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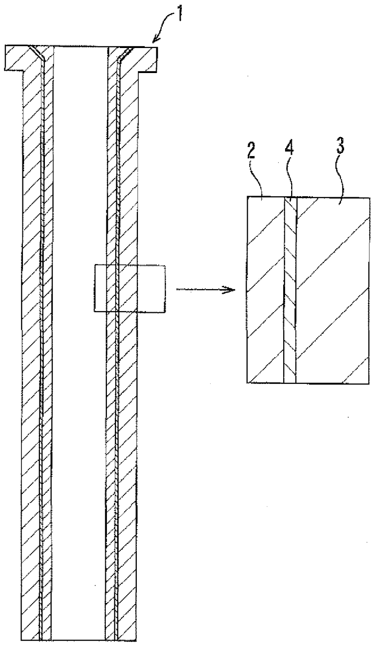
(54) NOZZLE FOR CONTINUOUS CASTING AND METHOD FOR MANUFACTURING THE SAME

(57) Disclosed is a continuous casting nozzle, which comprises a layer formed to have high functions, such as high corrosion resistance and high anti-deposition capability, and disposed on the side of an inner bore thereof to serve as an inner bore- side layer, so as to enhance durability, wherein the continuous casting nozzle is capable of preventing expansion cracking of an outer periphery- side layer serving as a nozzle body thereof, due to a difference in thermal expansion between respective compositions of the inner bore- side layer and the outer periphery- side layer, while preventing peel-off of the inner bore- side layer during casting. The continuous casting nozzle has a structure in which respective opposed boundary surfaces between the inner bore-side layer 2 and an intermediate layer 4 and between the intermediate layer 4 and the outer periphery- side layer 3, are in direct contact with each other, wherein a bonding strength between the intermediate layer and each of the inner bore- side layer and the outer periphery- side layer adjacent to the intermediate layer is in the range of 0.01 to 1.5 MPa, as measured in a non-oxidation atmosphere at 1000□ C, and a compressive rate (%) of the intermediate layer in a non-oxidation atmosphere at 1000□ C and under a pressure oaf 2.5 MPa is in the range of 10 to 80 %.

Fig. 1



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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a nozzle for continuous casting of molten metal, and more particularly to a continuous casting nozzle which comprises a tubular refractory structure having an inner bore formed along an axial direction thereof to allow molten metal to pass therethrough, wherein a part or an entirety of the tubular refractory structure includes an inner bore- side layer, an intermediate layer and an outer periphery-side layer.

[0002] As used herein, the term "tubular" means any configuration of a refractory structure having an inner bore formed along an axial direction thereof, irrespective of a cross-sectional shape thereof in a direction orthogonal to the axial direction. That is, the cross-sectional shape in the direction orthogonal to the axial direction is not limited to a circular shape, but may be any other shape, such as an oval shape, a rectangular shape or a polygonal shape.

[0003] As used herein, the term "inner bore-side layer" collectively means any refractory layer located on the side of the inner bore relative to a central region (e.g., intermediate layer), in a horizontal cross-section taken at any position of an overall length of a continuous casting nozzle in a molten-metal passing direction (i.e., vertical direction), and covers any layer structure. For example, the inner bore-side layer may be made up of a plurality of layers. In this case, a thermal expansion coefficient of the inner bore-side layer means a maximum one of respective thermal expansion coefficients of the plurality of inner bore-side layers.

[0004] As used therein, the term "outer periphery-side layer" collectively means any refractory layer located on the side of an outer periphery of a continuous casting nozzle relative to the central region (e.g., intermediate layer), in the above horizontal cross-section, and covers any layer structure. For example, the outer periphery-side layer may be made up of a plurality of layers (e.g., a two-layer structure consisting of an AG (i.e. Aluminum-Graphite)-based layer and a ZG(i.e. Zirconia-Graphite)-based layer located outside the AG-based layer). In this case, a thermal expansion coefficient of the outer periphery-side layer means a maximum one of respective thermal expansion coefficients of the plurality of outer periphery-side layers.

2. Description of the Background Art

[0005] A continuous casting nozzle, such as a long nozzle for discharging molten steel from a ladle into a tundish, or an immersion nozzle for pouring molten steel from a tundish into a continuous casting mold, comprises a tubular refractory structure having an inner bore formed approximately along an axial center thereof to allow molten metal, such as molten steel, to pass therethrough, wherein the molten steel passing through the inner bore causes a temperature gradient between inner bore-side and outer periphery-side layers of the continuous casting nozzle. Particularly, in an initial stage of discharging/passing of the molten steel, the above phenomenon becomes prominent due to rapid temperature rise in the inner bore-side layer.

[0006] Irrespective of whether a refractory body constituting the refractory structure is made up of a single layer or a multi-layer, the temperature gradient gives rise to a strain due to an internal stress of the refractory body, and becomes one factor causing breaking, such as cracking, particularly in the outer periphery-side layer. Further, as the temperature gradient becomes larger, and a thermal expansion coefficient of the inner bore-side layer is greater than that of the outer periphery-side layer to a larger degree, a thermal stress will be increased to cause a higher risk of breaking in the outer periphery-side layer.

[0007] In the continuous casting nozzle, a molten steel flow passes therethrough while violently colliding against an inner bore surface thereof. Thus, in particular, a region of the continuous casting nozzle adjacent to the inner bore surface is severely damaged due to abrasion caused by the molten steel, non-metal inclusions in the molten steel, etc., embrittlement of a matrix and washing (corrosion) due to oxidizing components of the molten steel, etc., and wear caused by a reaction with FeO and other component of the molten steel. Moreover, in connection with a recent trend of upgrading of steel which involves an increase in amount of non-metal inclusions in molten steel, such as alumina, deposition of inclusions (mainly, alumina) onto the inner bore surface of the continuous casting nozzle, or clogging of the inner bore of the continuous casting nozzle due to the inclusions, become one key factor determining a lifetime of the continuous casting nozzle.

[0008] In the above circumstances, there has been an increasing need for improving corrosion resistance and abrasion/wear resistance of an inner bore surface of a continuous casting nozzle, and reducing deposition of non-metal inclusions and others onto the inner bore surface or clogging of an inner bore of the continuous casting nozzle due to the non-metal inclusions and others, to achieve higher durability and safety (stable casting capability) of the continuous casting nozzle.

[0009] With a view to meeting the above needs, it has been attempted to extend a lifetime of a continuous casting nozzle, for example, by applying a refractory composition excellent in thermal shock resistance to a body (i.e., an outer periphery-side layer) of the nozzle, to form a skeleton of the nozzle, and applying a refractory composition excellent in abrasion/wear resistance and corrosion resistance, or a refractory composition resistant to deposition of inclusions such as alumina, to a region of the nozzle on the side of an inner bore surface thereof adapted to come into contact with a molten steel flow (i.e., inner bore-side layer) in such a manner as to define a part or an entirety of the inner bore surface.

[0010] Particularly, with regard to the inner bore-side layer, various functional enhancement techniques have been recently developed. For example, with a view to providing higher corrosion resistance, there has been developed a technique of incorporating a corrosion resistant component, such as Al_2O_3, ZrO_2 or MgO, into a material having a reduced amount of graphite and silica which are wear-nonresistant aggregates, or a material devoid of graphite and silica. Further, with a view to reducing or preventing deposition of inclusions, such as Al_2O_3, in molten steel, onto the inner bore surface, or clogging of the inner bore due to the inclusions, there has been promoted a practical use of a continuous casting nozzle, such as an immersion nozzle, having a refractory layer made of a basic material containing a CaO component highly reactive with an Al_2O_3 component, and inserted thereinto.

[0011] A refractory aggregate including the above components for obtaining such a highly-functional refractory composition has high thermal expansibility, and the highly-functional refractory composition contains the refractory aggregate in a relatively large amount. Thus, a thermal expansion amount of the inner bore-side layer is apt to be increased. Furthermore, due to an additional factor, such as an increase in thermal gradient caused by lowering in thermal conductivity of the inner bore-side layer relative to the outer periphery-side layer, in connection with a reduction in carbon content, a difference between respective thermal expansion amounts of the inner bore-side layer and the outer periphery-side layer, and a resulting thermal stress, are apt to be more increased, which leads to increasing risk of breaking of the continuous casting nozzle, particularly cracking in the outer periphery-side layer caused by thermal expansion of the inner bore-side layer (hereinafter referred to as "expansion cracking").

[0012] A typical countermeasure against breaking of a continuous casting nozzle due to a temperature gradient (thermal stress) therein includes a technique of reducing a thermal stress based on an increase in thermal conductivity, a reduction in thermal expansion amount, and/or a lowering in elastic modules, for example, by incorporating graphite into a refractory composition of the continuous casting nozzle in a relatively large amount, or by adding or quantitatively increasing fused silica having a relatively small thermal expansion coefficient. On the other hand, the increased content of graphite or fused silica has a negative effect causing deterioration in durability, such as abrasion/wear resistance and corrosion resistance, due to deterioration in oxidation resistance, enhancement in reactivity with other refractory components and components in molten steel, etc. Thus, the above technique is not effective as a realistic solution due to restrictions in application to the inner bore-side layer.

[0013] In the above situation, with a view to avoiding the risk of breaking of a continuous casting nozzle, there has been employed a technique of, for example, in a structure where a shaped member serving as an inner bore-side layer is installed on the side of an inner bore of an outer periphery-side layer, forming a mortar layer therebetween using mud-like mortar which comprises a fine powder mainly consisting of a refractory material such as a conventional oxide, and a nonorganic binder such as silicate containing a relatively large amount of solvent, in such a manner that the mortar layer has a relatively large porosity to reduce a strength thereof so as to allow a stress caused by thermal expansion of the inner bore-side layer to be relieved based on breakage of the mortar layer itself, i.e., a technique employing mortar capable of exhibiting a relatively high porosity although it has a relatively low bonding force, to avoid cracking of the nozzle. However, this anti-cracking technique based on mortar has the following problems.

(1) The mortar layer containing an excess amount of solvent has a property that the solvent in the mortar layer is absorbed in materials of the remaining layers through contact with the materials of the remaining layers. Thus, the porosity of the mortar layer is apt to become gradually lower or denser toward a boundary surface with each of the remaining layers, so that, particularly, when the mortar layer is used in a continuous casting nozzle and formed to have a small thickness of several mm, the stress relief function of the mortar layer itself after installation will deteriorate or disappear.

(2) It is substantially impossible to control an apparent porosity. Specifically, a pore distribution allowing for buckling at a given stress or less cannot be controlled, and thereby it is essential to contain an excessive amount of solvent to preclude achievement of a good balance with bondability (i.e., bonding capability).

(3) The stress relief function of the mortar layer is based on a mechanism where an allowance for thermal deformation of the inner bore-side layer is created to absorb a stress by an irreversible breaking of a matrix of the mortar layer defining pores, to relieve a stress in the inner bore-side layer. Thus, when the matrix is broken once, the bondability is lost to increase a risk of drop-off. Moreover, a gap resulting from breaking of the mortar layer due to changes in temperature allows molten metal, such as molten steel and slag, to easily intrude thereinto, and the intruding molten steel and slag are highly likely to cause cracking and corrosion, which leads to damage of the remaining layers or the continuous casting nozzle.

[0014] For example, as another approach to preventing breaking due to a thermal stress while seeking higher durability such as corrosion resistance, the following Patent Document 1 discloses a casting nozzle comprising: a carbon-free refractory layer formed to have high thermal expansibility and high corrosion resistance and installed only on the side of an inner bore of the nozzle; a carbon-containing refractory layer formed to have excellent spalling resistance and installed on the side of the remaining part, i.e., outer periphery, of the nozzle; and a separating layer allowing at least 80% or more of a contact surface between the two refractory layers to be separated from each other, wherein the separating layer is formed by setting a burnable material, such as polypropylene or nylon, and then the burnable material is vanished.

[0015] However, in the casting nozzle disclosed in the Patent Document 1, less than 20% of the contact surface between the two refractory layers is bonded together. Even if a bonded region is fairly small, it will be an origin of an expansion cracking phenomenon, because a stress causing expansion cracking is transmitted from the carbon-free refractory layer (i.e., inner bore-side layer) to the carbon-containing refractory layer (i.e., outer periphery-side layer) through the bonded region. If the bonded region is set at zero %, it causes a basic problem that the inner bore-side layer cannot be structurally supported. Moreover, molten steel easily intrudes into the separating layer to cause problems, such as fissures in the refractory layers due to solidification shrinkage of the molten steel occurring when it undergoes changes in temperature, and expansion of the solidified steel occurring when it is heated, and peel-off due to no bonding between the inner bore-side layer and the outer periphery-side layer.

[0016] The following Patent Document 2 discloses a technique intended to suppress deposition of inclusions, wherein a CaO nozzle member containing 70 wt% or more of CaO and having an apparent porosity of 50% or less is inserted into a nozzle body of an immersion nozzle, in such a manner that a gap depending on a thermal expansion amount of the CaO nozzle member is provided between the CaO nozzle member and the nozzle body. The Patent Document 2 also discloses a technique of packing thin ceramic fibers or a small amount of mortar between an end of the CaO nozzle member and the nozzle body to fix the CaO nozzle member to the nozzle body, according to need.

