(12) **INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)**

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
18 November 2021 (18.11.2021)

(10) **International Publication Number**
WO 2021/229263 A1

(51) **International Patent Classification:**
C21C 1/02 (2006.01) *C21C 7/072* (2006.01) *C21C 5/46* (2006.01) *F27D 3/00* (2006.01) *C21C 7/00* (2006.01) *F27D 3/18* (2006.01) *C21C 7/064* (2006.01) *F27D 3/16* (2006.01)

(21) **International Application Number:** PCT/IB2020/054439

(22) **International Filing Date:** 11 May 2020 (11.05.2020)

(25) **Filing Language:** English

(26) **Publication Language:** English

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) **Title:** STIRRING METHOD OF LIQUID METAL AND ASSOCIATED DEVICE

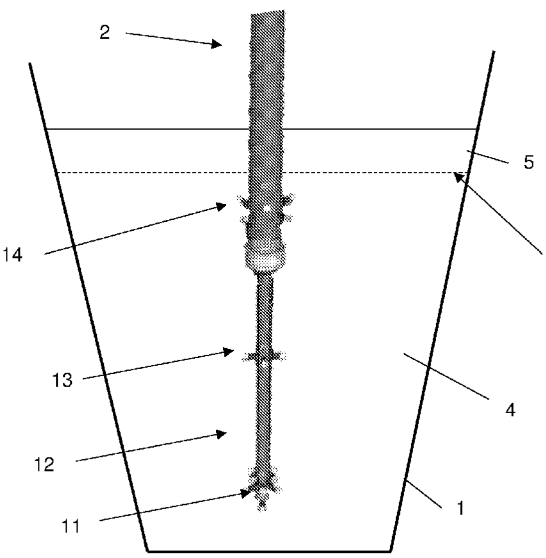

Figure 1

(57) **Abstract:** A method to stir liquid metal contained into a steelmaking vessel, said liquid metal being surrounded by a slag layer, the method comprising injection of a gas, optionally containing a powder, by at least two injection means located at at least two different injection points along the depth of the liquid metal, the first injection point being located in the bottom half of the liquid metal and the second injection point being located in the vicinity below the interface between liquid metal and slag layer. Associated device.

WO 2021/229263 A1

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Published:

— *with international search report (Art. 21(3))*

Stirring method of liquid metal and associated device

[001] The invention is related to a method for stirring liquid metal in a steelmaking vessel and to a stirring device allowing to perform such a method.

[002] During the hot-metal pre-treatment or refining of steel, liquid steel, or more generally liquid metal, is poured into a steelmaking vessel, such as a ladle, so as to be brought to a targeted composition. This targeted composition of the liquid steel depends notably on the required composition of the final cast semi-product and so of its grade. Newly developed grades, notably for the automotive industry, require a strict control of impurities into the liquid steel to avoid subsequent issues in the manufacturing process or defects in the final product. This makes the efficiency of the refining step(s) in both terms of production time and reliability essential.

[003] One of the most unwanted impurities is sulphur. Sulphur is present in most raw materials used for steelmaking (iron ore, coke and coal) and may also come the use of low-quality scrap. Sulphur increases the brittleness of steel and decreases the weldability and corrosion resistance. Therefore, sulphur needs to be removed, to typically below 0,015% and up to 0,0010% for low-sulphur grades. This may be done at different stage along the steelmaking process route, in the blast furnace, in the torpedo car, in the converter but also in the later stages of steelmaking when sulphur is present in the liquid steel. It can be done through a specific desulphurization step or in parallel with other refining steps.

[004] The main reaction for sulphur transfer which can occur at high temperature combines dissolved sulphur (S) in the liquid metal and calcium ions in the slag to form calcium sulphide which can be dissolved in the slag, depending on its “sulphide capacity”:

$$S + (CaO) = (CaS) + O$$

Therefore, conditions for an efficient desulphurization imply reducing conditions, including low content in oxygen O in steel and low FeO +MnO in the slag , a basic slag near the lime saturation having high sulphide capacity to ensure a high partition ratio of sulphur and an efficient stirring to boost kinetics toward the equilibrium.

