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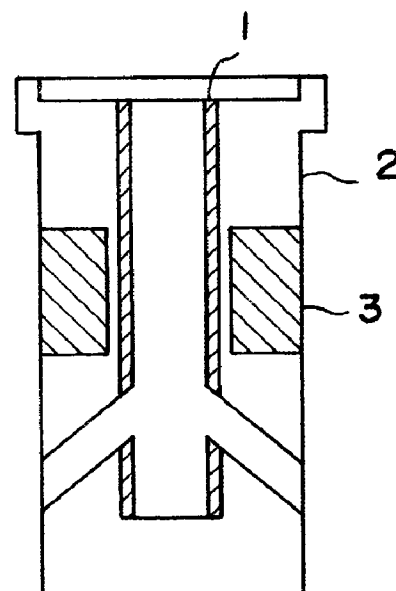
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(54) **NOZZLE FOR CONTINUOUS CASTING OF STEEL**

(57) A nozzle for use in continuous casting of steel, which is free from blockage and has melt-damage resistance, is provided. A nozzle for use in continuous casting of steel according to the present invention is characterized in that at least an interior surface of the nozzle and/or portions that come into contact with molten steel are composed of a refractory material comprising, as mineral phase, spinel, or spinel and periclase.

**FIG. 1**



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**Description**Industrial Field of the Invention

5 [0001] The present invention relates to a nozzle used in continuous casting of steel, such as a submerged nozzle, a long nozzle, etc.

Prior Art

10 [0002] In the continuous casting of steel, conventionally,  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -C nozzles having superior resistance to spalling have been the most widely used. However, in the case where the nozzles made with  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -C material are used for the casting of aluminum killed steel, there arises a problem of blockage of the nozzle due to the adhesion of  $\text{Al}_2\text{O}_3$  inclusions in the molten steel. Also, in the case of using the above nozzles for casting high oxygen content steel, high manganese content steel or stainless steel, a problem conversely arises in which the nozzles are melt-damaged. The  
15 blockage or melt-damage of nozzles not only causes the deterioration of the service life of refractory materials, but also hinders the operation of steel manufacture and adversely affects the quality of steel materials. Accordingly, the development of a nozzle that is free from blockage and has melt-damage resistance for use in continuous casting of steel is of great importance.

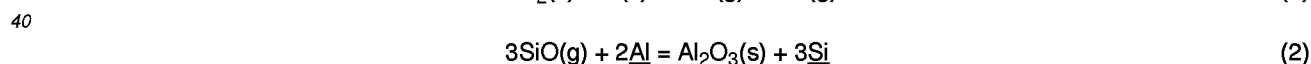
[0003] Under the circumstances, as a countermeasure to this, Japanese Patent Laid-open No. 3-243258 discloses a  
20 nozzle in which materials containing a) not less than 90% by weight of  $\text{Al}_2\text{O}_3$ ; b) not less than 90% by weight of  $\text{MgO}$ ; or c) not less than 90% by weight of  $\text{ZrO}_2$  are formed into cylindrical sleeves, and one or two of them are inserted in combination with each other to be used as a nozzle.

[0004] Further, Japanese Patent Laid-open No. 5-237610 proposes, for the purpose of decreasing the blockage of  
25 the nozzle, the use of a refractory material, as a material for an interior body of the submerged nozzle, in which respective contents of carbon and  $\text{SiO}_2$  are less than 1% by weight, spinel content is 1 to 40% by weight,  $\text{MgO}$  content is 0.5 to 15% by weight, and the rest is  $\text{Al}_2\text{O}_3$ .

Problems the Invention Aims to solve

30 [0005] The main mechanism that causes blockage of  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -C nozzles in the casting of aluminum killed steel is as follows:

[0006] Firstly, in a refractory at high temperature, reaction of the following Equation (1) occurs between  $\text{SiO}_2$  and C used as raw materials.  $\text{SiO}$  (gas phase, hereinafter referred to as (g)) and  $\text{CO}$  (g) diffuse at the interface between the  
35 nozzle and molten steel, and reactions with Al in the molten steel occur in accordance with the following Equations (2) and (3). As a result, a network layer of alumina is formed on the working surface of the nozzle and melt-adhered onto the nozzle surface to initiate the adhesion of  $\text{Al}_2\text{O}_3$  infusions thereto. As the adhesion of  $\text{Al}_2\text{O}_3$  infusions progress, nozzle blockage will become worse.



45 [0007] In the above equations, (s) represents solid phase, and  $\text{Al}$ ,  $\text{Si}$  and  $\text{C}$  each represent the molten Al, Si and C in the molten steel.

