

EUROPEAN PATENT APPLICATION

Application number: 81300574.1

Int. Cl.³: **B 22 D 11/10**
B 22 D 1/00, C 21 C 7/00

Date of filing: 12.02.81

Priority: 13.02.80 PC T US80 00155

Date of publication of application:
26.08.81 Bulletin 81 34

Designated Contracting States:
BE DE FR GB IT

Applicant: **CATERPILLAR TRACTOR CO**
100 Northeast Adams Street
Peoria Illinois 61629(US)

Inventor: **Frantzreb, John Gordon SR.**
509 W. Forrest Lawn Avenue
Peoria Illinois 61615(US)

Representative: **Wardrobe, Alexander James**
Brownlie et al,
Frank B. Dehn & Co. Imperial House 15-19 Kingsway
London WC2B 6UZ(GB)

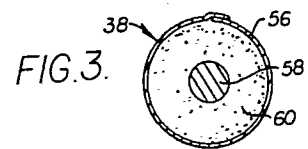
Filled tubular article and method for casting boron treated steel.

The invention provides a filled tubular article (38) for controlled dissolution in a molten metal for making boron treated steel, comprising:

an elongate conduit of ferrous material (56)

an elongate, non-particulate member located within the conduit, the member being primarily of aluminum material (58) and

a preselected particulate master composition (60) including particles being made of a material containing a preselected amount of the chemical element boron. The invention also provides a method of casting a boron treated steel article by introducing molten steel into a mold (20), the improvement comprising: the introduction below the surface of the molten steel (13) in the mold of preselected percentages by weight of aluminum in the form of a non-particulate elongate member and boron in the form of particles of a material containing the chemical element boron, said elongate member and particles being within an outer conduit of ferrous material of a filled tubular article (38)



- 1 -

FILLED TUBULAR ARTICLE AND METHOD
FOR CASTING BORON TREATED STEEL

5 This invention relates generally to casting of boron treated steel, and more specifically to an improved filled tubular article and method of controlled insertion of preselected materials within the filled tubular article into the molten metal as it is being cast.

10 Up to the present time a number of difficulties have been experienced with the continuous casting of boron treated steels because of the need to add boron, alloying elements, deoxidants and denitriders to the molten metal near the time of pouring. For example, such steels have been typically produced by adding
15 aluminum to the molten metal immediately prior to the introduction thereof into the mold. However, the aluminum in these aluminum killed steels forms oxides and a reaction with the silicates in the melt to plug the nozzles that meter the molten metal to the tundish
20 and to the mold. Titanium also forms oxides and tends to plug the nozzles in much the same way. Such slag formation at the nozzles not only detrimentally affects the controlled flow rate of molten metal into the mold, but detrimentally affects the ratio of external surface
25 area of the poured stream to the total stream cross section so that there is undesirably an increased oxidation and nitriding tendency. The formation of slag also detracts from the amount of residual aluminum available for obtaining the desired grain refinement.

- 2 -

The material additions such as titanium, zirconium and boron, in singular or combined form, which have been made to the tundish or ladle to improve the response of the material to heat treatment have heretofore been relatively ineffective because there has been a reaction with the atmosphere and a fading phenomena as a result of prolonged exposure of the additional materials to the atmosphere at the elevated temperature. In other words, the article or billet that is formed has a less homogeneous and coarser structure than it should have for the expense of the material additions and a lower hardenability than is desired. Typically, several feet of the continuously cast billets are not usable because of imperfections, and so such sections are cut off resulting in a waste of time and material.

Another approach to minimizing the exposure of the highly reactive additive materials to the atmosphere is to shroud the outlet stream and/or to use an inert gas such as argon to isolate the stream as it is being poured into the mold. Obviously, this adds a considerable cost to the process.

Less prevalent in the continuous casting of boron treated steels is the introduction of an aluminum alloy rod near the entry to the mold as is recommended by Kawecki Berylco Industries, Inc. of Reading, Pennsylvania. This late addition of aluminum, as well as preselected amounts of titanium and boron integrally formed with the aluminum, has been only partially satisfactory. This is in part due to the aluminum alloy rod melting prematurely so that there is an undesirable reaction with the atmosphere that decreases the effectiveness of the material additions, and in part due to a less than satisfactory selection of the basic elements and their proportions.

