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② Designated Contracting States: **DE FR GB SE** 7) Applicant: NKK CORPORATION
1-2 Marunouchi 1-chome, Chiyoda-ku
Tokyo(JP)

Inventor: Nishio, Hiroaki c/o NKK Corporation 1-2, Marunouchi 1-chome Chiyoda-ku Tokyo(JP) Inventor: Takahashi, Tatsuhito NKK Corporation 1-2, Marunouchi 1-chome Chiyoda-ku Tokyo(JP) Inventor: Yabuta, Kazuya NKK Corporation

1-2, Marunouchi 1-chome Chiyoda-ku Tokyo(JP) Inventor: Kato, Akira NKK Corporation 1-2, Marunouchi 1-chome

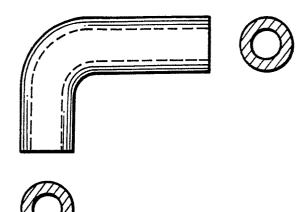
Chiyoda-ku Tokyo(JP)

Representative: Patentanwälte Grünecker, Kinkeldey, Stockmair & Partner Maximilianstrasse 58 D-8000 München 22(DE)

(54) Decay mold.

\$\sqrt{57}\$ A decay mold comprising a powder material having a transition accompanied with a volume change occurring at a temperature lower than the sintering temperature and a binder thereof, comprising a material thermally decomposable at a temperature lower than the sintering temperature, or comprising a material soluble at least in one solvent in which the molding assistant to impart formability to the powder to be molded is insoluble. By using the mold of the invention, an arbitrary form of sintered products can be manufactured without damaging it at the demolding.

FIG. I





DECAY MOLD

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BACKGROUND OF THE INVENTION

SUMMARY OF THE INVENTION

Field of the Invention

This invention relates to molds for molding powder and then sintering it to produce a product of ceramic, sintered metal or the like.

Description of the Prior Art

In the process for manufacturing a ceramic product, a sintered metal product or the like from powder through sintering, there is a molding process to mold the powder into an arbitrary form. In the molding process, the powder is molded into a prescribed form by filling it into a metal mold followed by pressuring, or by suspending it into solvent together with a binder such as water followed by casting into a porous mold, or by kneading it together with resin followed by injecting into a metal mold. In general, the molded body of the powder is separated from the mold prior to the sintering process. The mold has a separable structure so as to demold the molded body without damage.

However, when a part having an undercut portion like shown in Figure 2 is molded, the molded body cannot be taken out of the mold without damage by the above methods. Therefore, in the conventional molding methods of powder, the moldable forms are restricted by the mold employed.

On the other hand, in precision molding of metal, it is conducted to mold an arbitrary form by shell molding process where the mold used can be removed by the destruction of the mold utilizing external mechanical force, and therefore, a form having an undercut can be molded by the shell molding. The shell mold used for the precision molding should be excellent in heat resistance, thermal shock, and strength, because a molten metal is poured therein. However, the molded body formed of powder keeps its form by entaglement of the powder particles theirselves or by binding the powder particles through resin, inorganic binder or the like. Therefore, the strength of the molded body is very weak compared with the shell mold used for precision molding of metal. Thus, it is considered to be difficult to remove the shell mold from the molded body of powder without damage, and the shell mold has never been utilized therefor. An object of the invention is to provide a decay mold capable of molding powder without damaging the molded body irrespective of its form.

Another object of the invention is to provide a decay mold capable of molding powder without dividing the mold into several pieces irrespective of its form and thereby capable of improving the reliability of the sintered body and the simplicity of the manufacturing process.

The present invention provides decay molds achieved the above objects, and are characterized by destroying decomposing or dissolving the shell mold utilizing the volume change occuring at a transition, thermal decomposition or dissolution of the mold without damaging the molded body.

Thus, a decay mold of the invention comprises a powder material having a transition accompanied with a volume change occurring at a temperature lower than the sintering temperature and a binder thereof.

Another decay mold of the invention comprises a material thermally decomposable at a temperature lower than the sintering temperature.

Another decay mold of the invention comprises a material soluble at least in one solvent in which the molding assistant to impart formability to the powder to be molded is insoluble.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 and Figure 2 illustrate a sintered product molded by the mold of the invention, and Figure 1 indicates a curved pipe and

Figure 2 indicates a square bowl having an undercut portion.