[005] One of the ways to decrease the sulphur content in liquid metal is thus to improve the stirring efficiency in the vessel and notably to avoid the presence of so-called dead zones, i.e. areas where the interactions between injected agents and the liquid metal is not effective and/or where the flow velocity is lower than the average flow velocity in the vessel.

Stirring is usually performed by injection of an inert gas, such as nitrogen or argon, into the liquid metal. This stirring may be performed by a lance comprising injection holes immersed into the metal and/or by a porous plug located in the bottom of the steelmaking vessel. However, with those techniques big dead zones are observed on the circumference of the vessel farthest from the gas injection points. One way to improve stirring would be to increase the flow rate of injected gas but it would create metal splashes which are extremely dangerous for operators working around and which may damage equipments.

[006] In order to improve stirring efficiency of the liquid metal, a rotating stirring device has been proposed. This device is a lance with gas injection ports in the lower end of the lance which is immersed into the liquid bath and is rotative around the vertical axis. This allows to reduce the dead zones areas in the lower region of liquid metal in the vessel. However, this kind of device does not give sufficient results in terms of desulfurization efficiency.

[007] There is so a need for a stirring method allowing to improve the desulfurization, and more generally the cleanliness, of liquid metal. There is also a need for a stirring method which reduces the presence of dead zones into the stirred liquid metal without being detrimental to the productivity.

[008] This problem is solved by a method according to the invention, wherein gas, optionally containing a powder is injected into a liquid metal poured into a steelmaking vessel and surrounded by a slag layer, by at least two injection means located at at least two different injection points along the depth of the liquid metal, the first injection point (being located in the bottom half of the liquid metal and the second injection point being located in the vicinity below the interface between liquid metal and slag layer.

[009] The method of the invention may also comprise the following optional characteristics considered separately or according to all possible technical combinations:

- the second injection point is located at less than 500 millimetres below the interface between liquid metal and slag layer,
- the injection is performed while rotating injection means along the vertical axis of the vessel,
- rotation speed is comprised between 60 and 150 rpm,
- each injection mean is independently controlled from one another in terms of injection flow rate and pressure.

[0010] The invention is also related to a stirring device allowing to perform a stirring method according to the invention, the device comprising a lance provided with at least two injection means, the first injection mean being located at the end of the lance intended to be immersed into the liquid metal and the second injection mean being located so as to be in the vicinity below the interface between liquid metal and slag layer when the device is immersed into the steelmaking vessel.

[0011] The device of the invention may also comprise the following optional characteristics considered separately or according to all possible technical combinations:

– the second injection mean is located at less than 500 millimetres below the interface between liquid metal and slag layer when the device is immersed into the steelmaking vessel,

– at least a part of the lance is able to rotate along the vertical axis of the vessel,

– each injection mean is provided with its own control mean able to control the flow rate and pressure of the gas injected by said injection mean independently from the other injection means,

– the second injection mean comprises at least four injectors, each of the injectors making an angle β with the axis perpendicular to the vertical axis Z of the lance comprised between 25 and 35°,

– the device further comprises an additional injection mean located at the tip of the lance intended to be immersed into the liquid metal,

– the device further comprises an additional injection mean located at the middle of the lance part immersed into the liquid metal,

– the injection means are injection nozzles.

[0012] Other characteristics and advantages of the invention will emerge clearly from the description of it that is given below by way of an indication and which is in no way restrictive, with reference to the appended figures in which:

- Figure 1 illustrates a steelmaking vessel and a stirring device to perform a method according to the invention
- Figure 2 illustrates a stirring device according to one embodiment of the invention
- Figure 2A illustrates a 1st injection mean according to one embodiment of the invention
- Figure 2B illustrates a 2nd injection mean according to one embodiment of the invention
- Figure 3A illustrates a projection of the 1st injection mean along a plan A-A perpendicular to the vertical axis of the lance

- Figure 3B illustrates a projection of the 2nd injection mean along a plan A-A perpendicular to the vertical axis of the lance
- Figure 4 is a simulation of flow of liquid metal when using a stirring method according to prior art or according to the invention

Elements in the figures are illustrations and may not have been drawn to scale.