- 3 -

Even though the advantageous teachings of U. S. Patent No. 3,991,808 issued to J. R. Nieman, et al on November 16, 1976 have been widely recognized, such teachings have not resulted in the formation of a single additive rod capable of effectively making boron treated steel and while taking into account the diverse chemical reactions that occur. Not only do the reaction capabilities of the materials of the rod itself have to be taken into proper account, but also one must consider the reaction thereof to the composition of the molten metal and to the gases in the atmosphere. Furthermore, the flexibility of the rod should be maintained to permit coiling thereof on a containment reel. Hence, the additive rod should not be too stiff or brittle, and if particulate material is contained within the rod it should be capable of being drawn for improved densification thereof.

Thus, what is desired is a single rod, capable of being easily handled and fed into molten steel, and containing such hardenability intensifiers and additives as are precisely tailored for the production of fine grain, boron treated steels in an effective and economical manner. As one would suspect, the full boron effect is likely to be obtained only with a rod having a preselected construction and material composition. In this regard, it should be recognized that a substantial number of inoculating rods are known to the industry which are constructed specifically for completely different casting purposes. For example, the following U. S. patents disclose inoculating rod constructions which are representative of the general state of the art:

3,056,190 to D. S. Chisholm, et al
on October 2, 1962
3,367,395 to S. I. Karsey
on February 6, 1968
5 3,921,700 to J. G. Frantzreb, Sr.
on November 25, 1975
4,174,962 to J. G. Frantzreb, Sr. et al
on November 20, 1979

However such inoculating rods are totally unsatisfactory
10 for making boron treated steels.

According to one aspect of the present invention
we provide a filled tubular article for controlled dissolution
in a molten metal for making boron treated steel,
comprising:

15 an elongate conduit of ferrous material;
an elongate, non-particulate member located
within the conduit, the member being primarily of aluminum
material; and
a preselected particulate master composition
20 including particles being made of a material containing
a preselected amount of the chemical element boron.

The filled tubular article of the invention
preferably has an elongate ferrous metal conduit, an
elongate substantially aluminum member in the conduit,
25 and a master composition including ferriboron and
ferrotitanium particulate materials in the conduit.
Advantageously, the master composition also includes
ferrovanadium particulate material.

According to a further aspect of the present
30 invention we provide a method of casting a boron treated
steel article by introducing molten steel into a mold,
the improvement comprising: the introduction below the
surface of the molten steel in the mold of preselected
percentages by weight of aluminum in the form of a non-
35 particulate elongate member and boron in the form of
particles of a material containing the chemical element

boron, said elongate member and particles being within an outer conduit of ferrous material of a filled tubular article.

5 In a further aspect of the invention, a method of casting boron treated steel includes introducing aluminum in the form of a non-particulate elongate member and ferroboron particulate material in preselected percentages by weight below the surface of the molten steel in the mold by means of a containing conduit.

10 Advantageously, the method of the present invention may successfully be used to make boron treated steel in a continuous as-cast round bar manufacturing facility by introducing preselected amounts of ferroboron, ferrotitanium, and ferrovanadium particulate materials and an
15 aluminum rod in a protective conduit and effecting melting thereof at a preselected depth below the level of the molten steel in the mold. Its success has been determined by a study of boron factors, performance criteria, and chemical analyses of the elements of a plurality of heat-
20 treated parts including experimental tests and comparison base tests.

A preferred embodiment of the present invention is described below by way of example and with reference to the accompanying drawings in which:-

25 Fig. 1 is a diagrammatic, elevational view of a continuous casting facility including an apparatus for progressively feeding a filled tubular article constructed in accordance with the present invention into molten metal in the mold;

30 Fig. 2 is an enlarged, fragmentary and diagrammatic elevational view of the upper portion of the casting facility of Fig. 1 with a portion illustrated in section to better illustrate details of the present invention;

35 Fig. 3 is an enlarged, diagrammatic, cross sectional view of the filled tubular article illustrated in Figs. 1 and 2;

Fig. 4 is a graph showing the relationship

between actual boron factor and carbon content; and

Fig. 5 is a tabular listing of seven experimental rod members and the additive material ratio additions in each.