[0008] On the other hand, the mechanism of melt-damage of  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -C nozzle in the casting of high oxygen content steel, high manganese content steel or stainless steel is as follows:

[0009] Firstly, carbon in the working surface of refractory material dissolves into the molten steel. That is, the following  
50 Equation (4) is established, and the working surface is rendered into  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -C oxide.



[0010] Thereafter,  $\underline{\text{Mn}}$ ,  $\underline{\text{O}}$ , and  $\underline{\text{Fe}}$  in the molten steel penetrate, in the form of  $\text{MnO}$  and  $\text{FeO}$ , into the working surface.  
55 That is, the following Equations (5) and (6) are established.





[0011] Furthermore, MnO-FeO inclusions in the molten steel collide onto the working surface, and are adhered thereto. The MnO and FeO that have penetrated into the working surface because of the above two reasons, react with  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  in the working surface to form a liquid slag of  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -MnO-FeO. When the slag is lost in the stream of molten steel, the melt-damage of refractory material is caused.

[0012] However, the above-mentioned conventional nozzles are effective in some extent to prevent the blockage of nozzles but less effective in suppressing the melt-damage of nozzles. Conversely, some conventional nozzle may suppress the melt-damage of nozzles but not the blockage of nozzles.

[0013] Accordingly, an object of the present invention is to provide a nozzle for use in continuous casting of steel, which can overcome the above-mentioned problems, and is free from blockage and has melt-damage resistance.

#### Means for Solving the Problem

[0014] A nozzle for use in continuous casting of steel according to the present invention is characterized in that at least an interior surface of the nozzle and/or portions that come into contact with molten steel are composed of a refractory material comprising, as mineral phase, spinel, or spinel and periclase.

[0015] Further, a nozzle for use in continuous casting of steel according to the present invention is characterized in that the refractory material of at least the interior surface of the nozzle and/or the portions that come into contact with molten steel are manufactured by using spinel raw materials.

[0016] Still further, a nozzle for use in continuous casting of steel according to the present invention is characterized in that the refractory material of at least the interior surface of the nozzle and/or the portions that come into contact with molten steel are composed of raw refractory material having a grain size of 1,000  $\mu\text{m}$  or less and in which the ratio of grains of 500  $\mu\text{m}$  or less is at least 60% by weight.

[0017] Furthermore, a nozzle for use in continuous casting of steel according to the present invention is characterized in that the thickness of the refractory material of at least the interior surface of the nozzle and/or the portions that come into contact with molten steel are 2 to 20 mm.

#### Brief Description of the Drawings

[0018]

Fig. 1 shows an embodiment of a distribution pattern of materials in a nozzle of the present invention;

Fig. 2 shows another embodiment of the distribution pattern of materials in the nozzle of the present invention;

Fig. 3 shows another embodiment of the distribution pattern of materials in the nozzle of the present invention;

Fig. 4 shows another embodiment of the distribution pattern of materials in the nozzle of the present invention;

Fig. 5 shows another embodiment of the distribution pattern of materials in the nozzle of the present invention; and

Fig. 6 shows a distribution pattern of materials in a conventional nozzle.

#### Embodiment

[0019] The present invention will now be described in detail.

[0020] A nozzle for use in continuous casting of steel according to the present invention is characterized in that at least an interior surface of the nozzle and/or portions that come into contact with molten steel are composed of a refractory material comprising, as mineral phase, spinel or/and periclase.

[0021] The refractory material of the present invention does not contain carbon and  $\text{SiO}_2$ . Accordingly, when the refractory material is used in the casting of aluminum killed steel, reactions according to the above-mentioned Equations (1) to (3) do not take place with the result that no network layer of  $\text{Al}_2\text{O}_3$  is formed on the working surface of the refractory material. As a result, adhesion of  $\text{Al}_2\text{O}_3$  inclusions onto the working surface and blockage of the nozzle due to the adhesion of the inclusions are remarkably suppressed.

[0022] Further, the refractory material of the present invention is a mineral phase comprising spinel, or spinel and periclase, and contains no free  $\text{Al}_2\text{O}_3$ . Accordingly, when the refractory material is used for the casting of high oxygen content steel, high manganese content steel, and stainless steel, melt-damage of the refractory materials may be

suppressed.

