(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 1 715 065 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
25.10.2006 Bulletin 2006/43

(51) Int Cl.:
C21C 7/00 *(2006.01)*

(21) Application number: **06008183.3**

(22) Date of filing: **20.04.2006**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK YU

(30) Priority: **20.04.2005 EP 05075937**

(71) Applicant: **Corus Staal BV**
1970 CA Ijmuiden (NL)

(72) Inventors:
- **Tiekink, Wouter Karel**
  1944 NG Beverwijk (NL)
- **Kooter, Rob**
  1964 BC Heemskerk (NL)

(74) Representative: **Kruit, Jan et al**
Corus Technology BV
PO Box 10000
1970 CA IJmuiden (NL)

(54) **A wire for injecting into a steel melt and process of treating a steel melt using said wire**

(57) A wire for injecting into a steel melt in an injection direction, the wire comprising a metallic tubular shell enclosing a core, the core comprising calcium or a calcium containing compound, wherein the core also comprises a distribution enhancing compound for distributing the calcium or calcium containing compound in the steel melt in a direction substantially perpendicular to the injection direction wherein the distribution enhancing compound comprises a compound having a vapour pressure which is higher than the vapour pressure of calcium at liquid steel temperatures for obtaining a more homogeneous distribution of the calcium or calcium containing compound in the steel melt. The invention also relates to a process of treating a steel melt using said wire, the use of said wire and the resulting continuously cast steel product.

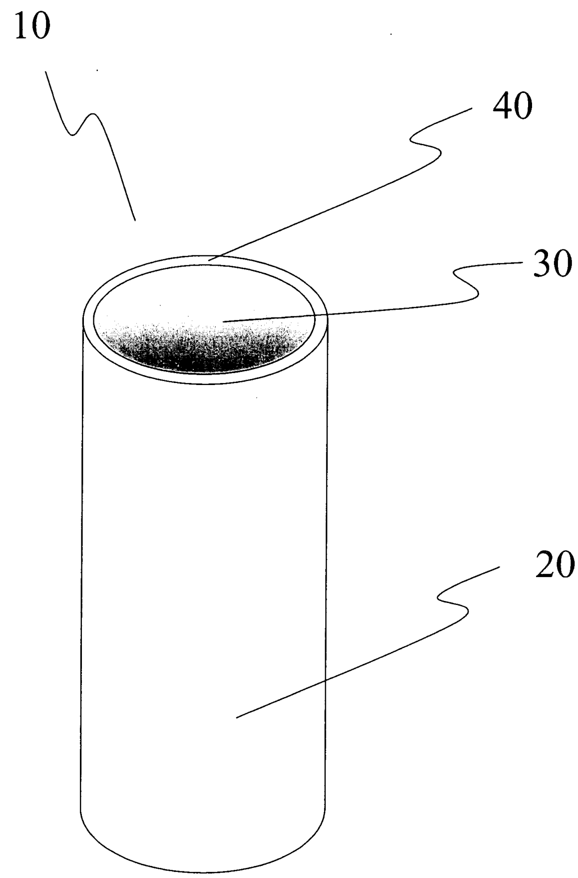

Figure 1

EP 1 715 065 A2

Description

[0001] This invention relates to a wire for injecting into a steel melt in an injection direction, the wire comprising a metallic tubular shell enclosing a core, the core comprising calcium or a calcium containing compound. The invention also relates to a process of treating a steel melt using said wire and the use of said wire. The invention further relates to a continuously cast steel product produced by said method using said wire.

[0002] Calcium (Ca) is used in the steel industry, particularly in the continuous casting of steel billet, slabs or strip to improve the castability of aluminium-killed steel. The calcium treatment results in the fluxing of alumina inclusions into a calcium aluminate composition that is liquid at casting temperatures. These calcium aluminates are therefore unlikely to cause clogging of the refractory casting tubes which are used to convey the liquid steel from the ladle into the tundish and particularly those used to convey the liquid steel from the tundish into the casting mould.

