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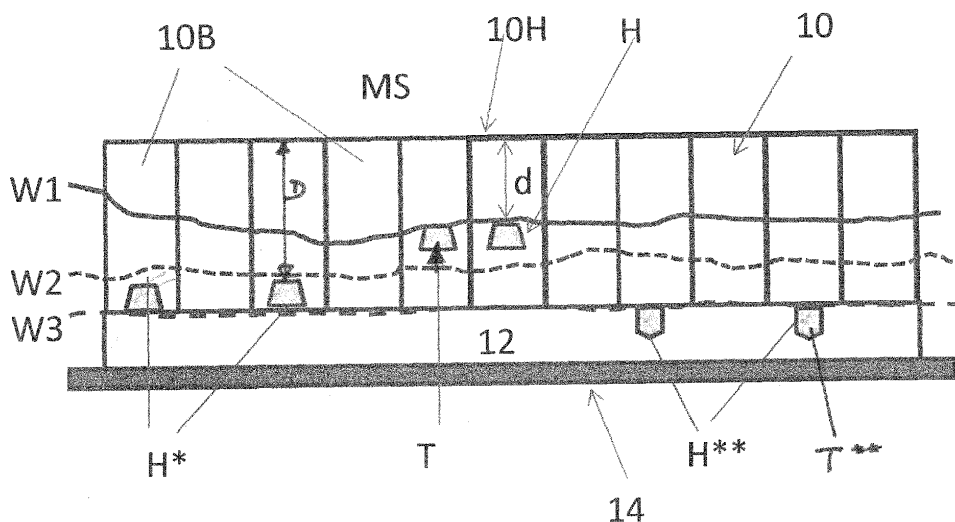
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(54) **A METHOD FOR DETECTING A PREDETERMINED WEAR OF A REFRACTORY LINING OF A METALLURGICAL VESSEL AND A CORRESPONDING REFRACTORY LINING**

(57) The invention relates to a method for detecting a predetermined wear of a refractory lining of a metallurgical vessel, in which a metal melt is treated, wherein
d) the refractory lining is applied in one or more layers of refractory ceramic material, which layer(s) define an inner surface of the refractory lining, adjacent to the metal melt, and an outer surface of the refractory lining, adjacent to an outer envelope of the metallurgical vessel, and
e) the refractory lining comprises, at defined areas and

in defined quantities, at least one tracer, which is not a basic component of the metal melt or of a corresponding slag,
f) analyzing the metal melt or the slag or both at least until a predetermined threshold of said tracer in said metal melt or said slag respectively is identified, which threshold corresponds to a predetermined wear of the refractory lining.



Description

[0001] The invention relates to a method for detecting a predetermined wear of a refractory lining of a metallurgical vessel, in which a metal melt is treated, and a corresponding refractory lining.

[0002] To withstand the high temperatures of a metal melt (often $>1.000^{\circ}\text{C}$) it is known to protect the outer envelope of a metallurgical treatment vessel, in most cases a metallic construction, by a refractory (high temperature resistant) lining on its inside.

[0003] This is true for vessels (like a ladle, tundish or the like) in which a ferrous metal like steel is treated, as well as for non-ferrous metal applications like in Peirce-Smith converters, Teniente converters, or copper refining furnaces in general as disclosed in CA2,760,352.

[0004] Corrosion of the refractory ceramic lining material in such pyrometallurgical operations by the molten metal and/or a corresponding slag cannot be avoided and is a major concern for the furnace operator as refractory wear or failure inevitably results in reduced production efficiency.

[0005] Numerous attempts have been made to increase the service life of the refractory material, but even longer lifetimes leave the problem to identify a critical wear of the refractory lining and need for a repair or replacement of the refractory ceramic lining.

[0006] To detect and predict the refractory lifetime it is crucial to have an understanding of any corrosion progress during regular production.