[0013] In figure 1 is illustrated a steelmaking vessel 1 containing liquid metal 4 surrounded by a slag layer 5. The term liquid metal 4 is used to encompass both hot metal or liquid steel. This steelmaking vessel 1 may for example be a ladle or any other suitable vessel allowing to perform actions on hot metal or liquid steel composition. This vessel 1 may be used for different steps of the steelmaking process such has hot-metal pre-treatment, liquid steel refining, secondary metallurgy, desulphurization…wherein a stirring is necessary to enhance reactions between liquid metal 4 and slag 5. This stirring is performed with a stirring device 2. In a method according to the invention the stirring is performed by injection of an inert gas, eventually containing powder at at least two distinct injection points along the depth of the liquid metal. The gas may be argon or nitrogen. The powder maybe lime, magnesium, fluorspar, calcium carbide, calcium aluminates, synthetic slags or even soda ash. According to the invention, the first injection point 12 is located in the bottom half of the liquid metal, preferably as deep as possible in the liquid metal 4. In a preferred embodiment, it is located at less than 100mm from the vessel bottom, by vessel bottom it is meant the internal bottom, refractories layer excluded when there is one. This location depends on the size of the vessel 1. The second injection point 14 is located in the vicinity below the interface 6 between liquid metal 4 and slag layer 5, preferably at less than 500mm below said interface 6. As previous, this location depends on the size of the vessel 1. Combination of those two injection points allow to improve mass transfer between slag 5 and liquid metal 4 at the interface while not creating any dead zones. This thus globally improves desulphurisation of the liquid metal by promoting the formation of calcium sulphides and reduce the desulphurization time. It also prevents agglomeration, coalescence and flotation of inclusions improving thus cleanliness of the liquid metal. Each of the injection mean may be independently controlled in terms of flow rate and pressure, it means each injection mean may have its own gas injection channel pipe and/or be provided with its own flow control mean, such as a valve, so that flow rate can be independently controlled from one injection mean to another.

[0014] Figure 2 illustrates a device 2 to perform a stirring method according to the invention. This device 2 comprises a lance 3 and at least two injection mean 11,12,13,14 located at different locations along the length of the lance 3. The 1st injection mean 12 is located at the end 21 of the lance 3 intended to be immersed into the liquid metal 4 and the 2nd injection mean 14 is located so as to be in the vicinity, preferably at less than 500mm, more preferably less than 300mm, below the interface 6 between liquid metal 4 and slag layer 5 when the device 2 is immersed into the steelmaking vessel 1. In another embodiment, the device 2 comprises a third injection mean 11 located at the tip of the lance 3. The device 2 may also comprise in addition or in replacement of this third injection mean 11, a fourth injection mean 13 located at the middle of the lance 3. In a preferred embodiment the lance 3 is able to rotate around its vertical axis Z. The lance 3 may rotate as one single body or may comprise several parts being able to rotate independently from one another. The rotation speed is preferably comprised between 60 and 150rpm (rotation per minute). The rotation of the lance 3, as well as the addition of additional injection means 11,13, allows to improve homogenization and reduce the gradients of concentration of elements and temperature in the liquid metal, thus improving process performances such as decrease of the mixing time, better dissolution of fluxes loaded into the vessel for process purposes, improved cleanliness of the liquid metal.

[0015] Figure 2A illustrates an embodiment of a 1st and 3rd injection means 11, 12. In this embodiment the 1st injection mean is composed of eight injection holes split in two levels of four holes and symmetrically distributed around the circumference of the lance 3. A projection of this 1st injection mean 12 on a plan A-A perpendicular to the vertical axis Z of the lance 3 is illustrated in figure 3A. In a most preferred embodiment, each of the injection hole makes an angle β with the axis perpendicular to the vertical axis Z of the lance 3, said angle β being preferably the same for each injection hole. This angle β is preferentially comprised between 25 and 35° and most preferably of 30°. In this specific embodiment the injection mean comprises eight injection holes, but the configuration, both in terms of symmetry and angle β can be applied to any mean comprising at least four injection holes. This configuration allows to get a better distribution of the gas into the liquid metal and to improve the stirring efficiency. The 3rd injection mean 11 is a single injection hole located at the tip of the lance 3.