[0003] DE2421743 discloses the use of a mixture or an alloy of calcium with elements such as aluminium, magnesium, strontium, barium, lithium, cerium or rare earth metals for desulphurisation or desoxidation. Calcium is used to desulphurize the steel by forming solid calcium sulphide particles (CaS). These particles also form nucleation sites for manganese sulphide (MnS) particles to precipitate on during solidification, thereby forming globular MnS-CaS precipitates. The formation of pure MnS-particles in the steel is thereby prevented. These MnS-particles are easily rolled out during hot rolling and may serve as a stress raiser in a later application of the steel in a product. However, a large calcium concentration at a given location in the melt will result in formation of too much calcium sulphide, which lowers the amount of calcium available to form calcium-aluminates, which in turn adversely affects the clogging tendency.

[0004] It is known that for a consistent steel quality, and for uninterrupted operation of the casting equipment, a homogeneous distribution of the calcium over the liquid steel is important.

[0005] In general, calcium is added after the liquid steel has been killed by adding aluminium to the liquid steel. The calcium addition usually takes place by injecting a filled wire into the liquid steel, the wire comprising a shell, which is usually metallic, and a calcium containing core or filling. DE2421743 discloses the use of a filled steel shell for desulphurization and desoxidation. In the context of this description, the shell of the wire is to be understood to be elongated, and usually hollow. The wire is injected into the liquid steel by means of an injecting device which injects or shoots a chosen amount of wire into the melt. Due to the high temperature of the melt, the metallic shell melts and the core or filling of the wire is released into the steel melt. Preferably, the wire is injected into the melt at such a velocity that the wire melts before it hits the bottom of the ladle wherein the liquid steel is contained.

[0006] The problems with injecting calcium containing wire into liquid steel is that the calcium addition is not spread or distributed homogeneously over the steel melt during calcium wire injection. The injection of the wire only ensures a good distribution of the wire and thus of the calcium addition in the injection direction of the wire.

[0007] It is an object of this invention to provide a filled wire for injection into liquid steel ensuring an improved distribution of the calcium addition during the calcium treatment of a liquid steel.

[0008] It is also an object of this invention to provide a filled wire for injection into liquid steel having an improved yield of the calcium during the calcium treatment of a liquid steel.

[0009] One or both of these objects are reached according to the invention by providing a wire for injecting into a steel melt in an injection direction, the wire comprising a metallic tubular shell enclosing a core, the core comprising calcium or a calcium containing compound, wherein the core also comprises a distribution enhancing compound for distributing the calcium or calcium containing compound in the steel melt in a direction substantially perpendicular to the injection direction wherein the distribution enhancing compound comprises a compound having a vapour pressure which is higher than the vapour pressure of calcium at liquid steel temperatures for obtaining a more homogeneous distribution of the calcium or calcium containing compound in the steel melt.

[0010] By injecting the wire in the steel melt, the calcium or calcium containing compound is introduced in the melt in the injection direction of the wire. This injection ensures a good penetration of the calcium or calcium containing compound substantially in the injection direction. As a result of buoyancy or of the action of bottom bubbling, the calcium or calcium containing compound rises through the melt, thereby ensuring a good distribution of the calcium or calcium containing compound in the vertical direction, which is preferably substantially the same direction as the injection direction. The presence of the distribution enhancing compound ensures that the calcium or calcium containing compound from the wire is given an additional speed component in a second direction which is directed away from the injection direction, the second direction preferably being substantially perpendicular to the injection direction and therefore preferably substantially perpendicular to the vertical direction. This additional speed component ensures an improved lateral distribution of the calcium or calcium containing compound and thereby a more homogeneous distribution of the calcium or calcium containing compound in the steel melt. This in turn results in an improved yield of the calcium or calcium containing compound because the formation of calcium sulphide is prevented thereby making the calcium or calcium containing compound available for the formation of calcium-aluminates, and thus preventing clogging of the ceramic tubes more effectively. Upon injecting in the steel melt, the shell of the wire quickly melts, thereby releasing the calcium or calcium containing compound and the distribution enhancing compound. The distribution enhancing compound, having a vapour pressure under the circumstances in a steel melt particularly at the liquid steel temperature of about 1600 °C, for instance in the ladle in a steel plant, which is higher than that of the calcium or calcium containing compound. This higher vapour pressure boosts the calcium or calcium containing compound in a direction away from the wire, preferably substantially perpendicularly to the injection direction of the wire.