[0007] According to prior art, corrosion of the refractory material is analysed by visual methods with the help of inspection ports, by calculating heat transfers within the remaining lining as well as by ultrasonic or electromagnetic methods. None of these known methods leads to reliable results about the wear of the refractory lining material.

[0008] Therefore it is an object of the invention to provide an alternative to identify a predetermined wear of a refractory lining in a metallurgical vessel, in particular to identify a critical wear in order to allow a suitable repair work and/or replacement of the refractory lining in good time before any serious operation problems may occur.

[0009] The invention is based on the following considerations:

[0010] The quality (including wear behavior/wear resistance/corrosion resistance) of ceramic refractory materials used for lining a metallurgical vessel was improved over the past decades. It may even be improved further, but the lifetime (service time) of the refractory items will remain finite.

[0011] Insofar the invention does not deal with improvements of the wear resistance of refractory ceramics but in fact focusses on a new concept to diagnose its wear reliably and is based on the following cognitions:

- The wear starts at the so-called hot-side of a refractory lining, i.e. the inner side of the lining, which

stands in contact with the hot metal melt and a corresponding slag.

- The wear develops from the hot-side to the cold-side of the lining, i.e. the outer side of the lining, adjacent to the outer envelope of the vessel; in other words: dependent on time, the lining becomes thinner. Depending on the refractory material and metallurgical application, the wear may develop over hours, days, months or years until it reaches a critical value. A critical wear is reached if the refractory material cannot fulfil its tasks any more in a reliable manner; in other words: when the lining material has reached a critical remaining thickness (depths).
- The invention allows to identify this critical thickness by integrating a wear indicator (tracer) into the refractory ceramic material at predetermined locations, which will be released from the ceramic material and discharged into a metal melt and/or its slag, when the refractory lining has been worn to a corresponding depth.
- Tracers are defined as substances which typically are not part (a basic/standard component) of the melt and/or any corresponding slag or which are part of the melt/slag in negligible quantities (impurities). Insofar these tracers become part of the ceramic material of the refractory lining material but only in areas of the lining, which are arranged at a distance to the hot side of a new, yet unused lining.
- Accordingly any wear of the newly developed refractory lining material will not lead to any changes in the wear behavior compared with prior art systems unless the wear has reduced the thickness of this lining to a predetermined degree and the indicators/tracers mentioned will be set free and move into the metal melt and/or the corresponding slag, where these tracers can be identified by a corresponding (in particular chemical) analysis.

[0012] This general teaching is independent of whether the refractory lining is a monolithic lining, a lining made of shaped elements like bricks or a combination of both. As long as the regular (standard) refractory material at the hot side of the lining is lost/worn by corrosion or any other wear mechanism like metallurgical, thermal, mechanical or chemical attack, the effect equals that in prior art constructions.

[0013] The effect achievable by the invention only starts, when the refractory material has been worn to a depth, where the refractory lining material includes these further ingredients (tracers). In that case additional wear of the refractory material leads to the effect that these foreign substances are separated (released) from the ceramic refractory material and transferred into the metal melt and/or its slag, thereby changing the chemical com-

position and/or physical properties of the melt/slag, which may be detected by corresponding tests (analysis) of the metal melt or the slag respectively. Insofar the invention includes a refractory lining with integrated tracer materials as well as a method to determine a critical wear of this lining.

[0014] In its most general embodiment the invention relates to a method for detecting a predetermined wear of a refractory lining of a metallurgical vessel, in which a metal melt is treated, wherein

- the refractory lining is applied in one or more layers of refractory ceramic material, which layer(s) define an inner surface of the refractory lining, adjacent to the metal melt, and an outer surface of the refractory lining, adjacent to an outer envelope of the metallurgical vessel, and
- the refractory lining comprises, at defined areas and in defined quantities, at least one tracer, which is not a basic component of the metal melt or of a corresponding slag,
- analyzing the metal melt or the slag or both at least until a predetermined threshold of said tracer in said metal melt or said slag respectively is identified, which threshold corresponds to a predetermined wear of the refractory lining.