**[0023]** These particular reasons therefor may be described based on the experimental results in the following examples:

- 5 •  $\text{Al}_2\text{O}_3$  is present in the form of composite oxide (spinel) with MgO to thereby lower the thermodynamic activity of  $\text{Al}_2\text{O}_3$  with the result that MnO and FeO from molten steel can hardly penetrate to the refractory materials.
- The reactivity between periclase and molten steel is small with the result that MnO and FeO from molten steel can hardly penetrate to periclase.
- 10 • The solid-phase line temperature of MgO-spinel refractory materials exceeds 2,000°C, which is extremely high, with the result that even if MnO and FeO do penetrate, a liquid slag phase hardly occurs.

**[0024]** As described above, the feature of the nozzle of the present invention is to control the mineral composition of the refractory material to be used. In other words, even if the refractory material has a similar chemical composition, when the mineral compositions (crystal structure) are different from each other, the reactivity thereof with molten steel is naturally different, resulting in a large difference in the melt-damage of the refractory materials.

**[0025]** In the present invention, the refractory material of the interior surface of the nozzle and/or the portions that come into contact with molten steel are composed of spinel crystal, which is a composite oxide of  $\text{Al}_2\text{O}_3$  and MgO, or spinel crystal and periclase crystal consisting of MgO. However, when the refractory material of the present invention is prepared by using a practical refractory raw material, unavoidable impure minerals may exist therein, which may be accompanied by unavoidable impure components. It is preferable to suppress the unavoidable impure minerals as much as possible. Therefore, the content of impure components other than  $\text{Al}_2\text{O}_3$  and MgO, which are used for the formation of spinel and periclase, is preferably 3% or less by weight. If the content exceeds 3% by weight, the melt-damage resistance of the impure minerals that accompany the impure components is so low that the portions of the impure minerals is melt-damaged earlier than spinel and periclase, which is not preferable. More preferably, the content is 1% or less by weight.

**[0026]** The refractory material of the present invention used in the nozzles may be preferably applied to the interior surface and/or the portions that come into contact with molten steel of any nozzle used in continuous casting such as long nozzles or submerged nozzles. With respect to manufacturing the nozzle, the nozzle may be manufactured by the following methods: A method (simultaneous molding method) may be used, in which the blend of the refractory raw material of the present invention that forms the interior surface and/or the portions to come into contact with molten steel and the blend of refractory raw material that forms the main body of the nozzle are simultaneously pressure molded to form a nozzle having a predetermined shape. Also, a method (finishing method) may be used, in which the blend mixed with the refractory raw material of the present invention composing the interior surface and/or the portions to come into contact with molten steel is cast-molded or pressure molded into the main body of a nozzle that has been preformed, then dried and occasionally sintered. In addition,  $\text{Al}_2\text{O}_3$ -C refractory material or  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -C refractory material, which has been conventionally used as refractory that forms the main body of the nozzle, may be appropriately used.

**[0027]** Examples of distribution patterns of the refractory materials in accordance with the present invention are given in Figs. 1 to 5. Here, Figs. 1 to 4 show the submerged nozzles with  $\text{ZrO}_2$ -C refractory material (3) arranged around a powder line. The powder line is a zone that comes into contact with a highly corrosive mold powder when the submerged nozzle is used. Accordingly,  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -C refractory material (2) composing the main body of the nozzle has been replaced in this region by the  $\text{ZrO}_2$ -C refractory material (3), which has superior corrosion resistance, to reinforce the powder line zone. Incidentally, the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -C refractory materials and  $\text{ZrO}_2$ -C refractory materials of ordinary composition may be used, for instance,  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -C refractory material composed of 30 to 90% by weight of  $\text{Al}_2\text{O}_3$ , 0 to 35% by weight of  $\text{SiO}_2$ , and 10 to 35% by weight of C, or  $\text{ZrO}_2$ -C refractory material composed of 66 to 88% by weight of  $\text{ZrO}_2$ , 2 to 4% by weight of CaO, and 10 to 30% by weight of C, for example, when CaO stabilized  $\text{ZrO}_2$  is used. Further, CaO stabilized  $\text{ZrO}_2$  is widely used as the  $\text{ZrO}_2$  raw material, but MgO stabilized  $\text{ZrO}_2$ ,  $\text{Y}_2\text{O}_3$  stabilized  $\text{ZrO}_2$ , baddeleyite, etc., may also be used. In Figs. 1 to 5, reference numeral 1 denotes a refractory material comprising as mineral phase spinel or spinel and periclase, that is, the refractory material according to the present invention. It should be understood that the distribution patterns of materials in the nozzle of the present invention are not limited to those shown in Fig. 1 to 5.

