



AU9650542

(12) PATENT ABRIDGMENT (11) Document No. AU-B-50542/96
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 695890

(54) Title
IMMERSED METALLURGICAL POURING NOZZLES

International Patent Classification(s)
(51)⁶ **B22D 041/54**

(21) Application No. : **50542/96**

(22) Application Date : **09.04.96**

(30) Priority Data

(31) Number	(32) Date	(33) Country
9507444	10.04.95	GB UNITED KINGDOM

(43) Publication Date : **24.10.96**

(44) Publication Date of Accepted Application : **27.08.98**

(71) Applicant(s)
DIDIER-WERKE AG

(72) Inventor(s)
STEPHEN JOHN LEE

(74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122

(56) Prior Art Documents
JP 07-051818

(57) Claim

1. An immersed metallurgical pouring nozzle comprising a body of refractory material which defines a flow passage, and an annular member of refractory material whose erosion resistance is higher than that of the body of the nozzle, the annular member being situated, in use, in the region of the slag line of the nozzle and wholly encapsulated in the material of the body of the nozzle, wherein an annular portion of the body of the nozzle which is situated outside the annular member is made of a refractory material whose erosion resistance is greater than that of the remainder of the body of the nozzle but is less than that of the annular member, and wherein all of the materials of the body of the nozzle are co-pressed.

AUSTRALIA

Patents Act 1990

**ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT**

Application Number:

Lodged:

Invention Title: IMMERSED METALLURGICAL POURING NOZZLES

The following statement is a full description of this invention, including the best method of performing it known to us :-

IMMERSED METALLURGICAL POURING NOZZLES

5 The present invention relates to immersed metallurgical
pouring nozzles, that is to say pouring nozzles of which
a portion, typically the downstream end, is immersed in
a pool of molten metal, in use. The invention is
particularly concerned with so-called submerged entry
10 nozzles (SEN's) for pouring molten steel, that is to say
pouring nozzles which conduct molten steel from a tundish
or other metallurgical vessel into a mould, typically a
continuous casting mould from which the solidified metal
is continuously withdrawn. The invention does, however,
15 relate to other types of pouring nozzle, such as so-
called ladle shrouds for conducting molten steel from a
metallurgical vessel into a tundish, whose downstream end
is also submerged, in use, in molten metal.

20 When continuously casting steel, molten steel is
continuously introduced into the open upper end of the
mould through an SEN whose lower end is submerged in the
metal in the mould. The surface of the steel in the
mould is thus exposed to the air and is thus subject to
reoxidation. In order to prevent this and to minimise
25 the heat loss from the exposed surface, the surface of
the molten steel is typically covered by a layer of
insulating powder comprising a combination of fluxing
agents or glasses together with carbon, silica and
alumina. The powder melts into a glassy layer which
30 shields and insulates the molten steel surface and tends
to be drawn down between the molten steel and the sides
of the water-cooled mould and thus to act as a lubricant.
However, this molten glassy layer has a highly aggressive
and corrosive tendency with respect to the material of

the SEN. The outer surface of the SEN tends to be rapidly eroded away by the glassy layer at the slag line, that is to say at the region at which the SEN passes through the surface of the molten steel and glass, and it is this erosion which limits the service life of the SEN and necessitates its being replaced relatively frequently.

SEN's for casting steel are typically made of a mixture of alumina and graphite. The graphite is added to impart thermal shock resistance to the alumina because it will be appreciated that at the commencement of operation, even if the SEN is preheated, as is common, a relatively cold SEN is contacted by molten steel at a temperature of ca. 1550°C which represents a very substantial thermal shock. Pure alumina would tend to crack when subjected to this thermal shock but graphite has a high coefficient of thermal conductivity and thus tends to accelerate the dissipation of thermal gradients and also has considerable lubricant characteristics and thus permits slight relative movement of the constituent alumina particles of an SEN without cracking occurring.

However, the presence of the graphite in the alumina reduces the resistance to erosion by the glassy layer at the slag line by its influence on the bonding matrix. Accordingly the graphite content need be as high as possible to produce one of the necessary characteristics of SEN's, namely thermal shock resistance, and as low as possible to achieve the other necessary characteristic, namely resistance to erosion at the slag line. The construction and composition of all SEN's thus necessarily constitutes a compromise between these two conflicting requirements.