[0017] In the above structure where a gap equivalent to a thermal expansion amount of the CaO nozzle member on the side of an inner bore of the immersion nozzle (i.e., inner bore-side layer) is provided between the nozzle body on the side of an outer periphery of the immersion nozzle (i.e., outer periphery-side layer) and the CaO nozzle member, the expansion cracking phenomenon of the outer periphery-side nozzle body caused by the highly-expandable CaO nozzle member can be suppressed. However, in view of the description "the gap is preferably set to be 3% or more of an outer diameter of the CaO nozzle member, during preheating" in the paragraph [0022] of the Patent Document 2, it is assumed that the inner bore-side CaO nozzle member is not in close contact with the outer periphery-side nozzle body in a high-temperature state (a thermal expansion coefficient of a CaO-based material is about 2% or less at about 1500□ C, even in a material consisting substantially only of CaO and having a maximum level of thermal expansion coefficient). If the CaO nozzle member is not in close contact with the nozzle body in the high-temperature state, i.e., during use of the immersion nozzle, the CaO nozzle member is likely to have displacement or drop off due to a compression stress receiving during use. Moreover, molten steel easily intrudes into the gap between the CaO nozzle member and the nozzle body. This involves a risk of damage of the CaO nozzle member and the outer periphery-side nozzle body due to solidification shrinkage of the molten steel and thermal expansion of the solidified steel. Furthermore, a material, such as CaO, capable of reacting with deoxidation products in molten steel to produce a low-melting point compound is fundamentally premised on wearing out. Thus, the CaO nozzle member involves a risk of drop-off or breaking due to reduction in thickness caused by wear, and the structure having no support base therebehind.

[0018] As above, if a joint portion between the inner bore-side layer and the outer periphery-side layer, such as the separating layer in the Patent Document 1 or the gap in the Patent Document 2, is set to be excessively broad, a resulting intrusion of molten steel is likely to cause peel-off and damage of the inner bore-side layer, and damage of the outer periphery-side layer. Further, if the joint portion is set to be excessively narrow, a tensile stress acting on the outer periphery-side layer in a circumferential direction thereof due to thermal expansion of the inner bore-side layer is likely to cause occurrence of longitudinal crack along an axial direction of the tubular refractory structure, or transverse crack (crack along a direction having an angle relative to the axial direction; so-called "fracture", etc.)

[0019] Thus, in a continuous casting nozzle having a highly-expandable inner bore-side layer installed therein, it would be critical to form a matrix structure capable of preventing intrusion or passing of molten metal, and have a function of allowing the inner bore-side layer to be bonded to an outer periphery-side layer, in addition to a function of reducing an influence of a stress from the inner bore-side layer. However, heretofore, a solution for giving the above three functions or structures has seldom been discussed.

[0020] Further, as disclosed in the Patent Documents 1 and 2, a conventional installation process essentially includes a step of preparing the outer periphery-side layer as a nozzle body of the continuous casting nozzle, and the inner bore-side layer, separately from each other, and a step of assembling the two layers together in a final stage by use of mortar or the like. This causes deterioration in productivity and an increase in production cost. Moreover, in the assembling of the refractory layers prepared as separate components, the layers are brought into contact with each other through respective flat and smooth surfaces thereof. Thus, it is difficult to obtain a bonding strength and a fixing force therebetween sufficient to solve the above problems, which leads to a need for additional means to enhance the bonding strength, based on an adhesive or the like.

[Patent Document 1] JP 60-152362A
[Patent Document 2] JP 07-232249A

SUMMARY OF THE INVENTION

[0021] It is an object of the present invention to provide a continuous casting nozzle comprising a refractory layer formed to have high functions, such as high corrosion resistance and high anti-deposition capability, and disposed on the side of an inner bore thereof to serve as an inner bore-side layer, so as to enhance durability, wherein the continuous casting nozzle is capable of preventing expansion cracking of an outer periphery-side layer serving as a nozzle body thereof, due to a difference in thermal expansion between respective compositions of the inner bore-side layer and the outer periphery-side layer, while preventing displacement and peel-off of the inner bore-side layer during casting. It is another object of the present invention to provide a method of producing the continuous casting nozzle in a stable and easy manner.

[0022] More specifically, in a continuous casting nozzle comprising a tubular refractory structure which has an inner bore formed along an axial direction thereof to allow molten metal to pass therethrough, and at least partly includes an inner bore-side layer disposed on the side of the inner bore, and an outer periphery-side layer disposed on a radially outward side relative to the inner bore-side layer, wherein the inner bore-side layer has the thermal expansion greater than that of the outer periphery-side layer, it is an object of the present invention to (1) prevent breaking of the outer periphery-side layer, and (2) enhance stability of the inner bore-side layer during casting, while (3) preventing intrusion of molten steel and others between respective ones of a plurality of layers including an intermediate layer. In other words, it is an object of the present invention to provide a continuous casting nozzle having a structure capable of satisfying these functions. It is another object of the present invention to provide a production method capable of stably obtaining the continuous casting nozzle in an optimized and laborsaving manner.

[0023] In order to achieve the above objects, according to one aspect of the present invention, there is provided:

(1) a continuous casting nozzle comprising a tubular refractory structure which has an inner bore formed along an axial direction thereof to allow molten metal to pass therethrough, and at least partly includes an inner bore-side layer disposed on the side of the inner bore, and an outer periphery-side layer disposed on a radially outward side relative to the inner bore-side layer, wherein the inner bore-side layer has the thermal expansion greater than that of the outer periphery-side layer. The continuous casting nozzle is characterized in that the tubular refractory structure includes an intermediate layer having compressability and lying between the inner bore-side layer and the outer peripheiy-side layer, wherein: the inner bore-side layer, the intermediate layer and the outer periphery-side layer are simultaneously integrated together during a forming process to form a multi-layer structure; a bonding strength between the intermediate layer and each of the inner bore-side layer and the outer periphery-side layer adjacent to the intermediate layer is in the range of 0.01 to 1.5 MPa, as measured in a non-oxidation atmosphere at 1000□ C; and the intermediate layer has a compressive rate K (%) satisfies the following Formula 1 as measured in a non-oxidation atmosphere at 1000□ C under a pressure of 2.5 MPa,

$$K \,\square\, [(Di \times \square\, i - Do \times \square\, o) / (2 \times Tm)] \qquad \text{--- Formula 1}$$

wherein:

Di is an outer diameter (mm) of the inner bore-side layer;
Do is an inner diameter (mm) of the outer peripheiy-side layer;
Tm is an initial thickness (mm) of the intermediate layer at room temperature;
□ i is a maximum thermal expansion coefficient (%) of the refractory composition of the inner bore-side layer in a temperature range of room temperature to 1500□ C; and
□ o is a thermal expansion coefficient (%) of the refractory composition of the outer periphery-side layer at a temperature at start of discharge or pouring of molten metal through the continuous casting nozzle (i.e., passing of molten steel) (claim 1).

(2) Preferably, in the continuous casting nozzle set forth in the appended claim 1, the intermediate layer in a state after being subjected to a heat treatment in a non-oxidation atmosphere at 600□ C or more contains expanded

expansive graphite particles (hereinafter referred to as "expanded graphite particles") (claim 2).

(3) Preferably, in the continuous casting nozzle set forth in the appended claim 1 or 2, the intermediate layer in a state after being subjected to a heat treatment in a non-oxidation atmosphere at 1000□ C contains a carbon components (except any carbon compound with the remaining components) in a total amount of 16 mass% or more (including 100 mass%) (claim 3).

(4) Preferably, in the continuous casting nozzle set forth in the appended claim 1 or 2, the intermediate layer in a state after being subjected to a heat treatment in a non-oxidation atmosphere at 1000□ C contains a carbon component (except any carbon compound with the remaining components) in a total amount of 16 mass% or more, with the remainder other than the carbon component being a refractory material comprising one or more selected from the group consisting of oxide, carbide, nitride and metal.

According to another aspect of the present invention, there is provided:

(5) a method of producing a continuous casting nozzle comprising a tubular refractory structure which has an inner bore formed along an axial direction thereof to allow molten metal to pass therethrough, and at least partly includes an inner bore-side layer, an intermediate layer and an outer periphery-side layer which are arranged in this order in a radially outward direction with respect to the inner bore. The method comprises the steps of: preparing a mixture (ingredients) for the intermediate layer, which contains un-expanded expansive graphite particles in an amount ranging from 5 to 45 mass%, and burnable particles in an amount ranging from 55 to 95 mass%, and further contains an organic binder in a given mass% with respect to a total mass% of the un-expanded expansive graphite particles and the burnable particles, and in addition to the total mass%, wherein the given mass% of the organic binder is set to allow a ratio of a carbon component only of the organic binder (except any carbon compound with the remaining components) to an entire refractory composition of the intermediate layer, in a state after the refractory composition of the intermediate layer is subjected to a heat treatment in a non-oxidation atmosphere at 1000□ C, to fall within the range of 2.5 to 15 mass%; subjecting the mixture (ingredients) for the intermediate layer to a pressure forming using a cold isostatic press (CIP) machine, simultaneously and integrally together with a mixture (ingredients) for the inner bore-side layer and a mixture (ingredients) for outer periphery-side layer, to obtain a single shaped body; and subjecting the shaped body to a heat treatment at a temperature of 600 to 1300□ C to allow the burnable particles contained in the mixture (ingredients, i.e., green body after pressing) for the intermediate layer in the shaped body to be vanished so as to form voids, and then expand the un-expanded expansive graphite particles contained in the mixture (ingredients, i.e., green body after pressing) for the intermediate layer in the shaped body so as to allow the voids to be filled with the expanded graphite particles (claim 5).

According to another aspect of the present invention, there is provided:

(6) a method of producing a continuous casting nozzle comprising a tubular refractory structure which has an inner bore formed along an axial direction thereof to allow molten metal to pass therethrough, and at least partly includes an inner bore-side layer, an intermediate layer and an outer periphery-side layer which are arranged in this order in a radially outward direction with respect to the inner bore. The method comprises the steps of: preparing a mixture (ingredient) for the intermediate layer, which contains un-expanded expansive graphite particles in an amount ranging from 5 to 45 mass%, and burnable particles in an amount ranging from 55 to 95 mass%, a refractory material which is one or more selected from the group consisting of oxide, carbide, nitride and metal, in a total amount of 40 mass% or less, and further contains an organic binder in a given mass% with respect to a total mass% of the un-expanded expansive graphite particles, the burnable particles and the refractory material which is one or more selected from the group consisting of oxide, carbide, nitride and metal, and in addition to the total mass%, wherein the given mass% of the organic binder is set to allow a ratio of a carbon component only of the organic binder (except any carbon compound with the remaining components) to an entire refractory composition of the intermediate layer, in a state after the refractory composition of the intermediate layer is subjected to a heat treatment in a non-oxidation atmosphere at 1000□ C, to fall within the range of 2.5 to 15 mass%; subjecting the mixture (ingredients) for the intermediate layer to a pressure forming using a cold isostatic press (CIP) machine, simultaneously and integrally together with a mixture (ingredients) for the inner bore-side layer and a mixture (ingredients) for outer periphery-side layer, to obtain a single shaped body; and subjecting the shaped body to a heat treatment at a temperature of 600 to 1300□ C to allow the burnable particles contained in the mixture (ingredients, i.e., green body after pressing) for the intermediate layer in the shaped body to be vanished so as to form voids, and then expand the un-expanded expansive graphite particles contained in the mixture (ingredients, i.e., green body after pressing) for the intermediate layer in the shaped body so as to allow the voids to be filled with the expanded graphite particles (claim 6).

[0024] Specifically, in order to achieve the above objects, a continuous casting nozzle of the present invention is intended to meet the following fundamental requirements:

(1) to install an intermediate layer having a stress relief function, between the inner bore-side layer and the outer periphery-side layer;

(2) to maintain a layer configuration of the intermediate layer so as to prevent breaking and other adverse effect due to layer destruction, i.e., to enhance layer stability; and

(3) to simultaneously integrate the intermediate layer, the inner bore-side layer and the outer periphery-side layer together during a forming process to form a multi-layer structure so as to fixedly bond between the intermediate layer and each of the inner bore-side layer and the outer periphery-side layer.

[0025] (The above requirements (1), (2) and (3) will hereinafter be referred to as respectively as "compressability requirements", "stability requirement" and "bondability requirement".)

[0026] Each of the above requirements will be specifically described below.

(1) COMPRESSABILITY REQUIREMENT

[0027] As mentioned above, with a view to enhancement in corrosion resistance and abrasion/wear resistance, suppression of elution of a carbon component from a refractory composition into molten steel, and prevention of deposition of inclusions, mainly nonmetal inclusions such as alumina, onto an inner bore surface or nozzle clogging due to the inclusions, the inner bore-side layer tends to be made of a refractory composition having an increased amount of Al_2O_3, MgO, ZrO_2 and/or CaO and exhibiting excellent corrosion resistance and abrasion/wear resistance.

