



(11)

EP 2 434 025 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

21.03.2018 Bulletin 2018/12

(51) Int Cl.:

C21C 1/02 (2006.01)

(86) International application number:

PCT/JP2010/061366

(21) Application number: **10794262.5**

(22) Date of filing: **29.06.2010**

(87) International publication number:

WO 2011/002094 (06.01.2011 Gazette 2011/01)

(54) METHOD OF DESULFURIZATION OF MOLTEN IRON

VERFAHREN ZUR ENTSCHEFELUNG VON GESCHMOLZENEM EISEN

PROCÉDÉ DE DÉSULFURATION DE FER FONDU

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO SE SI SK SM TR**

(30) Priority: **30.06.2009 JP 2009155148**

25.12.2009 JP 2009294022

29.06.2010 JP 2010147015

(43) Date of publication of application:

28.03.2012 Bulletin 2012/13

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Description

Technical Field

5 **[0001]** The present invention relates to a method for desulfurizing hot metal (molten iron) by blowing a desulfurization agent from a top lance to the surface of hot metal that is being stirred with an impeller in a mechanical stirring desulfurization apparatus fitted with the impeller.

Background Art

10 **[0002]** Due to the recent increase in the amount of low-sulfur steel being produced, an efficient desulfurization treatment at the stage of hot metal processing is needed. A common hot metal desulfurization process uses a solid desulfurization agent such as calcium oxide (CaO). For example, there is an injection desulfurization process in which a CaO-based desulfurization agent is blown from a blowing injection lance to hot metal contained in a hot metal transport container
15 such as a torpedo car or a hot-metal ladle, or a mechanical stirring desulfurization process in which a stirring blade (also referred to as "impeller") is immersed in hot metal in a hot metal transport container and a CaO-based desulfurization agent is top-added to the hot metal that is being stirred with the rotating impeller.

[0003] In the desulfurization reaction using a CaO-based desulfurization agent, increasing the reaction interfacial area is effective in achieving high efficiency of the desulfurization reaction. Accordingly, the desulfurization reaction
20 efficiency is enhanced by reducing the size in diameter of the desulfurization agent that is added. In an actual mechanical stirring desulfurization process, the desulfurization agent supplied from a hopper is generally top-added into a treatment container such as a hot-metal ladle through a charging gate that is disposed above the treatment container. If the desulfurization agent in the form of fine particles is added in this manner, a large amount of the desulfurization agent will scatter (fly apart) or will be lifted by an updraft, resulting in a low addition yield of the desulfurization agent. As a
25 result, an efficient desulfurization treatment is not feasible.

[0004] To solve this problem, PTL 1 proposes a method for desulfurizing hot metal using a mechanical stirring desulfurization apparatus, in which a desulfurization agent is blasted together with a carrier gas through a top lance onto the surface of hot metal that is being stirred with an impeller, thereby performing a desulfurization treatment.
30 PTL 1 describes that blasting a fine particulate desulfurization agent having excellent reactivity together with a carrier gas reduces the occurrence of scattering during the addition of the desulfurization agent and improves the addition yield of the desulfurization agent.

It further describes that the fine particulate desulfurization agent has a large reaction interfacial area which promotes the desulfurization reaction, resulting in a markedly improved desulfurization rate. To permit the blasted desulfurization agent to be scattered (or dispersed), smoothly into the hot metal, PTL 1 describes that the horizontal distance R from
35 the center of the impeller to the blasting position of the desulfurization agent preferably satisfies the relation:

$$d/3 \leq R \leq d/2 + 1/3 \times (D - d)$$

40 (Formula (2), wherein D is the inner diameter of the treatment container containing the hot metal, and d is the diameter of the impeller) (paragraphs [0017] to [0020]).

Citation List

45 Patent Literature

[0005] PAL 1: Japanese Unexamined Patent Application Publication No. 2005-179690

Summary of Invention

50 Technical Problem

[0006] A substantial increase in reaction interfacial area is important in order to improve the desulfurization reaction efficiency per unit mass of the desulfurization agent. According to PTL 1, a powder desulfurization agent is blasted together with a carrier gas from a top lance onto the hot metal surface in order to avoid the aggregation of the desulfurization agent which can be a problem in top-adding the desulfurization agent from above the treatment container as well as to increase the substantial reaction interfacial area. As used herein, the term aggregation refers to a phenomenon in which

the particles of the added desulfurization agent combine together into spherical masses within or on the hot metal. It is necessary that the aggregation be suppressed in order to substantially increase the reaction interfacial area. Adding a desulfurization agent of finer particle size is a possible approach for suppressing the aggregation and reducing the size of the aggregates. However, a desulfurization agent that has been excessively reduced in size suffers a low addition yield even when the agent is blasted from a top lance.

[0007] Studying PTL 1 from the above viewpoint reveals that PTL 1 does not specify the size in diameter of the desulfurization agent and thus it must be said that it is difficult to add the desulfurization agent with a high addition yield as well as to achieve a stable desulfurization treatment with suppressed aggregation of the added desulfurization agent.

[0008] In a hot metal pretreatment process, hot metal is often subjected to a desiliconization treatment or a dephosphorization treatment prior to the desulfurization treatment. In such a case, the desulfurization treatment is carried out after the slag produced in the desiliconization treatment or the dephosphorization treatment is removed. However, the slag formed in the precedent step cannot be removed completely and a portion of the slag generated in the precedent step is inevitably mixed in the hot metal in variable amounts. Since both the desiliconization treatment and the dephosphorization treatment are refining treatments utilizing an oxidation reaction, the slag mixed in the hot metal is highly oxidized. This contaminant slag is incorporated in the hot metal when the hot metal is stirred with an impeller, and is reduced with carbon present in the hot metal. This phenomenon is the same as if oxygen is added to the hot metal, and thus the desulfurization treatment that is a reductive refining treatment is adversely affected. That is, the mixed slag inhibits the desulfurization reaction. This phenomenon is more influential in the blowing addition of a desulfurization agent through a top lance than in the top addition. The reason for this is that in the top addition method, the mixed slag and the desulfurization agent (the top-added flux) aggregate on the hot metal surface with the result that the mixed slag is not directly incorporated into the hot metal and thus is less likely to inhibit the desulfurization reaction, whilst blowing the desulfurization agent through a top lance permits the agent (the top-blown flux) to be present in so small an amount on the hot metal surface that the mixed slag is more likely to be incorporated directly.

[0009] The invention has been made in view of the problems described above. It is therefore an object of the invention to provide a method for desulfurizing hot metal by blowing a desulfurization agent from a top lance onto the surface of hot metal that is being stirred with an impeller in a mechanical stirring desulfurization apparatus fitted with the impeller, the method being capable of adding the desulfurization agent with a high addition yield while preventing the aggregation of the added desulfurization agent, and thereby desulfurizing the hot metal stably and highly efficiently.