**[0028]** Also, when manufacturing by simultaneous molding, the raw material blend of the refractory material such as  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -C refractory material composing the main body of the nozzle, which has been mixed with phenolic resin or polysaccharide as a binder, and the raw material blend of the refractory material according to the present invention composing the interior surface and/or the portions to come into contact with molten steel, may be filled into their given positions in the mold, formed by CIP, etc., and dried to obtain an unfired or fired product. The refractory material composing the main body of the nozzle and the refractory material according to the present invention composing the interior surface and/or the portions to come into contact with molten steel are preferably mixed with the same kind of binder.

**[0029]** When manufacturing by finishing, a starting material blend mixed with the same binder used in the main body of nozzle or a binder such as silicate, phosphate, etc., may be cast around the main body of a nozzle, which has been preformed by a conventional method, molded or pressure molded, then dried and occasionally fired.

**[0030]** However, it is not preferable to insert and load the interior portions (interior surface and/or portions to come into contact with molten steel), which have been made separately by pressure molding, cast molding or injection molding, into the main body, which has been conventionally preformed, because the interior portions do not easily stick to the refractory material composing the nozzle body. In particular, in order to maintain stable adhesion when heated at a high temperature in use, the above-mentioned simultaneous molding or finishing is preferable, because the refractory material according to the present invention composing the interior surface and/or the portions to come into contact with molten steel is composed of spinel, or spinel and periclase, so that it may have a greater expansion coefficient than that of the  $\text{Al}_2\text{O}_3\text{-C}$  or  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-C}$  refractory material composing the main body of the nozzle.

**[0031]** Similarly, the refractory material composing the main body of the nozzle and the refractory material composing the interior surface and/or the portions to come into contact with molten steel are preferably mixed with the same kind of binder as described above to yield better affinity resulting in a stable adhesion

**[0032]** On the other hand, in the manufacture of the refractory material according to the present invention, it is desirable to use as raw material a spinel raw material, or a spinel raw material and a magnesia raw material comprising periclase. When magnesia and alumina starting materials are used simultaneously as starting materials, magnesia reacts with alumina during the firing or use of the refractory materials to form spinel. However, the materials expand as the reaction progresses, and there is a risk that the materials may cracks. Incidentally, spinel raw materials, in which the ratio of  $\text{MgO} : \text{Al}_2\text{O}_3$  composing spinel does not correspond to the theoretical composition and spinel and periclase coexist with an excess of  $\text{MgO}$ , or in which corundum crystals as free alumina are not found with an excess of  $\text{Al}_2\text{O}_3$ , can be used. Both spinel and magnesia raw materials may be used irrespective of an electro-molten or fired product.

**[0033]** The grain size of the starting materials blended to form the refractory material according to the present invention is preferably  $1,000 \mu\text{m}$  or less, in which the ratio of grains having a grain size of  $500 \mu\text{m}$  or less is not less than 60% by weight. If particles having a grain size exceeding  $1,000 \mu\text{m}$  are present, the grain size of the starting material in relation to the thickness of nozzle is too large, which will cause the refractory structure to become brittle, and will cause grains to fall out, etc., during use. Also, if the ratio of grains having a grain size of less than  $500 \mu\text{m}$  or less is less than 60% by weight, the molding property is deteriorated, especially in simultaneous molding, and a satisfactory molded product can seldom be obtained. Incidentally, if the raw materials having a grain size of less than  $0.5 \mu\text{m}$  exceeds 20% by weight, the resistance to spoiling of the refractory material is undesirably deteriorated, resulting in cracking.

**[0034]** Further, when the refractory material of the present invention is used for the interior surface of the nozzle and/or the portions that come into contact with molten steel, the thickness thereof is preferably with the range of 2 to 10 mm. Refractory material with a thickness of less than 2 mm, is weak and therefore not capable of withstanding the impact of the stream of molten steel, resulting in a risk that the nozzle will fall-out from the main body of the nozzle. Further, if the thickness exceeds 10 mm, the difference in thermal expansion coefficient with the refractory material composing the main body is large. Accordingly, there is a risk that cracking will result (deterioration of spoiling resistance), which is not desirable.

#### Effect of the Invention

**[0035]** Using the nozzle according to the present invention, blockage of the nozzle due to the adhesion of  $\text{Al}_2\text{O}_3$  inclusions during the casting of aluminum killed steel casting can be remarkably suppressed. Also, in the casting of high oxygen content steel, high manganese content steel stainless steel and Ca-treated steel, damage of the nozzles is remarkably reduced.

#### Example

**[0036]** The tests of spalling resistance,  $\text{Al}_2\text{O}_3$  inclusions adhesion resistance and melt-damaged resistance performed on each of the samples in the examples and comparative examples below will now be explained.

