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(54) **Method of forming shaped body from fine particles with carrier fluid under pressure gradient.**

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Description

The present invention relates to a method of forming a shaped body from fine particles such as powder, whiskers or short fibers of ceramics or metals, by employing a mold having a mold chamber.

5 It is known to manufacture ceramic or metallic articles from fine particles of the material such as powder, whiskers or short fibers by charging a mixture of the fine particles and a fluidal binder or binding agent into a mold chamber of a mold, compacting the mixture in the mold chamber to follow the shape of the mold chamber, removing the molded body out of the mold, expelling the binding agent out of the molded body, and sintering the fine particles to form an integral body.

10 In the above article manufacturing processes, the fluidal binding agent has been considered to be indispensable to give a smooth fluidity to a mass of fine particles so that it is readily deformable to fill a mold chamber uniformly up to every corner thereof and also to maintain the shape of the molded body prior to the sintering of the fine particles.

15 However, the process of expelling the binding agent out of the molded body, which is generally to heat the molded body under ventilation of atmosphere, takes a relatively long time, and further, if the heating is not carried out at an appropriate condition, there is a high probability that an undesirable shrinkage occurs and cracks are generated.

In order to meet with these problems, it has been proposed in Japanese Patent Publication 3-9064 (= US-A-4.731.208) to use a super critical fluid as mixed in the mixture of fine particles and a binding agent, 20 noting that a super critical fluid presents a high dissolubility to the binding agent due to its high density, and thus it works as a good extraction agent in expelling the binding agent out of the molded body.

Further, in Japanese Patent Publication 3-12122 (=US-A-5.028.363) it has been proposed to first replace the binding agent in the molded body by a super critical fluid and then to remove the super critical fluid from the molded body, while shifting the super critical state of the fluid directly to a gaseous state 25 without crossing the liquid-gas border line, so that no state of coexistence of liquid and gas is encountered in the micro pores in the molded body, thereby avoiding that the micro structure of the molded body is damaged by the capillary action of the fluid in the micro pores.

In view of the difficulties concerned with the removal of the binding agent from the molded body as described above, it is the object of the present invention to provide a method of forming a shaped body 30 from fine particles such as powder, whiskers or short fibers of ceramics or metal, without using any binding agent, so that no process of removing the binding agent from the molded body is required.

US-A-3.165.570 discloses a method without using a binding agent; a carrier fluid, such as air, is used to transport the particulate material into the mold.

The present invention provides a method of forming a shaped body in accordance with Claim 1.

35 When fine particles such as powder, whiskers or short fibers of ceramics or metal are supplied, as mixed with a carrier fluid, under a pressure elevated substantially above atmospheric pressure, into a mold chamber of a mold through an inlet port thereof open to the mold chamber at a first portion thereof, and when the mold has an outlet port open to the mold chamber at a second portion thereof substantially opposite to said first portion and adapted to exhaust substantially only the carrier fluid in a gaseous state 40 out of the mold chamber, a continuous flow of the carrier fluid is generated across the mold chamber from the inlet port to the outlet port, whereby a suspension of the fine particles by the carrier fluid enough to carry the fine particles to every corner in the mold chamber is available, and then, as the carrier fluid which has carried the fine particles is exhausted through the outlet port, the fine particles are gradually stacked up, starting from the location of the outlet port toward the location of the inlet port, forming a tight stack of 45 the fine particles having such a micro structure that each fine particle is most stably received in a micro space afforded by several preceding fine particles and is subsequently pressed among those preceding fine particles by the flow of the carrier fluid as well as a pressure gradient across a succeeding stack of the fine particles. Thus, when the pressure to supply the mixture of the fine particles and the carrier fluid into the mold chamber is appropriately selected, a molded body of the fine particles is available in any reasonable 50 shape to have a high integrity enough to maintain its shape unchanged during the succeeding sintering process.

According to the present invention, said carrier fluid is at a super critical state when said mixture is supplied into said mold chamber, said carrier fluid being in a gaseous state at room temperature and atmospheric pressure.