[0016] Figure 2B illustrates an embodiment of a 2nd injection mean 14. In this embodiment the 2nd injection mean 14 is composed of eight injection holes split in two levels of four holes and symmetrically distributed around the circumference of the lance 3. In this embodiment the first level injection holes 14A are perpendicular to the vertical axis Z of the lance 3. The second level injection holes 14B makes an angle γ with the axis perpendicular to the vertical axis Z of the lance 3, said angle γ being preferably the same for each injection hole. This angle γ is preferentially comprised between 25 and 35° and most preferably of 30°. A projection of this 2nd injection mean 14 on a plan A-A perpendicular to the vertical axis Z of the lance 3 is illustrated in figure 3B. When projected on the plan A-A perpendicular to the vertical axis Z, each first level injection hole 14A makes an angle α with a second level injection hole 14B comprised between 40 and 50°. The angle α is preferably of 45°. In this specific embodiment the injection mean comprises eight injection holes, but the configuration, both in terms of symmetry and angles can be applied to any mean comprising at least four injection holes. This configuration allows to get a better distribution of the gas into the liquid metal and to improve the stirring efficiency.

[0017] In the embodiment of a device according to the invention as illustrated in figure 2, the lance 3 further comprises a fourth injection mean 13 located in the middle of the lance part defined to be immersed into the liquid metal. This fourth injection mean preferentially comprise four injection holes symmetrically distributed around the circumference of the lance 3. Those injection holes are preferably perpendicular to the vertical axis Z of the lance 3.

[0018] As a matter of illustration for a ladle able to comprise 300Tons of liquid steel, having as internal dimensions (without the refractory layer) a height of 4700mm and a diameter of 4100mm, the lance 3 has a length of 6000mm and is immersed over 3600mm into the liquid steel. The first injection mean 12 is located at 100mm above the ladle bottom and the 2nd injection mean 14 is located at 300mm below the interface 6 between slag layer 5 and liquid steel 4.

<u>Examples</u>

[0019] A simulation by CFD (Computational Fluid Dynamics) was performed, results of which are represented in figure 4. First simulation (Figure 4A) is when using a stirring device according to prior art with a lance and an injection nozzle located at the tip of the lance. Second simulation (Figure 4B) is when using a rotating stirring device as described in preamble with a lance with gas injection ports in the lower end of the lance which is immersed into the liquid bath and rotative around the vertical axis. Third simulation (Figure 4C) is when using a device according to the embodiment described in figure 2.

[0020] What is represented is the liquid metal velocity (expressed in m/s) at the liquid metal / slag interface in a steady state, 2,5 min after the start of gas injection. The stirring device is located at the centre of the circle.

[0021] The dark outer circle corresponds to velocity close to zero in the three cases as no stirring happens in those area close to the vessel's walls. We can however see that with a device and thus a method according to the invention (figure 4C), the thickness of this circle is reduced, which means there is a smaller zone with no stirring.

[0022] Moreover, we can also see that with a device and thus a method according to the invention, the area around the centre is darker than with the two other devices. This means that we have higher velocity and thus more important exchanges at the interface between liquid and slag. In the meantime, we don't see any "open eye". This open eye is the fact that when stirring push away the metal from the device, it creates an opened surface in the liquid metal, this exposing it to the external atmosphere. This would be detrimental to the steel quality and/or cleanliness, as the presence of an open-eye implies that the slag is no longer covering the liquid metal which is thus in direct contact with air and will be oxidised. This has to be avoided. Contrary with what could have been expected, the presence of an injection point near the metal /slag interface does not imply generation of open-eye.

[0023] Results presented in Table 1 have been obtained with a water model using a small-scale lance according to prior art (1 to 2) and according to the invention (3 to 6). Injection means 11,12,13,14 were activated or not (X means the injection mean is ON and inject gas, 0 means is OFF and no gas is injected through this mean). Location of injection means 12 and 13 is according to the invention. Rotation was activated or not (0 rpm means rotation is not activated, rpm stand for number of rotations per minute), global flow rate in litres per minute (lpm) was varied, and mixing time was measured using NaCl as chemical tracer to calculate the mixing time through the measurements of the water conductivity over time.