**[0037]** In the spalling tests, samples  $40 \times 40 \times 230 \text{ mm}$  in dimension preheated at  $800^\circ\text{C}$  for one hour were immersed for 5 minutes in  $1,580^\circ\text{C}$  of molten steel that was prepared by dissolving 200 kg of steel in a high frequency furnace, and then pulled up to be cooled in air. Samples after cooling were evaluated on the basis of crack formation. Ten samples were prepared and were evaluated by the total number of samples in which cracks had formed.

**[0038]** In the melt-damage tests, samples of 40 mm in diameter and 230 mm in height were immersed in molten high oxygen content steel at  $1,580^\circ\text{C}$  in argon and rotated for 60 minutes at a speed of 100 rpm, then evaluated by the decrease in diameter of each sample.

**[0039]** In the  $\text{Al}_2\text{O}_3$  inclusions adhesion tests, samples of 40 mm in diameter and 230 mm in height were immersed in molten aluminum killed steel at  $1,580^\circ\text{C}$  in argon, rotated for 60 minutes at a speed of 100 rpm, then evaluated based

on the thickness of  $\text{Al}_2\text{O}_3$  adhesion layer on the working surface of each sample.

Example 1

5 **[0040]** Two percent by weight (outer percentage) of phenol resin as binder were added to the starting material blends shown in Table 1 below, blended, CIP molded under a pressure of  $1,000 \text{ kgf/cm}^2$ , and then dried at  $250^\circ\text{C}$  for 3 hours to prepare samples. In this example, a spinel raw material having a nearly theoretical composition, in which the weight ratio of  $\text{MgO} : \text{Al}_2\text{O}_3$  is 28 : 72, and a magnesia rich spinel raw material, in which the weight ratio of  $\text{MgO} : \text{Al}_2\text{O}_3$  is 50 : 50, were used.

10 **[0041]** The samples thus obtained were subjected to the spolling, melt-damage and  $\text{Al}_2\text{O}_3$  adhesion tests described above. The results obtained are given in Table 1.

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Table 1

		INVENTIVE PRODUCT							Comparative Product			
		1	2	3	4	5	6	7	1	2	3	4
BLEND (wt%)	Magnesia (0.5-300 $\mu\text{m}$ )	85	60	20	10	-	20	-	80	-	78	
	Magnesia (<0.5 $\mu\text{m}$ )	5	10	10	-	-	-	-	20	-	-	
	Spinel of theoretical composition (500-1000 $\mu\text{m}$ )	3	-	20	10	35	-	-	-	10	-	
	Spinel of Theoretical Composition (0.5-500 $\mu\text{m}$ )	7	28	50	70	60	-	-	-	25	-	
	Spinel of Theoretical Composition (<0.5 $\mu\text{m}$ )	-	2		10	5	-	-	-	-	-	
	MgO rich Spinel (500-1000 $\mu\text{m}$ )	-	-				30	10	-	-	-	
	MgO rich Spinel (0.5-500 $\mu\text{m}$ )	-	-				40	80	-	-	-	
	MgO rich spinel (<0.5 $\mu\text{m}$ )	-	-				10	10	-	-	-	
	Alumina (100-500 $\mu\text{m}$ )	-	-				-	-	-	65	22	
Chemical Composition (wt%)	MgO	93	78	50	35	28	60	50	100	10	78	-
	Al <sub>2</sub> O <sub>3</sub>	7	22	50	65	72	40	50	-	90	22	41
	SiO <sub>2</sub>	-	-	-	-	-	-	-	-	-	-	28
	C	-	-	-	-	-	-	-	-	-	-	31
Mineral Phase		P.S	P.S	P.S	P.S	S	P.S	P.S	P	C.S	P.C	C.M
Test Results	Spalling resistance	0	0	0	0	0	0	0	5	0	3	0
	Melt-damage resistance	0	0	0	0	0	0	0	0	5	1	10
	Al <sub>2</sub> O <sub>3</sub> inclusions Adhesion resistance	0	0	0	0	0	0	0	0	0	0	10

**[0042]** In Table 1, symbols in the row of 'Mineral Phase' indicate the following: P; periclase, S; spinel, C; corundum, and M; Mullite, respectively.

**[0043]** From the results shown in Table 1, the following can be ascertained:

- 1) Comparative Product 1, which had a composition of 100% by weight of MgO, and Comparative Product 3, which

had a composition of 78% by weight of MgO, 22% by weight of Al<sub>2</sub>O<sub>3</sub>, and had periclase and corundum as mineral phase, had poor spalling resistance, but there were no such problems with any of the other samples.

2) Damage resistance was poorest in Comparative Product 4 (conventional Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-C refractory material), followed by Comparative Products 2 and 3, but there were no such problems with any of the other samples.