5 Referring to Figs. 1 and 2 a rotary continuous casting facility 10 is illustrated of the type utilized by the MacSteel Division of Quanex Corporation and located in Jackson, Michigan. Such facility produces continuous as-cast round bars by utilizing a large
10 bottom pour ladle 12 to pour argon-gas-stirred molten steel 13 into a tundish 14. Liquid steel is teemed from the tundish via a bent nozzle 16 having a relatively small outlet opening at 18, for example about 16 mm (5/8") dia., and into a water cooled mold 20 at a
15 precise angle with respect to a central vertical axis 22. The generally cylindrical mold 20 is of copper and has a precisely contoured or tapered internal bore 24 to allow for solidification shrinkage and to maintain mold contact with the solidifying hot bar for optimum
20 cooling.

As is diagrammatically indicated in Fig. 2, the copper mold 20 has an enlarged annular head portion or top end 26 and a lower cylindrical body portion or bottom end 28, and vertically spaced apart seal means
25 30 are provided between the mold and a suitable support member 32 to define a chamber 34 through which liquid coolant such as water is circulated. Through a mechanism, not shown, the mold 20 is oscillated at a rate of about 60 cycles per minute through a range of about 16 mm
30 (0.625") in the direction of the vertical axis 22 on which it is centered, while at the same time it is rotated at a speed of about 60 revolutions per minute as is schematically shown in Fig. 1 by the movement indicating arrows "A" and "B" respectively. The emerging

bar or strand depends from the mold and passes through a water spray system 35. Thereafter the bar is cut to length by a carriage mounted saw, not shown, that clamps to the bar and travels with it during the cut.

5 In actuality, the continuous casting facility
10 so far described and used during the development of the present invention, is a twin strand unit having side-by-side molds 20 and associated nozzles 16 to allow simultaneous manufacture of a pair of bars.
10 Since the construction and operation of each strand is the same, a description of one can suffice for the other and only one unit need be illustrated in the drawings. The straight bar length or overall height "OH" is about 10 m (33'), and the bar diameter "D" can
15 be varied from, for example, about 100 to 180 mm (4 to 7").

 An apparatus for introducing additives into the casting mold 20 is generally indicated by the reference numeral 36. The additives utilized in the
20 present invention are in the form of a relatively ductile filled tubular article or treating rod 38 having a lower or distal end 40. The filled tubular article is progressively urged downwardly when viewing the drawings by a wire feed mechanism 42 which unreels
25 the article from a rotatable reel 44. A feed rate of about 64 mm/sec. ($2 \frac{1}{2}$ " /sec.) was found to be satisfactory in one instance. A hollow tubular guide member 46 is located below the feed mechanism, and is generally aligned with a plane through the central axis 22;
30 however, the guide member has a preselected angle of inclination with respect to the axis so that the distal end 40 of the filled tubular article is below a surface 48 of the molten steel 13 in the mold 20 by a preselected distance "L" as indicated in Fig. 2 and so that the
35 distal end is adjacent the central axis thereat. For

further details of the apparatus 36 reference is made to U. S. Patent No. 3,991,808 issued November 16, 1967 to J. R. Nieman, et al.

Thus, it can be appreciated that as the
5 molten steel 13 is added to the mold 20 the filled
tubular article 38 melts at its distal end 40 to add
preselected materials below the surface 48 simultaneously
with reciprocation and rotation of the mold. Moreover,
heat is removed from the copper mold by the water in
10 the chamber 34, and progressive solidification occurs
at the periphery of the tapered bore 24 so that a
cylindrical bar 50 is continuously formed along the
axis 22. In the instant example the retraction rate or
formation rate of the bar is about 2m/min. (79"/min.).
15 It is to be understood that the central part of the bar
does not immediately solidify, but rather the solidifi-
cation progresses radially inwardly with time and with
the downward movement of the bar. This phenomenon is
graphically or schematically portrayed in Fig. 2 by the
20 tapered phantom solidification demarcation lines desig-
nated by the reference numeral 52. At a distal end 54
of the downwardly converging lines 52 the liquid center
of the treated molten metal has solidified. For example,
the distal end 54 is typically reached at a distance
25 "H" of about 5.5m (18') from the top of the mold for a
bar diameter of about 140mm (5.5").