Various different constructions of SEN have been proposed and used in an attempt to minimise these problems and certain of these are illustrated schematically in Figure 1.

5

Figure 1a shows a simple SEN which is of uniform alumina graphite construction with its lower end immersed in a pool of molten steel 2 on which a glassy protective layer 4 of molten mould powder floats. As may be seen, the body 6 of the SEN is eroded very substantially at the slag line and the rate of wear or erosion is typically 7 to 10 mm per hour. The composition of such nozzles includes 40 to 65%, typically 51%, by weight Al_2O_3 and 20 to 35%, typically 31%, by weight C and has a bulk density of 2.20 to 2.65, typically 2.40 g/ml.

15

The modified SEN shown in Figure 1b includes an annular body 8 of zirconia graphite which is copressed with the alumina graphite and affords the external surface of the SEN in the region of the slag line. The alumina graphite has the same composition as that set forth above and the zirconia graphite has a composition including 65 to 82%, typically 74%, by weight ZrO_2 and 17 to 25%, typically 20%, by weight C and a bulk density of 3.20 to 3.60, typically 3.60, g/ml. In this construction, the rate of erosion can be reduced to typically 1.5 to 3.5 mm per hour and whilst this represents a substantial improvement the rate of erosion is still substantial. The reason for this is that the zirconia graphite insert necessarily includes a significant graphite content in order that it has the necessary thermal shock resistance and this graphite content renders the bonding matrix of the insert subject to substantial rates of erosion at the slag line.

20

25

30

The further modified construction shown in Figure 1c is very similar but in this case the entire lower portion of the SEN is made of zirconia graphite whose composition is the same as that set forth above. The performance and disadvantages of this construction are the same as those of the construction of

5 Figure 1b.

Figure 1d represents a different approach in which a preformed, high temperature fired annular sleeve of sintered zirconia is secured by refractory cement to the external surface, in the region of the slag line, of an SEN of otherwise conventional shape. The zirconia sleeve has a very high erosion

10 resistance, whereby the erosion is reduced to typically 0.2 to 0.5 mm per hour, but due to the absence of graphite its thermal shock resistance is lower which means that in practice this construction is unacceptable due to the possibility of thermal shock failure of the sleeve and/or its refractory cement connection to the SEN, especially if the preheating conditions are not accurately controlled.

15 It is an object of the present invention to provide an immersed metallurgical pouring nozzle, particularly an SEN for pouring steel, which avoids the problems referred to above and which in particular has a reduced tendency to erosion at the slag line but which nevertheless is not subject to thermal shock failure.

20 According to the present invention there is provided an immersed metallurgical pouring nozzle, particularly an SEN, of the type comprising a body of refractory material which defines a flow passage and an annular member of refractory material whose erosion resistance is higher than that of the body of the nozzle.

25 The annular member is wholly encapsulated in the material of the body of the nozzle,

An annular portion of the body of the nozzle which is situated outside the annular member is made of a refractory material whose erosion resistance is greater than that of the remainder of the body of the nozzle but is less than that

30 of the annular member, all of the materials of the body of the nozzle being compressed.



The main body of the nozzle may be preferably made of a refractory material e.g. alumina graphite.

Thus the nozzle in accordance with the invention is provided with a band or annular member of erosion resistant material, as in the known constructions, but differs from the known constructions in that the erosion resistant material does not constitute a part of the outer surface of the nozzle but is surrounded by a layer of material forming part of the body of the nozzle.

In the known nozzles, at the beginning of pouring, the molten metal and erosive glass layer come directly into contact with the erosion resistant material which is thus subjected to a substantial temperature gradient and thermal shock and must be constructed to resist this. However, in the nozzle in accordance with the present invention, the molten metal and erosive glass layer do not initially come into direct contact with the erosion resistant material but instead contact the material of the body of the nozzle inside and outside it which means that the temperature gradient and thus the thermal shock to the erosion resistant material is subjected are substantially reduced. This means that the erosion resistant material need no longer represent the same compromise between thermal shock resistance and erosion resistance, or at least not to the same extend as previously, and thus that it may have a lower graphite content, preferably 0 to 10% and more preferably 6% or less, than was previously possible whilst still having adequate resistance to the reduced thermal shock to which it is subjected. Its erosion resistance may thus be substantially higher than was previously possible. The covering layer of the material of the body of the nozzle is rapidly eroded at the slag line but by the time the molten glass layer contacts the erosion resistant material it has already substantially reached the temperature of the molten metal and is not then subjected to a further substantial thermal shock.