[0028] In many cases, the outer periphery-side layer (including an outer periphery-side layer as a part of a nozzle body) to be designed while placing great important on thermal shock resistance has a smaller content of Al_2O_3, MgO, ZrO_2 and/or CaO as compared with the inner bore-side layer. Thus, a thermal expansion coefficient of the inner bore-side layer inevitably becomes greater than that of the outer periphery-side layer.

[0029] When a refractory composition having a larger thermal expansion coefficient than that of the outer periphery-side layer is used for the inner bore-side layer, breaking of a continuous casting nozzle due to fissures and expansion cracking in the outer periphery-side layer caused by the inner bore-side layer will more frequently occur. Even if the inner bore-side layer and the outer periphery-side layer are made of the same refractory composition or, made of respectively, of refractory compositions having the same level of thermal expansion characteristic, the breaking occurs when the inner bore-side layer is heated up to a temperature greater than that of the outer periphery-side layer due to preheating or rapid heating from the side of the inner bore, passing of molten steel or the like, to create a large temperature gradient between the inner bore-side layer and the outer periphery-side layer.

[0030] That is, in the present invention, the requirement that "the inner bore-side layer has the thermal expansion greater than that of the outer periphery-side layer" means not only a condition that a maximum thermal expansion coefficient of the refractory composition of the inner bore-side layer at 1500□ C (substantially close to a casting temperature region) or less is greater than that of the refractory composition of the outer periphery-side layer at 1500□ C or less, but also a condition that a level of thermal expansion of the inner bore-side layer becomes greater than that of the outer periphery-side layer, due to a temperature difference between the inner bore-side layer and the outer periphery-side layer occurring during heating, such as receiving of molten steel or preheating from the side of the inner bore, even though each of the inner bore-side layer and the outer periphery-side layer has the same maximum thermal expansion coefficient or exhibits the same thermal expansion behavior (e.g., a material having the same composition and structure).

[0031] In cases where there is no stress relief function or only an extremely low stress relief function, between an inner bore-side layer and an outer periphery-side layer, a stress of the inner bore-side layer is applied to the outer periphery-side layer as a compression stress oriented in a radial direction on a horizontal section of the nozzle. Further, if the outer periphery-side layer is designed to extend to cover opposite longitudinally or axially outward ends of the inner bore-side layer, the stress of the inner bore-side layer is also applied to the outer periphery-side layer as a compression stress oriented in the axial direction. Then, the radial compression stress is converted to a tensile stress oriented in a circumferential direction, and the axial compression stress is converted to a tensile stress in the axial direction. Subsequently, when these tensile stresses become greater than a tensile strength limit of the refractory composition of the outer periphery-side layer, the circumferential tensile stress causes an axial (vertical) crack, and the axial tensile stress causes a horizontal (transverse) crack to damage the outer periphery-side layer.

[0032] In the present invention, as means to provide the stress relief function between the inner bore-side layer and the outer periphery-side layer having the above relationship, the intermediate layer having compressability and bondability during a nozzle preheating operation and during hearing up to 1500□ C (substantially close to a casting temperature region) is installed.

[0033] This allows a stress due to thermal expansion of the outer periphery-side layer to be applied to the installed intermediate layer as a compression stress without being directly applied to the outer periphery-side layer. During this process, in response to the compression stress, a thickness of the intermediate layer itself is reduced in the radial direction, and in the axial direction at the axial end. In other words, a stress due to thermal expansion the intermediate layer can be relieved by reducing a volume of the intermediate layer. In the present invention, such a capability to be reduced in thickness and volume is referred to as "compressability".

[0034] Generally, in a tubular refractory structure comprising an Al_2O_3-C based material which is a typical material of an outer periphery-side layer of a conventional immersion nozzle, the outer periphery-side layer is broken by a pressure of about 2.5 MPa applied to an inner wall surface thereof. For example, in an Al_2O_3-graphite based refractory structure comprising an outer periphery-side layer which has practically minimum radial dimensions (inner diameter ϕ = 80 mm, outer diameter ϕ = 135 mm) and a maximum tensile strength of 6 MPa, when a pressure load is applied from the side of an inner wall surface of the outer periphery-side layer, the outer periphery-side layer reaches breaking when the pressure load is applied to the inner wall surface at about 2.5 MPa, according to calculation using a formula for a thick-walled cylinder.

[0035] In a continuous casting nozzle where an intermediate layer and an inner bore-side layer are disposed on the side of an inner bore relative to an outer periphery-side layer, the intermediate layer itself is required to exhibit a deformation behavior in order to relieve a stress due to thermal expansion of the inner bore-side layer, which is oriented toward the outer periphery-side layer. That is, the stress oriented toward the outer periphery-side layer has to be reduced to 2.5 MPa or less by deformation (contraction) of the intermediate layer.

[0036] Thus, during heating of the inner bore-side layer or during passing of molten steel, a tensile stress to be generated in the outer periphery-side layer is preferably reduced to 2.5 MPa or less, more preferably further reduced as low as possible to provide enhanced safety, and the intermediate layer itself is required to exhibit a deformation behavior capable of reducing a compression stress to a value corresponding to such a tensile stress value.

[0037] Compressability required for the intermediate layer under a pressing force of 2.5 MPa or more can be expressed as a compressive rate K (%) in the following Formula 1:

$$K \square \ [(Di \times \square i - Do \times \square o) / (2 \times Tm)] \qquad \text{--- Formula 1}$$

wherein:

Di is an outer diameter (mm) of the inner bore-side layer;
Do is an inner diameter (mm) of the outer periphery-side layer;
Tm is an initial thickness (mm) of the intermediate layer at room temperature;
□ i is a maximum thermal expansion coefficient (%) of the refractory composition of the inner bore-side layer in a temperature range of room temperature to 1500□ C; and
□ o is a thermal expansion coefficient (%) of the refractory composition of the outer periphery-side layer at a temperature at start of passing of molten metal.

[0038] Di and Do are, respectively, a diameter measured on an outer periphery-side surface of the inner bore-side layer and a diameter measured on an inner bore-side surface of the outer periphery-side layer, in respective horizontal cross-sections (i.e., cross-sections taken along a direction perpendicular to the axial direction) of the inner bore-side layer and the outer periphery-side layer. When a horizontal cross-sectional shape of each of the inner bore-side layer and the outer periphery-side layer is not circle, Di may be defined as a distance between two positions where a straight line extending radially from a center of the horizontal cross-sectional shape of the inner bore-side layer intersects with the outer periphery-side surface of the inner bore-side layer, and Do may be defined as a distance between two positions where the above straight line intersects with the inner bore-side surface of the outer periphery-side layer in the cross-section. Then, the entire dimensions may be determined to satisfy the Formula 1.

[0039] With regard to compressability in an axial end of the nozzle, Di may be replaced with an axial distance between respective opposite axially outward end surfaces of the inner bore-side layer, and Do may be replaced with an axial distance between respective opposite axially inward surfaces of the outer periphery-side layer each facing a corresponding one of the axially outward end surfaces of the inner bore-side layer, in respective vertical cross-sections of the inner bore-side layer and the outer periphery-side layer, taken along a longitudinal (vertical) axis of the nozzle.

[0040] In the Formula 1, □ i is a maximum thermal expansion coefficient (%) of the refractory composition of the inner bore-side layer in a temperature range of room temperature to 1500□ C, which means that □ i is a maximum thermal expansion coefficient of the refractory composition of the inner bore-side layer in a temperature range of room temperature to substantially a molten steel temperature. Further, □ o is a thermal expansion coefficient (%) of the refractory composition of the outer periphery-side layer at a temperature at start of passing of molten metal, and the temperature to which the outer periphery-side layer is exposed at start of passing of molten metal, varies depending on operation conditions, such as a preheating condition. Thus, □ o is determined for each job site on a case-by-case basis.

[0041] In cases where the continuous casting nozzle is used without preheating, a temperature of the outer periphery-side layer is equal to room temperature (ambient temperature). In this case, □ o may be considered as a thermal expansion coefficient at room temperature which is a reference point of a measurement of thermal expansion coefficient, i.e., "zero", and therefore the Formula 1 can be expressed as the following Formula 2:

$$K \square \ [(Di \times \square\, i) / (2 \times Tm)] \qquad \text{--- Formula 2}$$

[0042] The compressive rate K satisfying the Formula 2 is a value in consideration of the most severe condition, i.e., a condition that a difference in thermal expansion between the inner bore-side layer and the outer periphery-side layer is maximized. Thus, if the compressive rate K is determined at a value satisfying the Formula 2, the outer periphery-side layer will never be broken. Preferably, the compressive rate K is set at a value satisfying the Formula 2 in all the operation conditions.

[0043] The compressive rate K is a value determined under a condition that a target refractory composition (sample) is not oxidized, for example, in a non-oxidation atmosphere, such as a reducing gas atmosphere or an inert gas atmosphere, or in an oxidizing gas atmosphere, such as an air atmosphere, under a condition that an antioxidant is applied on a surface of the target refractory (sample). During an actual use of the continuous casting nozzle, the intermediate layer is placed in a non-oxidation atmosphere. If a target sample is oxidized during a measurement of the compressive rate K, properties of the sample cannot be accurately figured out.

[0044] Preferably, in the present invention, the compressive rate K of the intermediate layer is fundamentally set in the range of 10 to 80%.

[0045] A thickness of the intermediate layer can be adjusted depending on the compressive rate K of the intermediate layer to absorb expanded dimensions of the inner bore-side layer. If the compressive rate K is less than 10%, the thickness of the intermediate layer will be increased depending on a difference in thermal expansion coefficient between the inner bore-side layer and the outer periphery-side layer. Thus, due to restrictions on an overall wall thickness of the continuous casting nozzle, a wall thickness of the nozzle body is inevitably reduced to cause a problem about deterioration in structural strength. If the compressive rate K is greater than 80%, an excessively reduced thickness of the intermediate layer is likely to cause a problem about production difficulty in forming such a thin intermediate layer, and a problem about deterioration in bonding strength between the inner bore-side layer and the outer periphery-side layer, although the thickness of the intermediate layer can be sufficiently reduced to prevent occurrence of the above problem about deterioration in structural strength. For example, on an assumption that the inner diameter of the outer periphery-side layer, the thermal expansion coefficient of the inner bore-side layer, and the thermal expansion coefficient of the outer periphery-side layer, are set, respectively, at about 80 mm ϕ, 2.0% and 0.8%, which are close to the smallest size in conventional continuous casting nozzles, the thickness of the intermediate layer is about 4 mm, and the compressive rate necessary for the refractory composition of the intermediate layer is 10%. Further, on an assumption that the inner diameter of the outer periphery-side layer, the thermal expansion coefficient of the inner bore-side layer, and the thermal expansion coefficient of the outer periphery-side layer, are set, respectively, at about 150 mm ϕ, 2.0% and 0.8%, which are close to the largest size in conventional continuous casting nozzles, the thickness of the intermediate layer is about 1.2 mm, and the compressive rate necessary for the refractory composition of the intermediate layer is 78%.

[0046] The above compressive rate may be measured by the following method, and a resulting measured value can be regarded as the compressive rate.

[0047] A columnar refractory body (20 mm ϕ × 5 mm t) made of a mixture having a characteristic of exhibiting compressability after being formed under a pressure equal to a shaping pressure and subjected to a heat treatment is put in a holding cavity of a carbon-based member having the same shape as that of the columnar refractory body, and subjected to a heat treatment under a non-oxidation atmosphere in a given temperature rise pattern to allow a burnable component to be vanished so as to obtain a columnar sample (about 20 mm ϕ × about 5 mm t). This heat-treated columnar sample is disposed between respective end surfaces of two refractory jigs each having a size of 20 mm ϕ × 40 mm L. Further, a cylindrical sample guide made of a refractory composition and formed to have an inner diameter 20 mm ϕ, an outer diameter of 50 mm) ϕ and a height of 78 mm is fitted on the sample in order to prevent the sample from dropping off laterally during an operation of longitudinally pressing the columnar sample clamped between the jigs, to obtain a measurement sample.