With reference now to the cross sectional
view of Fig. 3, the filled tubular article 38 can be
seen to include an elongate metal conduit 56, an elongate,
30 non-particulate member 58 located within the conduit,
and a preselected particulate master composition 60
compactly contained within the conduit. Specifically,
the master composition 60 includes ferroboron, the non-
particulate member 58 is primarily of aluminum material,
35 and the conduit 56 is of preferably a ferrous material

for formability. For example, the conduit 56 can have the following composition in percentage by weight:

	C	About 0.10%
	Mn	0.25 - 0.50%
5	S	About 0.05%
	P	About 0.01%
	Fe	Balance

It has been determined that the master composition 60 should preferably include preselected weight percentages of ferrotitanium and ferrovanadium particulate materials intermixed with a preselected weight percentage of ferroboration particulate material. It has been found it desirable to compact the master composition 60 within the conduit 56 to a relatively dense state in order to assure rapid internal dissolution of the conduit. For example, the preferred density of the core is equivalent to a degree of compaction in excess of 10% above the tapped density thereof. The term "tapped density" as used herein, refers to the known procedure described in "HANDBOOK OF METAL POWDERS" - Poster, Reinhold Publishing Co., New York, New York, 1966, page 57.

More particularly, it has been found that boron treated steel can be made especially advantageously by progressively inserting a filled tubular article 38 consisting essentially of the following elements in the proportions indicated into and below the surface of molten metal in the mold:

		Broad Range (Wt.%) *	Preferred Range (Wt.%) *	Most Desirable (Wt.%) *
30				
	1) aluminum portion of member 58	0.015 - 0.070	0.015 - 0.030	0.016
35	2) boron portion of ferroboration	0.0008 - 0.00462	0.0011 - 0.00308	0.0018

- 10 -

	3) titanium portion of ferrotitanium	0.038 - 0.150	0.038 - 0.088	0.050
5	4) vanadium portion of ferrovanadium	0.022 - 0.147	0.044 - 0.103	0.044

*Note: Reflected as a percentage of the molten metal addition to the mold.

It may be noted that the ferrous metal portions of the protecting conduit 56 and the selected three particulate materials designated immediately above is not significant since such ferrous portions have a negligible diluent influence on the molten metal. Rather this compatibility factor can be utilized with advantage because ferroalloys of boron, titanium and vanadium are available in the marketplace at economical prices and because the reaction thereof is less vigorous than the reaction of the purer basic element forms.

Another way to state the preferred material relationship is to designate the ratio of the four elements as about 9:1:28:24 which reflects the weight analysis ratio of aluminum, boron, titanium and vanadium in the filled tubular article 38.

In the aforementioned preferred composition of the novel filled tubular article 38, low cost aluminum serves as an effective deoxidizer and denitrider and imparts the desired degree of grain refinement in the cast article by removing dissolved gases from the melt. Above a level of about 0.070 Wt.% the ductility of the cast article can be expected to be adversely affected and an undesired amount of inclusions noted therein. Below a level of about 0.015 Wt.% the amount would probably be ineffective as a grain refiner. It should be present in a non-particulate or non-powder form for the reason

that if aluminum were present in the form of relatively small particles an excessive amount of external surface area would be provided; such larger surface area would at least partly oxidize even within the confines of the conduit 56, for example, and result in a marked decrease in effectiveness of the aluminum additive. While it is preferred that the aluminum member 58 be present as a cylindrical rod centrally located within the conduit 56, it also is contemplated that it could be formed as a coating on the inside surface of the conduit. However, if the conduit itself were made of aluminum such construction would be unsatisfactory because the larger surface area thereof would be exposed to the atmosphere and it would melt too fast so that the aluminum and master composition 60 would be prematurely exposed to atmospheric contamination. The aluminum that was used was over 99% pure since it is commercially available in that form.