[0015] "Defined areas" are areas within the refractory lining (at a certain distance to the hot surface of the new lining), representing a wear of the lining material to a certain extend (depth), which wear is to be detected. "Defined quantities" are quantities sufficient to be detected (analyzed) as a melt or slag component after the tracer was transferred into the melt/slag

[0016] The invention further comprises a refractory lining of a metallurgical vessel for a treatment of a metal melt, wherein the refractory lining

- is made of one or more layers of refractory ceramic material, which layer(s) define an inner surface of the refractory lining, adjacent to the metal melt, and an outer surface of the refractory lining, adjacent to an outer envelope of the metallurgical vessel, and comprises a wear indicator, defined by at least one tracer which is integrated into at least part of the refractory ceramic material at a distance to the inner surface of the refractory lining, wherein said distance corresponds to a predetermined wear of the refractory lining to be detected.

[0017] The term "tracer" (=tracer material/tracer substance/indicator) includes detection metals reflecting an important type of a substance, which may be used as a "wear indicator", as tracer metals are easily detectable within the metal melt, treated within the metallurgical vessel, although other substances may be used as well for

this purpose with the proviso, that these substances must be detectable within the metal melt and/or the corresponding slag, within the vessel or after the melt/slag has been discharged or tapped. Insofar it is preferred to use tracers (substances) like detection metals or metal oxides, which are not present in the metal melt or slag (or in negligible quantities) and thus detectable even in very small amounts.

[0018] The benefit of the invention is, that wear of the refractory lining can be detected without any inspection ports, without any measurements of heat transfer or other experimental equipment. Insofar the invention is also applicable in "closed furnace constructions" like an EAF (electric arc furnace) without any openings for visual inspections.

[0019] During industrial production an analysis of the final products (in particular: the treated metal melt or the (tapped) slag) is always done and insofar the invention does not require any additional expenditures or efforts except analyzing for an additional component (the tracer(s)) of the metal melt (alloy) or slag.

[0020] The method can also be used as an emergency indicator, when a minimum thickness of the refractory lining has been reached and prevent from a run out.

[0021] The areas of the refractory lining "doped" by said tracers may extend over the whole lining or parts of it. At different depths (distances) to the hot inner side of the yet unworn lining, different tracers and/or tracers in different concentrations (amounts) may be arranged to allow a step wise wear detection.

[0022] As mentioned, the type of the lining is not crucial. The refractory lining can present

- an inner layer, which is made of bricks,
- an outer brick layer,
- an outer monolithic layer,
- an inner monolithic layer,

or combinations thereof.

[0023] Typically the wear indicator (zone characterized by the presence of one or more tracers) within the refractory lining is arranged closer to its outer surface (the cold side) than to its inner surface (the hot side). Throughout the description and claims the position of the hollow spaces and tracers refers to the "new lining", i.e. the yet unworn lining.

[0024] According to one embodiment the wear indicator within the refractory lining is arranged in an outer layer of a multi-layer refractory lining.

[0025] The tracer substance(s) of the wear indicator may be evenly distributed within a corresponding wear indicating zone of the refractory ceramic material, meaning that the doped zone extends over the complete lining.

[0026] Alternatively the tracers are sectionally distributed within the refractory ceramic material, meaning that only certain sections of the lining are doped with said tracer substances. These sections can be hollow spaces within the refractory lining material, which are filled, at

least partially, with the one or more tracer substances. These sections can be sections of increased wear, for example adjacent to gas purging elements, nozzles etc.. The tracer can be prepared as a powder, granules, pellets or the like.

[0027] To avoid sintering of the tracer material before its release into the metal melt, a tracer material with a corresponding melting point is selected, for example a Wolfram or Zirconia based tracer substance, with a melting point of a at least hundred degrees above a typical metal melt temperature.

