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

(11) Publication number: **0 044 183**
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 81303066.5

(22) Date of filing: 06.07.81

(51) Int. Cl.³: C 21 C 7/00
C 21 C 7/06, C 21 C 7/064
C 21 C 1/10, C 22 B 9/10

(30) Priority: 09.07.80 GB 8022513

(43) Date of publication of application:
20.01.82 Bulletin 82/3

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

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(54) Metallurgical treatment agents.

(57) Method of making wire-like treatment agent for metal melts e.g. ferrous ones comprises heating metal tube (1) e.g. of steel, introducing into the tube (1) a melt (3) having a temperature below melting point of the metal of the tube and comprising a reactive metal e.g. magnesium and cooling the tube (1) and the melt inside it to solidify the melt in the tube (1). Wire-like treatment agent itself comprises solidified melt (11) comprising a reactive metal encased in a preformed tube (1) of metal of higher melting point than that of the reactive metal.

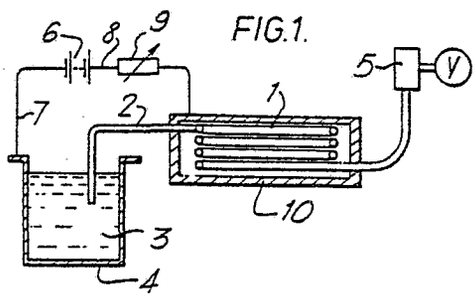

FIG.1.

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METALLURGICAL TREATMENT AGENTS

The invention concerns metallurgical treatment agents, in particular such agents in wire-like form, and their manufacture and use.

It is well known that certain reactive metals, e.g. magnesium, are useful for treating molten metals, e.g. iron and steel, to produce effects such as deoxidation, desulphurisation, inclusion modification and nodularisation. The reactive metals are generally of relatively low melting point in the sense that their melting points are substantially lower than the temperatures of the metallic melts to be treated and the boiling point may also be below the temperature of the melt to be treated. These factors and the reactivity of the reactive metals create problems in making and using treatment agents comprising the metals.

Numerous proposals have been made concerning temporarily protecting the reactive metal by providing it within a container that, in use, permits release of the reactive metal. In particular it has been proposed to sheath the reactive metal with a non-reactive metal of higher melting point to yield a wire-like product and to conduct the treatment by feeding the wire-like product into the metallic melt to be treated. One such proposal is described in U.S. patent specification 3915693 which discloses, for example, a steel tube filled with calcium-silicon powder and aluminium powder. After the tube has been filled, it is said that the tube may be

drawn to a desired smaller diameter. Mention is made of filling the tube by evacuating it of gas and permitting it to fill with the powder by suction. Another such proposal is described in U.S. patent specification 4134196 which discloses, for example, extruding particulate magnesium as a wire and enveloping it in steel tape aligned with the axis of the wire, one edge of the tape being tightly folded over the other.

The known wire-like treatment agents all have one or more disadvantages regarding their manufacture and/or use.

According to one aspect of the invention a method of making a wire-like treatment agent for metal melts comprises heating a metallic tube, introducing into the tube a melt having a temperature below the melting point of the metal of the tube and comprising a reactive metal and causing or allowing the tube and melt so to cool that the melt solidifies in the tube.

The method of the invention has the advantage of not requiring the reactive metal used to be initially in any particular form. In the invention the melt introduced into the tube may be made by melting, for example, magnesium in ingot form. Such reactive metals as calcium and magnesium when in particulate form are hazardous to handle and transport and tend to become contaminated by reaction with atmospheric oxygen and moisture. Moreover it is difficult to fill relatively long and narrow preformed tubes with particulate material and if initially a relatively short and wide tube is filled with the particulate material and is then drawn to a desired smaller diameter, the drawing constitutes an additional manufacturing step. Also, any method of providing a tube filled with particulate material tends to result in the material being relatively loosely packed and in non-uniform packing. By use of the method of the invention a relatively long and narrow tube can be completely and uniformly filled and without any need for a drawing operation.

The method of the invention has a particular advantage over any method involving forming a tube around the desired contents in that a preformed tube is used and so there is no need for equipment to form the tube around the contents. Furthermore, if a tube is formed around particulate material there is a risk that air and moisture may be trapped in the product whereas this can be avoided in the method of the invention.

The method of the invention has a yet further advantage over any method involving using a strip of metal to form a tube around the desired contents, in that any such method means that the matter forming the tube must have one or more joins, e.g. a longitudinal join, and possibly also an overlapped portion. A join is a potential weakness that in use of the product could give rise to premature and non-uniform release of the reactive metal and an overlapped portion, because of the increased thickness of the tube in the area of overlap, is also liable to give rise to non-uniform release of the reactive metal. These disadvantages are avoided by the use of a preformed tube in the method of the invention.