55 However, said carrier fluid may also be at a liquid state when said mixture is supplied into said mold chamber, said carrier fluid being in a gaseous state at room temperature and atmospheric pressure.

As viewed from another aspect of carrying out the method of the present invention, said mixture may be prepared to be at said elevated pressure in a pressure vessel equipped with a heating means and an

agitation means, and is supplied into said mold chamber by the pressure in said pressure vessel.

Alternatively, said mixture may be prepared in a vessel equipped with a heating means and an agitation means, and is supplied from said vessel into said mold chamber through a pump means which compresses said mixture.

5 CO₂ is one of the most desirable materials to be used as said carrier fluid in the method according to the present invention.

In the accompanying drawing,

Fig. 1 is a diagrammatical illustration of a device to carry out an embodiment of the present invention;

Fig. 2 is an example of a molded body of fine particles produced by the device shown in Fig. 1; and

10 Fig. 3 is a view similar to Fig. 1, showing another embodiment of the present invention.

In the following the present invention will be described in more detail with respect to some preferred embodiments with reference to the accompanying drawings.

Referring to Fig. 1, 10 designates a storage container of CO₂ which supplies CO₂ through a conduit 12, a pump 14 and a conduit 16 to a mixing vessel 18 having a mixing chamber 20. The CO₂ is selectively
15 heated by a heater 22 while it is conducted through the conduit 16. The mixing vessel has a heater 24 arranged around the mixing chamber 20 and an agitator 28 for mixing fine particles 26 charged in the mixing chamber 20 and the CO₂ introduced into the mixing chamber 20. The mixture of the fine particles and the CO₂ is conducted through a shutoff valve 30 and a conduit 32 to a mold 34 through an inlet port 36. The mold 34 is made of an upper mold half 38 and a lower mold half 40 defining in combination a mold
20 chamber 42. A small clearance left between the two mold halves at a location opposite to the inlet port 36 provides an outlet port 44 adapted to pass substantially only gas therethrough.

Example 1:

25 A molded body was made from a silicon nitride powder by employing the device shown in Fig. 1.

First, a fine particle material consisting of a silicon nitride powder of 0.4 micron mean particle diameter forming 96 parts in weight, a yttrium oxide powder of 0.2 micron mean particle diameter forming 2 parts in weight and an alumina powder of 0.1 micron mean particle diameter forming 2 parts in weight was charged into the mixing chamber 20.

30 Then, with the shutoff valve 30 being kept closed, the mold chamber space was heated by the heater 24 up to 35 °C, which is higher than the critical temperature 31.1 °C of CO₂. Then, operating the pump 14, opening a port valve (not shown in Fig. 1) of the storage container 10, and operating the heater 22, CO₂ from the storage container 10 was charged into the mixing chamber 20 until the pressure in the mixing chamber 20 reached 400atm, which is higher than the critical pressure 73.8atm of CO₂, thus rendering the
35 CO₂ in the mixing chamber 20 in a super critical state.

The agitator 28 was also operated to mix the fine particles with the super critical CO₂, thus suspending the fine particles in turbulent flows of the CO₂. Then, opening the shutoff valve 30, the mixture was supplied from the mixing vessel into the mold chamber 42 through the inlet port 36. In the meantime, CO₂ gas was exhausted from the outlet port 44. When the mold chamber 42 was completely filled with a stack of the fine
40 particles forming a body 46, the shutoff valve 30 was closed, and all of the heaters 22 and 24, the pump 14 and the agitator 28 were stopped.

Although it was unable to see the behaviour of the fine particles and the super critical CO₂ in the mold chamber 42, it is guessed that, as a part of the super critical CO₂ existing adjacent the outlet port 44 in the mold chamber 42 is exhausted through the outlet port 44 while changing its state into a gas, the fine
45 particles suspended by such part of the CO₂ were laid around the outlet port 44 to form a layer of stacked fine particles, and then, as the thickness of the stack layer gradually increased, it provided a flow resistance layer against the flowing out of the CO₂ in the mold chamber through the outlet port 44, thereby generating a pressure gradient across the stack layer toward the outlet port, successively letting each fine particle be most stably received in each micro space afforded by several preceding fine particles already formed into
50 the stack layer, by the force generated according to the pressure gradient, or the flow of CO₂ and the compression of the stack layer exerted thereby.