Ferroboron particulate material provides the desired degree of hardenability to the steel article while replacing an appreciable percentage of more expensive alloying ingredients. Above a boron level of about 0.00462 Wt.% an undesirable secondary reaction occurs involving the precipitation of iron borides that tend to embrittle the article. Below a level of about 0.0008 Wt.% there is insufficient boron available to provide the hardenability effect on the heat treatment of the article. The ferroboron particulate material that was used had 1 1/2 Wt.% boron.

The preferred addition of ferrotitanium serves as a powerful deoxidizer and denitrider. Above a titanium level of about 0.150 Wt.% there is so much titanium that some would be available to link up with the carbon and detrimentally affect the heat treatment capability of the cast article and its hardenability. This is so because titanium is an exceptionally strong

carbide former. Furthermore, the formation of stable inclusions can occur that would adversely affect machinability. Below a titanium level of about 0.038 Wt.% the effectiveness of the boron addition would be
5 minimized since the boron would tend to link with the available oxygen and nitrogen in place of titanium. The ferrotitanium particulate material that was used had 70 Wt.% titanium.

Lastly, the preferred ferrovanadium addition
10 serves as a somewhat weaker deoxidizer, a stabilizer, a hardenability agent, a grain refiner and a means of increasing the strength of the boron steel article. Above a level of about 0.147 Wt.% vanadium there would be massive carbide precipitation that would result in a
15 loss of hardenability. Below a level of about 0.022 Wt.% there would not be the degree of system stability desired; in other words, there would be an excessively large variation in the microstructure and hardenability of the final product article. Moreover, there would be
20 an undesirable loss in strength if the level is below that recommended. The ferrovanadium particulate material that was used had 54 Wt.% vanadium.

With the aforementioned proportions, about 50% of the total weight of the master composition 60 is
25 ferrovanadium, about 43 1/2% is ferrotitanium, and about 6 1/2% is ferroboron.

Initially, experimental tests were conducted on casting boron steel by introducing a filled tubular article including a metallic sheath containing pre-
30 selected additives into the molten metal flowing into a casting mold substantially as set forth in U. S. Patent No. 3,991,808 mentioned previously. One of the objects of the testing was to try to obtain a satisfactory boron factor at a reasonable cost, and without adding

undesirable amounts of the additives to the chemical analysis of the final castings.

In connection with the so-called boron factor, reference is made to the pioneering work of Marcus A. Grossman, such as his AIME Paper of February, 1942 on Hardenability Calculations from Chemical Compositions, and to ASTM Specification A255 relating to a standard method of End-Quench Test for hardenability of steel. The actual boron factor is generally defined as the actual D.I. in inches calculated from Jominy divided by D. I. in inches calculated from the chemistry (without boron). When steel is properly made, the boron factor, or its contribution to increased hardenability, is an inverse function of the carbon content. The higher the amount of carbon, the lower the boron factor and the less the contribution to increasing hardenability. This is observable by reference to the chart identified as Fig. 4, wherein the actual boron factor is plotted in the vertical direction of the ordinate and the carbon content of the steel is plotted in the horizontal direction of the abscissa. A target value or normal expectancy value is represented in Fig. 4 by the substantially straight shaded band or region identified by the reference letter A. The further the actual boron factor is below the target value in the band when viewing the chart, the more undesirable it is.

Initially, steels having a chemistry similar to 10B30 Mod., 41B30, and 10B30 Mod. with high silicon (0.5 - 0.63 Wt.%) were experimentally poured. It was found that there was no apparent correlation between the boron factor and the micro-alloying content, since the 0.25-0.40 Wt.% Cr and 0.08-0.15 Wt.% Mo in the 41B30 alloy steel did not influence the boron factor. Furnace or ladle additions of aluminum, with and without additions of ferrotitanium and silicon zirconium, were

made to the melt before pouring and various filled tubular articles or rods were inserted into the casting cavity at the time of pouring. For example, some rods contained particulate ferrotitanium and/or silicon zirconium along with particulate ferroboration. The actual boron factors obtained varied from less than 1.0 to 2.07 and fluctuated too widely as may be noted by reference to the zone designated by the reference letter "B" in Fig. 4. From this and the chemical analyses of the various heats the conclusions were reached that furnace and ladle additions were erratic and wasteful, and that ferrotitanium additions within the rod were highly desirable. Furthermore, while zirconium additions within the sheath exhibited some degree of success on hardenability, the cost thereof was excessive for the effectiveness obtained. It was also learned that boron factors did not appear to relate to boron content.