[0048] The measurement sample is set inside a furnace of a material testing machine adapted to controllably adjust a temperature, an atmosphere and a pressing speed. Then, after increasing a furnace temperature up to a given value under a non-oxidation atmosphere, and holding the temperature until it is uniformed, a pressing operation is initiated to carry out the measurement. Specifically, an initial thickness t0 (mm) of the cylindrical measurement sample is firstly measured under a pressureless condition. After holding a temperature of the measurement sample at a given value, the measurement sample is compressed from upward and downward directions while setting a crosshead moving speed in the range of 0.001 to 0.01 mm/sec, in such a maimer as to increase a pressing force up to 2.5 MPa, and then a displacement (i.e., deformation amount) h1 (mm) of the measurement sample is measured. Furthermore, in order to measure a blank value (i.e., a value in a measurement sample devoid of the intermediate layer), under the same temperature and the same load of the refractory jigs for clamping the measurement sample, the measurement sample is pressed under the same conditions, except that it is clamped, to measure a displacement h2. These measured values can be assigned to the following Formula 3 to calculate the compressive rate K (%) at each temperature:

$$K = (h1 - h2) / t0 \times 100\ (\%) \qquad \text{----- Formula 3}$$

[0049] The compressive rate K can also be measured from an actual casting nozzle having a structure where the inner bore-side layer is continuously integrated with the outer periphery-side layer through the intermediate layer during the forming process. Specifically, the actual casting nozzle is subjected to core boring at 20 mm ϕ from the outer periphery-side layer toward an axis of a refractory body of the nozzle in a direction perpendicular to the axis, to obtain a core sample integrally including respective portions of the inner bore-side layer, the intermediate layer and the outer periphery-side layer, and having a diameter of about 20 mm ϕ and opposite curved ends consisting of respective portions of an inner bore surface and an outer peripheral surface of the nozzle. In order to uniformly measure the compressive rate of the intermediate layer, the core sample is bonded to two refractory jigs after flatly machining each of top and bottom curved surfaces of the ends, or bonded to refractory jigs each having the same curvature as that of a corresponding one of the ends of the core sample, to obtain a measurement sample including the inner bore-side layer, the intermediate layer and the outer periphery-side layer and having a size of 20 mm ϕ × 80 to 100 mm L (when the measurement sample is smaller than this size, conditions, the measurement may be performed under a condition that parameter values, such as a unit area and a unit length, are set at the same level as those in the above measurement sample on a calculation basis, and then a measured value may be subjected to conversion). Then, in the same manner as that in the above method, the initial thickness t0 (mm) of the intermediate layer is accurately measured under a pressureless condition. Further, the displacement h1 of the intermediate layer is measured in a non-oxidation atmosphere, and the displacement h2 as a blank value in a state devoid of the intermediate layer is measured, so as to calculate the compressive rate K. The measurement sample obtained from the actual nozzle makes it possible to accurately measure compressability of the intermediate layer.

(2) STABILITY REQUIREMENT AND BONDABILITY REQUIREMENT

[0050] The intermediate layer is required to satisfy the above compressability requirement, and maintain sufficient stability and bondability relative to the inner bore-side layer and the outer periphery-side layer after production and during use of the continuous casting nozzle.

[0051] As mentioned in the section "Background Art", the conventional technique of obtaining compressability based on buckling or destruction of a large amount of low-strength mortar or a matrix having a high porosity, the matrix after buckling or destruction is simply formed as powder, and thereby neither the interlayer bonding force nor the intermediate layer itself can be maintained. If a gap exists between the inner bore-side layer and the outer periphery-side layer due to the powdered intermediate layer, i.e., the layers are in a peeled state without being fixed to each other, the intermediate layer itself is locally destroyed due to a stress unevenly applied thereto to further increase a volume of gap. If the intermediate layer is vanished, the inner bore-side layer is likely to become movable and cause drop-off or destruction, and the inner bore-side layer is likely to be locally brought into contact with the outer periphery-side layer and cause stress concentration and destruction. Moreover, such a gap allows intrusion of molten metal, such as molten steel, which is likely to accelerate layer destruction and interlayer peeling.

[0052] Thus, the intermediate layer having compressability is required to maintain healthy matrix and given bondability (as will be described later) relative to the inner bore-side layer and the outer periphery-side layer, even after being compressed.

[0053] It is understood that the given bondability of the intermediate layer relative to the inner bore-side layer and the outer periphery-side layer is based on an assumption that the refractory composition itself of the intermediate layer has a certain level or more of layer strength necessary for exhibiting the given bondability, to allow a healthy layer condition to be maintained.

[0054] In order to enhance stability of the intermediate layer and fixability of the intermediate layer relative to the inner bore-side layer and the outer periphery-side layer, the present invention is intended to enhance bondability of the intermediate layer relative to the inner bore-side layer and the outer periphery-side layer.

[0055] Bondability, i.e., joinability or fixability, can be evaluated as bonding strength (as mentioned above, on the assumption that stability enough to exhibit the bonding strength is ensured, the bondability is evaluated). The inventers have found that an optimal value of the bonding strength is in the range of 0.01 to 1.5 MPa, as measured in a non-oxidation atmosphere at 1000□ C.

[0056] The minimum value "0.01 MPa" of the bonding strength is determined based on a result of various experimental tests, and a value which allows a frictional resistance between the layers to be obtained in a minimum level for maintaining each of the inner bore-side layer and the outer periphery-side layer in its installation position. If the bonding strength is less than 0.01 MPa, a retention capability for the inner bore-side layer is low although it might prevent drop-off of the inner bore-side layer before start of passing of molten steel, and thereby the inner bore-side layer is likely to be peeled off, due to shock at start of passing of molten steel, vibration caused by changes in flow speed of molten steel, or occurrence of local wear in the inner bore-side layer. Moreover, in various stages, such as transportation of the continuous casting nozzle, installation of the continuous casting nozzle to a continuous casting apparatus, preheating and passing of molten steel, external force in each of the stages is likely to cause displacement from a predetermined position, peel-off or drop-off of the inner bore-side layer. Furthermore, in connection with the above phenomena, a portion of the intermediate layer becomes impossible to satisfy the above compressability requirement to cause a higher risk of breaking of the inner bore-side layer or the outer periphery-side layer.

[0057] If the bonding strength is increased to a value greater than 1.5 MPa, the strength of the refractory composition itself of the intermediate layer will be increased accordingly. That is, a strength of an internal matrix of the intermediate layer is also largely increased at the same level as that of the bonding strength, to spoil the compressability of the intermediate layer. This makes it easy to transmit a stress due to thermal expansion of the inner bore-side layer to the outer periphery-side layer without being relived, to increase a risk of occurrence of breaking of the continuous casting nozzle.

[0058] As shown in FIG. 3, the bonding strength may be measured by cutting a portion of a continuous casting nozzle having an inner bore-side layer 2, an intermediate layer 4 and an outer periphery-side layer 3, along two planes parallel to a horizontal cross-section of the nozzle (taken along a direction perpendicular to a longitudinal or axial direction of the nozzle), to obtain a cylindrical slice-shaped sample 10 having a thickness of about 100 mm, pushing only the inner bore-side layer 2 downwardly using a pushing member 11 (a columnar pusher made of a refractory composition and formed to have a flat end) having an outer diameter approximately equal to that of the inner bore-side layer, wherein a full weight overall load is divided by a bonding area to derive the bonding strength. The measurement is performed in a non-oxidation atmosphere at a temperature of 1000□ C.

[0059] The reason for performing the measurements of the compressability and the bonding strength in a non-oxidation atmosphere at a temperature of 1000□ C, and defining components of the refractory composition of the intermediate layer in a state after the intermediate layer is subjected to a heat treatment in a non-oxidation atmosphere at a temperature of 1000□ C, is that 1000□ C corresponds to a temperature at which a volatile component in the organic binder is sufficiently volatilized to establish a carbon-based joint matrix so as to provide stable compressability and bonded state.

[0060] In the present invention, the refractory structure at least partly has an integral multi-layer structure obtained by forming the inner bore-side layer simultaneously together with the intermediate layer and the outer periphery-side layer during a forming process. The integral multi-layer structure means that respective matrix portions of the three layers around boundaries therebetween are joined to each other in a direct contact manner without any gap therebetween.

[0061] Specifically, in the present invention, respective mixtures (ingredients) for the inner bore-side layer, the intermediate layer and the outer periphery-side layer are simultaneously subjected to a cold isostatic pressing (CIP) process to form an integral continuous structure, as will be described later.

[0062] A conventional technique based on installation of adhesive or mortar, for example, a technique of forming each of the inner bore-side layer, the intermediate layer and the outer periphery-side layer into a shaped body separately, and then bonding the shaped bodies together through a silicate-based adhesive or the like (the "adhesive or mortar" will hereinafter be referred to collectively as "mortal/adhesive") involves the following problems.

(1) During an operation of charging mortar etc., into a narrow gap with, an un-bonded zone is likely to be created due to occurrence of an unfilled zone and/or mixing of large air bubbles, to cause instability in quality of the mortar/adhesive region.

(2) A large amount of liquid is contained to ensure operation efficiency. Thus, the liquid is liable to be absorbed in a target layer to cause shrinkage of the mortars, which leads to shrinkage crack in the mortal/adhesive itself or formation of a gap (peel-off) on a bonding surface.

(3) A boundary region between the respective layers has a sudden change in matrix phase. Thus, stress concentration is likely to occur in the boundary region to cause destruction or peel-off of a bonded portion.

(4) In a high-temperature region, e.g., during passing of molten steel, components of mortal/adhesive react with components of the layers. Thus, the mortal/adhesive is softened or molten to cause deterioration in bonding strength, and the layers themselves shrink and deform to cause deterioration in fixing force of the layers, which increases a risk of occurrence of drop-off or peel-off of the inner bore-side layer, or breaking of the outer periphery-side layer.

[0063] Differently from the above conventional technique, the integral structure in the present invention employs a bonding mechanism based on a mechanical entanglement between respective components of the layers. This provides the following effects.

(1) During preparation of a mixture (ingredients), a given amount of burnable particles can be uniformly dispersed over the mixture (ingredients), so that voids resulting from vanishment of the burnable particles caused by a heat treatment are substituted and filled with expansive graphite particles having micro-voids. This makes it possible to control a compression amount uniformly and stably.

(2) A bonding through a binder component, such as a carbonaceous material, in the intermediate layer, is also developed during the heat treatment, to provide enhanced uniformity and stability.

(3) The micro-voids of the expansive graphite particles are finely dispersed over the entire matrix during a heat treatment after the forming process. The expanded graphite particle region having micro-void layers in the intermediate layer stretches and contracts in an accordion manner, so that a bonding force can be maintained without significant destruction of the matrix of the intermediate layer, to uniformly absorb a thermal expansion of the inner bore-side layer.

[0064] The above effects make it possible to obtain robust fixability between the respective layers or stability in each of the three layers while reducing the risk of occurrence of drop-off or peel-off of the inner bore-side layer or breaking of the outer periphery-side layer.

[0065] Further, as compared with the conventional technique based on installation of mortal/adhesive, the simultaneous integral forming process makes it possible to obtain the continuous casting nozzle having the above features, with a high degree of accuracy, i.e., while suppressing variation in matrix structure and dimensions such as thickness (the uniformization is promoted because, during a course of expansion of the expansive graphite particles, the expansion generates a pressure inside the intermediate layer, to allow components, mainly the expansive graphite particles in the intermediate layer, to be automatically charged and dispersed in the voids resulting from vanishment of the burnable particles), and to achieve simplification and laborsaving in a production process, and reductions in required production lead time and cost.

[0066] In order to ensure the compressability, the bondability and the stability, the intermediate layer in the present invention may have a structure where a plurality of carbonaceous lamellar unit layers each having a thickness of 1 □ m or less are arranged in a layered pattern while interposing a space therebetween (this arrangement will hereinafter be referred to simply as "laminar configuration". This structure mainly comprises graphite particles having expansibility, wherein the graphite particles are in an expanded state (in the present invention, the graphite particles before expansion will be referred to as "expansive graphite particles", and the graphite particles after expansion will be referred to as "expanded graphite particles").

[0067] In the present invention, the compressability of the intermediate layer is provided primarily based on a phenomenon that the expanded graphite particles arranged in the laminar configuration compress the spaces between the laminar layers, in response to an external force, and each of the laminar unit layers is flexibly deformed. When each of the carbonadoes laminar unit layers has a thickness of 1 □ m or less, a property of being flexibly deformed by an external force while maintaining the original configuration of the carbonadoes laminar unit layer is enhanced, and the spaces each formed between adjacent ones of the carbonadoes laminar unit layers at a distance of about 10 to 200 □ m serve as a space necessary for deformation and displacement of the carbonadoes laminar unit layers. The carbonadoes laminar unit layers and the spaces exist in such a manner as to be entangled with each other 3-dimentionally and complicatedly, so that a stress can be dispersed in all directions to enhance the compressability, i.e., the stress relieve function.

[0068] In the present invention, a mixture (ingredients) for the intermediate layer is used in such a manner that it contains un-expanded expansive graphite particles in an amount ranging from 5 to 45 mass%, and burnable particles in an amount ranging from 55 to 95 mass%, and further contains an organic binder in a given mass%, with respect to a total mass% of the un-expanded expansive graphite particles and the burnable particles, and in addition to the total mass%, wherein the given mass% of the organic binder is set to allow a ratio of a carbon component of the organic binder to an entire refractory composition of the intermediate layer, to fall within the range of 2.5 to 15 mass%, as a corresponding value in a state after the refractory composition of the intermediate layer is subjected to a heat treatment in a non-oxidation atmosphere at 1000□ C. This makes it possible to form the intermediate layer having both desired compressive rate and bondability without crack and peeling, through a heat treatment in a non-oxidation atmosphere at 600 to 1300□ C.