After the completion of the above molding operation, the mold halves were opened and the molded body 46 in the form of a rectangular parallelepiped block such as shown in Fig. 2 was obtained. The block had three dimensions precisely coinciding with those of the mold chamber 42. There was no shrinkage and
55 no crack in the block.

The density and the bending strength of the molded body 46 were tested. The density was substantially uniform over all portions thereof and was 1.50 g/cm³, presenting a volumetric density of 48%. The molded body was firm enough to maintain its shape for subsequent sintering process. It was confirmed that no CO₂

remained in the molded body.

Example 2:

The device was modified as shown in Fig. 3 so that the pump 14 is positioned in the conduit 32 and can supply a mixture of fine particles and a carrier fluid prepared in the mixing vessel 18 into the molding chamber 42 under a compression applied thereby.

A mixture of 10kg silicon nitride powder of 0.5 micron mean particle diameter, 500g yttrium oxide of 0.1 micron mean particle diameter and 500g alumina powder of 0.1 micron mean particle diameter was charged into the mixing chamber 20 of the mixing vessel 18. Then, with the shutoff valve 30 being kept closed, CO₂ was supplied into the mixing chamber 20 at 5kg/cm². Then, operating the heater 24, while also operating the agitator 28, the mixing chamber space was heated so that the temperature rised up to 80 °C and the pressure rised up to 120kg/cm², thus rendering the CO₂ in a super critical state.

Then, opening the shutoff valve 30, while operating the pump 14, the mixture of the fine particles and the super critical CO₂ was pumped up to 300kg/cm² and supplied to the mold chamber 20. The supply of the mixture under the pumping was continued, while allowing CO₂ gas to exhaust through the outlet port 44, until the mold chamber 20 was completely filled with a stack of the fine particles. Then, the shutoff valve 30 was closed, and the pump 14 was stopped. Then, the mold halves were opened, and the mold body 46 was taken out.

For the sake of comparison, several molded bodies were produced from the same mixture but without operating the pump 14, so that the pressure of supplying the mixture into the mold chamber 42 gradually lowered according to the consumption of the mixture in the mixture vessel 18.

The difference in density of the molded body according to the mixture supply pressure in the mold chamber was as follows:

Pressure (kg/cm ²)	Density (g/cm ³)
300	1.40
120	1.31
112	1.29
103	1.27
95	1.24
86	1.22
78	1.20

The molded body produced by the mixture supply pressure of 300kg/cm² and the molded body produced by the mixture supply pressure of 95kg/cm² were sintered in N₂ atmosphere at 1700 °C for 4 hours. The density of the sintered bodies was measured. Further, 40 samples for the bending test according to JIS R1601 were produced from each molded body, and were tested. The mean values of the density, the strength and the Weibull coefficient with respect to the samples obtained under the pressures of 300kg/cm² and 95kg/cm² were respectively as follows:

Pressure	Density	Strength	Weibull coefficient
300kg/cm ²	3.27g/cm ³	1260MPa	16
95kg/cm ²	3.22g/cm ³	920MPa	7

Example 3:

A mixture of 10kg silicon nitride powder of 0.5 micron mean particle diameter, 500g yttrium oxide powder of 0.1 micron mean particle diameter and 500g alumina powder of 0.2 micron mean particle diameter was charged into the mixing chamber 20 of the mixing vessel in the device shown in Fig. 3. Then, with the shutoff valve 30 being kept closed, CO₂ under pressure was charged into the mixing chamber 20. The pressure and the temperature in the mixing chamber space were adjusted to be 100kg/cm² and 23 °C, respectively, so that the CO₂ was in a liquid state. The amount of CO₂ charged in the mixing chamber 20 was 3.5kg.