[0010] JP-A-2008 050659 discloses a method according to the preamble of claim 1.

Solution to Problem

[0011] To achieve the above object, the present invention is directed to a method for desulfurizing hot metal using a mechanical stirring desulfurization apparatus, the method including the steps recited in claim 1.

[0012] Optionally, the desulfurization agent is blasted after a desulfurization slag that has been generated beforehand in a desulfurization treatment with a CaO-based desulfurization agent has been added onto the surface of the hot metal and thereafter the stirring of the hot metal with the impeller has been initiated.

Advantageous Effects of Invention

[0013] According to the present invention, the size in diameter of the CaO-based desulfurization agent that is blown from a top lance is specified to be in the range of 30 to 400 μm . Since the desulfurization agent does not contain fine particles that are scattered easily, the scattering during the blowing of the desulfurization agent is prevented. In addition, because the desulfurization agent does not contain large particles having a small reaction interfacial area and further because the aggregation of the added desulfurization agent is prevented, a large desulfurization reaction interfacial area is obtained to allow for stable and highly efficient desulfurization treatment. As a result, the methods of the invention provide industrial advantages such as the reduction of consumption of the desulfurization agent and the associated reduction of the amount of slag.

Brief Description of Drawings

[0014]

[Fig. 1] Fig. 1 is a schematic view of a mechanical stirring desulfurization apparatus used in the invention.

[Fig. 2] Fig. 2 is a diagram showing a relationship between the size in diameter of a CaO-based desulfurization agent (horizontal axis: mm) and the scatter (fly apart) ratio (vertical axis: %).

[Fig. 3] Fig. 3 is a diagram showing a relationship between the size in diameter of a CaO-based desulfurization agent (horizontal axis: mm) and the average size in diameter of desulfurization slag (vertical axis: mm).

[Fig. 4] Fig. 4 is a diagram showing a relationship between the size in diameter of a CaO-based desulfurization agent (horizontal axis: mm) and the sulfur concentration in desulfurized hot metal (vertical axis: mass %).

Description of Embodiments

[0015] The present invention will be described in detail hereinbelow.

[0016] The present inventors have carried out hot metal desulfurization tests using a mechanical stirring desulfurization apparatus. In detail, the desulfurization of hot metal was tested using an actual mechanical stirring desulfurization apparatus by blasting a CaO-based desulfurization agent together with a carrier gas through a top lance while changing the size in diameter of the desulfurization agent to determine the optimum range of the size in diameter of the desulfurization agent to be added. A schematic view of the mechanical stirring desulfurization apparatus used in the desulfurization tests is shown in Fig. 1.

[0017] Referring to Fig. 1, a hot-metal ladle 2 which contains hot metal 3 tapped from a blast furnace has been mounted on a carrying truck 1 and has been transported into the mechanical stirring desulfurization apparatus. The mechanical stirring desulfurization apparatus has a refractory impeller 4 that can be immersed or buried in the hot metal 3 contained in the hot-metal ladle 2 and can be rotated to stir the hot metal 3. The impeller 4 is configured so as to be capable of ascending and descending in a substantially vertical direction by an elevating device (not shown) and so as to be rotatable about a shaft 4a by a rotating device (not shown). Further, the mechanical stirring desulfurization apparatus is fitted with a top lance 5 for blasting a CaO-based desulfurization agent 7 onto the hot metal 3 in the hot-metal ladle 2. The top lance 5 is connected with a supply unit that is composed of a dispenser 8 containing the powdery CaO-based desulfurization agent 7 and a supplying device 9 for supplying predetermined amounts of the agent from the dispenser 8. The mechanical stirring desulfurization apparatus is configured such that the powdery CaO-based desulfurization agent 7 together with a carrier gas 10 can be supplied from the top lance 5 at the desired time. The carrier gas 10 may be a reducing gas, an inert gas or a non-oxidative gas. A dust hood 6 is provided above the hot-metal ladle 2, covering the hot-metal ladle 2. Exhaust gas and dust that are generated during the treatment are suctioned by a dust collector (not shown) through an exhaust gas duct (not shown) attached to the dust hood 6. In the illustrated desulfurization apparatus, the shaft 4a of the impeller 4 and the top lance 5 are provided so as to penetrate the dust hood 6 and to be vertically movable.

[0018] In the desulfurization tests, CaO-20 mass % Al_2O_3 having sizes in diameter of 10 to 1000 μm was used as the CaO-based desulfurization agent 7. The tests examined the scattering behavior of the CaO-based desulfurization agent 7, the particle diameter of the desulfurization slag resulting from the treatment, and the desulfurization behavior. Table 1 describes the desulfurization treatment conditions. In the present invention, the size in diameter of the desulfurization agent is defined based on sieving. Even if a particle has a spindle shape with a longer diameter that is larger than the opening of the sieve, the particle is defined as being smaller than the opening of the sieve as long as it can pass through the sieve. In the desulfurization tests in which the diameter of the desulfurization agent was changed to various diameters, the size in diameter of the CaO-based desulfurization agent 7 had been adjusted to be the average size in diameter $\pm 10\%$.

[Table 1]

[0019]

Table 1

Hot metal	Mass		300 tons
	Temperature		1280 to 1320°C
	Chemical composition	C	4.2 mass %
		Si	0.02 mass %
		P	0.10 mass %
		Mn	0.2 mass %
S		0.03 mass %	
Desulfurization agent	Composition		CaO-20 mass % Al ₂ O ₃
	Size in diameter		10 to 1000 μm
	Addition amount		7 kg/hot metal-ton
Inner diameter of treatment container			4 m

(continued)

Stirring	Impeller diameter	1.45 m
	Rotational speed	120 rpm
	Time	15min

[0020] The hot-metal ladle 2 containing 300 tons of the hot metal 3 at 1280 to 1320°C was mounted on the carrying truck 1. The truck 1 carrying the hot-metal ladle 2 was positioned such that the impeller 4 would be located substantially at the center of the hot-metal ladle 2. The impeller 4 was then lowered and immersed in the hot metal 3. After the impeller 4 was immersed in the hot metal 3, rotation of the impeller 4 was initiated and the rotational speed was increased to a predetermined rotational speed (120 rpm). After the rotational speed of the impeller 4 reached the predetermined rotational speed, the supplying device 9 was activated to blow the CaO-based desulfurization agent 7 contained in the dispenser 8, together with the carrier gas, from the top lance 5 onto the surface of the hot metal 3, thereby performing desulfurization treatment. In this desulfurization test, the top lance 5 was located at a position such that the distance (A) was equal to $(1/2) \times D$ wherein A was the horizontal distance (m) from the center of the hot-metal ladle 2 to the center of the top lance 5, and D was the inner radius (m) of the hot-metal ladle 2 that was the treatment container, and further such that the distance from the still, namely, unruffled surface of the hot metal 3 in the hot-metal ladle to the tip of the top lance 5 (also referred to as "lance height") was 1.0 m. The distance (A) was larger than the impeller radius (R) (m). The top lance 5 was located at this position so as to face down in the vertical direction. The carrier gas was nitrogen gas.