[0069] Alternatively, in the present invention, a mixture (ingredients) for the intermediate layer is used in such a manner that it contains un-expanded expansive graphite particles in an amount ranging from 5 to 45 mass%, and burnable particles in an amount ranging from 55 to 95 mass%, with the remainder being 40 mass% or less of refractory material which is one or more selected from the group consisting of oxide, carbide, nitride and metal, and further contains an organic binder in a given mass%,[with respect to a total mass% of the un-expanded expansive graphite particles, the burnable particles and the refractory material, and in addition to the total mass%, wherein the given mass% of the organic binder is set to allow a ratio of a carbon component of the organic binder to an entire refractory composition of the intermediate layer, to fall within the range of 2.5 to 15 mass% as a corresponding value in a state after the refractory composition of the intermediate layer is subjected to a heat treatment in a non-oxidation atmosphere at 1000□ C. This makes it possible to form the intermediate layer having both desired compressive rate and bondability without crack and peeling, through a heat treatment in a non-oxidation atmosphere at 600 to 1300□ C.

[0070] In the present invention, the compressability of the intermediate layer is provided based on a phenomenon that, during a course of allowing a component of the burnable particles and the organic binder, which does not form a carbon bond, to be vanished, a part or entirety of voids resulting from the vanishment is substitute with the expanded graphite particles. Preferably, the expansive graphite particle is made of a material which initiates expansion at approximately the same temperature as that at which the organic binder initiates burning and vanishment. The material is appropriately selected from expansive graphite particles different in expansion initiation temperature, in conformity to the vanishment initiation temperature of the burnable particles. Typically, the material is appropriately selected from expansive graphite particles having an expansion initiation temperature of 130 to 350□ C. A particle size of the expansive graphite particle is preferably set in the range of 50 to 800□ m, more preferably in the range of 100 to 600 □ m. If the particle size is less than 50 □ m, the expansibility during heating deteriorates to cause difficulty in obtaining desired compressability, although a capability to fill the micro-voids is enhanced. If the particle size is greater than 800 □ m, the 3-dimensional entanglement of the expanded graphite particles is reduced to cause deterioration in bonding strength, although the expansibility is improved to provide enhanced compressability.

[0071] In the components of the refractory composition of the intermediate layer after the heat treatment in a non-oxidation atmosphere at 1000□ C, the remainder other than the expanded graphite particles may include a refractory material comprising one or more selected from the group consisting of oxide, carbide, nitride and metal.

[0072] Among them, particularly the refractory material particles constituting the remainder other than the carbon component take on a function of ensuring corrosion resistance of the intermediate layer. Specifically, the particles have a function of suppressing or preventing molten metal, such as molten steel, from coming into direct contact with the outer periphery-side layer having relatively low corrosion resistance, when the intermediate layer is damaged, and a function of ensuring corrosion resistance and abrasion/wear resistance of the intermediate layer itself The particles also have a skeletal function for maintaining the strength of the intermediate layer as a refractory body.

[0073] In addition to a damageable portion of the inner bore-side layer itself, a boundary portion between the inner bore-side layer and the nozzle body, a locally damageable portion having brittleness, such as a gas-injecting gas spool portion or a joint portion between the respective layers, the continuous casting nozzle has a portion to be directly exposed to molten steel all the time as a product of a continuous casting nozzle, such as an outlet portion of an immersion nozzle. For example, if the portion to be directly exposed to molten steel has poor collusion resistance and abrasion/wear resistance, a selective loss of the portion causes a breaking of the continuous casting nozzle which is a fatal problem in operation of continuous casting, due to intrusion of molten steel between the inner bore-side layer and the outer periphery-side layer.

[0074] As a refractory material for use in a refractory portion of the intermediate layer to be directly exposed to molten steel, a refractory aggregate comprising one or more selected from the group consisting of Al_2O_3, SiO_2, MgO, CaO and ZrO_2, specifically, alumina-silica based aggregate (e.g., corundum, mullite, sillimanite, kyanite and kaolinite; in view of obtain corrosion resistance to molten steel, it is preferable to select one of them in the above order); alumina-magnesia based spinel; zirconia; zircon; and/or alkaline earth metal oxide, may be selectively used depending on a level of corrosion resistance required under individual casting operation conditions, or other factor. It is recommended to avoid the use of a refractory material consisting only of silica, and a glassy refractory material including an alkali metal component, because they have a problem about oxidation of a carbon component, and formation of a low-melting point substance resulting from a reaction with other refractory material.

[0075] Further, with a view to suppressing oxidation of the refractory composition of the intermediate layer, carbide such as silicon carbide or titanium carbide, and nitride such as BN or silicon nitride, may be contained in the refractory composition of the intermediate layer.

[0076] The refractory material for the above mentioned remainder is not an essential component. Thus, if there is not a need for relying on the refractory composition as the remainder, to ensure corrosion resistance and/or abrasion/wear resistance in view of individual casting operation conditions, a situation of damage of the continuous casting nozzle, and other factor, the refractory material for the remainder is not necessarily contained.

[0077] In the present invention, the refractory composition of the intermediate layer primarily comprises carbon having high stability even in a high-temperature range, specifically of about 1000□ C or more at which sintering of oxide or the like, and a reaction for a low-melting point substance are initiated or accelerated, so that the intermediate layer itself definitely has high stability. In addition, the expanded graphite particles are disperse in such a manner as to cover the remaining refractory material particles. This makes it possible to almost prevent sintering, shrinkage and formation of a low-melting point substance, due to a reaction between respective remaining refractory aggregates, such as oxides, while preventing generation of voids caused by sintering and softening of the refractory composition of the intermediate layer. This is also an advantage of the present invention using the expanded graphite particles as a primary component of the intermediate layer.

[0078] The refractory material particles constituting the refractory composition of the intermediate layer are bound to each other through the binder. In view of maintaining the compressability of the refractory composition of the intermediate layer, and preventing softening or melting of the refractory composition of the intermediate layer so as to maintain a bonding function even at high temperatures, the binder is preferably made of thermosetting resin, tar or pitch, as a starting material, wherein it has a carbonaceous bondable matrix in a state after a heat treatment at 600□ C or more.

[0079] Thus, in the present invention, the organic binder is added to allow a ratio of a content of a carbon component of the binder as a corresponding value in a state after being subjected to a heat treatment in a non-oxidation atmosphere at 1000□ C, to a component (including a carbon component other than the carbon component of the binder) of the entire refractory composition of the intermediate layer in a state after being subjected to a heat treatment in a non-oxidation atmosphere at 1000□ C, to fall within the range of 2.5 to 15 mass%. If the ratio is less than 2.5 mass%, a sufficient bonding strength between the inner bore-side layer and the outer periphery-side layer cannot be obtained, although it is favorable to expansion of the expansive graphite particles and compressability of the intermediate layer. If the ratio is greater than 15 mass%, the expansion of the expansive graphite particles during the heat treatment is hindered to cause difficulty in ensuring required compressability of the intermediate layer, although it is favorable to the bonding strength.

[0080] Further, the expanded graphite particles as the carbon component are required to contain 13.5 mass% or more in the intermediate layer, in order to ensure required compressability and a healthy matrix. If the content is less than 13.5 mass%, the matrix of the intermediate layer is more likely to have a brittle portion to increase a risk of occurrence of shrinkage crack and deterioration in the bondability relative to the outer periphery-side layer.

[0081] Thus, in the present invention, the intermediate layer after being subjected to the heat treatment in a non-oxidation atmosphere at 1000□ C includes expanded graphite particles and an organic binder component, and contains respective carbon components (except any compound, such as SiC, B_4C and AIC, with the remaining components) of the expanded graphite particles and the organic binder component, in a total amount of 16 mass% or more (including 100 mass%). Specifically, 16 mass% as a lower limit of the total of the carbon components is a sum of 13.5 mass% as a minimum content of the expanded graphite particles, and 2.5 mass% as a minimum content of the organic binder component. A portion exceeding 16 mass% may consist only of the organic binder component (maximum content: 15 mass%) and the expanded graphite particles, or may comprise a carbonaceous component, such as flaky graphite or carbon black, other than the expanded graphite particles and the organic binder component.

[0082] When the total of the carbon contents is in the range of 16 to less than 100 mass%, a refractory material which is one or more selected from the group consisting of oxide, carbide, nitride and metal, may be contained in the remainder, in a total amount of 84 mass% or less.

[0083] The bonding strength is changed depending on a balance between a content of the binder and a content of the burnable particles in the mixture (ingredients).

[0084] It is recommended to avoid the use of a binder containing a large amount of alkali metal, because it is likely to cause softening or melting of oxides, or vaporization of the carbon components, which leads to degradation in matrix of the intermediate layer or the adjacent layers. Particularly, in view of maintaining a matrix strength in a low-temperature region (e.g., 600□ C or less), an organic resin which does not remain in the form of a carbon component may be used.

[0085] A production method for obtaining the refractory composition of the intermediate layer in the present invention, and a continuous casting nozzle comprising the intermediate layer having the refractory composition, will be described below.

[0086] A continuous casting nozzle having the compressable intermediate layer can be obtained by a production method which comprising the steps of: preparing three types of mixtures (ingredients) for the inner bore-side layer, the intermediate layer and the outer periphery-side layer, on a layer-by-layer basis; providing to a forming mold a plurality of cavities for forming the inner bore-side layer, the intermediate layer and the outer periphery-side layer, wherein the cavities are separated from each other to allow each of the cavities to have a given size and configuration; filling each of the cavities of the forming mold with a corresponding one of the mixtures (ingredients), and allowing adjacent ones of the mixtures (ingredients) to be brought into direct contact with each other, for example, by removing partitions; subjecting the mixtures (ingredients) in direct contact with each other, to a pressure forming process using a CIP machine to form a shaped body; and subjecting the shaped body to a heat treatment at a temperature of 600 to 1300□ C, in a non-oxidation atmosphere, or an oxidation atmosphere after subjecting a surface of the shaped body to an anti-oxidation treatment. The production method may further includes, in advance of the above mentioned heat treatment step, an independent step of subjecting the shaped body to a heat treatment at a temperature less than the above temperature, to remove a volatile component and cure a resin therein.

[0087] While a fundamental handling/operation and a required apparatus in each of the steps are the same as that in a conventional continuous casting nozzle production method, the continuous casting nozzle production method of the present invention has the following first to third features.

[0088] The first feature is a composition of the refractory mixture (ingredients) for the intermediate layer (intermediate-layer mixture (ingredients)). The intermediate-layer mixture (ingredients) contains, as a powder component except a volatile component, (1) un-expanded expansive graphite particles in an amount ranging from 5 to 45 mass%, (2) burnable particles in an amount ranging from 55 to 95 mass%, and (3), as needed, a refractory material which is one or more selected from the group consisting of oxide, carbide, nitride and metal, in a total amount of 40 mass% or less (including zero), as the remainder, and further contains an organic binder in a given mass%, with respect to a total mass% of the powder component, and in addition to the total mass%, wherein the given mass% of the organic binder is set to allow a ratio of a carbon component only of the organic binder (except any carbon compound with the remaining components) to an entire refractory composition of the intermediate layer, in a state after the refractory composition of the intermediate layer is subjected to a heat treatment in a non-oxidation atmosphere at 1000□ C, to fall within the range of 2.5 to 15 mass%;

[0089] The second feature is to simultaneously integrate the three layers together by a CIP process, without any joint at boundary regions therebetween.

[0090] The third feature is to remove the burnable particles in the shaped body of the intermediate-layer mixture (ingredients) to form voids therein, and then expand the un-expanded expansive graphite particles, in the step of subjecting the integrated shaped body to a heat treatment at 600 to 1300□ C.

[0091] The above features will be more specifically described below.

[0092] It is practically difficult to obtain the refractory composition of the intermediate layer in the present invention which contains the expanded graphite particles as a primary component, by using a refractory composition or a mixture (ingredients) for the intermediate layer which already has compressive rate approximately equal to the aforementioned compressability required in a state after a continuous casting nozzle is formed as a product (this compressability has the same meaning as the compressive rate satisfying the Formula 1; hereinafter referred to as "product compressability"), and installing the refractory composition or mixture (ingredients) into an integral structure simultaneously together with other layers during a step of farming the continuous casting nozzle. Specifically, in a CIP process (typically, a forming pressure is far greater than 2.5 MPa) designed to produce a continuous casting nozzle based on an apparatus and a fundamental handling/operation according to a conventional continuous casting nozzle production method, the refractory composition having compressability is compressed during the forming step, and thereby the refractory composition after the forming step will lose the compressability. Therefore, it is difficult to achieve a balance between the purpose of producing a continuous casting nozzle using a refractory composition or a mixture (ingredients) which already has compressability approximately equal to product compressability, and the purpose of obtaining a continuous casting nozzle having an integral structure with the product compressability.