After full agitation of the mixture by the agitator 28, opening the shutoff valve 30, while operating the pump 14, the mixture was pumped up to 200kg/cm² and supplied into the mold chamber 42. The pumping supply of the mixture into the mold chamber was continued, while CO₂ gas was exhausted through the outlet port 44, until the mold chamber 42 was completely filled with a stack of the fine particles. Then, the shutoff valve was closed, the pump 14 was stopped, and the molded body was taken out from the mold in the same rectangular parallelepiped block form.

The molded body showed three dimensions precisely coinciding with those of the mold chamber 42. The density was 1.37g/cm³. No CO₂ remained in the molded body.

The molded body was sintered in N₂ atmosphere at 1750 °C for 4 hours. 40 samples for the bending test according to JIS R1601 were produced from the sintered body, and tested. The mean values of the strength and the Weibull coefficient were 1210 MPa and 14, respectively.

From the foregoing it will be appreciated that according to the present invention molded bodies of fine particles such as powder, whiskers or short fibers of ceramics or metal to be turned into integral ceramic or metallic articles by a subsequent sintering process are obtained to have a shape and dimensions defined by a mold chamber at high fidelity, with no use of binding agent, thereby obviating the difficulties concerned with expelling the binding agent from the molded bodies. Therefore, a high productivity is available in the manufacture of shaped articles of ceramics or metal starting from fine particles of the material.

Claims

1. A method of forming a shaped body from fine particles such as powder, whiskers or short fibers of ceramics or metal by preparing a mold (34) having a mold chamber (42), an inlet port (36) open to said mold chamber at a first portion thereof, and an outlet port (44) open to said mold chamber at a second portion thereof substantially opposite to said first portion, and supplying a mixture of said fine particles and a carrier fluid into said mold chamber through said inlet port under a pressure elevated substantially above atmospheric pressure while exhausting said carrier fluid out of said mold chamber through said outlet port in a gaseous state, characterized in that said carrier fluid of said mixture supplied into said mold chamber through said inlet port is either at a super critical state or at a liquid state, said carrier fluid being in a gaseous state at room temperature and atmospheric pressure.
2. A method according to Claim 1, wherein said mixture is prepared to be at said elevated pressure in a pressure vessel (18) equipped with a heating means (24) and an agitation means (28), and is supplied into said mold chamber (42) by the pressure in said pressure vessel.
3. A method according to Claim 1, wherein said mixture is prepared in a vessel (18) equipped with a heating means (24) and an agitation means (28), and is supplied from said vessel into said mold chamber (42) through a pump means (14) which compresses said mixture.
4. A method according to any one of Claims 1 - 3, wherein said carrier fluid is CO₂.

Patentansprüche

1. Verfahren zur Bildung eines Formkörpers aus feinen Partikeln, wie etwa aus Pulver, Whiskern oder Kurzfasern aus Keramiken oder Metall durch Anfertigung einer Form (34) mit einer Formkammer (42), einer zu einem ersten Abschnitt der Formkammer offenen Einlaßöffnung (36) und einer zu einem zweiten, dem ersten Abschnitt im wesentlichen gegenüberliegenden zweiten Abschnitt der Formkammer offenen Auslaßöffnung (44) und zur Zuführung eines Gemisches der feinen Partikel und eines Trägerfluids durch die Einlaßöffnung in die Formkammer bei einem wesentlich über dem atmosphärischen Druck erhöhten Druck, während das Trägerfluid über die Auslaßöffnung im gasförmigen Zustand aus der Formkammer ausströmt,
dadurch gekennzeichnet, daß
das Trägerfluid des über die Einlaßöffnung in die Formkammer eingespeisten Gemisches entweder im überkritischen Zustand oder im flüssigen Zustand ist, wobei sich das Trägerfluid bei Raumtemperatur und atmosphärischem Druck im gasförmigen Zustand befindet.
2. Verfahren nach Anspruch 1, wobei das Gemisch vorbehandelt wird, um bei erhöhtem Druck in einem mit einer Heizeinrichtung (24) und einer Röhreinrichtung (28) ausgestatteten Druckkessel (18) zu sein,

und mittels dem Druck im Druckkessel in die Formkammer gespeist wird.