[0028] In an application with tracers being sectionally distributed within the refractory ceramic material, namely at different distances perpendicular to the inner surface of the (new) refractory lining and/or at a distance to each other, the invention provides the possibility to give different alerts at different degrees of wear, in particular if different indicators (tracer materials) are arranged at different positions (in particular at different depths) within the refractory lining.

[0029] The type, amount and placement of a tracer within the refractory ceramic lining material, is selected according to the required wear indicating and according to the exactness of the method and analysis to identify the tracer in the melt or slag.

[0030] According to one embodiment the at least one tracer comprises at least one detection metal and/or at least one metal combination/compound like a metal oxide which is not included in the metal melt or slag before the at least one tracer gets in contact with the metal melt and/or slag to be detected.

[0031] The one or more tracer of the wear indicator may comprise at least one substance of the group: Aluminium (Al), Magnesium (Mg), Silicium (Si), Barium (Ba), Molybdenum (Mo) and Titanium (Ti), as metals, as oxides or both. Other metals like Hf, V, Ni as well as other oxides based on - for example - La, Eu, Co, In etc. may be used as well.

[0032] The metal melt can be a non-ferrous metal melt, like a copper melt, or a steel melt.

[0033] The invention will now be described in further details by way of an example and with reference to the attached Figure which displays in a schematic way :

a sectional view of a refractory lining of a Pierce-Smith converter

[0034] The Peirce-Smith converter as displayed is used for treating a non-ferrous metal melt. It has an inner diameter of 4m and a length of 12m, a capacity of about 300.000kg copper matte (german: Kupferstein) and an inner refractory lining made of an inner brick layer 10 and an outer monolithic layer 12.

[0035] The brick layer 10 is made of $\text{MgO-Cr}_2\text{O}_3$ bricks 10B. Bricks 10B are standard tapered bricks of 150mm length, 78/65 mm width (at both ends) and 375mm height, thus featuring an overall volume of 4020cm^3 per brick.

[0036] The inner brick layer 10 is followed by the re-

fractory monolithic outer layer 12 adjacent to a metallic outer envelope 14 of said converter, wherein said layer 12 has a thickness of 20mm (perpendicular to said envelope 14).

[0037] The copper melt and a corresponding slag (commonly identified by MS) are in permanent contact with a hot-side/hot surface 10H of the refractory lining, causing wear of the lining material. In Fig. 1 different degrees of wear are identified by lines W1 and W2, which will be explained in more detail hereinafter by way of examples.

[0038] Hollow spaces H of a first type are prepared within some of the bricks 10B at a distance "d" to the hot surface 10H of the yet unused (new) bricks 10B and filled with a tracer T, namely a BaO powder of a grain size $d_{50} < 100\mu\text{m}$. The said distance "d" corresponds to a first degree of wear, symbolized by line W1. As displayed this "wear line" is never ideally linear, but irregular, according to different wear at different section. Insofar the arrangement of the tracer materials always represents an average wear behaviour.

[0039] If wear has reached one or more of said hollow spaces H, the tracer material may flow out of said hollow space(s) and into the metal melt and the associated slag, thus changing the chemical composition of the slag correspondingly.

[0040] Further hollow spaces H^* are arranged at the outer (cold) end of said bricks 10B, adjacent to the monolithic outer layer 12, i.e. at a distance " D^* " being larger than "d".

[0041] In the displayed example said hollow spaces 10H are arranged in the vicinity of a (non-displayed) tuyere zone (gas purging zone) of the Peirce-Smith Converter, i.e. in a part of the converter, which undergoes high wear. Said hollow spaces H^* are either arranged behind said hollow spaces H (as displayed) in the gas purging zone and/or in other parts of the converter, which are characterized by a more moderate wear behavior compared with the tuyere zones.

[0042] Said hollow spaces H^* are filled with another tracer, namely MoO_3 , prepared as MoO_3 -pellets, 90% of which featuring a diameter between 0,1 and 1mm.

[0043] As soon as wear has reached the hollow spaces H^* (see wear line W2, which roughly corresponds to distance D) said MoO_3 tracer will be released more or less spontaneously and may then be analyzed as part of the slag.