[0093] Thus, at least in the step of forming the mixtures (ingredients) simultaneously and integrally under a high pressure, the mixture (ingredients) to be formed must not have compressability approximately equal to product compressability, except compressability equivalent to volume shrinkage occurring in a filling step during a CIP process for a powder of a refractory composition for a conventional continuous casting nozzle (the volume shrinkage will hereinafter referred to as "compaction" in order to discriminate from the "compressability").

[0094] The production method of the present invention is intended to obtain a continuous casting nozzle having an integral structure, wherein an intermediate layer has a refractory composition exhibiting product compressability.

[0095] In the mixture (ingredients) having the composition as described in the fist feature, the expanded expansive graphite particles as a primary component taking a major roll in compressability in a product state has almost no significant compressability in its un-expanded state. Thus, even if the mixture (ingredients) is exposed to a high pressure during a CIP process, a volume of the composition is not reduced, and this volume shrinkage can be limited to about the compaction. This makes it possible to ensure a given volume, such as a wall thickness and an axial dimension, of the intermediate layer.

[0096] The mixture (ingredients) resistive to a CIP process allows the intermediate-layer mixture (ingredients) to be formed simultaneously and integrally together with other refractory mixtures (ingredients) for the inner bore-side layer and the outer periphery-side layer.

[0097] The un-expanded expansive graphite particles in the intermediate layer is preferably contained in the range of 5 to 45 mass%. If the content is less than 5 mass%, compressability of the refractory composition of the intermediate layer after the heat treatment is excessively lowered. Thus, it is necessary to excessively increase a thickness of the intermediate layer to satisfy the Formula 1 about compressability, which leads to an undesirable situation where a thickness of a continuous casting nozzle is restricted in design, and a variation in compressability is likely to occur in each region of the intermediate layer. If the content of the un-expanded expansive graphite particles is greater than 45 mass%, the expansive graphite particles are excessively expanded beyond a volume of voids generated by banishment of the burnable particles, and a pressure in the refractory composition of the intermediate layer is excessively increase due to an expansion of the intermediate layer, to cause a problem about deterioration in production yield.

[0098] The burnable particles in the intermediate-layer mixture (ingredients) is preferably contained in the range of 55 to 95 mass%. If the content is less than 55 mass%, a volume of voids vanished by heating of the burnable particles during the heat treatment in the production process is excessively reduced to cause difficulty in sufficiently ensuring a space between respective laminar layers of the expanded graphite particles after the voids are filled according to expansion of the expansive graphite particles, which increases a risk of deterioration in compressability. If the content is greater than 95 mass%, a volume of voids after vanishment of the burnable particles is excessively increased, and thereby a space including a space between respective laminar layers of the expanded graphite particles is excessively created after the voids are filled according to expansion of the expansive graphite particles, to increase a risk of deterioration in strength and bondability of the intermediate layer itself The amount of the burnable particles is preferably set at a value equal to greater than the amount of the expansive graphite particles. As the burnable particle, a polyethylene particle, a polyester powder or a grain powder may be used. Preferably, the burnable particle has a minimum particle size, such as about 45 □ m or less, to evenly form voids and obtain an even distribution of the expanded graphite particles.

[0099] The respective amounts of the un-expanded expansive graphite particles and the burnable particles in the intermediate-layer mixture (ingredients) may be determined by relatively adjusting them to satisfy the Formula 1 about compressability.

[0100] The remainder contained the intermediate-layer mixture (ingredients) in an amount of 40 mass% or less (a minimum amount of the un-expanded expansive graphite particles is 5 mass%, and a minimum amount of the burnable particles is 55 mass%. Thus, a maximum value of the remainder is 100 - 5 - 55 =40, and a minimum thereof amount is zero) may be a refractory material comprising one or more selected from the group consisting of oxide, carbide, nitride and metal. This component is not essential, i.e., may not be contained. The refractory material, such as a type, a combination and amount thereof, may be determined depending on conditions of individual casting operation and a structure and configuration of equipment, i.e., a level of corrosion resistance required for the intermediate layer, and depending on an amount of the expansive graphite particles and the burnable particles in conformity to a level of compressability, and in consideration of control of a reaction with respective materials of the inner bore-side layer and the outer periphery-side layer.

[0101] Thus, in the continuous casting nozzle of the present invention, a maximum amount of carbon component in the refractory composition of the intermediate layer in a state after being subjected to a heat treatment at 600□ C or more may be set at 100 mass%, with respect to the entire refractory composition except the binder, or the entire refractory composition including the binder when the binder consists only of a carbonaceous material.

[0102] When the intermediate-layer mixture (ingredients) contains the un-expanded expansive graphite particles, the burnable particles, and the additional refractory material particles as the remainder, these refractory material particles (hereinafter referred to collectively as "raw material powder") are uniformly mixed. Then, a binder is added (a solvent may be used. In this case, a solvent is also added) to the uniformly mixed raw material powder while uniformly kneading the mixture, to give fluidity, wettability, shape-retainability and bonding function to the raw material powder.

[0103] The mixture (ingredients) is required to ensure shape-retainability during the forming step and a subsequent step, and strength of the refractory composition after the heat treatment. Thus, in the present invention, an organic binder, such as one or more selected from the various types of tars, pitches, phenol resins and furan resins, is added in such a manner as to allow a ratio of the organic binder to an entire refractory composition of the intermediate layer, to fall within the range of 2.5 to 15 mass% in terms of a carbon component of the organic binder in a state after being subjected to a heat treatment in a non-oxidation atmosphere at 1000□ C. Preferably, the organic binder is added in such a manner as to allow a total mass of a solid of the organic binder (a sum of an amount of carbon component after a heat treatment in a non-oxidation atmosphere at 1000□ C, and an amount of additional organic binder which does not remain in the form of a carbon component in the state after the heat treatment in a non-oxidation atmosphere at 1000□ C, in terms of a solid except a solvent, at room temperature) to fall within the range of 5 to 30 mass%, with respect to total 100 mass% of a power component consisting of the expansive graphite particles, the burnable particles and the refractory material as the remainder, and in addition to the power component. The reason is that the amount of the solid of the organic binder is less than 5 mass% or greater than 30 mass%, the mixture (ingredients) deteriorates in fluidity and compressability during the forming step, and the refractory composition deteriorates in strength after the forming step.

[0104] With a view to ensuring strength in a low temperature range of room temperature to about 300□ C, primarily in order to ensure shape-retainability after the forming step, an organic binder which does not remain in the form of a carbon component (carbon bond) at about 600□ C or more (hereinafter referred to as "second organic binder") may be used in combination with the aforementioned organic binder (hereinafter referred to as "first organic binder").

[0105] As the additional, second, organic binder which does not remain in the form of a carbon component (carbon bond), an organic adhesive material/resin, such as an acrylic resin, a vinyl acetate resin, a polyester resin or a polyacrylonitrile resin, may be used.

[0106] When the second organic binder is used in combination with the first organic binder, the second organic binder may be added in such a manner as to allow a sum of an amount of solid of the second organic binders, except a solvent (at room temperature), and an amount of carbon component of the first organic binder in a state after a heat treatment in a non-oxidation atmosphere at 1000□ C, to fall within the range of 5 to 30 mass%, in addition to the total mass% of the powder component.

[0107] Preferably, with a view to enhancing strength after the heat treatment in the continuous casting nozzle production method of the present invention, a ratio of pitches to be used may be increased. This strength is set on the assumption that it is equal to or grater than the bonding strength, and the above binder bondable to carbon contributes to enhancement in strength of the intermediate layer itself.

[0108] In an operation of bonding a commonly used oxide, for example, using mortar/adhesive containing an inorganic binder, such as silicate (or forming a layer corresponding to the intermediate layer), in a high-temperature range of 1000 to 1500□ C, for example, an oxide component and an alkali metal oxide are softened due to a reaction therebetween, and a bonding strength will be gradually lowered. Further, at a temperature of 1200□ C or more, due to occurrence of melting, the bonding strength is significantly lowered to cause shrinkage or thermal decay, and gap between the layers, which spoils a healthy structure of a continuous casting nozzle, in many cases.

[0109] The joint structure in the present invention can solve the above conventional problem, because it has a structure primarily based on carbon bond, which is almost free of a component causing acceleration of sintering or formation of a low-melting point substance, and high-temperature degradation.

[0110] Separately from the intermediate-layer mixture (ingredients), the respective mixtures (ingredients) for the inner bore-side layer and the outer periphery-side layer are prepared.

[0111] Respective compositions of the mixtures (ingredients) for the inner bore-side layer and the outer periphery-side layer may be determined in conformity to conditions and an intended purpose of individual continuous casting, and based on a premise that they has characteristics, such as fillability, shape-retainability and strength performance, which allow for formation simultaneously with the intermediate layer by a CIP process.

[0112] Then, an inner space of a forming mold for a CIP process is divided into a plurality of cavities each having a given size and configuration to form the inner bore-side layer, the intermediate layer and the outer periphery-side layer, and each of the cavities is with a corresponding one of the mixtures (ingredients).

[0113] Subsequently, adjacent ones of the mixtures (ingredients) are brought into direct contact with each other without being spaced apart from each other. This step may comprise providing a plurality of cavities divided by partition plates to allow each of the cavities to be filled with a corresponding one of the mixtures (ingredients), filling each of the cavities with a corresponding one of the mixtures (ingredients), and removing the partition plates to allow the intermediate-layer mixture (ingredients) to be brought into direct contact with adjacent ones the mixtures (ingredients) of the inner bore-side layer and the outer periphery-side layer in a borderless manner. Alternatively, the step may comprise temporarily forming the mixture (ingredients) for one or two of the inner bore-side layer, intermediate layer and the outer periphery-side layer into a given shape (forming a temporary shaped body), setting the temporary shaped body in a forming mold for a CIP process, and filling given cavities with the mixtures (ingredients) for the layers adjacent to the temporary shaped body. Further, the mixtures (ingredients) may be supplied in the same mold to fill the respective cavities in a stepwise manner, and compressed plural times every filling operation, and finally simultaneously pressed to integrate them.

[0114] Then, the mixtures (ingredients) are subjected to a press forming process using a CIP machine. Forming conditions, such as a pressure and a compression time, may be the same as those for a conventional process for a continuous casting nozzle (e.g., about 150 MPa).

[0115] Through the above steps, an integral shaped body having the respective refractory compositions of the layers formed as a multi-layer structure can be obtained.

[0116] The obtained shaped body may be subjected to a drying process at about several hundred □ C or less. Then, the shaped body is subjected to a heat treatment in a non-oxidation atmosphere, or in an oxidation atmosphere after subjecting a surface of the shaped body to an anti-oxidation treatment, at 600 to 1300□ C. In this heat operation step, burnable material (burnable particles, solvent, etc.) in the shaped body of the intermediate-layer mixture (ingredients) are vanished to form voids therein, and then the un-expanded expansive graphite particles are expanded to fill the voids formed by banishment of the burnable materials with the expanded graphite particles).

[0117] Specifically, a volume occupied by the burnable particles in the mixture (ingredients) is substituted with particles constituting a laminar structure consisting of a plurality of carbonaceous layers as the result of expansion of the expansive graphite particles. This makes it possible to obtain a refractory layer exhibiting compressability based on evenly distributed small spaces.

[0118] The vanishment of the burnable material and the expansion phenomenon of the un-expanded expansive graphite particles are promoted at a temperature of about several hundred □ C. Preferably, the intermediate-layer mixture (ingredients) is treated at a temperature of 600□ C or more to reliably complete the above phenomena. If the heat treatment temperature is greater than 1300□ C, properties, such as thermal shock resistance, of the refractory compositions of a portion of the continuous casting nozzle other than the intermediate layer in the present invention, such as a refractory composition of the nozzle body, is more likely to undesirably change. Thus, a maximum heat treatment temperature is set at 1300□ C.

[0119] Subsequently, the heat-treated body may be subjected to machining /treatment., such as cutting, grinding and anti-oxidation treatment. Through the above steps, the continuous casting nozzle of the present invention can be obtained.

[0120] The production method of the present invention having the above features makes it possible to obtain a continuous casting nozzle excellent in compressability and bondability. In addition, as compared with the conventional continuous casting nozzle, i.e., a production method comprising the steps of preparing separate members for respective layers, assembling and joining them together using mortar/adhesive, and subjecting the joined body to a drying process, the production method of the present invention makes it possible to achieve significant reduction in the number of production processes and cost, and provide enhanced productivity and enhanced accuracy, such as dimensional accuracy, of the continuous casting nozzle.

[0121] As mentioned above, the present invention can prevent expansion cracking of the outer periphery-side layer due to a difference in thermal expansion between the inner bore-side layer and the outer periphery-side layer, in a continuous casting nozzle where a layer having a high function, such as a capability to prevent deposition of inclusions, is disposed on the side of an inner bore to enhance durability, i.e., the inner bore-side layer has a thermal expansion coefficient greater than that of the outer periphery-side layer, or in a continuous casting nozzle having a large thermal gradient due to rapid heating even though the inner bore-side layer has a thermal expansion coefficient approximately equal to that of the outer periphery-side layer.