[0011] In an embodiment of the invention the distribution enhancing compound comprises one or more of a compound selected from the group of compounds comprising magnesium, magnesium-oxide, sodium, sodium-oxide, zinc, zinc-oxide.

[0012] It was found by the inventors that magnesium, magnesium-oxide, sodium, sodium-oxide, zinc, zinc-oxide provide a vapour pressure under the circumstances in a steel melt resulting in an improved lateral distribution of the calcium or calcium containing compound. Preferably the vapour pressure generated by the distribution enhancing compound is higher than that generated by the calcium or calcium containing compound. It is noted that cadmium or cadmium-oxide also provides a vapour pressure under the circumstances in a steel melt which is higher than the vapour pressure of calcium, but due to the level of toxicity of cadmium, the industrial applicability of such an addition as a distribution enhancing compound is limited. It is also noted that the magnesium-oxide, sodium-oxide or zinc-oxide may also be provided in the form of a magnesium-oxide containing compound, a sodium-oxide containing compound or a zinc-oxide containing compound such as sodium-silicate anhydride ($Na2O.SiO2$) in the case of a sodium-oxide addition.

[0013] In a preferred embodiment of the invention the distribution enhancing compound comprises magnesium and/or magnesium oxide.

[0014] It was found by the inventors that magnesium (Mg) and/or magnesium oxide (MgO) provides a very high vapour pressure under the circumstances in a steel melt, thereby providing a very effective lateral distribution of the calcium or calcium containing compound. The vapour pressure in the melt of the magnesium is significantly higher than that of the calcium. It should be noted that the magnesium oxide will be reduced to magnesium by the calcium also present in the wire. The magnesium thus formed will also vaporise and contribute to the very effective lateral distribution of the calcium or calcium containing compound. It should be noted that the same holds for sodium and sodium oxide, which also provide an effective lateral distribution of the calcium or calcium containing compound as a result of the higher vapour pressure in comparison to the vapour pressure of calcium in the melt. It should be noted that the amount of magnesium must be carefully trimmed to avoid too much turbulence and too much MgO pick up in the calcium aluminates. Preferably the weight ratio of magnesium to calcium is between 1 to 10%, preferably at most 8%, more preferably at most 5%. Preferably the ratio of magnesium to calcium is at least 1.5%, more preferably at least 2%.

[0015] In an embodiment of the invention, the steel in the steel melt is an unalloyed or low-allow steel, such as low carbon steel having a carbon content of about 0.1% in weight or less, an extra low-carbon steel having a carbon content of about 0.04% or less, an ultra low carbon steel having a carbon content of about 0.01% or less, carbon-manganese steel, microalloyed steel or the like. By using the wire according to the invention, a steel product after solidification can be produced with a total magnesium content of between 0.5 and 10 ppm, and wherein the magnesium in solid solution is below 2 ppm.

[0016] According to a second aspect of the invention, a process of treating a steel melt is provided wherein a wire as described above is introduced in the melt in an injection direction, preferably a substantially vertical injection direction, and wherein the calcium or calcium containing compounds are distributed substantially perpendicularly to the injection direction by the distribution enhancing compound. It is noted that a substantially vertical injection direction includes the vertical injection direction and injection directions deviating slightly from the vertical as a result of a principal inability to obtain an absolutely vertical direction under practical conditions in a steelworks. In practice, substantially vertical means vertical $\pm$ 5°.

[0017] In an embodiment of the invention the distribution enhancing compound comprises a compound having a vapour pressure which is higher than the vapour pressure of calcium at liquid steel temperatures.

[0018] In an embodiment of the invention the distribution enhancing compound comprises one or more of a compound selected from the group of compounds comprising magnesium, magnesium-oxide, sodium, sodium-oxide, zinc, zinc-oxide, preferably wherein the distribution enhancing compound comprises magnesium and/or magnesium oxide.

[0019] According to a third aspect of the invention, the use of a wire as described above for improving the lateral or spatial distribution of calcium or a calcium containing compound in a steel melt after injection of the wire in the steel melt by injection means is provided.