[0021] After a predetermined amount (7 kg/hot metal-ton) of the CaO-based desulfurization agent 7 was added and stirring was performed for a predetermined time (15 min), the operation of the impeller 4 was terminated. When the rotation of the impeller 4 stopped, the impeller 4 was raised and held above the hot-metal ladle 2. The produced desulfurization slag surfaced and covered the surface of the hot metal. When the desulfurization slag became static, the desulfurization treatment of the hot metal 3 was complete.

[0022] After the completion of the desulfurization treatment, a sample was collected from the hot metal 3 and was analyzed to determine the sulfur content in the hot metal. In addition, 10 kg of the desulfurization slag floating on the hot metal was collected, and the average size in diameter of the desulfurization slag was calculated by particle size distribution measurement. Further, the amount of the CaO-based desulfurization agent 7 that had been trapped on the filter of the dust collector during the desulfurization treatment was measured. The scatter ratio was determined by expressing the measured amount relative to the amount of the added desulfurization agent as a percentage. Similarly to the size in diameter of the desulfurization agent, the size in diameter of the desulfurization slag is defined based on sieving. Even if a particle has a spindle shape with a longer diameter that is larger than the opening of the sieve, the particle is defined as being smaller than the opening of the sieve as long as it can pass through the sieve. The average size in diameter of the desulfurization slag measured herein is a weighted average size in diameter determined using the method described in "Huntai Kougaku Sousho (Powder Engineering Library), Vol. 1, Huntai no Kiso Bussei (Basic Properties of Powder), edited by The Society of Powder Technology, Japan, published from THE NIKKAN KOGYO SHIMBUN, LTD., pp. 8-12". Of the distribution references r (0 (number), 1 (length), 2 (area) and 3 (volume)) that are described in the literature, the reference 1 is adopted in the invention. (Namely, the length distribution is adopted as the distribution reference.)

[0023] The relationship between the size in diameter of the CaO-based desulfurization agent (horizontal axis: mm) and the scatter ratio (vertical axis: %) is shown in Fig. 2. Fig. 3 shows the relationship between the size in diameter of the CaO-based desulfurization agent and the average size in diameter of the desulfurization slag (vertical axis: mm). As shown in Figs. 2 and 3, the scatter ratio markedly increased to 80% or more when the size in diameter of the desulfurization agent was less than 30 μm ; on the other hand, although the average size in diameter of the desulfurization slag increased with increasing size in diameter of the desulfurization agent, the increase in the average size in diameter of the desulfurization slag was small when the size in diameter of the desulfurization agent was 400 μm or less. When the size in diameter of the desulfurization agent was more than 400 μm , the scatter ratio was low but the average size in diameter of the desulfurization slag was so large that an increase in reaction interfacial area was not expected.

[0024] The relationship between the size in diameter of the CaO-based desulfurization agent and the sulfur concentration in the desulfurized hot metal (vertical axis: mass %) is shown in Fig. 4. As was expected from the results of the scatter ratio and the average size in diameter of the desulfurization slag, the tests showed that controlling the size in diameter of the CaO-based desulfurization agent 7 within the range of 30 to 400 μm allowed for stable desulfurization to the level of low-sulfur steel. The size in diameter of the desulfurization agent on the horizontal axis in Figs. 2 to 4 was the average size in diameter of the desulfurization agent that had been classified in terms of size in diameter so as to have the average size in diameter $\pm 10\%$.

[0025] The present invention was made on the basis of the test results described above. That is, the method for

desulfurizing hot metal using a mechanical stirring desulfurization apparatus according to the invention includes blasting a CaO-based desulfurization agent having a size in diameter of 30 to 400 μm , together with a carrier gas, through a top lance onto the surface of hot metal that is being stirred with an impeller to desulfurized the hot metal.

[0026] Furthermore, tests were carried out in which the CaO-based desulfurization agent 7 having a size in diameter of 30 to 400 μm was blasted while changing the position of the top lance 5 in the direction of the radius of the hot-metal ladle 2. Provided that the radius of the impeller 4 was R (m), the impeller radius (R) was not more than 1/2 of the inner radius (D) of the hot-metal ladle 2 ($R \leq (1/2) \times D$). The top lance 5 was provided so as to be facing down in the vertical direction, and the lance height was constant at 1.0 m. The impeller 4 was positioned at substantially the center of the hot-metal ladle 2.

[0027] In the tests, good results were stably obtained when the horizontal distance (A) from the center of the hot-metal ladle 2 to the center of the top lance 5 was equal to or greater than the distance from the center of the impeller 4 to the outer periphery of the impeller 4, namely, the impeller radius (R), and was equal to or less than half (1/2) the inner radius (D) of the hot-metal ladle 2, i.e., ($R \leq A \leq (1/2) \times D$). Within this range, the average sulfur concentration in the desulfurized hot metal was 0.0007 mass % (variations: 0.0006 to 0.0015 mass %), the scatter ratio of the desulfurization agent was 5 to 10%, and the size in diameter of the desulfurization slag was 5 to 10 mm.

[0028] When the top lance 5 was located more inside toward the center of the hot-metal ladle 2 than the above preferred range (i.e., when the top lance was located at a position from the center of the hot-metal ladle to a position within the outer periphery of the impeller 4, $0 \leq A < R$), the desulfurization agent formed into a giant mass in the vicinity of the position at which it was added. Consequently, the size in diameter of the desulfurization slag became excessively large, and the desulfurization agent attached to the shaft 4a of the impeller 4 and its performance in the desulfurization reaction deteriorated. When the position was outside the above preferred range ($(1/2) \times D < A \leq D$), the scatter ratio of the desulfurization agent was increased and the size in diameter of the desulfurization slag became larger as the position became further outside.

[0029] These results were ascribed to the fact that the vortex produced by the impeller 4 formed a region on and within the hot metal in which the flow was downward in the vertical direction, and the desulfurization agent 7 which was blasted onto this region was incorporated into the hot metal and the desulfurization reaction proceeded. If the top lance was too close to the center of the hot-metal ladle 2, the desulfurization agent 7 accumulated to form a mass on the part of the hot metal which was rotating at the same speed as the impeller 4. If the top lance was located too far outside, the addition of the desulfurization agent took place on the flow that was upward in the vertical direction on and within the hot metal. In such case, the agent required some time before it was incorporated into the hot metal and scattered and aggregated during that period.