3. Verfahren nach Anspruch 1, wobei das Gemisch in einem mit einer Heizeinrichtung (24) und einer Rühreinrichtung (28) ausgestatteten Kessel (18) vorbehandelt wird und von dem Kessel über eine das Gemisch verdichtende Pumpeneinrichtung (14) in die Formkammer (42) gespeist wird.
4. Verfahren nach einem der Ansprüche 1 bis 3, wobei das Trägerfluid CO₂ ist.

Revendications

1. Un procédé de moulage d'un corps façonné à partir de fines particules, telles que poudres, trichites ou fibres courtes de céramiques ou de métaux par préparation d'un moule (34) comprenant une cavité de moule (42), un orifice d'entrée (36) débouchant dans ladite cavité de moule, dans une première partie de celle-ci, et un orifice de sortie (44) débouchant dans ladite cavité de moule dans une seconde partie de celle-ci, sensiblement à l'opposé de ladite première partie, et l'alimentation d'un mélange desdites fines particules et d'un fluide porteur dans ladite cavité de moule à travers ledit orifice d'entrée sous une pression élevée, sensiblement supérieure à la pression atmosphérique tandis que ledit fluide porteur est évacué à l'état gazeux de ladite cavité de moule à travers ledit orifice de sortie, caractérisé en ce que ledit fluide porteur dudit mélange alimenté dans ladite cavité de moule à travers ledit orifice d'entrée est, soit à un état super critique, soit à un état liquide, ledit fluide porteur étant à l'état gazeux à la température ambiante et à la pression atmosphérique.
2. Un procédé selon la revendication 1, dans lequel ledit mélange est préparé pour être amené à ladite pression élevée dans un récipient sous pression (18) équipé de moyens de chauffage (24) et de moyens d'agitation (28) et est alimenté dans ladite cavité de moule (42) par la pression régnant dans ledit récipient sous pression.
3. Un procédé selon la revendication 1, dans lequel ledit mélange est préparé dans un récipient (18) équipé de moyens de chauffage (24) et de moyens d'agitation (28) et est alimenté à partir dudit récipient dans ladite cavité de moule (42) par l'intermédiaire de moyens de pompage (14) qui compriment ledit mélange.
4. Un procédé selon l'une quelconque des revendications 1 à 3, dans lequel ledit fluide porteur est de l'anhydride carbonique.

FIG. 1

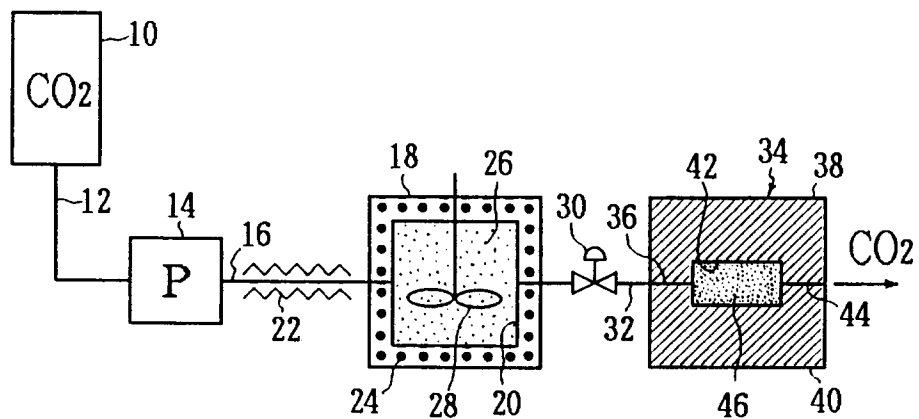


FIG. 2

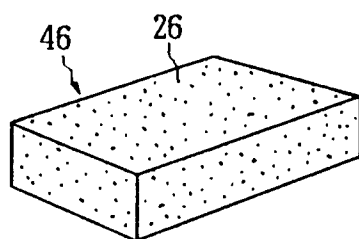


FIG. 3