With this background, further experimental tests were conducted using four different filled tubular articles or rods for comparison purposes. These rods were designated as Nos. 1-4 in the chart identified as Fig. 5, and different quantities thereof were melted by the following 10B38 carbon steel composition in percentage by weight as it was poured at a preselected pour temperature into the casting cavity at an average pour rate of about 11.3 kg/sec (25 lbs/sec.):

	C	0.35 - 0.43%
	Mn	About 1.13%
30	S	0.050% Max.
	P	0.040% Max.
	Si	0.15 - 0.30%
	Fe	Balance

Identical generally cylindrical ingots were produced and tested for chemistry, oxygen and nitrogen levels, hardenability and microstructure. From these data the actual boron factors were obtained for each ingot heat.

5 The steel heats associated with rod Nos. 1 and 3 were prepared by ladle additions of a preselected quantity of aluminum pellets generally in accordance with conventional practices, while there was no aluminum addition to the ladle during the pouring of the heats
10 of rod Nos. 2 and 4. Rather, in accordance with one aspect of the invention, the aluminum wire 58 was incorporated within the ferrous metal conduit 56 of rod Nos. 2 and 4 and surrounded by the particulate master composition 60 including preselected proportions of ferrotitanium and ferroboration as indicated by Fig. 5. The total weight percentage of the aluminum addition in each of the various heats associated with rod Nos. 1 and 2 was maintained the same, as was the aluminum addition in the heats of rod Nos. 3 and 4. For continuity the
15 total weight percentage of the boron addition was kept constant throughout this stage of the experimental tests.

 The results of the tests of rod Nos. 1 - 4 were enlightening. Particularly, it was noted that the
25 amount of aluminum present in the ingots associated with rod Nos. 2 and 4 generally doubled in comparison with the ingots associated with rod Nos. 1 and 3, indicating that an unexpectedly high recovery rate was exhibited. Since the average boron factor dropped from
30 about 1.8 to about 1.60 in comparable heats of rod Nos. 1 and 2, and the average boron factor dropped from about 1.93 to about 1.61 in comparable heats of rod Nos. 3 and 4, there was cause to believe that this was due at least in part to the presence of excessive
35 amounts of aluminum and that the amount of aluminum and

titanium needed within the rod could be reduced substantially and still retain the desired level of hardenability. The extra titanium in the heats of rod No. 3 when compared with the heats of No. 1 caused a higher boron factor, but not a sufficient increase to justify the added expense. Moreover, the amount of retained titanium in some of the ingots was noted to be higher than desired, for example above about 0.10 Wt.%.

Several heats using rod No. 5 were thereafter run to take into account the above mentioned factors. Rod No. 5 differed from the first four rods by containing a preselected quantity of ferrovanadium. Boron factors in the neighborhood of 1.90 were noted indicating a definite success with that rod as a result of the vanadium influence. However, the chemical analyses of the ingots indicated that a relatively high residual proportion of the additive elements was retained and that the ratio of the elements within the rod was therefore too rich.

Rod No. 6 was provided to reduce the amount of aluminum and titanium substantially, while keeping the amount of boron constant. Upon examining the ingots thus produced it was found that the same high boron factors of about 1.90 were observed. Thus, unexpectedly good results were obtained with less additive material, and this time the chemical analysis of the ingots indicated only minimal amounts of the additives present. This was the best rod of the seven listed in Fig. 5.

Another rod, rod No. 7 was evaluated, and is reported here to show that while columbium (otherwise known as niobium) is in the same general family as vanadium, the direct substitution thereof for vanadium is not productive insofar as hardenability is concerned. Specifically, the boron factor dropped so much that such substitution was indicated to be entirely unsatisfactory.