[0030] Thus, it has been found that when the top lance 5 is located so as to face down in the vertical direction under the conditions where the impeller radius (R) satisfies the relationship of Equation (1) below with respect to the inner radius (D) of the hot-metal ladle 2, a high desulfurization rate is achieved by locating the top lance 5 at a position satisfying the relationship of Equation (2) below.

$$R \leq (1/2) \times D \cdots (1)$$

$$R \leq A \leq (1/2) \times D \cdots (2)$$

[0031] In Equations (1) and (2), D is the inner radius (m) of the treatment container containing the hot metal, R is the radius (m) of the impeller, and A is the horizontal distance (m) from the center of the treatment container to the center of the top lance.

[0032] In actual operation, the above conditions and so on are preferably regulated so as to control the scatter ratio of the desulfurization agent to not more than 40% and the size in diameter of the desulfurization slag to not more than 14 mm. The impeller 4 (and the rotational shaft) is not necessarily positioned at the center of the treatment container and may be positioned eccentrically without any problems in stirring.

[0033] The size of the impeller and the treatment container may be determined appropriately in accordance with the amount of hot metal to be treated (generally 250 to 350 tons) and the desired level of stirring. As a guideline, R is preferably D/3 or more from the viewpoint of stirring.

[0034] The carrier gas for blowing the CaO-based desulfurization agent 7 through the top lance 5 may be a reducing gas, an inert gas or a non-oxidative gas. Examples of the reducing gases include hydrocarbon gases. An example of the inert gases is argon gas. An example of the non-oxidative gases is nitrogen gas. Because the desulfurization reaction of hot metal is a reduction reaction, a reducing gas is best suited as the carrier gas. That is, the carriage with the reducing gas is advantageous over the other gases because it lowers the oxygen partial pressure at the reaction interface and

accelerates the desulfurization reaction. In particular, the oxygen partial pressure at the hot metal-desulfurization agent interface can be ideally lowered under conditions where the fine particulate desulfurization agent is incorporated into the hot metal.

[0035] The CaO-based desulfurization agent 7 may be any substance that is based on calcium oxide (CaO) or, in other words, contains CaO at not less than 50 mass %. In particular, burned lime and limestone or the like may be used singly or as a mixture with Al_2O_3 or CaF_2 or the like as an agent which promotes melting. Further, dolomite (CaO-MgO) or the like may be used as the CaO-based desulfurization agent 7. Increasing the Al_2O_3 proportion in, for example, a CaO-based, CaO- Al_2O_3 desulfurization agent 7 (containing 5 mass % or less of residual impurities) results in an increased amount of the liquid phase. However, excessive formation of the liquid phase is not recommended because it facilitates the aggregation of the particulate desulfurization agent and leads to the reduction of the reaction interfacial area. Namely, it has been found that the Al_2O_3 proportion has an appropriate range in the CaO- Al_2O_3 desulfurization agent through the study of the present inventors- The metallic aluminum added herein (for example, aluminum contained in aluminum ash as the raw material) is regarded as an active ingredient that is the Al_2O_3 source in the CaO- Al_2O_3 -based desulfurization agent.

[0036] In the present invention, it is preferable that a desulfurization slag have been collected beforehand which has been produced in a desulfurization treatment with a CaO-based desulfurization agent prior to the desulfurization treatment. This collected desulfurization slag is added onto the hot metal in the hot-metal ladle 2 prior to the initiation of the stirring of the hot metal 3 with the impeller 4 and thereafter the hot metal 3 is stirred with the impeller 4 to incorporate the added desulfurization slag into the hot metal. Alternatively, the collected desulfurization slag is top-added onto the hot metal 3 that is being stirred with the impeller 4, thereby incorporating the added desulfurization slag into the hot metal. Thereafter, the CaO-based desulfurization agent 7 is added from the top lance 5. The reason why the addition of the CaO-based desulfurization agent 7 from the top lance 5 is initiated after the desulfurization slag is incorporated into the hot metal is that the powdery CaO-based desulfurization agent 7 added from the top lance 5 can be efficiently incorporated into the hot metal. That is, the added desulfurization slag remains on the surface of the hot metal for some time even though the hot metal 3 is being stirred with the impeller 4, and the presence of such a slag inhibits the incorporation of the desulfurization agent from the top lance 5 into the hot metal 3. The time required for the added collected slag to be incorporated into the hot metal varies in accordance with the facility or operation conditions, but the incorporation can be easily visually confirmed.

[0037] Generally, hot metal tapped from a blast furnace is initially subjected to a desiliconization treatment and/or a dephosphorization treatment. After the desiliconization treatment and/or the dephosphorization treatment, the slag containing iron oxide that has been generated in the treatment is discharged. However, it is difficult that the slag be completely discharged from the container, and a portion of the slag containing iron oxide remains. That is, such a slag containing iron oxide has remained in the hot-metal ladle 2 before the initiation of the desulfurization treatment.

[0038] Even in the case where the desulfurization treatment is the first step, blast furnace slag or desiliconization slag generated at a blast furnace runner finds its way into the hot-metal ladle 2 and comes to be present in the desulfurization treatment. In this case, the desulfurization reaction is adversely affected by the components in the slags that have come to be present in the desulfurization treatment step, namely iron oxide contained in a desiliconization agent and a dephosphorization agent, and SiO_2 contained in the desiliconization slag, the dephosphorization slag and the blast furnace slag.

[0039] Iron oxide is disadvantageous for the desulfurization reaction that is a reduction reaction. SiO_2 in combination with CaO that is the main component of the desulfurization agent lowers the basicity in the reaction site and decreases the desulfurization performance.

[0040] By adding the previously collected desulfurization slag into the hot-metal ladle before the CaO-based desulfurization agent 7 is added to the hot metal 3 and subsequently stirring the hot metal 3 together with the added desulfurization slag, the residual iron oxide-containing slag or the residual SiO_2 -containing slag is mixed with the desulfurization slag, and the desulfurization slag adheres to the surface of the iron oxide-containing slag or the SiO_2 -containing slag with the result that the residual slag is coated (sort of) with the desulfurization slag. Even if the iron oxide-containing slag or the SiO_2 -containing slag is incorporated into the hot metal, such a slag has been surrounded by the high-melting desulfurization slag and does not contact directly with the hot metal 3. Thus, the iron oxide-containing slag or the SiO_2 -containing slag is prevented from adversely affecting the desulfurization reaction.

[0041] That is, the addition of the previously collected desulfurization slag prevents the supply of oxygen from the residual iron oxide-containing slag to the hot metal 3 or prevents the residual SiO_2 -containing slag from lowering the basicity in the reaction site. As a result, the residual slags are prevented from inhibiting the desulfurization reaction that is a reduction reaction.