In the method of the invention the tube is preferably heated to a temperature in the range of 150°C below the melting point of the matter to be introduced into the tube to 150°C above that melting point. The heating is preferably maintained throughout the introduction of the melt into the tube. The tube is not heated to a temperature as high as the boiling point of the melt.

The heating of the tube can be effected by passing an electric current through it and instead of, or in addition to this, heating of the tube may be achieved by induction and/or in an oven.

The heating of the tube serves to prevent premature solidification of the melt in the tube and achieving this object can be further aided by heating the melt to be introduced into the

tube to a temperature above the melting point of its ingredient(s).

The introduction of the melt into the tube is preferably achieved by connecting one end of the tube to a supply of the melt to be introduced and applying a vacuum to the other end of the tube. Alternatively, or in addition, the melt may be forced into the tube by an applied pressure of inert gas. In any event, the introduction of the melt into the tube can be aided by use of a siphoning effect. By means of the method the product can be produced in very long continuous lengths e.g. 500 m.

The tube is preferably of iron or steel if the treatment agent is for treatment of ferrous metals. The diameter of the tube is preferably 1 to 20 mm, especially 5 to 15 mm, and its wall thickness 0.05 to 3 mm, especially 0.1 to 1 mm. It is particularly preferred that the melt introduced into the tube should contain or consist of magnesium or a magnesium alloy.

When a wire-like product in the form of magnesium in a steel tube is introduced into a ferrous metal melt at a temperature of say 1350°C a layer of the melt solidifies around the wire-like product and the temperature of the surface of the steel tube itself may be only about 1200°C but this is in the range in which magnesium has a substantial vapour pressure. Depending on a number of variables, an explosive pressure may develop within the steel tube and bubbles of magnesium vapour may rise too quickly through the ferrous metal melt and cause splashes of this melt and burn on the surface and cause wastage of magnesium. Also, pieces of the wire-like product may become broken off and float up and burn on the surface, again causing wastage of magnesium.

If a wire-like product of the invention is to be used in circumstances where the undesirable phenomena mentioned above might tend to occur, it is preferred to produce in the product, after the tube has been filled with the solidified melt comprising a reactive

metal, a number of holes in the tube, these holes being uniformly disposed around the tube and along its length. By this means a desirable controlled release of the contents of the tube can be achieved. The holes, which may be generally circular, preferably have a size in the range of 0.1 to 2 mm. The holes may be produced by, for example, passing the filled tube between one or more pairs of spiked rollers. A lubricant may be applied to the tube in connection with the making of the holes and an oily film may remain and serve to protect the reactive metal, exposed at the holes, from atmospheric attack. In any event, after the holes have been formed, they can be closed with a material which is readily removed in use but serves to prevent access of oxygen and moisture. Oils and waxes are suitable materials for this purpose.

To control the rate of vaporisation of reactive metal within the tube, the tube may be given a porous internal coating of refractory material before it is filled with the melt comprising the reactive metal. The refractory coating if present preferably comprises one or more of carbon, zirconia, alumina and magnesia. Furthermore, before the tube is filled with the melt, it may be given an internal coating of another metal desired to achieve an additional metallurgical reaction when the product is used. Examples of metals for providing such a coating include aluminium, cerium, zirconium, titanium, columbium, silicon and lead.

For treatment of metal melts having very high temperatures e.g. steel melts with products of the invention containing volatile reactive metals such as magnesium it can be desirable to reduce the vapour pressure of the matter within the tube. For this purpose it is preferred to use any magnesium or other highly volatile metal in the tube in the form of an alloy or mixture with another metal or other substance. Examples of suitable materials to provide the contents of the tube include magnesium-calcium, magnesium-zirconium and magnesium-nickel alloys and mixtures of magnesium with aluminium

or compounds, e.g. carbides, of metals such as calcium.

In addition to the method, the wire-like products themselves are an aspect of the invention. Thus, according to the invention a wire-like product for introducing a treatment agent comprising a reactive metal into a metal melt comprises a solidified melt comprising a reactive metal encased in a preformed tube of metal of higher melting point than that of the reactive metal. Preferred features of the product are as described above.

A yet further aspect of the invention comprises treating a melt of metal by feeding into the melt a product of the invention. The purpose of the treatment may be to effect one or more of desulphurisation, deoxidation, inclusion modification and nodularisation. The product of the invention is especially useful for treatment of ferrous metals, particularly iron. A length of the wire-like product may be fed continuously into the metal melt to be treated and the feeding rate can readily be varied or otherwise controlled. The wire-like product may be fed into the melt through a refractory tube, the outlet from which may be beneath the surface of the melt, or the product may be fed directly into the melt, in which case the product must be sufficiently rigid that it can be fed well below the surface of the melt and the casing must be such that the product does not disintegrate until a sufficient depth below the surface of the melt is reached.