The experience gained by analyzing the ingot castings made by using rod Nos. 1-7 as discussed immediately above permitted more extensive testing to be conducted with a reasonable promise of success. Accordingly, even though boron treated steel utilizing a minimum of additive material and having a reasonably high boron factor had never been advanced to the desired level in a continuous casting facility, three more experimental tests were conducted using plain or low carbon steel, medium carbon steel and medium carbon alloy steel having some chromium and molybdenum therein in the continuous casting facility described with reference to Figs. 1 and 2.

Specifically, the filled tubular article 38 having the preferred No. 6 rod construction (28 parts titanium; 1 part boron; 9 parts aluminum; and 24 parts vanadium) was inserted into a plain carbon steel having the following element analysis of primary interest in percentage by weight:

20	C	0.17%
	Mn	0.85%
	Si	0.25%
	S	0.022%
	Al	0.008%
25	P	0.005%

The filled tubular article 38 was inserted into the mold 20 as indicated in Fig. 2 at the rate of about 64 mm/sec. ($2\frac{1}{2}$ " /sec.), while the steel at about 1530°C (2790°F) was poured into the mold at a rate of about 4.60 kg/sec. (10.11 lbs./sec.). The filled tubular article at almost 8 mm dia. (5/16" dia.) exhibited a dissolution depth "L" of about 400 mm (16"). This corresponded to a rate of material addition of about 0.020 Wt.% Al, 0.0023 Wt.% B, 0.063 Wt.% Ti and 0.055 Wt.% V, reflected as a percentage of the molten metal addition to the mold. This enabled withdrawal of the

cylindrical bar 50 at a diameter of about 150 mm (5.875") at a rate of about 2m/min. (79"/min.). The result was the formation of an article having a highly desirable actual boron factor of 2.43, as indicated by the letter "C" on the graph of Fig. 4. This was achieved with reasonable levels of the additive ingredients remaining in the article. For example, 0.027 Wt.% Al, 0.0011 Wt.% B, 0.04 Wt.% Ti, and 0.040 Wt.% V were noted in the bar.

10 Secondly, the same filled tubular article 38 was inserted at approximately the same rate into a medium carbon steel having the following element analysis of primary interest in percentage by weight:

	C	0.35%
15	Mn	0.82%
	Si	0.29%
	Cr	0.06%
	S	0.023%
	Al	0.008% (Est.)
20	P	0.008%

In this second instance the corresponding rate of material addition was also about 0.020 Wt.% Al, 0.0023 Wt.% B, 0.063 Wt.% Ti, and 0.055 Wt.% V, and provided an article having a boron factor of 2.03 as indicated by the letter "D" on the graph of Fig. 4. This was achieved at a final chemistry retention level of about 0.03 Wt.% Al, .0020 Wt.% B, 0.07 Wt.% Ti and 0.06 Wt.% V.

In the third instance, the same filled tubular article 38 was inserted into a medium carbon alloy steel having the following element analysis of primary interest in percentage by weight:

	C	0.34%
	Mn	1.06%
	Cr	0.30%
	Si	0.25%
5	Mo	0.10%
	S	0.020%
	P	0.012%
	Al	0.008% (Est.)

In the third case the corresponding rate of material
10 addition was reduced to about 0.015 Wt.% Al, 0.0016
Wt.% B, 0.045 Wt.% Ti, and 0.040 Wt.% V as reflected as
a portion of the molten metal addition to the mold.
The leaner mixture provided an excellent actual boron
factor of 2.16 as indicated by the letter "E" on the
15 graph of Fig. 4 at a final chemistry retention level of
about 0.02 Wt.% Al, 0.0012 Wt.% B, 0.03 Wt.% Ti, and
0.035 Wt.% V.

Hence, it can be appreciated that the filled
tubular article and method for casting boron treated
20 steel in accordance with the present invention is
extremely successful by providing high boron factors,
by providing substantially the lowest practical levels
of material additions at a late stage to reduce fade
and contamination of the melt, and by providing a
25 manufactured article with relatively low chemistry
weight percentage levels of the additive elements. The
articles thus produced have exhibited an extremely
desirable clean microstructure morphology and/or a
minimum of nonmetallic inclusions that are often charac-
30 terized as "dirt". This is indicative that the recovery
rate is high, and the process economically efficient.