[0042] In particular, the addition of the desulfurization slag is more effective in the case where the desulfurization agent is blown from the top lance 5 to the hot metal surface.

[0043] The present inventors have confirmed that when the desulfurization treatment is performed after a desiliconization treatment, the addition of the previously collected desulfurization slag into the hot-metal ladle before starting the

stirring of the hot metal 3 with the impeller 4 results in a desulfurization slag in which the central portion has a high concentration of iron oxide and is based on SiO_2 , and the peripheral portion is based on CaO .

[0044] According to the present invention described hereinabove, the CaO -based desulfurization agent 7 that is blown from the top lance 5 has a size in diameter controlled within the range of 30 to 400 μm and thus can be prevented from scattering during the blowing. In addition, the aggregation of the added desulfurization agent is prevented and the desulfurization reaction interfacial area is increased, thereby realizing stable and highly efficient desulfurization treatment.

EXAMPLES

EXAMPLE 1

[0045] Hot metal was desulfurized using a mechanical stirring desulfurization apparatus illustrated in Fig. 1 and CaO -20 mass % Al_2O_3 as the CaO -based desulfurization agent (amount of added desulfurization agent: 7 kg/hot metal-ton). The results are described below. Nitrogen gas was used as the carrier gas for the CaO -based desulfurization agent. The impeller had four non-inclined blades. The impeller was located substantially at the center of the hot-metal ladle.

[0046] The operation conditions were as follows. Four levels of the size in diameter of the CaO -based desulfurization agent were adopted: 20 μm or less (Comparative Example 1), 500 to 1000 μm (Comparative Example 2), 200 to 400 μm (Inventive Example 1) and 30 to 100 μm (Inventive Examples 2 to 5). In Comparative Examples 1 and 2 and Inventive Examples 1 and 2, the top lance was located at a position satisfying Equation (2) described hereinabove to examine the influence of the size in diameter of the desulfurization agent on the desulfurization reaction. In Inventive Examples 3 and 4, the top lance was located at a position failing to satisfy Equation (2) described hereinabove to examine the influence of the position of the top lance on the desulfurization reaction. In Inventive Example 5, the top lance was located at a position satisfying Equation (2) described hereinabove and a previously collected desulfurization slag was added onto the hot metal before the impeller was rotated. The operation conditions other than the size in diameter of the CaO -based desulfurization agent and the position of the top lance were in accordance with Table 1. Each test consisted of 100 charges (ch). The operation conditions and the results are described in Table 2.

[Table 2]

[0047]

Table 2

	Size in diameter of desulfurization agent (μm)	Amount of recycled desulfurization slag (tons/ch)	Position of top lance (distance A)	Average S concentration in hot metal (mass %)		Maximum S concentration in desulfurized hot metal (mass %)	Rate of S < 0.003 mass % achievement after treatment (%)
				Before desulfurization	After desulfurization		
Comparative Example 1	≤ 20	0	$R \leq A \leq D/2$	0.029	0.0039	0.0080	20
Comparative Example 2	500 to 1000	0	$R \leq A \leq D/2$	0.028	0.0048	0.0110	11
Inventive Example 1	200 to 400	0	$R \leq A \leq D/2$	0.030	0.0009	0.0020	100
Inventive Example 2	30 to 100	0	$R \leq A \leq D/2$	0.029	0.0017	0.0034	90
Inventive Example 3	30 to 100	0	$0 \leq A < R$	0.031	0.0022	0.0050	80
Inventive Example 4	30 to 100	0	$D/2 < A \leq D$	0.031	0.0023	0.0052	77
Inventive Example 5	30 to 100	1.0	$R \leq A \leq D/2$	0.031	0.0007	0.0015	100
D: inner radius of hot-metal ladle; R: radius of impeller; A: distance from center of hot-metal ladle to center of top lance							

[0048] As shown in Table 2, Inventive Examples 1 and 2 achieved a lower average sulfur concentration in the desulfurized hot metal than in Comparative Examples 1 and 2. By comparing Inventive Examples 3 and 4 in which the position of the top lance was outside the preferred range according to the present invention with Inventive Example 2 in which the top lance was located in the preferred range of the invention, Inventive Example 2 was found to achieve higher desulfurization efficiency. Further, Inventive Example 5 which involved the recycling of desulfurization slag resulted in a further lowered average sulfur concentration in the desulfurized hot metal with smaller variations.

EXAMPLE 2

[0049] PTL 1 considers the locating position for a top lance from the viewpoint of the scattering or dispersion of a desulfurization agent into hot metal. In order to ascertain the relation of the locating position with the preferred position of the top lance in the present invention, a desulfurization treatment was carried out under various conditions described in Table 3. The operation conditions other than those shown in Table 3 were similar to those in EXAMPLE 1. Each test consisted of 100 charges.

[Table 3]

[0050]

Table 3

	Size in diameter of desulfurization agent (μm)	Addition amount of desulfurization agent (kg/t)	Amount of recycled desulfurization slag (kg/t)	Time until addition of desulfurization agent from top lance (minutes after starting operation)	Amount of Al_2O_3 mixed with desulfurization agent (weight % relative to the total amount of the agent)	Carrier gas for desulfurization agent from top lance	Position of top lance (distance A (m))'	Average S concentration in hot metal (mass %)		Maximum S concentration in desulfurized hot metal (mass %)	Rate of S < 0.003 mass % achievement after treatment (%)	Desulfurization agent addition method
								Before desulfurization	After desulfurization			
Comparative Example 3	200 to 400	5	0	-	20	-	-	0.030	0.0150	0.0220	48	Top addition
Inventive Example 6	200 to 400	5	0	0	20	N_2	$0.50 \leq \frac{(2R)}{3 \leq A} < R$	0.027	0.0037	0.0130	67	Blasting
Inventive Example 7	200 to 400	5	0	0	20	N_2	$0.60 \leq \frac{(2R)}{3 \leq A} < R$	0.028	0.0035	0.0110	70	Blasting
Inventive Example 8	200 to 400	5	0	0	20	N_2	$\frac{D}{2} < A \leq \frac{(2D)}{3 + R/3}$	0.030	0.0039	0.0200	65	Blasting
Inventive Example 9	200 to 400	5	0	0	20	N_2	$\frac{D}{2} < A \leq \frac{(2D)}{3 + R/3}$	0.028	0.0042	0.0210	60	Blasting
Inventive Example 10	200 to 400	5	0	0	20	N_2	$0.75 \leq \frac{R}{A} \leq \frac{D}{2}$	0.030	0.0017	0.0027	100	Blasting

(continued)