3) Al<sub>2</sub>O<sub>3</sub> inclusions adhesion was poor in Comparative Product 4, but Al<sub>2</sub>O<sub>3</sub> adhesion layer was not observed in any of the other samples.

[0044] Consequently, in the nozzle of the present invention, the refractory material disposed in the interior surface of the nozzle and/or the portions that come into contact with molten steel can be seen to simultaneously provide spalling resistance, damage resistance, and Al<sub>2</sub>O<sub>3</sub> inclusions adhesion resistance.

Example 2

[0045] The blend of starting material shown in Table 2 below was used to prepare samples by the same method as in Example 1, and spalling, damage, and Al<sub>2</sub>O<sub>3</sub> inclusions adhesion tests were performed. The results obtained are given in Table 2.

Table 2

		INVENTIVE PRODUCT				Comparative Product	
		8	9	10	11	5	6
BLEND (wt%)	Magnesia (>1000 μm)	-	-	-	-	10	-
	Magnesia (0.5-300 μm)	65	60	60	52	50	54
	Magnesia (<0.5 μm)	5	10	10	18	10	16
	Spinel of Theoretical composition (>1000 μm)	-	-	-	-	2	-
	Spinel of Theoretical Composition (500-1000 μm)	10	-	5	15	23	14
	Spinel of Theoretical Composition (0.5-500 μm)	18	28	20	15	5	10
	Spinel of Theoretical Composition (<0.5 μm)	2	2	5	-	-	6
Chemical Composition (wt%)	MgO	78	78	78	78	78	78
	Al <sub>2</sub> O <sub>3</sub>	22	22	22	22	22	22
Mineral Phase		P.S	P.S	P.S	P.S	P.S	P.S
Test Results	Spalling resistance	0	0	0	0	*	4
	Melt-damage resistance	0	0	0	0	*	0
	Al <sub>2</sub> O <sub>3</sub> inclusions Adhesion resistance	0	0	0	0	0	0

\*The falling-out of coarse particles was detected.

[0046] From the results shown in Table 2, the following can be ascertained.

1) When the maximum grain size of the starting material exceeds 1,000 μm, coarse particles fall out of the surface of the samples.

2) When the ratio of starting materials of less than 0.5 μm is not more than 20% by weight, the spalling resistance



is barely affected, but when it exceeds 20% by weight, the spalling resistance lowers remarkably.

3) The particle size has little effect on the resistance to melt-damage and the adhesion of  $Al_2O_3$  inclusions.

### Example 3

**[0047]** Using a main body of the nozzle composed of the  $Al_2O_3$ - $SiO_2$ -C refractory material of Comparative Product 4 shown in Table 1 above, nozzles (external diameter of nozzle; 130 mm, internal diameter; 70 mm, length; 600 mm) with the interior material of the nozzle of Inventive Product 1 shown in Table 1 above were prepared while varying the thickness of the interior materials (1 mm, 2 mm, 5 mm, 8 mm, 10 mm, and 12 mm, but the thickness of the main body of the nozzle was constant). The samples were simultaneously molded by CIP method, left for 24 hours, and then dried at 105°C for 24 hours. The distribution pattern of the materials was as shown in Fig. 5.

**[0048]** The nozzle test samples thus obtained were immersed for 1 hour in 200 kg of molten steel, which was melted at 1,580°C in a high frequency furnace, and then compared for spalling resistance by crack formation. Ten test samples were prepared and the spalling resistance was evaluated by the number of test samples, in which cracks were formed.

The test results are shown in Table 3.

Table 3

	Inventive Product				Comparative Product	
	12	13	14	15	7	8
Thickness of interior material (mm)	2	5	8	10	1	12
Spalling resistance	0	0	0	0	*	4

\*The falling-out of interior material was detected.

**[0049]** From Table 3, it became clear that the interior material may be in danger of falling-out when the thickness of the interior surface is less than 2 mm, and that the spalling resistance deteriorates markedly when the thickness exceeds 10 mm.

### Example 4

**[0050]** An actual machine test run was performed to evaluate the effect of the nozzle according to the present invention. The submerged nozzle of Inventive Product 13 shown in Table 3 as well as a conventional nozzle as comparison, which was made of the combination of  $Al_2O_3$ - $SiO_2$ -C refractory material of Comparative Product 4 of Table 1 and  $ZrO_2$ -C refractory material (80% by weight of CaO stabilized  $ZrO_2$  and 20% by weight of graphite) with a distribution pattern of materials shown in Fig. 6, were tested. The tests were performed at a casting temperature of 1,580°C by using a low carbon aluminum killed steel (composition (wt%): C; 0.08, Si; 0.03, Mn; 0.2, P; 0.01, Al; 0.05, and O; 10 ppm). After casting for 250 minutes, the thickness of the maximum  $Al_2O_3$  inclusions adhesion layer in the comparative nozzle was 15 mm, whereas it was only 3 mm in the nozzle of the present invention, showing a significant reduction effect in the  $Al_2O_3$  adhesion. Further, there was no cracking and falling-out of the interior material of the nozzle, and safe operation could be carried out.