[0024] When comparing trials 1 and 2 with trials 3 to 6 we can see that, whatever the activation or not of rotation, the mixing time is reduced with a method according to the invention.

[0025]

Trial n°	Injection Means				Flow rate per injector (lpm)	Rotation (rpm)	Mixing time (s)
	11	12	13	14			
1	X	0	0	0	60	0	50
2	X	0	0	0	60	60	55
3	0	X	0	X	40	60	43
4	0	X	0	X	50	60	38
5	0	X	0	X	60	60	35
6	0	X	0	X	60	0	38

Table 2

With a method, and an associated device, according to the invention it is thus possible to improve the stirring efficiency and consequently to improve the desulphurisation efficiency. This allows to obtain a liquid metal with low sulphur level and a better cleanliness. Moreover, the invention provides a stirring metal which does not create open-eye, reduce the dead areas and the metal splashes.

CLAIMS

1) A method to stir liquid metal (4) contained into a steelmaking vessel (1), said liquid metal being surrounded by a slag layer (5), the method comprising injection of a gas, optionally containing a powder, by at least two injection means located at at least two different injection points (11,12,13,14) along the depth of the liquid metal, the first injection point (12) being located in the bottom half of the liquid metal and the second injection point (14) being located in the vicinity below the interface (6) between liquid metal (4) and slag layer (5).

2) A method according to claim 1 in which the second injection point (14) is located at less than 500 millimetres below the interface (6) between liquid metal (4) and slag layer (5).

3) A method according to claim 1 wherein the injection is performed while rotating injection means along the vertical axis of the vessel (1).

4) A method according to claim 3 wherein rotation speed being comprised between 60 and 150 rpm.

5) A method according to anyone of claims 1 to 4 wherein each injection mean is independently controlled from one another in terms of injection flow rate and pressure.

6) A stirring device (2) allowing to perform a method according to anyone of the previous claims said device comprising a lance (3) provided with at least two injection means (12,14), the first injection mean (12) being located at the end (21) of the lance intended to be immersed into the liquid metal (4), and the second injection mean (14) being located so as to be in the vicinity below the interface (6) between liquid metal (4) and slag layer (5) when the device (2) is immersed into the steelmaking vessel (1).

7) A stirring device according to claim 6 wherein the second injection mean (14) is located at less than 500 millimetres below the interface (6) between liquid metal (4) and slag layer (5) when the device (2) is immersed into the steelmaking vessel (1).

8) A stirring device according to claim 6 or 7 wherein at least a part of the lance (3) is able to rotate along the vertical axis of the vessel (1).

9) A stirring device according to anyone of the preceding claims wherein each injection mean is provided with its own control mean able to control the flow rate and pressure of the gas injected by said injection mean independently from the other injection means.

10) A stirring device according to anyone of the preceding claims wherein the second injection mean (14) comprises at least four injectors, each of the injectors making an angle β with the axis perpendicular to the vertical axis Z of the lance 3 comprised between 25 and 35°.

11) A stirring device according to anyone of the preceding claims further comprising an additional injection mean (11) located at the tip of the lance (3) intended to be immersed into the liquid metal.

12) A stirring device according to anyone of the preceding claims further comprising an additional injection mean (13) located at the middle of the lance part immersed into the liquid metal.

13) A stirring device according to anyone of the preceding claims wherein the injection means are injection nozzles.