	Size in diameter of desulfurization agent (μm)	Addition amount of desulfurization agent (kg/t)	Amount of recycled desulfurization slag (kg/t)	Time until addition of desulfurization agent from top lance (minutes after starting operation)	Amount of Al ₂ O ₃ mixed with desulfurization agent (weight % relative to the total amount of the agent)	Carrier gas for desulfurization agent from top lance	Position of top lance (distance A (m))'	Average S concentration in hot metal (mass %)		Maximum S concentration in desulfurized hot metal (mass %)	Rate of S < 0.003 mass % achievement after treatment (%)	Desulfurization agent addition method
								Before desulfurization	After desulfurization			
Inventive Example 11	200 to 400	5	0	0	20	N ₂	1.00 ≤ R ≤ A ≤ D/2	0.029	0.0018	0.0028	100	Blasting

D: inner radius of hot-metal ladle; R: radius of impeller; A: distance from center of hot-metal ladle to center of top lance
*Formula (2) which indicates a preferred condition in PTL 1 is represented as (2R)/3≤A≤(2D)/3+R/3 using the symbols used in the present invention. Accordingly, Inventive Examples 6 to 9 satisfy Formula (2) of PTL 1 but do not satisfy the preferred range R≤A≤D/2 according to the present invention.

[0051] In the tests carried out in Inventive Examples 6 to 9, the position of the top lance satisfied the preferred range according to PTL 1, i.e., $d/3 \leq R \leq d/2 + 1/3 \times (D - d)$ (or $(2R)/3 \leq A \leq R + (1/3) \times (2D - 2R)$) when expressed with the symbols used in the present invention, and the right side is rearranged to $(2D)/3 + R/3$, but failed to satisfy the preferred range according to the present invention, $R \leq A \leq (1/2) \times D$. Inventive Examples 6 to 9 resulted in improved desulfurization efficiency compared to Comparative Example 3 which adopted the conventional top addition method. However, Inventive Examples 10 and 11 satisfying the preferred range of the invention achieved further markedly improved desulfurization efficiency. That is, the maximum S concentration after the desulfurization and the rate of $S < 0.003$ mass % achievement in Inventive Examples 10 and 11 demonstrate that the present invention realizes a high level of desulfurization with very small variations.

EXAMPLE 3

[0052] A desulfurization treatment was carried out under various conditions shown in Table 4. The results are described in Table 4. The operation conditions other than those shown in Table 4 were similar to those in EXAMPLE 1. Inventive Examples 12 to 16 shown in Table 4 ascertained the influence of the stirring time starting from the addition of recycled desulfurization slag (collected slag) beforehand to the initiation of the addition of the desulfurization agent through the top lance. In Inventive Examples 17 to 22, the influence of the amount of Al_2O_3 mixed in the $CaO-Al_2O_3$ -based desulfurization agent was ascertained. Inventive Examples 23 and 24 ascertained the influence of the carrier gas used for the desulfurization agent.

[Table 4]

[0053]

Table 4

	Size in diameter of desulfurization agent (μm)	Addition amount of desulfurization agent (kg/t)	Amount of recycled desulfurization slag (kg/t)	Time until addition of desulfurization agent from top lance (minutes after starting operation)	Amount of Al_2O_3 mixed with desulfurization agent (weight % relative to the total amount of the agent)	Carrier gas for desulfurization agent from top lance	Position of top lance (distance A)	Average S concentration in hot metal (mass %)		Maximum S concentration in desulfurized hot metal (mass %)	Rate of S < 0.003 mass % achievement after treatment (%)
								Before desulfurization	After desulfurization		
Inventive Examples 12	200 to 400	5	1	0	20	N_2	$R \leq A \leq \frac{D}{2}$	0.029	0.0016	0.0042	87
Inventive Example 13	200 to 400	5	1	4	20	N_2	$R \leq A \leq \frac{D}{2}$	0.029	0.0019	0.0051	86
Inventive Example 14	200 to 400	5	1	5	20	N_2	$R \leq A \leq \frac{D}{2}$	0.030	0.0022	0.0066	85
Inventive Example 15	200 to 400	5	1	2	20	N_2	$R \leq A \leq \frac{D}{2}$	0.031	0.0011	0.0015	100
Inventive Example 16	200 to 400	5	1	3	20	N_2	$R \leq A \leq \frac{D}{2}$	0.031	0.0010	0.0020	100
Inventive Example 17	200 to 400	5	1	2	0	N_2	$R \leq A \leq \frac{D}{2}$	0.033	0.0045	0.0120	65
Inventive Example 18	200 to 400	5	1	2	35	N_2	$R \leq A \leq \frac{D}{2}$	0.031	0.0029	0.0055	82
Inventive Example 19	200 to 400	5	1	2	40	N_2	$R \leq A \leq \frac{D}{2}$	0.032	0.0036	0.0069	81

	Size in diameter of desulfurization agent (μm)	Addition amount of desulfurization agent (kg/t)	Amount of recycled desulfurization slag (kg/t)	Time until addition of desulfurization agent from top lance (minutes after starting operation)	Amount of Al ₂ O ₃ mixed with desulfurization agent (weight % relative to the total amount of the agent)	Carrier gas for desulfurization agent from top lance	Position of top lance (distance A)	Average S concentration in hot metal (mass %) Before desulfurization After desulfurization	Maximum S concentration in desulfurized hot metal (mass %)	Rate of S < 0.003 mass % achievement after treatment (%)
Inventive Example 20	200 to 400	5	1	2	20	N ₂	R ≤ A ≤ D/ 2	0.031 0.0011	0.0015	100
Inventive Example 21	200 to 400	5	1	2	30	N ₂	R ≤ A ≤ D/ 2	0.030 0.0013	0.0022	100
Inventive Example 22	200 to 400	5	1	2	10	N ₂	R ≤ A ≤ D/ 2	0.030 0.0015	0.0026	100
Inventive Examples 23	200 to 400	5	0	0	20	N ₂	R ≤ A ≤ D/ 2	0.029 0.0018	0.0028	100
Inventive Example 24	200 to 400	5	1	2	20	propane	R ≤ A ≤ D/ 2	0.033 0.0006	0.0010	100

D: inner radius of hot-metal ladle; R: radius of impeller; A: distance from center of hot-metal ladle to center of top lance

[0054] It had been confirmed that in the desulfurization apparatus used in EXAMPLES, it took approximately 1 minute for the added desulfurization slag (collected slag) to be incorporated into the hot metal. Of Inventive Examples 12 to 16, the desulfurization efficiency was particularly excellent in Inventive Examples 15 and 16 in which the stirring time was 2 minutes and 3 minutes, respectively. Inventive Examples 13 and 14 in which the stirring time was 4 minutes or more resulted in lower desulfurization efficiency, probably because with a given constant total stirring time assigned in the test, a sufficient time was not allowed after the desulfurization agent was added. Thus, in this mechanical stirring desulfurization apparatus, the stirring time was found to be particularly suitably 3 minutes or less.