[0044] The wear lines W1 and W2 - and thus the arrangement of the hollow spaces H and H^* - have been set by the responsible worker to allow identification of the corresponding degree of wear which requires repair or replacement of the refractory lining 10. In practice the hollow spaces H and H^* will be arranged at different zones, at one or more sections and/or at one or more distances to the hot side of a new refractory lining 10. The faster the expected wear is, the smaller the distance " d/D " will be chosen to arrange the hollow spaces, in order to allow a corresponding wear identification in due

time. Insofar the arrangement displayed in the Figure only serves to illustrate the principle of the invention by way of example.

[0045] It is assumed now that an amount of the tracer within hollows H shall be released (more or less spontaneously) from the refractory material into the copper slag. Conventional analysis methods and apparatus for metal slags allow a detection limit for Barium at about 50ppm. Correspondingly a reliable wear identification requires more than the detection limit (threshold) of 50ppm, for example 6kg (of released) BaO in 100.000kg slag, i.e. 60ppm BaO within said slag.

[0046] BaO was chosen as a suitable tracer as typically no Barium being present in a conventional copper slag and the detection level of Barium being quite low. A further criterion is that BaO will remain for long in the slag.

[0047] The size, number and distribution of the hollow spaces H or H* respectively is chosen in accordance with the expected wear and the required amount of the respective tracer.

[0048] During melt treatment within said converter the slag is chemically analyzed after certain times.

[0049] When the wear of the brick layer 10 has reached the hollow spaces H and the BaO tracer is released from said hollow spaces H in an amount exceeding the detection limit, it will take only a short time until the tracer can be analyzed as part of the corresponding slag.

[0050] Because of the ignoble characteristic of the BaO tracer (similar e.g. TiO_2), compared with iron, said tracer can be found more or less completely in the slag phase as long as no high amounts of iron oxides are present in said slag phase and as long as such iron oxides are not reduced to metallic iron. Dissolved in the slag phase the tracer can easily be detected by conventional analysis methods.

[0051] Although TiO_2 has a melting point of 1855°C , it is dissolved in the liquid slag at moderate contents (percentages) and does not form any solids (TiO_2 , FeTiO_3 , CaTiO_3). This is comparable with conventional slag compounds, which as pure substances show significantly higher melting temperatures than conventional slags (SiO_2 : 1713°C , CaO : 2580°C , MgO : 2852°C).

[0052] This is true analogously in case of a slag, yet undoped by the tracer, already including BaO but in an amount below the detection limit of 50ppm.

[0053] The detection of the tracer material in the slag as part of the method indicates that the brick wear has reached the "hollow spaces H" or H* and thus a depth "d" or "D" respectively. While said wear "opens" these space(s) the tracer is released into the adjacent metal melt and from there into the corresponding slag. The corresponding chemical analysis gives the worker a clear indication about the brick wear and residual life time of the refractory lining.

[0054] A 3rd group of hollow spaces H** is arranged in the outer layer 12 at its surface adjacent to bricks 10B, and filled with a third type of a tracer material T**. It becomes obvious that a wear of the lining down to corre-

sponding wear line W3 (=spaces H**) represents an emergency situation as the bricks 10B of the wear lining have already completely gone and the security of the vessel and the metallurgical process is only dependent on the permanent lining 12.