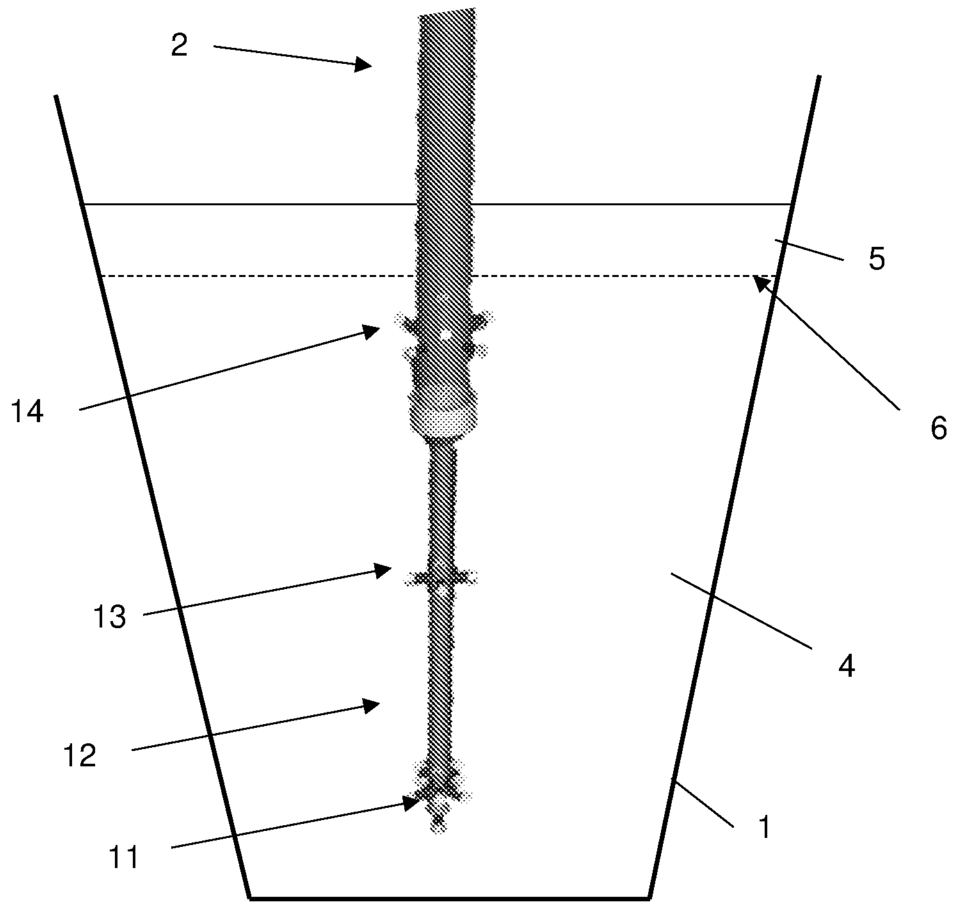


Figure 1

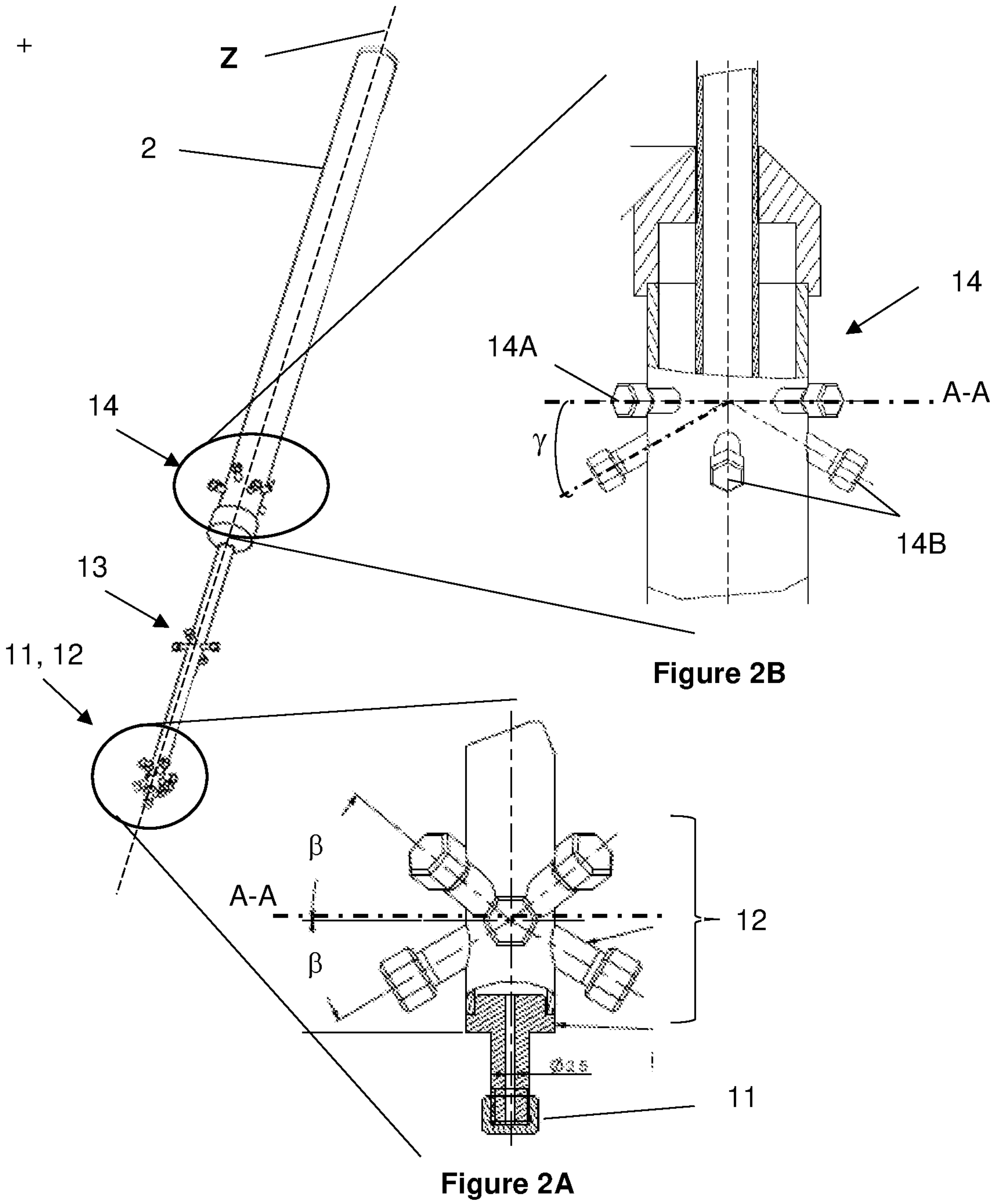


Figure 2B

Figure 2A

Figure 2