[0055] The results in Inventive Examples 17 to 22 showed that in the mechanical stirring desulfurization apparatus used in EXAMPLES, the amount of Al_2O_3 mixed in the $\text{CaO-Al}_2\text{O}_3$ desulfurization agent was particularly suitable in the range of 10 to 30% (weight % relative to the total amount of the agent). The results in Inventive Examples 23 and 24 confirmed that the desulfurization efficiency was further improved by using a reducing gas (propane gas (hydrocarbon gas) in Inventive Example 24) as the carrier gas.

[0056] It was also confirmed that the advantageous effects of the invention were achieved without any particular problems even when known desulfurization agents and known carrier gases other than those used in EXAMPLES were employed. However, the use of the $\text{CaO-Al}_2\text{O}_3$ desulfurization agent as the desulfurization agent was found to be advantageous in achieving the effects of the invention.

Industrial Applicability

[0057] The methods of the present invention realize highly efficient desulfurization treatment, namely desulfurization to a sulfur concentration of, for example, 0.003 mass %, with small variations of the results and with stability. As a result, the methods provide industrial advantages such as the reduction of consumption of the desulfurization agent and the associated reduction of the amount of slag.

Reference Signs List

[0058]

- 1 CARRYING TRUCK
- 2 HOT-METAL LADLE (TREATMENT CONTAINER)
- 3 HOT METAL
- 4 IMPELLER
- 4a IMPELLER SHAFT
- 5 TOP LANCE
- 6 DUST HOOD
- 7 CaO-BASED DESULFURIZATION AGENT
- 8 DISPENSER
- 9 SUPPLYING DEVICE
- 10 CARRIER GAS
- A HORIZONTAL DISTANCE FROM CENTER OF TREATMENT CONTAINER TO CENTER OF TOP LANCE
- R RADIUS OF IMPELLER
- D INNER RADIUS OF TREATMENT CONTAINER

Claims

1. A method for desulfurizing hot metal (3) using a mechanical stirring desulfurization apparatus, the method comprising blasting a CaO-based desulfurization agent (7) having a size in diameter of 30 to 400 μm , together with a carrier gas (10), through a top lance (5) onto the surface of hot metal (3) that is being stirred with an impeller (4) to desulfurize the hot metal (3), wherein the top lance (5) is provided so as to face down in the vertical direction;

characterized in that

the radius R of the impeller (4) satisfies the relation of Equation (1) below with respect to the inner radius D of the treatment container, and the horizontal distance A from the center of the treatment container to the center of the top lance (5) satisfies the relation of Equation (2) below with respect to the inner radius D and the radius R of the impeller (4):

$$R \leq 1/2 \times D \quad \dots (1)$$

$$R \leq A \leq 1/2 \times D \quad \dots (2) .$$

2. The method for desulfurizing hot metal (3) according to Claim 1, wherein the desulfurization agent (7) is blasted after a desulfurization slag that has been generated beforehand in a desulfurization treatment with a CaO-based desulfurization agent (7) has been added onto the surface of the hot metal (3) and thereafter the stirring of the hot metal (3) with the impeller (4) has been initiated.

Patentansprüche

1. Verfahren zum Entschwefeln flüssigen Metalls (3), das eine mechanische Rührentschwefelungsvorrichtung verwendet, wobei das Verfahren ein Strahlen eines CaO-basierten Entschwefelungsmittels (7) mit einer Größe im Durchmesser von 30 bis 400 μm zusammen mit einem Trägergas (10) durch eine obere Lanze (5) auf die Oberfläche des flüssigen Metalls (3), welches mit einem Impeller (4) gerührt wird, um das flüssige Metall (3) zu entschwefeln, aufweist, wobei die obere Lanze (5) so bereitgestellt ist, dass sie in der vertikalen Richtung nach unten weist; **dadurch gekennzeichnet, dass** der Radius R des Impellers (4) die Beziehung der Gleichung (1) unten in Bezug auf den inneren Radius D des Bearbeitungsbehälters erfüllt und der horizontale Abstand A vom Zentrum des Bearbeitungsbehälters zu dem Zentrum der oberen Lanze (5) die Beziehung der Gleichung (2) unten in Bezug auf den inneren Radius D und den Radius R des Impellers (4) erfüllt:

$$R \leq 1/2 \times D \quad \dots (1)$$

$$R \leq A \leq 1/2 \times D \quad \dots (2) .$$

2. Verfahren zum Entschwefeln flüssigen Metalls (3) nach Anspruch 1, wobei, nachdem eine zuvor in einer Entschwefelungsbehandlung mit einem CaO-basierten Entschwefelungsmittel (7) erzeugte Entschwefelungsschlacke auf die Oberfläche des flüssigen Metalls (3) aufgebracht wurde und danach das Rühren des flüssigen Metalls (3) mit dem Impeller (4) gestartet wurde, das Entschwefelungsmittel (7) gestrahlt wird.

Revendications

1. Procédé de désulfuration d'un métal chaud (3) en utilisant un appareil de désulfuration par agitation mécanique, le procédé comprenant la projection d'un agent de désulfuration (7) à base de CaO présentant une dimension en diamètre de 30 à 400 μm , avec un gaz vecteur (10), via une lance supérieure (5) sur la surface de métal chaud (3) qui est agitée avec une pâle (4) pour désulfurer le métal chaud (3), dans lequel la lance supérieure (5) est ménagée de manière à être tournée vers le bas en direction verticale ;

caractérisé en ce que

le rayon R de la pâle (4) satisfait la relation de l'Équation (1) ci-dessous par rapport au rayon interne D du récipient de traitement, et la distance horizontale A depuis le centre du récipient de traitement au centre de la lance supérieure (5) satisfait la relation de l'Équation (2) ci-dessous par rapport au rayon intérieur D et au rayon R de la pâle (4) :

$$R \leq 1/2 \times D \quad \dots (1)$$

$$R \leq A \leq 1/2 \times D \quad \dots (2)$$

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2. Procédé de désulfuration de métal chaud (3) selon la revendication 1, dans lequel l'agent de désulfuration (7) est projeté après qu'un laitier de désulfuration, qui a été généré auparavant dans un traitement de désulfuration avec un agent de désulfuration (7) à base de CaO , a été ajouté à la surface du métal chaud (3) et qu'ensuite l'agitation du métal chaud (3) avec la pôle (4) a été entrepris.