The invention is further described with reference to the accompanying diagrammatic drawings in which:

Figure 1 is a diagram showing apparatus for effecting the method of the invention,
Figure 2 is a view of one end and side of a portion of a product of the invention and
Figure 3 is an enlarged view of the end of the product as in Figure 2.

Referring to Figure 1, a coiled length of steel tube 1 communicates at one end with an angled metal pipe 2, the free end of which dips below the surface of molten magnesium 3 contained in a metal vessel 4. The end of the tube 1 remote from the vessel 4 opens into a chamber 5 provided with a suction pump V for applying a vacuum.

A source of electric direct current 6 is connected by a lead 7 to the metal vessel 4 and by a lead 8, via an adjustable resistance 9, to the end of the pipe 2 remote from the vessel 4. The tube 1 is positioned in an oven 10 for heating the tube.

To operate the apparatus of Figure 1, magnesium ingots are melted to provide the melt 3. The tube 1 is heated in the oven 10 to a temperature of about the melting point of magnesium. Electric direct current from the source 6 is passed through the lead 8, the adjustable resistance 9, the pipe 2, the melt 3 (which is electrically conductive) and the lead 7 and serves to keep the melt 3 molten and to heat the pipe 2 to a temperature of about the melting point of magnesium. The temperature of the tube 1 is maintained and vacuum applied by means of the pump V to fill the tube 1 with molten magnesium. The heating of the tube 1 is then discontinued and the tube and melt allowed to cool and the magnesium thereby caused to solidify in the tube, which is then disconnected from the angled pipe 2 and chamber 5. The use of the chamber 5 facilitates completely filling the tube 1 with the melt without any risk of any of the melt being drawn into the pump.

Referring to Figures 2 and 3, the wire-like product of which Figures 2 shows merely a short length comprises a preformed steel tube 1 and within that a core 11 of solidified molten magnesium. Through the steel tube 1 are uniformly distributed holes 12. The product can be made by first heating the steel tube (having no holes) to a temperature of about the melting point of magnesium, introducing

molten magnesium into the tube and allowing it to solidify there and then moving the tube through a device to create the holes 12.

CLAIMS

1. A method of making a wire-like treatment agent for molten metal characterised by heating a metallic tube (1), introducing into the tube (1) a melt (3) having a temperature below the melting point of the metal of the tube and comprising a reactive metal and causing or allowing the tube (1) and melt so to cool that the melt solidifies in the tube (1).

2. A method according to claim 1 in which the tube (1) is heated to a temperature in the range of 150°C below the melting point of the matter to be introduced into the tube (1) to 150°C above that melting point.

3. A method according to claim 1 or claim 2 in which the melt (3) is introduced into tube (1) by connecting one end of the tube (1) to a supply of the melt (3) to be introduced and applying a vacuum to the other end of the tube.

4. A method according to any of claims 1 to 3 in which, after the melt has solidified in the tube (1), holes (12) are formed in the tube (1) uniformly disposed around the tube (1) and along its length.

5. A wire-like treatment agent, for molten metal, comprising a metal sheath (1) around a reactive metal (11) of lower melting point characterised in that the sheath (1) is a preformed tube (1) and the reactive metal (11) is present in a melt solidified inside the tube (1).

6. A treatment agent according to claim 5 in which the tube (1) is of steel and the reactive metal (11) is magnesium or a magnesium alloy.

7. A treatment agent according to claim 5 or claim 6 in which the diameter of the tube (1) is from 5 to 15 mm and its wall thickness is from 0.1 to 1 mm.

8. A treatment agent according to any of claims 5 to 7 in which there are holes (12) uniformly disposed around the tube (1) and along its length.

9. A treatment agent according to claim 8 in which the holes have a size in the range of 0.1 to 2 mm.

FIG.1.

