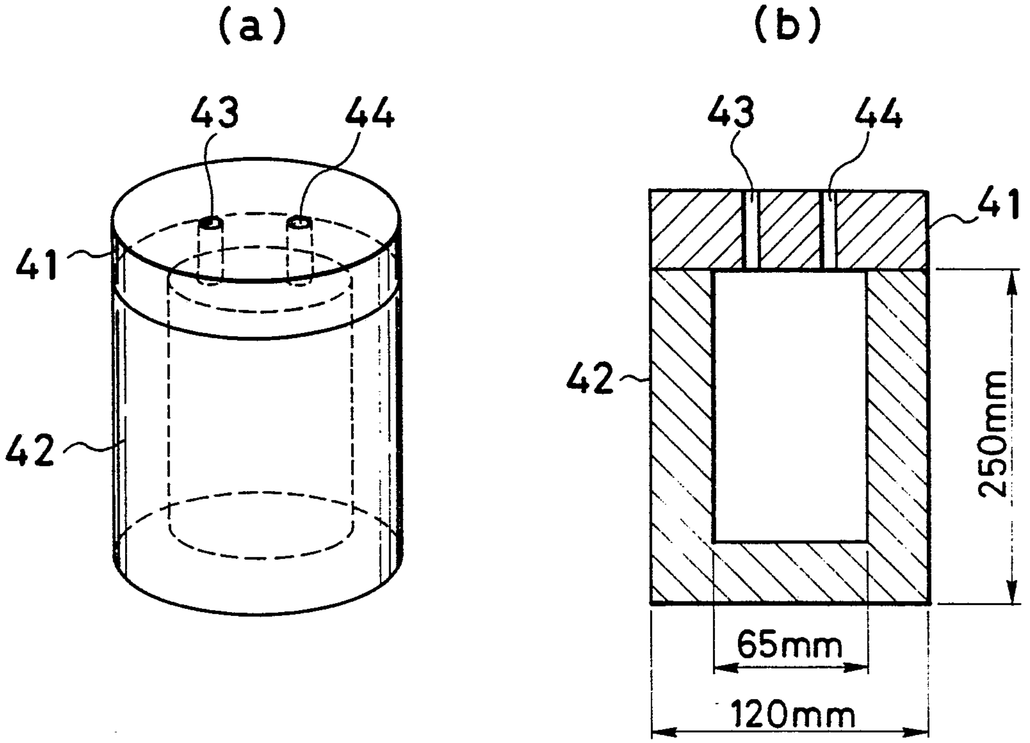

(a)
(b)
43
44
41
42
43
44
41
42
250mm
65mm
120mm

FIG.8

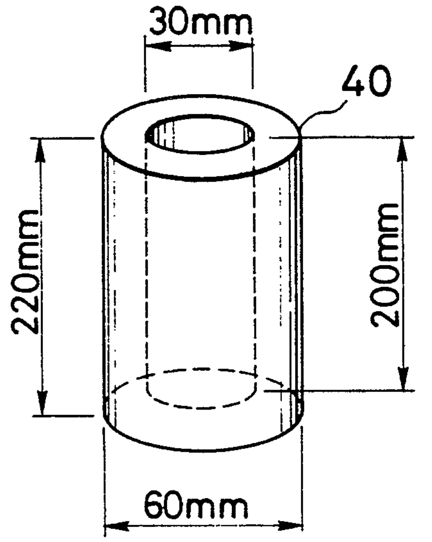
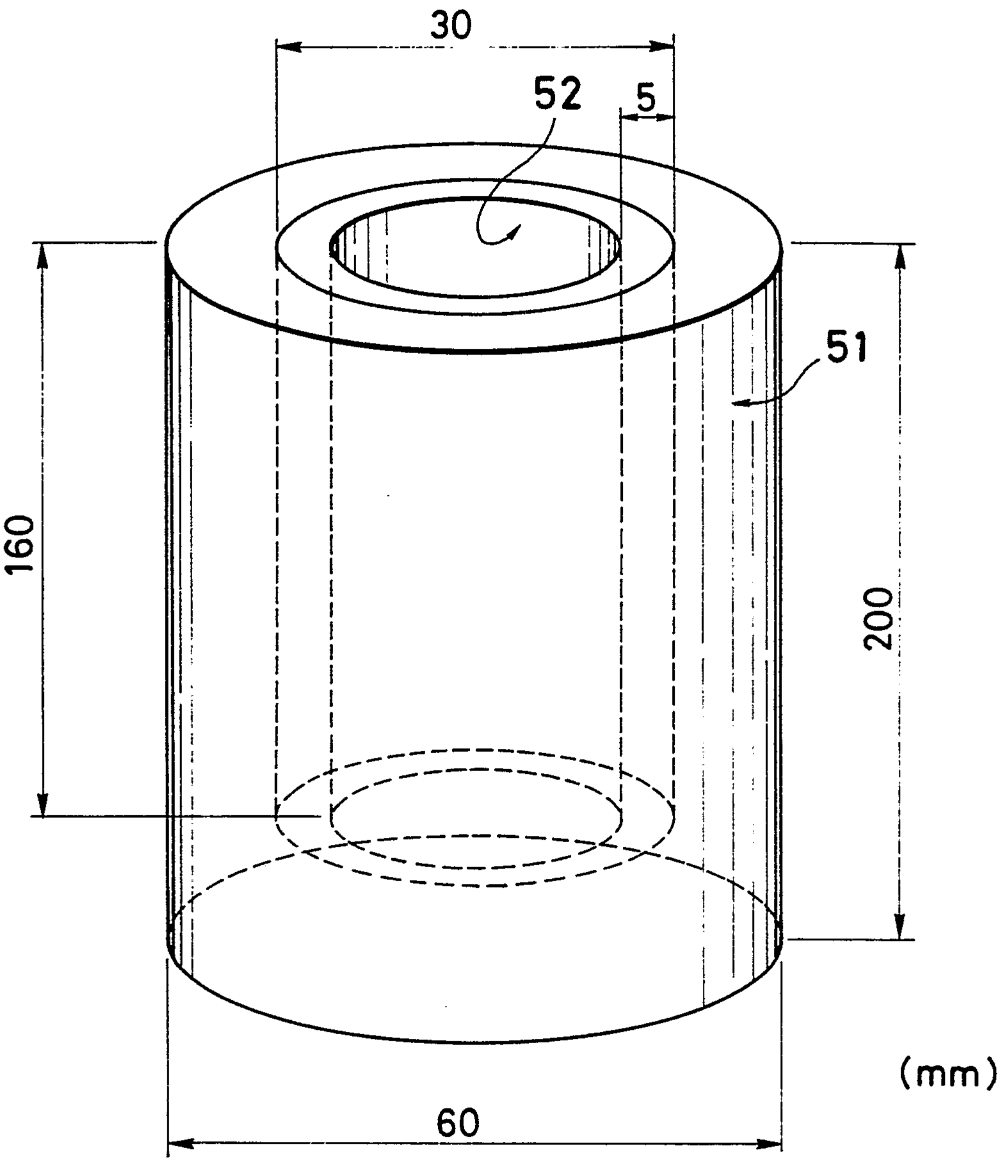

30mm
40
220mm
200mm
60mm

FIG. 9



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EUROPEAN SEARCH REPORT

Application number

EP 87 10 0559

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-2 876 122 (O.J. WHITTEMORE) * Column 1, lines 22-26,51-53; column 2, lines 26-31,46-49; claim 1 *	1-3,12,20	B 22 C 1/00 B 22 C 9/06
Y		7-11, 17,18, 21,23-26	

X	DE-A-2 047 041 (TOYOTA K.K.) * Claims 1,5 *	14-16	

Y	US-A-1 902 419 (R.A. PLANT et al.) * Claims 1-2,12 *	7-9	TECHNICAL FIELDS SEARCHED (Int. Cl.4)

Y	US-A-2 201 366 (V.A. GRODSKY) * Page 2, left-hand column, lines 51-53 *	10,11	B 22 C B 22 D

Y	US-A-3 460 606 (R.F. BODDEY) * Column 1, line 63 - clumn 2, line 6 *	17,23	

Y	GB-A-1 346 576 (SECRETARY OF STATE FOR DEFENCE) * Claims 1,3; page 6, lines 20-22 *	18,24, 25	
	--- -/-		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11-05-1987	DOUGLAS K.P.R.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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EUROPEAN SEARCH REPORT

Application number

EP 87 10 0559

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	US-H- 511 885 (D.R. HAYES et al.) * Claim 1; column 3, lines 55-57 * -----	21,26	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)

The present search report has been drawn up for all claims

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THE HAGUE	11-05-1987	DOUGLAS K.P.R.

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