DETAILED DESCRIPTION OF THE INVENTION

When the decay mold is comprised of the powder material having the transition, the powder material must be transformable, and the transition must be accompanied with a volume change. The volume change may be either of expansion or contraction. Moreover, the transition temperature of the powder material must be lower than the sintering temperature of the molded body. When the molded body of the powder sintering is calcined, the transition temperature is preferably lower than the calcination temperature. When the transition

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temperature is higher than the sintering temperature, the molded body is necessary to be heated higher than the sintering temperature in order to occur the transition resulting to break the molded body. A preferred particle size is 1 to 100 μ m. Suitable powder materials include zirconia, fused silica and zircon sand, zirconia is transformed with volume expansion in the vicinity of 1100 °C, and fused silica is transformed with volume shrinkage into cristobalite at higher than 1100 °C.

The binder binds the powder material to keep the molded form. A preferred binding strength of the powder material is destroyed readily by the volume change caused by the transition. Suitable binders include alumina sol, silica sol and zirconia sol.

The above decay mold may contain other materials than the powder material and the binder, such as alumina powder, silicon nitride powder, silicon carbide powder and mullite powder.

As the composition of the above mold a suitable content of the powder material is 30 to 90 wt. %, that of the binder is 10 to 30 wt. % and that of the other materials is less than 50 wt. %.

When the decay mold is comprised of the material thermally decomposable, the product of the thermal decomposition is preferably vapor or small pieces of solid matter at the temperature of the thermal decomposition in view of facilitating the removal of the destroyed mold. The thermal decomposition temperature must be a temperature not to damage the sintering material. On the other hand, when the molded body of the sintering material is calcined, the thermal decomposition temperature is preferably for the mold to resist at least up to the initial stage of the calcination.

The thermally decomposable material may be the material or a principal component of the mold, or a binder to bind the material forming the mold.

Suitable materials for the former case include gypsum and various resins. Gypsum decomposes in the vicinity of 300°C to produce gypsum anhydride and water, and further decomposes about 900°C. The resin may be thermoplastic resin or thermosetting resin. The resin may be porous. Various resins are commercialized, and the thermal decomposition temperature widely distributes from about 100°C to about 500°C. Therefore, a suitable resin can be selected from commercial resins according to the desired thermal decomposition temperature or the like. Preferred resins are not to evolve harmful gas such as HCI or HCN by the thermal decomposition.

When the thermally decomposable material is used for the binder, it may be selected from gysum and various resins. In this case, the material forming the mold is sufficient to be small pieces destroyed by the thermal decomposition of the

mold, and it may be powder, granules, rods, fiber or the like. Examples of the material forming the mold are ceramic powders such as alumina and titania and metal powders.

The above decay mold may be formed of the thermally decomposable material or a mixture of the thermally decomposable material and the material forming the mold alone, or may contain other components. A suitable content of the thermally decomposable material is more than 20 wt. %, preferably 35 to 80 wt %, a suitable content of the material forming the mold is more than 20 wt. %, preferably 35 to 60 wt. %, and a suitable content of other components is less than 10 wt. %.

When the decay mold is comprised of the material soluble at least in one solvent, the solvent may be water, alcohol, acetone, ether, benzene, toluene, hexane or the like. The solubility of the soluble material is preferably great. However, when the powder to be molded contains a binder (molding assistant), the solvent should be not to dissolve the binder. Besides, when the pattern is removed by dissolving it using a solvent after forming the mold, the soluble material should be insoluble at least in one solvent capable of dissolving the pattern, but should be soluble at least in one of the other solvents. In general, most of patterns are formed of paraffin. In this case, the soluble material is insoluble at least in one solvent capable of dissolving paraffin such as hexane, but is soluble at least one solvent other than the above solvent such as water. On the other hand, when the pattern is removed by another means such as melting, the solubility of the pattern is not necessary to be considered. Examples of the soluble materials are water-soluble urea resin, ethyl cellulose, methyl cellulose, polyvinyl butyral, polyvinyl alcohol and the like.