Claims

1. A method for detecting a predetermined wear of a refractory lining of a metallurgical vessel, in which a metal melt is treated, wherein
 - a) the refractory lining is applied in one or more layers of refractory ceramic material, which layer(s) define an inner surface of the refractory lining, adjacent to the metal melt, and an outer surface of the refractory lining, adjacent to an outer envelope of the metallurgical vessel, and
 - b) the refractory lining comprises, at defined areas and in defined quantities, at least one tracer, which is not a basic component of the metal melt or of a corresponding slag,
 - c) analyzing the metal melt or the slag or both at least until a predetermined threshold of said tracer in said metal melt or said slag respectively is identified, which threshold corresponds to a predetermined wear of the refractory lining.
2. The method according to claim 1, wherein analyzing of the metal melt or the slag or both is done continuously.
3. The method according to claim 1, wherein analyzing of the metal melt or the slag or both is done periodically.
4. The method according to claim 1, using a refractory lining without any tracer in a section of the refractory lining adjacent to its inner surface, in its primary condition.
5. The method according to claim 1, using a refractory lining wherein the tracer is arranged closer to the outer surface of the refractory lining than to its inner surface.
6. The method according to claim 1, using a refractory lining wherein the tracer is arranged in an outer layer of a multi-layer refractory lining.
7. The method according to claim 1, using a refractory lining wherein the tracer is evenly distributed within the refractory ceramic material.
8. The method according to claim 1, using a refractory lining wherein the tracer is sectionally distributed within the refractory ceramic material.

9. The method according to claim 1, using a refractory lining wherein the wear indicator is arranged in hollow spaces within the refractory material of the refractory lining.

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10. The method according to claim 1, using a refractory lining wherein one or more tracers are sectionally distributed within the refractory ceramic material at different distances perpendicular to the inner surface of the refractory lining.

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11. The method according to claim 10, wherein different tracers are used at sections of different distance perpendicular to the inner surface of the refractory lining.

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12. The method according to claim 1, using at least one metal oxide as a tracer, which metal oxide is not a component of the slag before the tracer gets in contact with the slag to be analyzed.

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13. A refractory lining (10) of a metallurgical vessel for a treatment of a metal melt, wherein the refractory lining (10)

- a) is made of one or more layers of refractory ceramic material, which layer(s) define an inner surface (10H) of the refractory lining (10), adjacent to the metal melt (MS), and an outer surface of the refractory lining (10), adjacent to an outer envelope (14) of the metallurgical vessel, and
- b) comprises a wear indicator, defined by at least one tracer (T) which is integrated into at least part of the refractory ceramic material at a distance to the inner surface (10H) of the refractory lining (10), wherein said distance corresponds to a predetermined wear (d) of the refractory lining (10) to be detected.

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Amended claims in accordance with Rule 137(2) EPC.

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1. A method for detecting a predetermined wear of a refractory lining of a metallurgical vessel, in which a metal melt is treated, wherein

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- a) the refractory lining is applied in one or more layers of refractory ceramic material, which layer(s) define an inner surface of the refractory lining, adjacent to the metal melt, and an outer surface of the refractory lining, adjacent to an outer envelope of the metallurgical vessel, and
- b) the refractory lining comprises, at defined areas and in defined quantities, at least one tracer, which is not a basic component of the metal melt or of a corresponding slag,
- c) analyzing the metal melt or the slag or both at least until a predetermined threshold of said

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- tracer in said metal melt or said slag respectively is identified, which threshold corresponds to a predetermined wear of the refractory lining;
- d) only certain sections of the refractory lining comprise said at least one tracer; and
- e) said sections are hollow spaces within said refractory lining.

2. The method according to claim 1, wherein analyzing of the metal melt or the slag or both is done continuously.

3. The method according to claim 1, wherein analyzing of the metal melt or the slag or both is done periodically.

4. The method according to claim 1, using a refractory lining without any tracer in a section of the refractory lining adjacent to its inner surface, in its primary condition.

5. The method according to claim 1, using a refractory lining wherein the tracer is arranged closer to the outer surface of the refractory lining than to its inner surface.

6. The method according to claim 1, using a refractory lining wherein the tracer is arranged in an outer layer of a multi-layer refractory lining.

7. The method according to claim 1, using a refractory lining wherein the tracer is evenly distributed within the refractory ceramic material.

8. The method according to claim 1, using a refractory lining wherein the tracer is sectionally distributed within the refractory ceramic material.