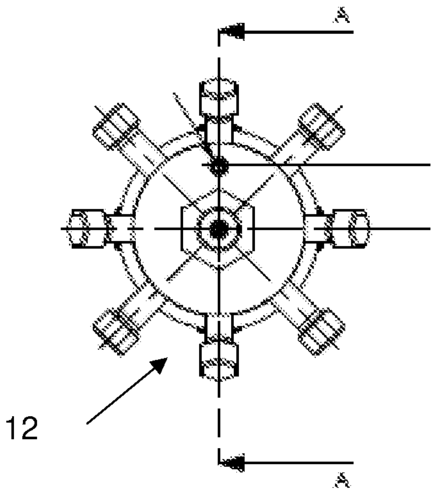


Figure 3A

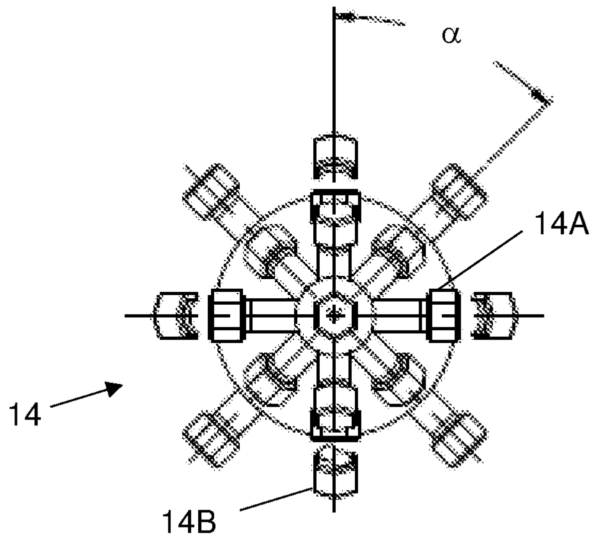
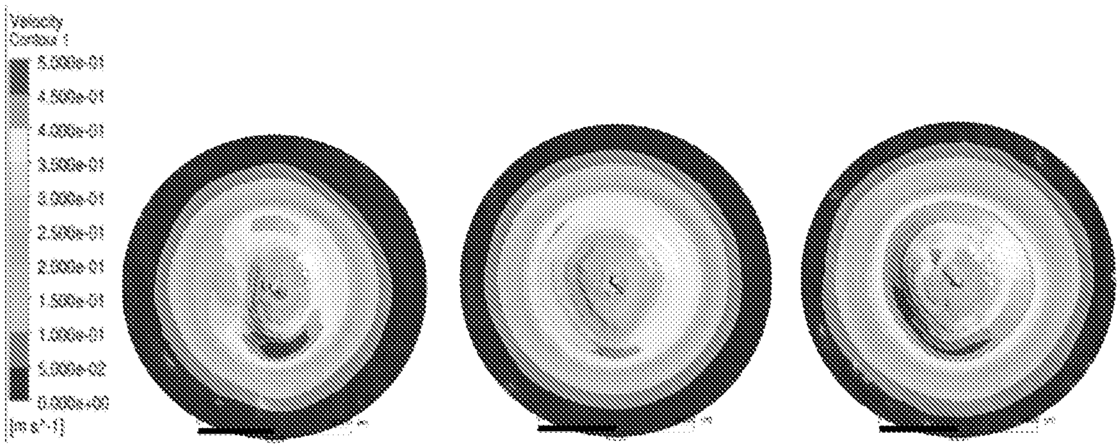