The soluble material may be the material of the mold or a principal component thereof or a binder to bind the material forming the mold. When the soluble material is used as the binder, the material forming the mold is sufficient to be small pieces destroyed by dissolving the soluble material, and it may be powder, granules, rods, fiber or the like. Examples of the material forming the mold are ceramic powders such as alumina and titania, metal powders, paper, yarn and the like.

The above decay mold may be formed of the soluble material or a mixture of the soluble material and the material forming the mold alone, or may contain other components. A suitable content of the soluble material is more than 10 wt. %, preferably 20 to 70 wt. %, a suitable content of the material forming the mold is more than 10 wt. %, preferably 40 to 80 wt. %, and a suitable content of other components is less than 20 wt. %.

As the forming process of the mold, first, a

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slurry containing the powder material and the binder, a slurry or solution of the thermally decomposable material or the soluble material are prepared. The slurry or the solution is applied to a pattern followed by drying. The mold can be completed by repeating the application and the drying. The application may be conducted by immersing or spraying as well as brushing. The solvent of the slurry or the solution may be water, methanol, ethanol, acetone, ether, hexane, toluene, benzene or the like. A suitable concentration of solid materials in sum of the powder material and the binder is 30 to 80 wt. %, and a suitable concentration of the thermally decomposable material or the soluble material is 20 to 80 wt. %. In the case of thermoplastic resins, they may be melted and then applied to the pattern. After the mold is formed, the pattern is removed by a suitable means such as dissolving using a suitable solvent or melting.

A sintered article can be produced using the mold of the invention by filling the raw powder for sintering in the mold by casting, injection molding, vibrational compression molding or the like, followed by calcination, if necessary. Subsequently, in the case of the mold comprised of the powder material having the transition, the mold is heated up to higher than the transition temperature of the powder material, and the mold is allowed to decay by the volume change caused by the transition. When the transition temperature is near the calcination temperature, the decay of the mold also proceeds during the calcination. The transition may be conducted twice or more times by lowering the temperature to the original state, then heating the mold again, or the like. In the case of the thermally decomposable material, the mold is heated up to higher than the thermal decomposition temperature of the thermally decomposable material, and the mold is allowed to decay or disappear by the thermal decomposition. When the thermal decomposition temperature is near or lower than the calcination temperature, the decay or disappearance of the mold also proceeds during the calcination. In the case of the soluble material, the mold can be allowed to decay or dissolve by adding a solvent capable of dissolving it. The destroyed mold is removed, and the molded body is sintered to obtain a sintered product. On the other hand, the molded body may be sintered in the state placed in the mold. In this case, the mold decays during sintering, and can be removed after the sintering.

Since a part or the whole of the mold of the invention is constructed by a material of which the principal component has a transition accompanied with a volume change, or it is thermally decomposable, or it is soluble in a solvent, the mold decays or disappears by the volume change due to the transition, when the mold is heated to higher

than the transition temperature or cooled to lower than the transition temperature or heated to higher than the decomposition temperature or immersed in the solvent. By using the mold of the invention, an arbitrary form of sintered products can be manufactured without damaging it at the demolding. The mold of the invention makes possible an integral molding of an article having a complex structure which was formed by molding divided into several parts followed by joining them. Thereby, the reliability of the sintered product is sharply improved, and the manufacturing process of the molded body can be simplicated.

EXAMPLES

Example 1

A pattern of the curved pipe shown in Figure 1 was prepared according to the pattern-making process used in the shell molding of precision casting. On the other hand, ZrO2 was supended in a commercial aqueous alumina sol in a concentration of 70 wt. %. The above pattern was immersed in the ZrO₂ suspension, and then, it was taken out followed by drying. This operation was repeated 5 times in total. The pattern coated with ZrO2-alumina sol was heated to about 200°C, and the pattern was removed by melting to obtain a shell mold. Ceramic powder was molded by injection molding using this mold, and dewaxed by heating to about 600°C. Subsequently, the mold was destroyed by heating to 1100 C in an oven to obtain a molded body of the ceramic powder in a form of the curved pipe without damage. The molded body was sintered under usual conditions. A test piece cut off the sintered body had a similar strength to a test piece cut off another sintered body obtained by molding through a CIP process and sintering under the same conditions.