### Example 5

**[0051]** The test was performed by using two submerged nozzles similar to those in Example 4 for continuous casting of high oxygen content steel (composition (wt%): C; 30 ppm, Si; 20 ppm, Mn; 0.3, P; 0.01, S; 0.01, Al; 10 ppm, and O; 600 ppm). As a result of testing, the maximum thickness damaged of the interior pipe after casting for 230 minutes in the comparative nozzle was 11 mm, whereas it was only 1 mm in the nozzle of the present invention, showing a significant decrease in damage in the submerged nozzle. In this case, too, there was no cracking and falling-out of the interior material of the nozzle, and safe operation could be carried out.

### Example 6

**[0052]** The test was performed by using two submerged nozzles similar to those in Example 4 for continuous casting of high manganese content steel (composition (wt%): C; 0.04, Si; 0.02, Mn; 1.5, P; 0.01, S; 0.01, and O; 100 ppm). As a result of testing, the maximum thickness damaged of the interior pipe after casting for 210 minutes in the comparative

nozzle was 13 mm, whereas it was only 1.5 mm in the nozzle of the present invention, showing a significant decrease in damage in the submerged nozzle. In this case, too, there was no cracking and falling-out of the interior material of the nozzle, and safe operation could be carried out.

5 Example 7

10 [0053] The test was performed by using two submerged nozzles similar to those in Example 4 for continuous casting of stainless steel (composition (wt%): C; 0.05, Si; 0.5, Mn; 1.0, P; 0.04, S; 0.02, Ni; 8.0, Cr; 18.0, and O; 50 ppm). As a result of testing, the maximum thickness damaged of the interior pipe after casting for 260 minutes in the comparative nozzle was 9 mm, whereas it was only 0.5 mm in the nozzle of the present invention, showing a significant decrease in damage in the submerged nozzle. In this case, too, there was no cracking and falling-out of the interior material of the nozzle, and safe operation could be carried out.

15 Example 8

20 [0054] The test was performed by using two submerged nozzles similar to those in Example 4 for continuous casting of calcium treating steel (composition (wt%): C; 0.05, Si; 0.3, Mn; 0.8, P; 0.01, S; 0.01, Al; 0.02, Ca; 30 ppm, and O; 20 ppm). As a result of testing, the maximum thickness damaged of the interior pipe after casting for 200 minutes in the comparative nozzle was 8 mm, whereas it was only 1 mm in the nozzle of the present invention, showing a significant decrease in damage in the submerged nozzle. In this case, too, there was no cracking and falling-out of the interior material of the nozzle, and safe operation could be carried out.

Claims

- 25 1. A nozzle for use in continuous casting of steel, characterized in that at least an interior surface of the nozzle and/or portions that come into contact with molten steel are composed of a refractory material comprising, as mineral phase, spinel, or spinel and periclase.
- 30 2. The nozzle for use in continuous casting of steel according to claim 1, wherein the refractory material is manufactured by using spinel raw materials.
- 35 3. The nozzle for use in continuous casting of steel according to claim 1 or 2, wherein the refractory material is composed of the raw refractory material having a grain size of 1,000  $\mu\text{m}$  or less and in which the ratio of grains of 500  $\mu\text{m}$  or less is at least 60% by weight.
- 40 4. The nozzle for use in continuous casting of steel according to any one of claims 1 to 3, wherein the thickness of the refractory material of at least the interior surface of the nozzle and/or the portions to come into contact with molten steel is 2 to 10 mm.