[0122] The continuous casting nozzle of the present invention has a structure where the three layers are integrated together. Thus, enhanced bonding force and fixing force between the respective layers can be obtained as compared with the joining technique based on adhesive, mortar or the like, without a need for a particular bonding material.

[0123] These make it possible to significantly enhance durability of the continuous casting nozzle, such as thermal shock resistance and stability, and promote achievement of higher function and high durability in the continuous casting nozzle, based on the multi-layer structure,

[0124] The production method of the present invention makes it possible to achieve a simultaneous internal forming process, to obtain the continues casting nozzle having the above excellent features, stably with high accuracy and high quality, and achieve simplification and laborsaving in a production process, and reductions in required production lead time and cost.

BRIEF DESCRIPTION OF THE DRAWINGS

[0125]

FIG. 1 is a sectional view showing a long nozzle according to one embodiment of the present invention.
FIG. 2 is a sectional view showing a continuous casting nozzle according to another embodiment of the present invention.
FIG. 3 is an explanatory diagram showing a measurement method of a hot bonding strength of an intermediate layer.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0126] The present invention will be more specifically described based on an embodiment thereof and an example.

[0127] The present invention was applied to a tubular refractory structure called "long nozzle" for use in transferring molten steel between a ladle and a tundish in a continuous casting process.

[0128] As shown in FIG. 1, in a refractory structure applied to a long nozzle 1 (diameter of an inner bore: 140 mm ϕ, diameter of a straight body: 226 mm ϕ, length: 1500 mm), an MgO-C based material (MgO = 77 mass%, C = 19 mass%) having a maximum thermal expansion coefficient at temperature of room temperature to 1500□ C of 1.8 % was used for an inner bore-side layer 2, and applied to the entire inner bore surface at a thickness of 10 mm, and an Al_2O_3-SiO_2-C material (Al_2O_3 = 50 mass%, SiO_2 = 25 mass%, C = 25 mass%) having a maximum thermal expansion coefficient at temperature of room temperature to 1500□ C of 0.5 %, was used for an outer periphery-side layer 3, and applied to the side of a region which is not immersed in molten steel bath (non-immersed portion). Further, a thickness of an intermediate layer 4 for reliving thermal expansion of the inner bore-side layer 2 was set at 3.0 mm.

[0129] A mixture (ingredients) for the intermediate layer 4 was prepared by; mixing un-expanded expansive graphite particles as the expansive material, polyethylene particles as the burnable particles, and alumina and magnesia as the refractory aggregate, together, and adding a pitch powder and an acrylic resin as the organic binder into the mixture; subjecting the mixture to a granulation process in a high-speed mixer; adjusting an amount of residual volatile component in a fluidized drying furnace to adjust plasticity during forming; and regulating the granulated mixture obtained through the drying, to have a particle size of 1 mm or less.

[0130] The derails are shown in Table 1. A compressive rate and a hot bonding strength (compressive shear strength) in Table I were measured by the aforementioned method. In the long nozzle 1 in this example, the compressive rate required for the intermediate layer, according to the Formula 1 is 34 % or more.

[0131] For comparison, the inner bore-side layer 2 was inserted into the outer periphery-side layer 3 using a conventional mud-like mortar to prepare Comparative Example 1. In Comparative Example 1, no compressability of the intermediate layer was observed in a measurement of a solid shape of the nozzle, and crack and peel-off occurred, respectively, in the outer periphery-side layer and the inner bore-side layer in a first cycle of pouring test.

TABLE 1

[0132]

【Table 1】

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Inventive Example 1	Inventive Example 2	Inventive Example 3	Comparative Example 4	Comparative Example 5	Inventive Example 4	Inventive Example 5	Inventive Example 6	Comparative Example 6	Inventive Example 7	Inventive Example 8	Comparative Example 7
Composition of mixture for intermediate layer (mass%)															
expansive graphite (600 μm or less)	45	50	45	45	45	45	45	0	15	10	5	4	5	5	5
non-expansive flaky graphite (600 μm or less)	0	0	0	0	0	0	0	45	0	0	0	0	0	0	0
polyethylene particle (45 μm or less)	0	50	55	55	55	55	55	55	85	90	95	96	55	55	50
Al_2O_3 fine particle (45 μm or less)	55	0	0	0	0	0	0	0	0	0	0	0	40	0	45
MgO fine particle (45 μm or less)	0	0	0	0	0	0	0	0	0	0	0	0	0	40	0
pitch powder (not included in 100 mass%, C source) *1	0	5	2	2.5	5	15	16	5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
acrylic resin (not included in 100 mass%, solid)	0	15	15	15	15	15	1.5	15	15	15	15	15	15	1.5	15
sodium silicate (not included in 100 mass%, solid)	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Chemical component of intermediate layer (mass%) *1															
C (carbon component)	43	100	100	100	100	100	100	10	100	100	100	100	16	16	14
Al_2O_3	52	0	0	0	0	0	0	0	0	0	0	0	84	0	86
MgO	0	0	0	0	0	0	0	0	0	0	0	0	0	84	0
SiO_2	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na_2O	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$K \geqq [(Di \times \alpha i - Do \times \alpha o)/(2 \times Tm)]$ *4	×	○	○	○	○	○	×	×	○	○	○	○	○	○	○
Compressive rate at 1000℃	4	58	72	65	62	49	29	14	75	77	78	81	72	68	67
at 1500℃	6	61	74	68	66	56	33	16	78	78	80	85	75	71	71
Hot bonding strength(MPa) at 1000℃	0.4	—	<0.01	0.3	0.5	1.4	1.8	<0.01	0.3	0.3	0.2	<0.01	0.1	0.3	<0.01
at 1500℃	<0.01	—	<0.01	0.2	0.4	1.2	1.6	<0.01	0.2	0.2	0.1	<0.01	0.1	0.2	<0.01
Yield of solid shape after firing *2															
state of outer periphery-side layer	○	×(K)	○	○	○	○	○	○	○	○	○	○	○	○	○
state of intermediate layer	×(S)	—	○	○	○	○	○	×(S)	○	○	○	○	○	○	×(S)
Pouring cycle repetition test (no preheating) *3															
1st cycle	×(C,P)	—	×(P)	○	○	○	×(C)	×(P)	○	○	○	×(P)	○	○	○
2nd cycle	—	—	—	○	○	○	—	—	○	○	○	—	○	○	×(P)
3rd cycle	—	—	—	○	○	○	—	—	○	○	○	—	○	○	—
Comprehensive evaluation *5	×	×	×	○	○	○	×	×	○	○	○	×	○	○	×

*1 The mass% of each material is a corresponding value to a chemical component after reducing firing at 1000℃

*2 ×(K): Occurrence of longitudinal crack in outer periphery-side layer, ×(S): occurrence of shrinkage crack, ○: good, no defect

*3 ○: no crack, ×(C): occurrence of crack, ×(P): peel-off of inner bore-side layer

*4 ○: satisfying conditional formula, × : failing to satisfy conditional formula

*5 ○: good, × : no good

[0133] A sample in Comparative Example 2 was prepared in such a manner as to contain 50 mass% of expansive graphite particles, with the remainder being 50 mass% of burnable particles, and further contain 5 mass part of pitch in addition to a total mass% of the expansive graphite particles and the burnable particles. In Comparative Example 2, expansion cracking occurred in the outer periphery-side layer during a heat treatment in a production process. The reason is that the expansive graphite particles is contained in an amount of 50 mass% which exceeds 45 mass% as the upper limit value, and thereby the outer periphery-side layer is pressed radially outwardly and broken by an expansion force of the expansive graphite particles during the heat treatment.

[0134] Inventive Examples 1 to 3 and Comparative Examples 3 and 4 are results of evaluation performed by setting an amount of the expansive graphite particles at a constant value of 45 mass%, and using a pitch powder as an organic binder, and changing, in the range of 2.0 to 16 mass%, an amount of carbon content of the pitch powder (hereinafter referred to as "pitch carbon component,") in terms of an amount of carbon content in a non-oxidation atmosphere at 1000□ C.

[0135] As increase in bonding strength along with an increase in the pitch carbon component is observed.

[0136] In Inventive Examples 1 to 3 and Comparative Example 3, the expansive graphite particles were sufficiently expanded during the heat treatment, and voids which have been occupied by the polyethylene particles were fully filled with the expanded graphite particles, so that a large compressive ratio could be obtained. However, in Comparative Example 3 where the pitch carbon component is reduced to 2 mass%, the bonding strength could not be sufficiently obtained to cause peel-off of the inner bore-side layer (inner bore-side member). Further, in Comparative Example 4 where the pitch carbon component is increased up to 16 mass%, the bonding strength was excessively increased, and the compensability was not sufficiently obtained. Consequently, crack occurred in the first cycle of the pouring test.

[0137] In Inventive Examples 1 to 3, excellent results could be obtained in "yield of solid shape" and "pouring cycle repetition test" without any problem.

[0138] In Comparative Example 5 where no expansive graphite particle is used, both the compressability and the bondability could not be obtained at a required level, and a peel-off phenomenon occurred in the pouring test.

[0139] In Inventive Examples 4 to 6 where an amount of the burnable particles is further increased, both the compressability and the bonding strength could be sufficiently obtained.

[0140] In Comparative Example 6 where the amount of the burnable particles is further increased, the bonding strength could not be sufficiently obtained, and a peel-off phenomenon occurred in the pouring test, although the compressability could be sufficiently obtained.

[0141] In Inventive Examples 7 and 8 where a part of the burnable particles is substituted with refractory particles, the compressability and the bonding strength could be sufficiently obtained, and excellent results could be obtained. In Comparative Example 7 where the amount of the refractory particles is further increased, the compressability could not be sufficiently obtained. Consequently, shrink crack was observed in the intermediate layer, and the bonding strength could not be sufficiently obtained. Moreover, a peel-off phenomenon occurred in the inner bore-side layer in a second cycle of poring test.

[0142] Although, in the above examples, the present invention is applied to the long nozzle illustrated in FIG. 1, a nozzle type to be covered by the present invention is not limited the long nozzle. For example, the present invention may be applied to a tubular refractory structure as shown in FIG. 2.

[0143] FIGS. 2(a) and (b) show two types of long nozzle utilizing the present invention as with the embodiment illustrated in FIG. 1. In the nozzle illustrated in FIG. 2(a), the outer periphery-side layer 3 is provided to extend up to a bottom end of the long nozzle 1, and the intermediate layer 4 is provided between a lower end of the inner bore-side layer 2 and the outer periphery-side layer 3. In FIG. 2(b), the refractory composition of the outer periphery-side layer 3 is provided to extend up to both top and bottom ends of the long nozzle 1, and the intermediate layer 4 is disposed between an upper end of the inner bore-side layer 2 and the outer periphery-side layer 3 and between the lower end of the inner bore-side layer 2 and the outer periphery-side layer 3.

[0144] FIG. 2(c) shows an example where the present invention is applied to an immersion nozzle. An immersion nozzle 1' illustrated in FIG. 2(c) comprises an outer peripheiy-side layer 3 consisting of an AG composition 3a and a ZG composition 3b, wherein the AG composition 3a is has a bottom wall, and a lateral wall formed with an outlet ports 5. An inner bore-side layer 2 also has a bottom wall, and an intermediate layer 4 is provided between the inner bore-side layer 2 and the outer periphery-side layer 3 to extend over substantially the entire region thereof.

Claims

1. A continuous casting nozzle comprising a tubular refractory structure which has an inner bore formed along an axial direction thereof to allow molten metal to pass therethrough, and at least partly includes an inner bore- side layer disposed on the side of said inner bore, and an outer periphery- side layer disposed on a radially outward side relative to said inner bore- side layer, wherein said inner bore-side layer has the thermal expansion greater than that of said outer periphery- side layer, said continuous casting nozzle being **characterized in that** said tubular refractory structure includes an intermediate layer having compressability and lying between said inner bore- side layer and said outer periphery- side layer, wherein:

   said inner bore- side layer, said intermediate layer and said outer periphery- side layer are simultaneously integrated together during a forming process to form a multi-layer structure;
   a bonding strength between said intermediate layer and each of said inner bore- side layer and said outer periphery- side layer adjacent to said intermediate layer is in the range of 0.01 to 1.5 MPa, as measured in a non-oxidation atmosphere at 1000□ C; and
   said intermediate layer has a compressive rate K (%) satisfies the following Formula 1 as measured in a non-oxidation atmosphere at 1000□ C under a pressure of 2.5 MPa,

   $$K \square \left[(Di \times \square i - Do \times \square o) / (2 \times Tm)\right] \qquad \text{--- Formula 1}$$

   wherein:

   Di is an outer diameter (mm) of said inner bore- side layer;
   Do is an inner diameter (mm) of said outer periphery- side layer;
   Tm is an initial thickness (mm) of said intermediate layer at room temperature;
   □ i is a maximum thermal expansion coefficient (%) of the refractory composition of said inner bore- side layer in a temperature range of room temperature to 1500□ C; and
   □ o is a thermal expansion coefficient (%) of the refractory composition of said outer periphery- side layer at a temperature at start of discharge or pouring of molten metal through said continuous casting nozzle.