Further features of the invention will be apparent from the following description of a specific embodiment of the invention which is given with reference to Figures 2 to 5 of the accompanying drawings, in which:

Figure 2 is a diagrammatic axial sectional view of an SEN for pouring molten steel in the as supplied state;



Figure 3 is a view of the SEN of Figure 2 shortly after the commencement of service;

Figure 4 is a view similar to Figure 2 of an alternative construction of SEN; and

- 5 Figure 5 is a view similar to Figure 2 of an SEN in accordance with an embodiment of the invention.

The SEN shown in Figure 2 comprises a tubular body 6 which defines a central flow passage 7 and is made of pressed alumina graphite, whose composition is the same as that described in connection with Figure 1. Wholly
10 encapsulated within the body at its lower end, that is to say in the vicinity of the slag line, i.e. where the nozzle will pass through the layer of molten mould powder when it is in use, is an annular member 8 of substantially higher erosion resistance, e.g. carbon bonded zirconia, optionally with a low content of graphite. At the commencement of operation the annular member 8 is not
15 directly contacted by molten steel or mould powder but is initially protected and insulated by the surrounding alumina graphite material of the nozzle body. It is therefore subjected to a substantially reduced thermal shock which it can adequately resist with only a low graphite content. The outer layer of alumina graphite is rapidly eroded at the slag line, as shown in Figure 3, until the slag
20 contacts the insert 8, whereafter the rate of erosion is significantly reduced, typically to less than 1 mm per hour.

The erosion resistant insert 8 may be a unitary, self-supporting member which is co-pressed with the alumina graphite of the nozzle body. It is preferred that the insert comprises carbon bonded zirconia comprising 85 to 92%,
25 typically 88%, weight ZrO_2 and 2 to 10%, typically 6%, by weight C and has a bulk density of 3.9 to 4.4, typically 4.1, g/ml. Alternatively, the insert may be presintered and incorporated into the nozzle body during its manufacture. In this event the insert will preferably contain 87 to 97%, typically 95.5%, by weight ZrO_2 and will have a bulk density of 4.1 to 4.6, typically 4.3, g/ml. However, the
30 fact that the insert is not exposed to the atmosphere and is wholly supported by the material of the nozzle, opens up the possibility of the insert 8 being carbon and graphite free and in powder or partially presintered form in the as supplied



state and then subsequently densifying and fully sintering under the action of the heat of the molten metal as the nozzle is first used. In this event the insert may comprise 84 to 94%, typically 92%, by weight ZrO_2 and will have a bulk density of 3.9 to 4.3, typically 4.0 g/ml. The material thus initially has a high thermal shock resistance which changes progressively to a high erosion resistance as sintering proceeds. If densification and sintering of the erosion resistant insert occurs in situ, this will be associated with a reduction in volume but this can be readily accommodated by providing a layer of compressible, refractory material, e.g. ceramic fibres adjacent the inner surface of the insert 8.

10 A combination of the concepts shown in Figures 1c and 2 may be utilised, whereby the erosion resistant insert 8, made of the material described in relation to Figures 2 and 3, is encapsulated within a zirconia graphite region 9, whose composition is the same as that described in relation to Figure 1c, of the SEN body which is co-pressed with the alumina graphite main body of the SEN
15 and this is shown in Figure 4.

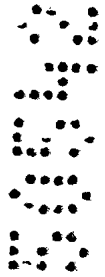
In contrast to the above SEN constructions, Figure 5 shows a SEN in accordance with the present invention. The SEN of Figure 2 is modified by replacing the layer of alumina graphite radially outside the insert 8 (that is the peripheral, annular region 11) with a layer of zirconia graphite 11. The insert 8
20 may have the same low-carbon or no-carbon content as described in connection with figures 2 to 4 but the outer layer 11 of zirconia graphite will be subject to the same compromise as regards carbon content as was discussed in connection with Figure 1 and will therefore have the same composition as described in connection with Figure 1c. The various materials are preferably co-pressed but it would also be possible for the components to be separately
25 preformed, fired and machined and then assembled and in this case the zirconia graphite component 11 may not only extend around the insert 8 but may also constitute the whole of the lower portion of the nozzle 6 below the insert.