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FIG. 1

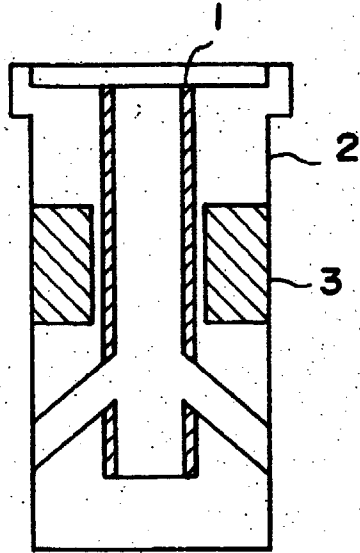
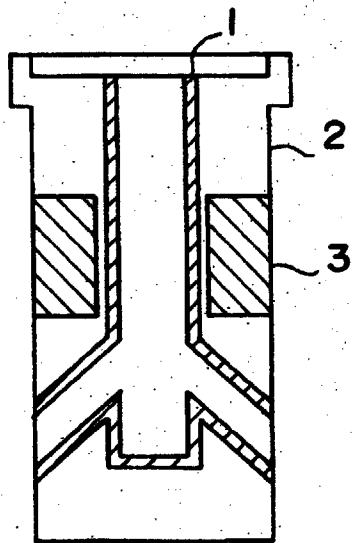
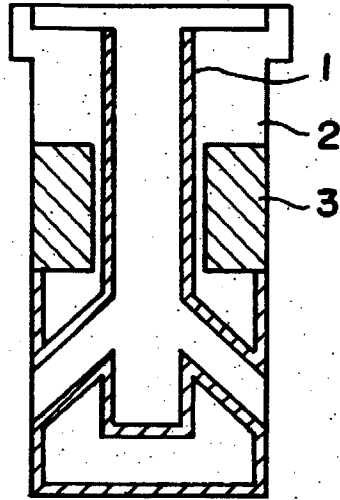


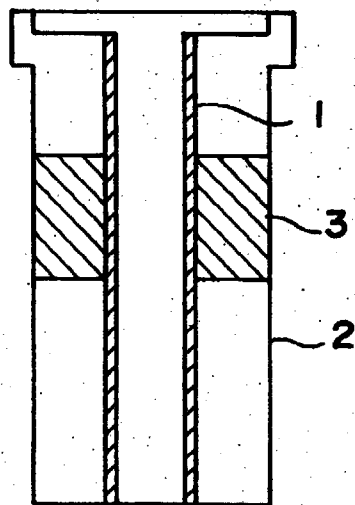
FIG. 2



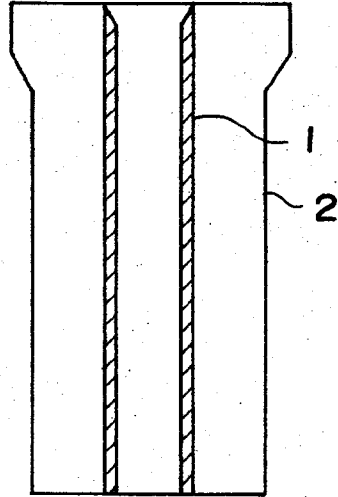
**FIG. 3**



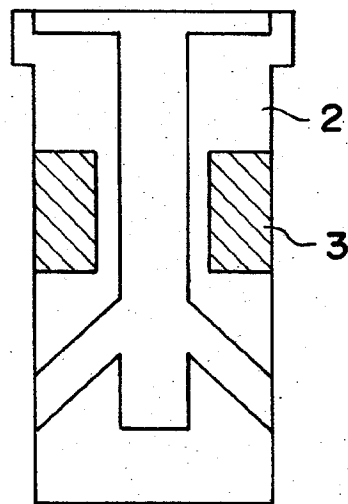
**FIG. 4**



**FIG. 5**



**FIG. 6**



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/01825

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. <sup>6</sup> B22D11/10, B22D41/54		
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) Int.Cl. <sup>6</sup> B22D11/10, B22D41/54, C04B35/44		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1997 Kokai Jitsuyo Shinan Koho 1971-1997 Jitsuyo Shinan Toroku Koho 1996-1998		
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.
Y	JP, 8-67558, A (Kawasaki Rozai K.K.), March 12, 1996 (12. 03. 96), Par. Nos. [0014], [0033], [0034] (Family: none)	1-4
Y	JP, 48-28008, A (Asahi Glass Co., Ltd.), April 13, 1973 (13. 04. 73), Claims ; Table 2 (Family: none)	1-3
Y	JP, 53-50215, A (Ibigawa Electric Industry Co., Ltd.), May 8, 1978 (08. 05. 78), Claims (Family: none)	1, 2
Y	JP, 7-330452, A (Harima Ceramic K.K., Nippon Steel Corp.), December 19, 1995 (19. 12. 95), Claims ; Tables 1, 2A (Family: none)	1-3
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search July 14, 1998 (14. 07. 98)	Date of mailing of the international search report July 21, 1998 (21. 07. 98)	
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer	
Facsimile No.	Telephone No.	

Form PCT/ISA/210 (second sheet) (July 1992)