Figure 3B



4A 4B 4C

Figure 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2020/054439

A. CLASSIFICATION OF SUBJECT MATTER
INV. C21C1/02 C21C5/46 C21C7/00 C21C7/064 C21C7/072
F27D3/00 F27D3/18 F27D3/16
ADD.

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)
C21C F27D

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP H06 221773 A (SUMITOMO METAL IND) 12 August 1994 (1994-08-12) paragraphs [0001], [0010], [0011], [0012], [0013], [0015], [0016], [0018], [0025]; claim 1; figures 1-4	1-13
X	US 2017/362672 A1 (EPPS LARRY J [US]) 21 December 2017 (2017-12-21) paragraphs [0019], [0049], [0053]; claims 1,6; figures 2,2f,2h,5,6	1-13
X	CN 106 987 684 A (SHANDONG IRON & STEEL CO LTD) 28 July 2017 (2017-07-28) paragraphs [0002], [0017], [0036]; claim 8; figures 1,2	1-13
	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 September 2020	24/09/2020

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Momeni, Mohammad

2

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2009/057964 A1 (COLAVITO DOMINICK M [US] ET AL) 5 March 2009 (2009-03-05) paragraph [0023]	1-13
A	US 9 259 780 B2 (ESM GROUP INC [US]) 16 February 2016 (2016-02-16) claim 1	1-13
A	WO 2011/049240 A1 (JFE STEEL CORP [JP]; UCHIDA YUICHI [JP] ET AL.) 28 April 2011 (2011-04-28) figure 1 Example 1	1-13

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2020/054439

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
JP H06221773	A	12-08-1994	NONE			
US 2017362672	A1	21-12-2017	NONE			
CN 106987684	A	28-07-2017	NONE			
US 2009057964	A1	05-03-2009	CA	2698492	A1	12-03-2009
			EP	2215275	A2	11-08-2010
			TW	200927945	A	01-07-2009
			US	2009057964	A1	05-03-2009
			WO	2009032067	A2	12-03-2009
			ZA	201001515	B	27-10-2010
US 9259780	B2	16-02-2016	AR	095419	A1	14-10-2015
			CA	2911839	A1	25-09-2014
			CN	105121670	A	02-12-2015
			EP	2971192	A1	20-01-2016
			MX	368726	B	14-10-2019
			PL	2971192	T3	29-11-2019
			RU	2015144054	A	27-04-2017
			US	2014263703	A1	18-09-2014
			WO	2014149645	A1	25-09-2014
WO 2011049240	A1	28-04-2011	BR	112012009231	A2	23-08-2016
			CN	102575306	A	11-07-2012
			JP	5644355	B2	24-12-2014
			JP	2011106028	A	02-06-2011
			KR	20120064710	A	19-06-2012
			TW	201130989	A	16-09-2011
			WO	2011049240	A1	28-04-2011