[0020] The invention is also embodied in a continuously cast steel produced using the process as described above, wherein the amount of magnesium added to the steel through the injection of the wire is between 0.5 and 50 ppm, or wherein the amount of MgO added to the steel through the injection of the wire is between 0.5 and 50 ppm, or wherein the amount of (Mg+MgO) added to the steel through the injection of the wire is between 0.5 and 50 ppm. Preferably the total magnesium content in the steel is between 0.5 and 10 ppm, and wherein the magnesium in solid solution is below 2 ppm.

[0021] It should be noted that ppm means grams of compound per ton of liquid steel. It should also be noted that with a continuously cast steel product a solidified product is meant. This cast product may be in the form of a slab, billet, thin slab or cast strip. The product according to the invention has been subjected to a calcium treatment with a more homogeneous distribution of calcium or calcium containing compound, and consequently, the final product will be more homogeneous in distribution of CaS, and consequently of globular MnS-precipitates. Also, the casting process can be performed more smoothly due to the reduced clogging tendency, and thereby the casting is not interrupted or not interrupted as often as would have been the case with a poorer distribution of calcium or calcium containing compound in the melt prior to casting the continuously cast steel product.

[0022] The invention is also embodied in a continuously cast steel product, produced as described above, wherein the total magnesium content in the steel is between 1.0 and 10 ppm, and wherein the magnesium in solid solution is below 2 ppm. It will be clear that the magnesium in solid solution can only be measured in the solidified condition of the continuously cast steel product.

[0023] The invention is also embodied in a continuously cast steel product, wherein the total magnesium content in the steel is between 1.0 and 10 ppm, and wherein the magnesium in solid solution is below 2 ppm.

[0024] It is noted that US 4,094,666 and 6,685,763 disclose the use of calcium and magnesium. US 4,094,666 injects an iron sheathed clad product comprising calcium and magnesium for desulphurisation and deoxidation purposes in such a way that the vaporization of the calcium and magnesium is deliberately prevented and a distribution enhancing effect of the calcium is consequently not reached, nor strived at. In US 6,685,763 the magnesium is added to keep the deoxidation inclusions in the liquid phase. A distribution enhancing effect of the calcium is neither obtained nor desired because the magnesium is also added alone without any calcium.

[0025] It is also noted that in some examples of US 4,094,666 and DE 2421743 magnesium additions are made to cast iron. These additions are intended to inoculate the nodular graphite in nodular cast iron. These additions do not result in any distribution enhancing effect of the calcium which may simultaneously be added for desulphurization or desoxidation purposes.

[0026] The invention will now be explained in more detail by means of the following, non-limiting example.

[0027] A wire having a diameter of 13 mm was injected into a steel melt, the wire comprising a metallic tubular shell having a wall thickness of 0.5 mm enclosing a core, the core comprising calcium or a calcium containing compound and iron (CaFe wire) and 3% magnesium as a distribution enhancing compound. The ratio of calcium and iron in the CaFe wire is about 30:70, containing about 73 g Ca/m of wire and 2 g Mg/m. The addition of a small amount of magnesium to the calcium wire will increase the vapour pressure inside the wire and give the Calcium particles, which are liquid or will just form a gas at the injection depth, more momentum to spread from the location where the wire dissolves into the liquid steel. In this way the calcium will react in a larger amount of steel than without magnesium and the formation of calcium aluminates is increased and the formation of CaS is reduced. CaS is mainly formed due to high calcium activities that are present in the steel during calcium injection. By distributing the Calcium over a larger volume of liquid steel by the distribution enhancing compound, the local calcium concentrations are reduced, thereby reducing the tendency of the CaS-formation. It should be noted that similar experiments using pure calcium wire instead of CaFe-wire were performed. The inventors found that when using wires with added magnesium as a distribution enhancing compound produced a higher yield of the calcium in the ladle as well as in the tundish, indicative for a more effective use of the added calcium and hence of a more effective calcium treatment.