Example 2

A shell mold was prepared in the same manner as Example 1, except that fused silica was suspended in a concentration of 65 wt. % instead of 70 wt. % of ZrO₂, and the pattern was immersed 7 times in the suspension. Using the shell mold, a ceramic sintered body was prepared in the same manner as Example 1, except the mold was destroyed by cooling from 1200°C to room temperature. The molded body was obtained without damage, and a test piece cut off the sintered body had a similar strength to a test piece cut off another

sintered body obtained by molding through a CIP process and sintering under the same conditions.

Example 3

A shell mold was prepared in the same manner as Example 1, except that the ZrO₂ suspension was relaced by a 70 wt. % commercial gypsum suspension. Ceramic powder was molded by cast molding using this mold, and dewaxed by heating to about 600° C. Most of the mold was fallen and the remaining part adhered to the molded body was destroyed by blowing using compressed air to obtain a molded body of the ceramic powder in a form of the curved pipe without damage. The molded body was sintered under usual conditions. A test piece cut off the sintered body had a similar strength to a test piece cut off another sintered body obtained by molding through a CIP process and sintering under the same conditions.

Example 4

A pattern of the curved pipe shown in Figure 1 was prepared according to the water-soluble pattern-making process used in the shell molding of precision casting. On the other hand; polyethylene was melted by heating at about 200 C. The above pattern was immersed in the polyethylene liquid, and then, it was taken out followed by drying. This operation was repeated 3 times in total. The pattern coated with polyethylene was immersed in water heated to a suitable temperature for the dissolution of the pattern, and the pattern was removed by dissolving to obtain a shell mold. Ceramic powder was molded by injection molding using this mold, and dewaxed by heating to about 600 C. The shell mold was decomposed together with the forming assistant during dewaxing to obtain a molded body of the ceramic powder in a form of the curved pipe without damage. The molded body was sintered under usual conditions. A test piece cut off the sintered body had a similar strength to a test piece cut off another sintered body obtained by molding through a CIP process and sintering under the same conditions.

Example 5

A paraffin pattern of the curved pipe shown in Figure 1 was prepared according to the pattern-making process used in the shell molding of precision casting. On the other hand, water-soluble urea resin was dissolved in water in a concentration of 50 wt. %. The above pattern was immersed in the

urea resin solution, and then, it was taken out followed by drying. This operation was repeated 10 times in total. The pattern coated with urea resin was immersed in hexane which can dissolve the paraffin but cannot dissolve the urea resin to remove the pattern. Ceramic powder was molded by low pressure injection molding, and immersed in water together with the mold. Thus, the shell mold was removed by dissolving to obtain a molded body of the ceramic powder in a form of the curved pipe without damage. The molded body was sintered under usual conditions. A test piece cut off the sintered body had a similar strength to a test piece cut off another sintered body obtained by molding through a CIP process and sintering under the same conditions.

Claims

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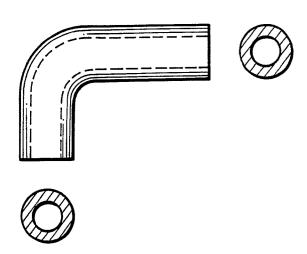
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- 1. A decay mold comprising a powder material having a transition accompanied with a volume change occurring at a temperature lower than the sintering temperature and a binder thereof.
- 2. The decay mold of claim 1 wherein said powder material is a member selected from zirconia, fused silica and zircon sand.
- 3. The decay mold of claim 1 wherein said binder is a member selected from alumina sol, silica sol and zirconia sol.
- 4. The decay mold of claim 1 composed of 30 to 90 wt. % of the powder material, 10 to 30 wt. % of the binder and less than 50 wt. % of other materials.
- 5. A decay mold comprising a material thermally decomposable at a temperature lower than the sintering temperature.
- 6. The decay mold of claim 5 wherein said material is a binder of the material forming the
- 7. The decay mold of claim 5 wherein said material is gypsum or a resin.
- 8. A decay mold comprising a material soluble at least in one solvent in which the molding assistant to impart formability to the powder to be molded is insoluble.
- 9. The decay mold of claim 8 wherein said material is a binder of the material forming the mold.
- 10. The decay mold of claim 8 wherein said material is a member selected from water-soluble urea resin, ethyl cellulose, methyl cellulose, polyvinylbutyral and polyvinylalcohol.

FIG.1



F1G.2