9. The method according to claim 1, using a refractory lining wherein one or more tracers are sectionally distributed within the refractory ceramic material at different distances perpendicular to the inner surface of the refractory lining.

10. The method according to claim 9, wherein different tracers are used at sections of different distance perpendicular to the inner surface of the refractory lining.

11. The method according to claim 1, using at least one metal oxide as a tracer, which metal oxide is not a component of the slag before the tracer gets in contact with the slag to be analyzed.

12. A refractory lining (10) of a metallurgical vessel for a treatment of a metal melt, wherein the refractory lining (10)

- a) is made of one or more layers of refractory

ceramic material, which layer(s) define an inner surface (10H) of the refractory lining (10), adjacent to the metal melt (MS), and an outer surface of the refractory lining (10), adjacent to an outer envelope (14) of the metallurgical vessel, and 5
b) comprises a wear indicator, defined by at least one tracer (T) which is integrated into at least part of the refractory ceramic material at a distance to the inner surface (10H) of the refractory lining (10), wherein said distance corresponds 10
to a predetermined wear (d) of the refractory lining (10) to be detected;
c) only certain sections of the refractory lining comprise said at least one tracer; and
d) said sections are hollow spaces within said 15
refractory lining.

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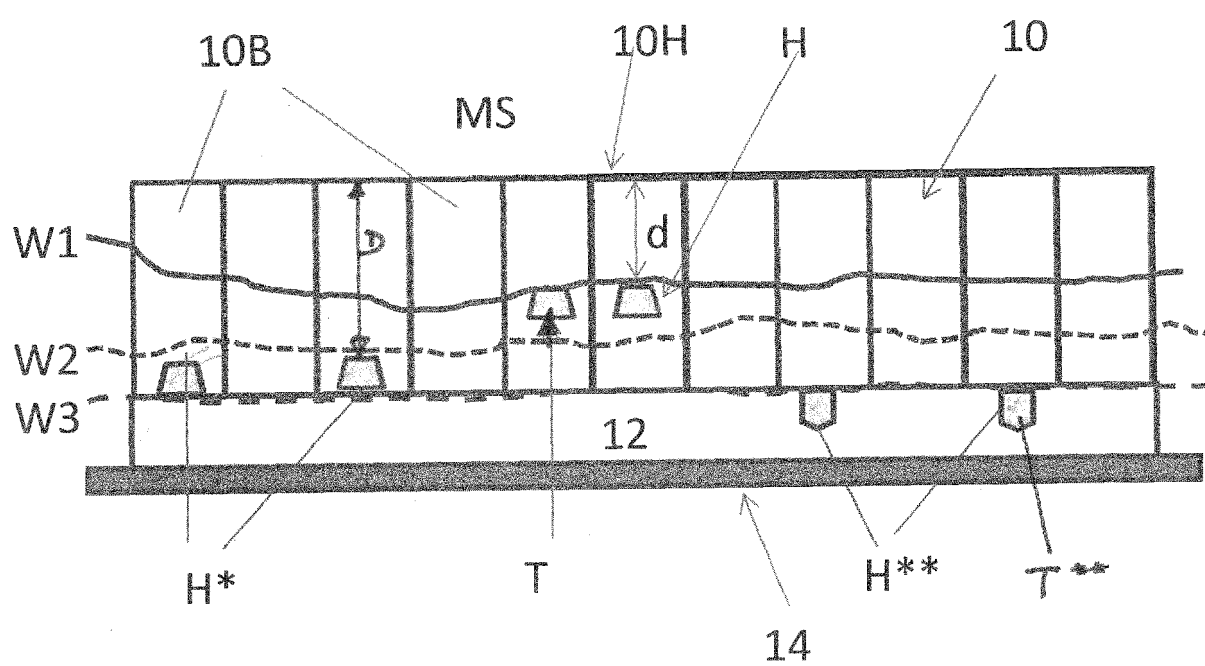
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EUROPEAN SEARCH REPORT

Application Number
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