[0028] The total addition of magnesium to the steel through the injected wire is 0.5 ppm to 50 ppm when the addition of calcium to the steel varies between 0.05 to 0.5 kg Ca/ton of steel. It should be noted that the amount of magnesium injected in the steel can be chosen independently of the amount of calcium injected in the steel for instance by using different wires with different ratios of magnesium to calcium. It was found by the inventors that the relative yield of the magnesium decreases when adding higher amounts of Magnesium. The total magnesium content in the steel after injection (total magnesium being magnesium in the inclusions and magnesium dissolved in the steel) is 0.5 to 10 ppm. The amount of magnesium in solid solution in the steel is below 2 ppm. Mass balances done on the inclusions in calcium treated steel show that practically all magnesium is present in the inclusions and the magnesium in solid solution, i.e. not in an inclusion, is below 2 ppm. It should be noted that the total magnesium content in the final steel product is the sum of magnesium already present in the steel prior to injecting, magnesium injected in the steel through the injection of the magnesium containing wire and magnesium added after the injection of the wire.

[0029] The invention will now be explained in more detail by means of the following, non-limiting Figure.

[0030] In Figure 1 a schematic drawing is presented of the wire 10 comprising a metallic tubular shell 20 having a certain thickness 40 enclosing a core 30. In Figure 1 the cross-section of the wire is substantially cylindrical, but it is noted that in general the cross-section may also be oval, triangular, square, rectangular, quadrangular or even multi-angular such as hexagonal, wherein the corners may be rounded or sharp. The core 30 comprises calcium or a calcium containing compound and a distribution enhancing compound such as magnesium as described above. The core may also comprise iron in case of the so-called CaFe wire. The shell 20 of the wire may be made of iron or steel. The core may in general be of a solid, a powdery or a granular constitution. It will be clear that Figure 1 only shows a small length of wire. In practice the length of wire is much longer.

[0031] It is of course to be understood that the present invention is not limited to the embodiments and examples described above, but encompasses any and all embodiments within the scope of the claims and the description and within the spirit of the invention as herein disclosed.

Claims

1. A wire (10) for injecting into a steel melt in an injection direction, the wire comprising a metallic tubular shell (20) enclosing a core (30), the core comprising calcium or a calcium containing compound, **characterised in that** the core also comprises a distribution enhancing compound for distributing the calcium or calcium containing compound in the steel melt in a direction substantially perpendicular to the injection direction wherein the distribution enhancing compound comprises a compound having a vapour pressure which is higher than the vapour pressure of calcium at liquid steel temperatures for obtaining a more homogeneous distribution of the calcium or calcium containing compound in the steel melt.

2. Wire according to claim 1, wherein the distribution enhancing compound comprises one or more of a compound selected from the group of compounds comprising magnesium, magnesium-oxide, sodium, sodium-oxide, zinc, zinc-oxide.

3. Wire according to any one of the preceding claims, wherein the distribution enhancing compound comprises magnesium and/or magnesium oxide.

4. Wire according to claim 3 wherein the weight ratio of magnesium to calcium is between 1 to 10%, preferably between 1.5 and 5%.

5. Wire according to any one of the preceding claims wherein the core has a powdery or granular constution.

6. Wire according to any one of the preceding claims wherein the shell is made of steel.

7. Process of treating a steel melt wherein a wire (10) according to any of the preceding claims is introduced in the melt in an injection direction, preferably a substantially vertical injection direction, and wherein the calcium or calcium containing compounds are distributed substantially perpendicularly to the injection direction by the distribution enhancing compound wherein the distribution enhancing compound comprises a compound having a vapour pressure which is higher than the vapour pressure of calcium at liquid steel temperatures.

8. Process according to claim 7 wherein the distribution enhancing compound comprises one or more of a compound selected from the group of compounds comprising magnesium, magnesium-oxide, sodium, sodium-oxide, zinc, zinc-oxide, preferably wherein the distribution enhancing compound comprises magnesium and/or magnesium oxide.

9. Use of a wire (10) according to any one of the claims 1 to 6 for improving the spatial distribution of calcium in a steel melt after injection of the wire in the steel melt by injection means.

10. Continuously cast steel produced using the process of claim 7 or 8, wherein the amount of magnesium added to the steel through the injection of the wire (10) is between 0.5 and 50 ppm, or wherein the amount of MgO added to the steel through the injection of the wire (10) is between 0.5 and 50 ppm, or wherein the amount of (Mg+MgO) added to the steel through the injection of the wire (10) is between 0.5 and 50 ppm.