30 The service life of a nozzle as shown in Figure 1a is sufficient to enable only one ladle of molten or even less to be poured before replacement is necessary due to slag line erosion. Nozzles as shown in Figures 1b and 1c



have an increased service life sufficient to pour, typically, four ladles of molten steel. However, the nozzle shown in Figures 2 and 4 is found to have a significantly improved service life sufficient to pour, typically, seven ladles. The inventive nozzle construction shown in Figure 5, however, has a yet further
5 enhanced service life and may be able to pour up to ten ladles.

It will be appreciated that, as an alternative to alumina graphite, the nozzle body 6 may be made of any material suitable for the purpose, such as fused silica, and that the erosion resistant insert 8 may comprise materials other than zirconia, e.g. magnesia or even alumina with a lower graphite content than
10 the nozzle body. The invention has been described principally in connection with nozzles for pouring steel but it is equally applicable to nozzles for pouring non-ferrous metals, such as aluminium, where similar nozzle erosion problems arise.



THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An immersed metallurgical pouring nozzle comprising a body of refractory material which defines a flow passage, and an annular member of refractory material whose erosion resistance is higher than that of the body of the nozzle, the annular member being situated, in use, in the region of the slag line of the nozzle and wholly encapsulated in the material of the body of the nozzle, wherein an annular portion of the body of the nozzle which is situated outside the annular member is made of a refractory material whose erosion resistance is greater than that of the remainder of the body of the nozzle but is less than that of the annular member, and wherein all of the materials of the body of the nozzle are co-pressed.

2. A nozzle as claimed in claim 1, wherein a carbon content of the annular member is between 0 and 10% by weight.

3. A nozzle as claimed in claim 1 or claim 2, wherein the materials of the body of the nozzle and of the annular member are co-pressed.

4. A nozzle as claimed in any one of claims 1 to 3, wherein the material of the annular member is sintered in situ.

5. A metallurgical pouring nozzle substantially as specifically herein described with reference to Figure 5 of the accompanying drawings.

DATED this 29th day of April, 1998

DIDIER-WERKE AG

WATERMARK PATENT & TRADEMARK ATTORNEYS
UNIT 1 THE VILLAGE
RIVERSIDE CORPORATE PARK
39-117 DELHI ROAD
NORTH RYDE NSW 2113
AUSTRALIA

IAS:CJS:GL

DOC 21

AU5054296.WPC



ABSTRACT

IMMERSED METALLURGICAL POURING NOZZLES

5

10

An immersed metallurgical pouring nozzle, such as a submerged entry nozzle for pouring molten steel, comprises a body (6) of refractory material, such as graphite alumina, which defines a flow passage (7). An annular member (8) of refractory material, such as zirconia with a very low or no-content of carbon, whose erosion resistance is higher than that of the body (6) of the nozzle is wholly encapsulated in the material of the body (6) of the nozzle.