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FIG. 1

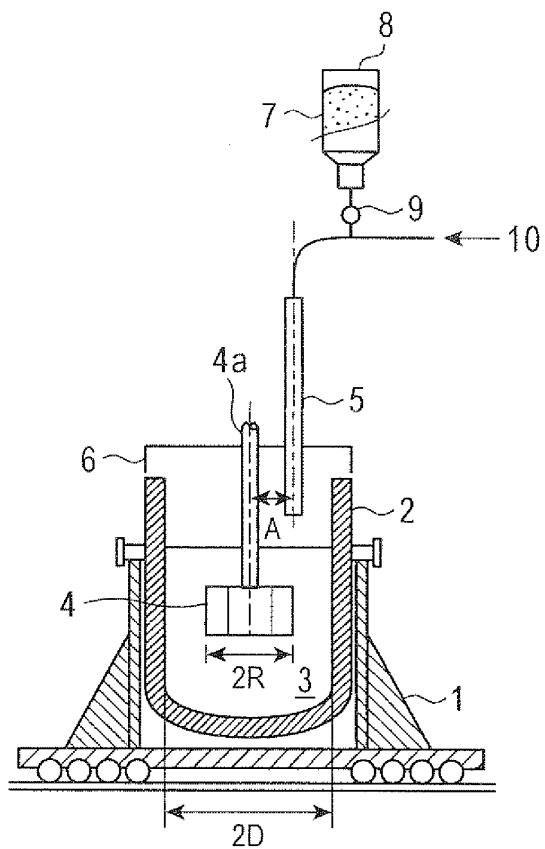


FIG. 2

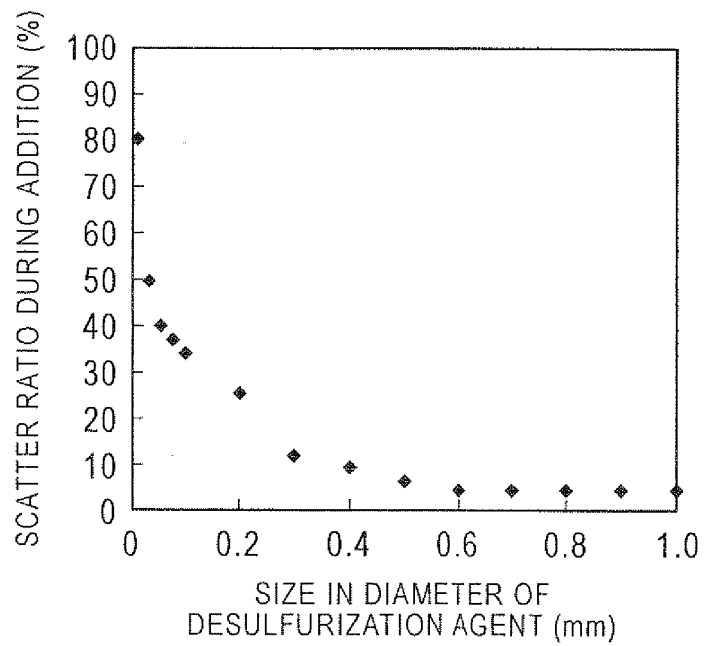


FIG. 3

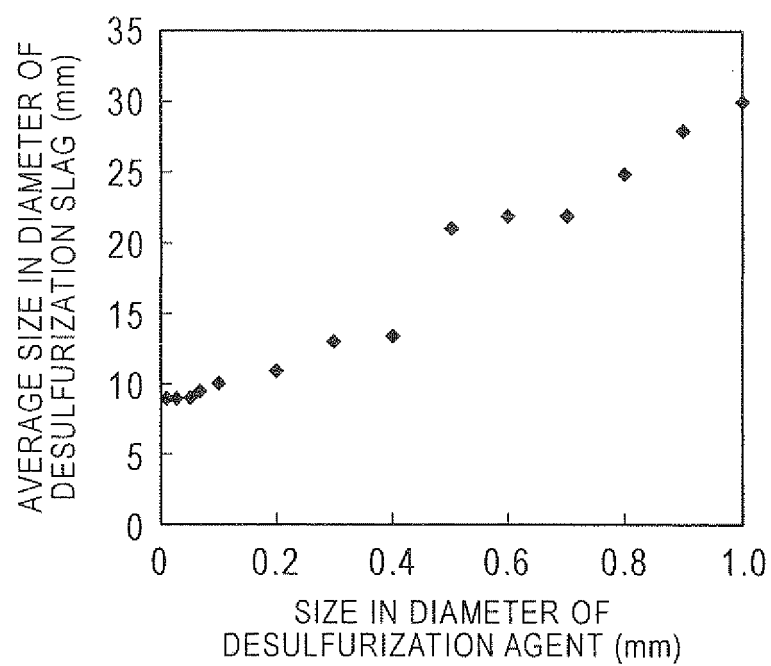
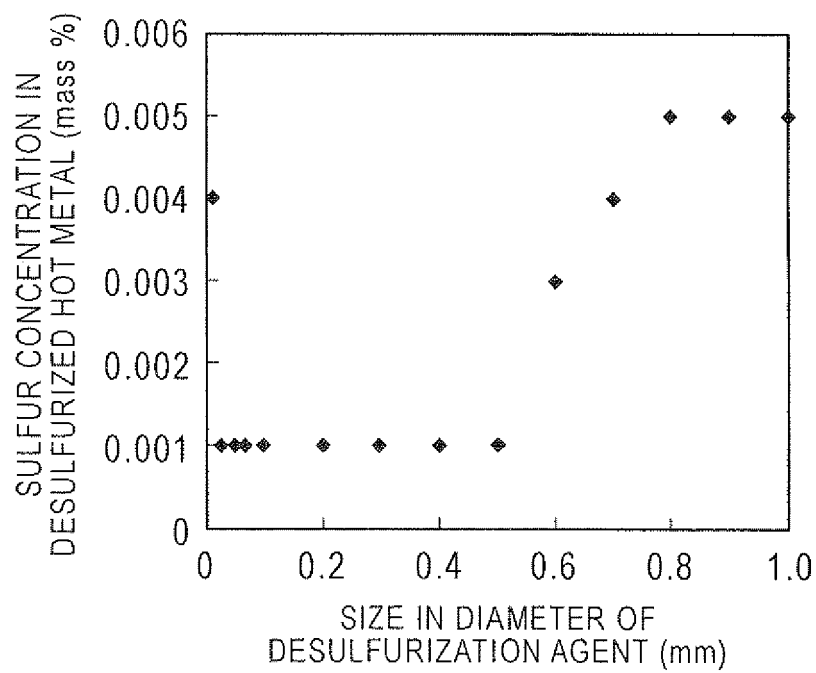


FIG. 4



REFERENCES CITED IN THE DESCRIPTION

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