11. Continuously cast steel product, produced using the process of claim 7 or 8, wherein the total magnesium content in the steel is between 0.5 and 10 ppm, and wherein the magnesium in solid solution is below 2 ppm

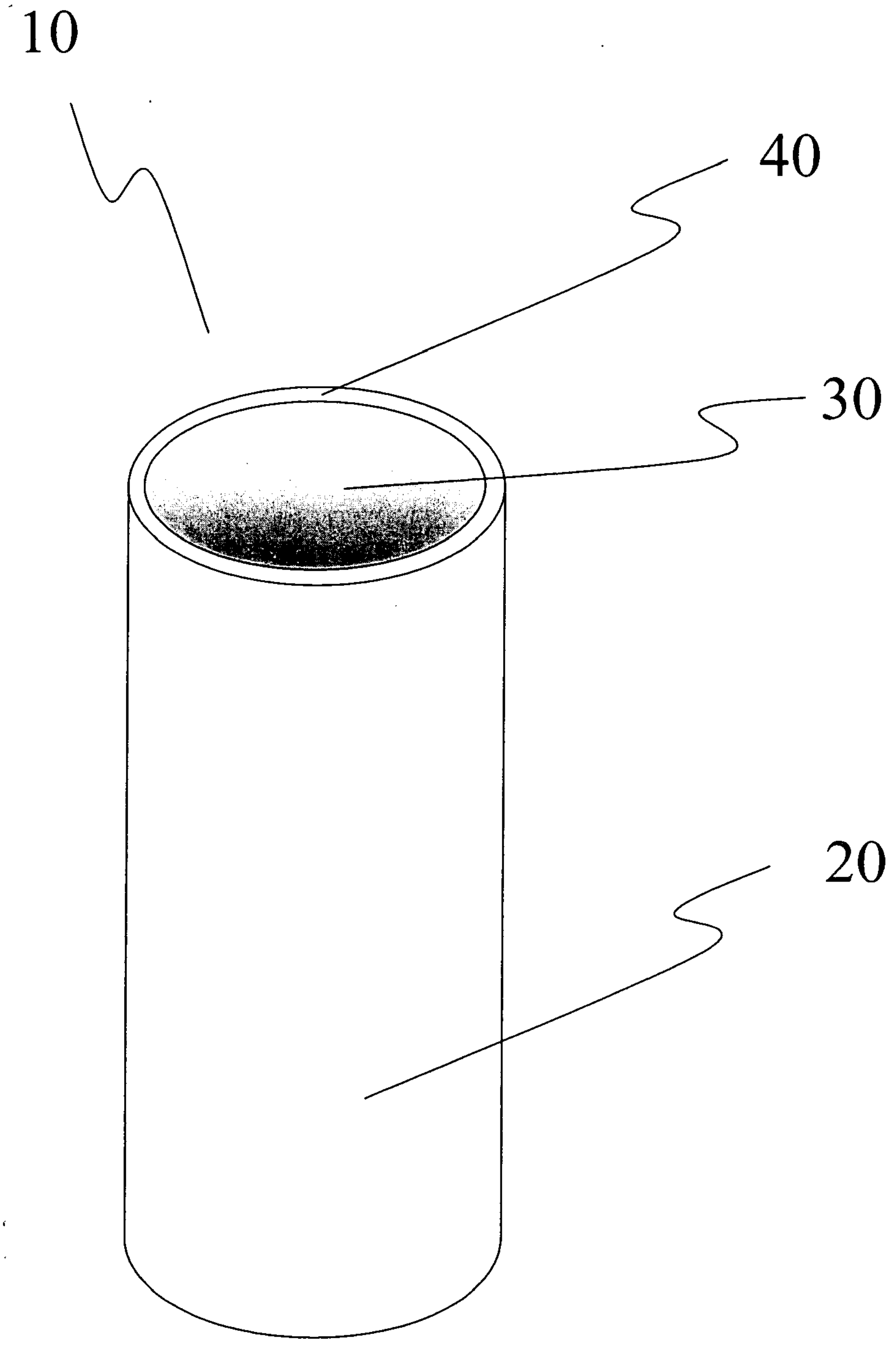

Figure 1

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- DE 2421743 **[0003] [0005] [0025]**
- US 4094666 A **[0024] [0024] [0025]**
- US 6685763 B **[0024] [0024]**