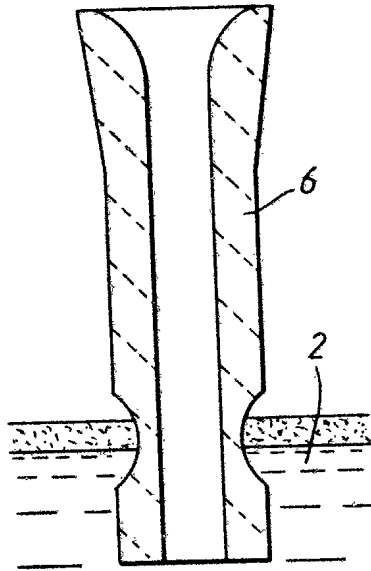


Fig. 1a

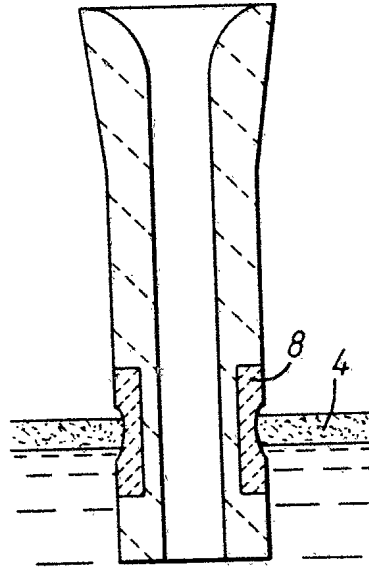


Fig. 1b

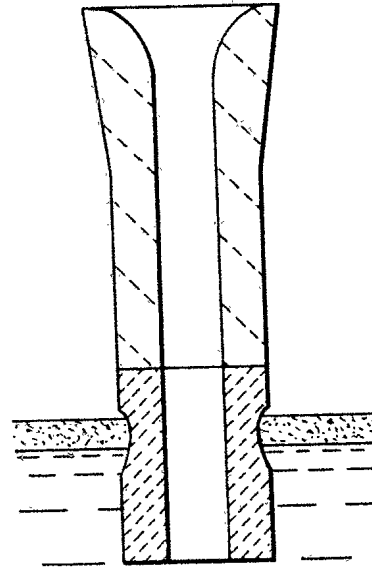


Fig. 1c

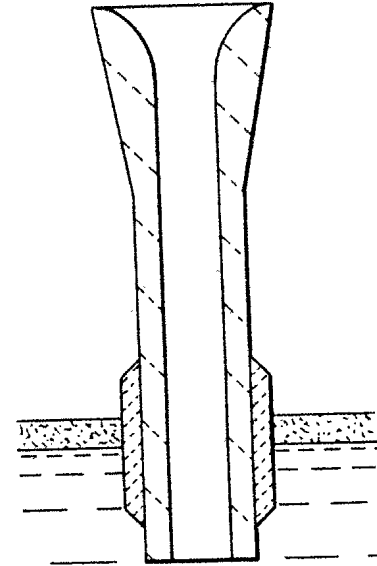


Fig. 1d

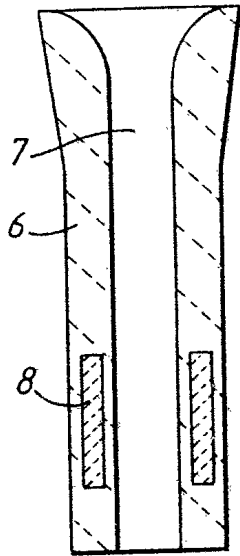


Fig. 2

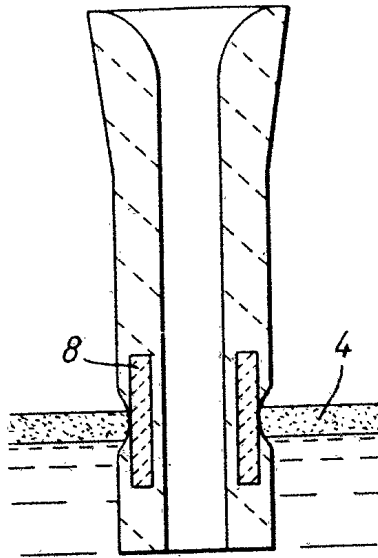


Fig. 3

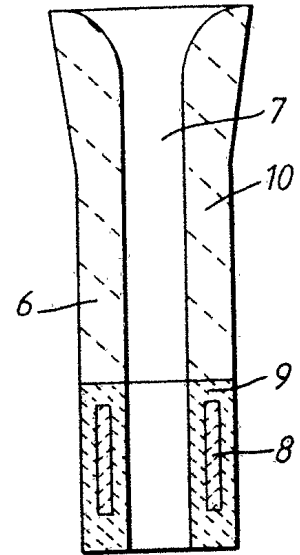


Fig. 4

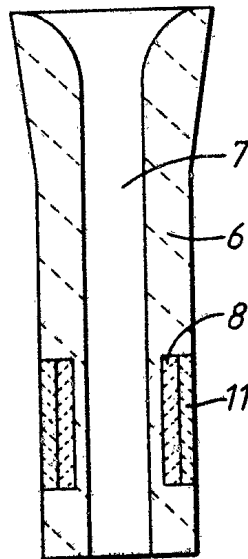


Fig. 5