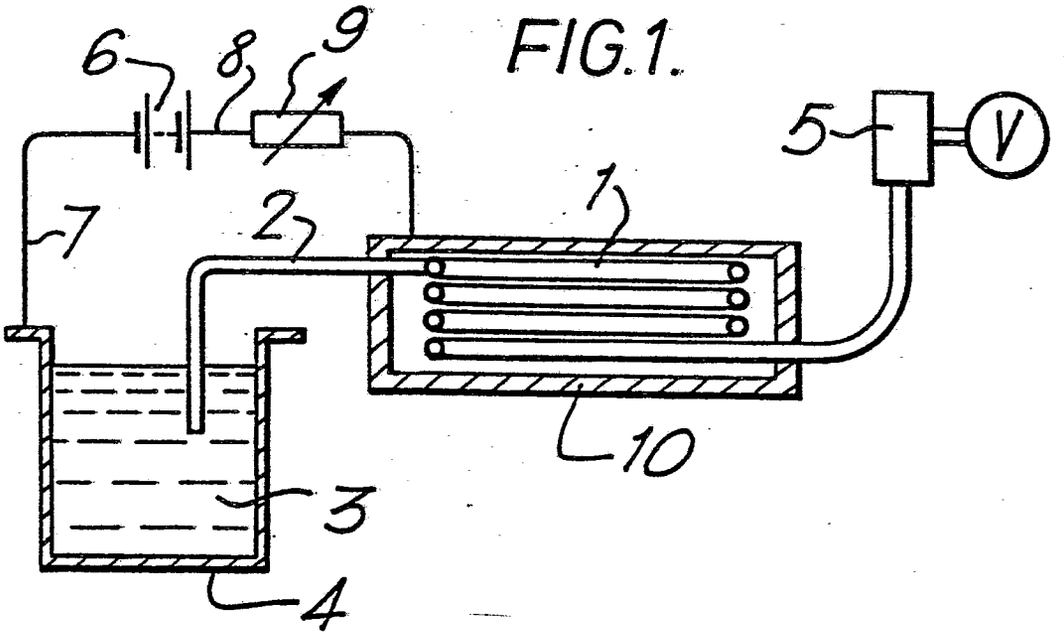


FIG.2.

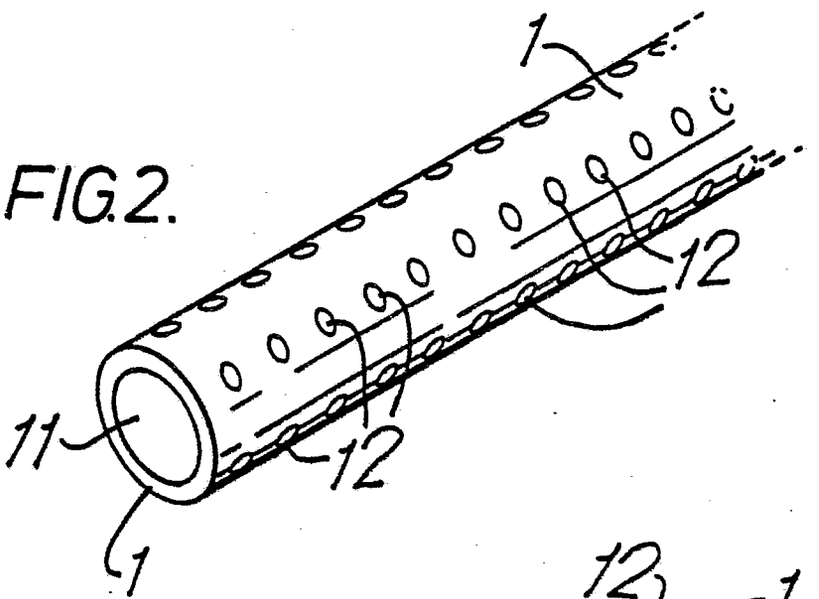
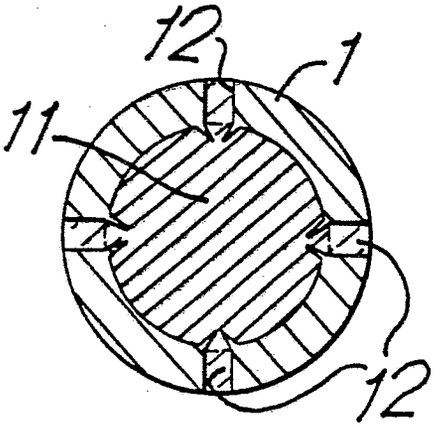


FIG.3.



0044183

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EUROPEAN SEARCH REPORT

Application number
EP 81 30 3066

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	DE - C - 974 835 (MAX-PLANCK-INSTITUT FUR EISENFORSCHUNG) * Claim 1(c)(d) and claim 2;page 2, lines 40-41 *	1,3,5,6
X	DE - A - 2 421 743 (OTOTANI) * Claims 1,6; page 4, lines 1-3 *	1,3,5,6
AD	US - A - 4 134 196 (YAMAJI et al.)	
AD	US - A - 3 915 693 (RASMUSSEN)	
A	WO - A - 79/00536 (CATERPILLAR TRACTOR)	

CLASSIFICATION OF THE APPLICATION (Int Cl ³)

C 21 C 7/00
7/06
7/064
1/10
C 22 B 9/10

TECHNICAL FIELDS SEARCHED (Int Cl ³)

C 21 C
C 22 B
B 22 D

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	19-10-1981	SCHROEDER