2. The continuous casting nozzle as defined in claim 1, wherein said intermediate layer in a state after being subjected to a heat treatment in a non-oxidation atmosphere at 600□ C or more contains expanded expansive graphite particles (hereinafter referred to as "expanded graphite particles").

3. The continuous casting nozzle as defined in claim 1 or 2, wherein said intermediate layer in a state after being subjected to a heat treatment in a non-oxidation atmosphere at 1000□ C contains a carbon component (except any carbon compound with the remaining components) in a total amount of 16 mass% or more (including 100 mass%).

4. The continuous casting nozzle as defined in claim 1 or 2, wherein said intermediate layer in a state after being subjected to a heat treatment in a non-oxidation atmosphere at 1000□ C contains a carbon component (except any carbon compound with the remaining components) in a total amount of 16 mass% or more, with the remainder other than said carbon component being a refractory material comprising one or more selected from the group consisting of oxide, carbide, nitride and metal.

5. A method of producing a continuous casting nozzle comprising a tubular refractory structure which has an inner bore formed along an axial direction thereof to allow molten metal to pass therethrough, and at least partly includes an inner bore- side layer, an intermediate layer and an outer periphery- side layer which are arranged in this order in a radially outward direction with respect to said inner bore, said method comprising the steps of:

preparing a mixture (ingredients) for said intermediate layer, which contains un-expanded expansive graphite particles in an amount ranging from 5 to 45 mass%, and burnable particles in an amount ranging from 55 to 95 mass%, and further contains an organic binder in a given mass%, with respect to a total mass% of said un-expanded expansive graphite particles and said burnable particles, and in addition to said total mass%, wherein said given mass% of said organic binder is set to allow a ratio of a carbon component only or said organic binder (except any carbon compound with the remaining components) to an entire refractory composition of said intermediate layer, in a state after the refractory composition of said intermediate layer is subjected to a heat treatment in a non-oxidation atmosphere at 1000□ C, to fall within the range oaf 2.5 to 15 mass%;
subjecting said mixture (ingredients) for said intermediate layer to a pressure forming using a cold isostatic pressing (CIP) machine, simultaneously and integrally together with a mixture (ingredients) for said inner bore-side layer and a mixture (ingredients) for outer periphery- side layer, to obtain a single shaped body; and
subjecting said shaped body to a heat treatment at a temperature of 600 to 1300□ C to allow said burnable particles contained in said mixture (ingredients, i.e., green body after pressing) for said intermediate layer in said shaped body to be vanished so as to form voids, and then expand said un-expanded expansive graphite particles contained in said mixture (ingredients, i.e., green body after pressing) for said intermediate layer in said shaped body so as to allow said voids to be filled with said expanded graphite particles.

6. A method of producing a continuous casting nozzle comprising a tubular refractory structure which has an inner bore formed along an axial direction thereof to allow molten metal to pass therethrough, and at least partly includes an inner bore- side layer, an intermediate layer and an outer periphery- side layer which are arranged in this order in a radially outward direction with respect to said inner bore, said method comprising the steps of:

preparing a mixture (ingredients) for said intermediate layer, which contains un-expanded expansive graphite particles in an amount ranging from 5 to 45 mass%, burnable particles in an amount ranging from 55 to 95 mass%, and a refractory material which is one or more selected from the group consisting of oxide, carbide, nitride and metal, in a total amount of 40 mass% or less, and further contains an organic binder in a given mass%, with respect to a total mass% of said un-expanded expansive graphite particles, said burnable particles and said refractory material which is one or more selected from the group consisting of oxide, carbide, nitride and metal, and in addition to said total mass%, wherein said given mass% of said organic binder is set to allow a ratio of a carbon component only of said organic binder (except any carbon compound with the remaining components) to an entire refractory composition of said intermediate layer, in a state after the refractory composition of said intermediate layer is subjected to a heat treatment in a non-oxidation atmosphere at 1000□ C, to fall within the range of 2.5 to 15 mass%;
subjecting said mixture (ingredients) for said intermediate layer to a pressure forming using a cold isostatic press (CIP) machine, simultaneously and integrally together with a mixture (ingredients) for said inner bore-side layer and a mixture (ingredients) for outer periphery- side layer, to obtain a single shaped body; and
subjecting said shaped body to a heat treatment at a temperature of 600 to 1300□ C to allow said burnable particles contained in said mixture (ingredients, i.e. green body after pressing) for said intermediate layer in said shaped body to be vanished so as to form voids, and then expand said un-expanded expansive graphite particles contained in said mixture (ingredients, i.e. green body after pressing) for said intermediate layer in said shaped body so as to allow said voids to be filled with said expanded graphite particles.

Fig. 1

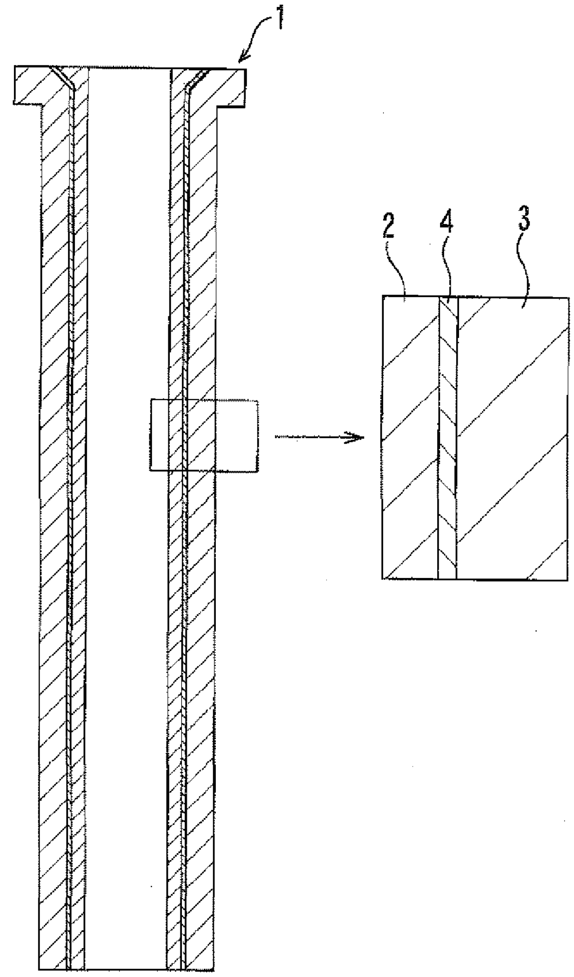
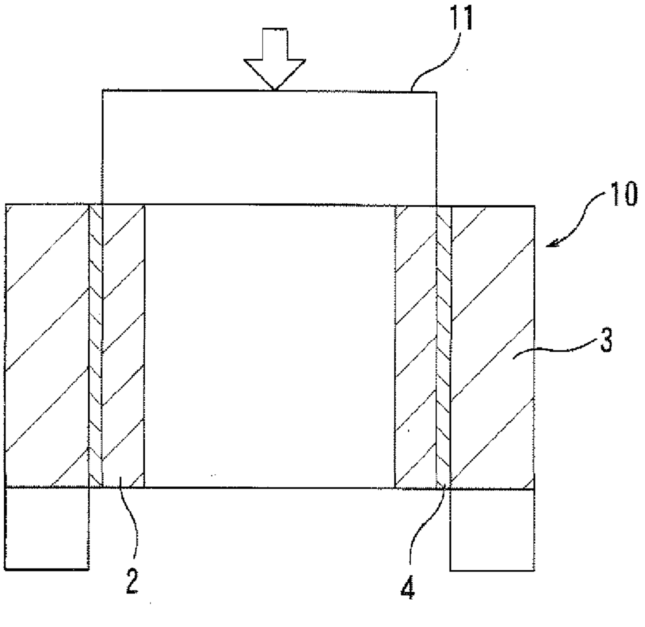


Fig. 3



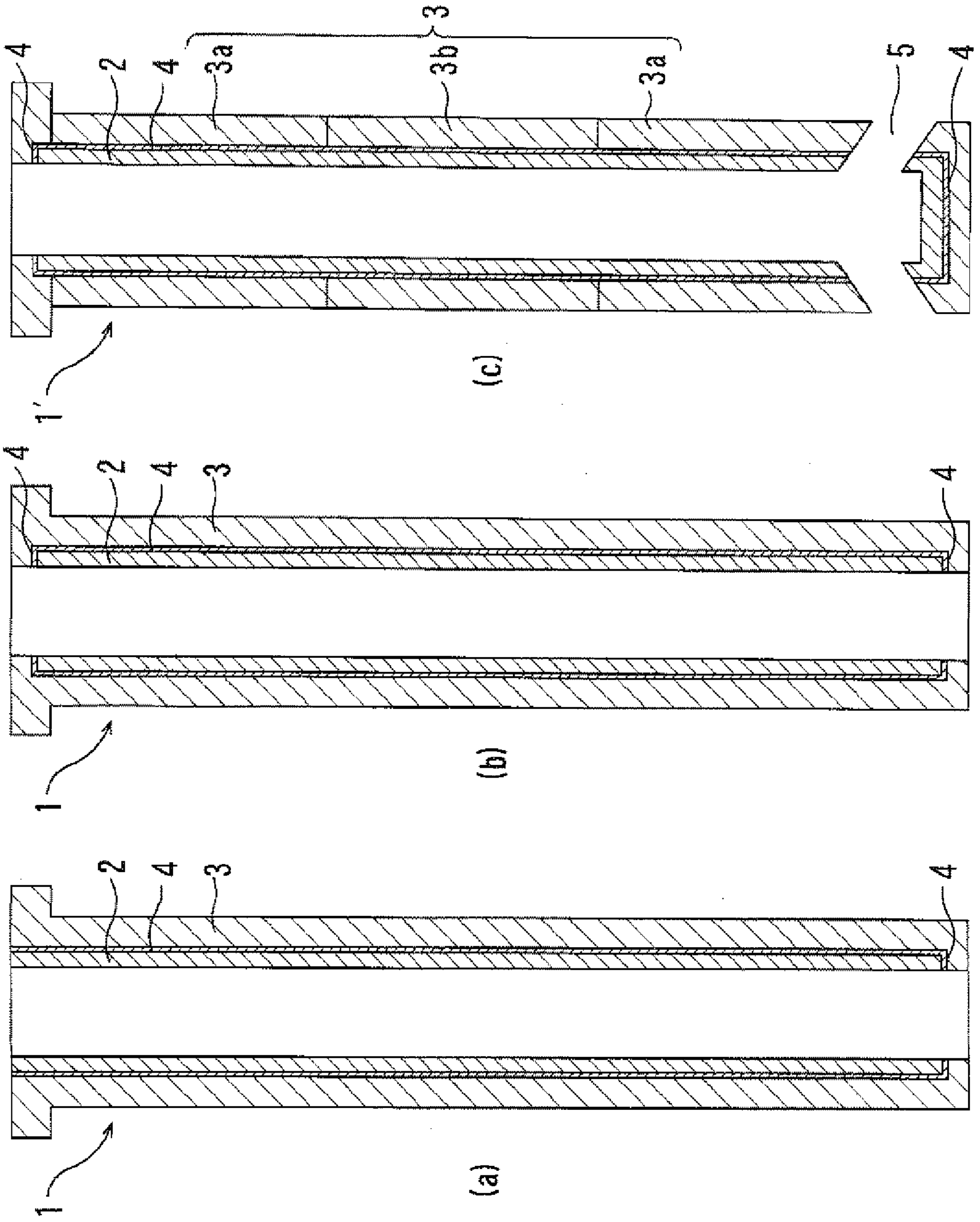


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2008/061928

A. CLASSIFICATION OF SUBJECT MATTER
B22D11/10(2006.01)i, *B22D41/50*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B22D11/10, B22D41/50

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2008
Kokai Jitsuyo Shinan Koho	1971-2008	Toroku Jitsuyo Shinan Koho	1994-2008

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2006-130555 A (Krosaki Harima Corp.), 25 May, 2006 (25.05.06), Par. Nos. [0057], [0069] (Family: none)	1-6
A	JP 2001-286995 A (Shinagawa Refractories Co., Ltd.), 16 October, 2001 (16.10.01), Claim 4 (Family: none)	1-6
A	JP 10-305357 A (Shinagawa Refractories Co., Ltd.), 17 November, 1998 (17.11.98), Fig. 2 (Family: none)	1-6

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 18 July, 2008 (18.07.08)	Date of mailing of the international search report 29 July, 2008 (29.07.08)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2007)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 60152362 A **[0020]**
- JP 7232249 A **[0020]**