CLAIMS:-

1. A filled tubular article (38) for controlled dissolution in a molten metal (13) for making boron treated steel, comprising:-

an elongate conduit (56) of ferrous material;

an elongate, non-particulate member (58) located within the conduit (56), the member (58) being primarily of aluminum material; and

a preselected particulate master composition (60) including particles being made of a material containing a preselected amount of the chemical element boron.

2. A filled tubular article (38) as claimed in claim 1 wherein the said master composition (60) comprises ferroboron particulate material.

3. A filled tubular article (38) as claimed in either of claims 1 and 2 wherein the non-particulate member (58) is present as a coating of preselected thickness internally of the conduit (56).

4. A filled tubular article (38) as claimed in either of claims 1 and 2 wherein the non-particulate member (58) is an elongate rod located generally centrally within the conduit (56).

5. A filled tubular article (38) as claimed in any of the preceding claims wherein the said master composition (60) includes ferrotitanium and/or ferrovanadium particulate material.

6. A filled tubular article (38) as claimed in any of the preceding claims wherefor one of the following conditions is satisfied:

(a) the chemical elements aluminum and boron are present therein in a weight ratio of about 9:1 respectively;

(b) the chemical elements aluminum, boron and titanium are present therein in a weight ratio of about 9:1:28 respectively; and

(c) the chemical elements aluminum, boron, titanium and vanadium are present therein in a weight

ratio of about 9:1:28:24 respectively.

7. A filled tubular article (38) as claimed in any one of the preceding claims wherein the said master composition (60) comprises a first plurality of particles being made of a material containing a preselected amount of the chemical element boron, a second plurality of particles being made of a material containing a preselected amount of the chemical element titanium and, if desired, a third plurality of particles being made of a material containing a preselected amount of the chemical element vanadium.

8. In a method of casting a boron treated steel article (50) by introducing molten steel (13) into a mold (20), the improvement comprising: the introduction below the surface (48) of the molten steel in the mold (20) of preselected percentages by weight of aluminum in the form of a non-particulate elongate member (58) and boron in the form of particles of a material containing the chemical element boron, said elongate member (58) and particles being within an outer conduit (56) of ferrous material of a filled tubular article (38).

9. A method as claimed in claim 8 wherein the particles of a material containing the chemical element boron comprise ferroboron particulate material.

10. A method as claimed in either of claims 8 and 9 including the steps of introducing a filled tubular article (38) into the molten steel so that a distal end (40) thereof melts below the surface (48) of the molten steel, the filled tubular article (38) having an outer conduit (56) of ferrous material, a non-particulate member (58) of substantially aluminum composition in the conduit (56), and particulate ferroboron in the conduit (56).

11. A method as claimed in any of claims 8 to 10 wherein together with ferroboron particulate material is introduced below the surface (48) of the molten steel in

the mold (20) ferrotitanium and/or ferrovanadium particulate material.

12. A method as claimed in any of claimed 8 to 11 wherein the said introduction fulfils at least one of the following conditions:

(a) relative to the weight of molten metal (13) introduced into the mold (20), 0.015 to 0.070% and 0.0008 to 0.00462% by weight of aluminum and boron respectively are introduced into the molten metal;

(b) relative to the weight of molten metal (13) introduced into the mold (20), 0.015 to 0.070%, 0.0008 to 0.00462% and 0.038 to 0.150% by weight of aluminum, boron and titanium respectively are introduced into the molten metal; and

(c) relative to the weight of molten metal (13) introduced into the mold (20), about 0.016%, about 0.0018% about 0.050% and about 0.044% by weight of aluminum, boron, titanium and vanadium respectively are introduced into the molten metal.

13. A method as claimed in any of claims 8 to 12 including the steps of (a) inserting a filled tubular article (38) into the mold (20) toward a dissolution depth level "L" in the molten steel (13), the filled tubular article (38) having a conduit (56) of ferrous material, an elongate substantially aluminum member (58) within the conduit (56), and a preselected master composition (60) including ferroboron particulate material within the conduit (56), and (b) delivering the filled tubular article (38) into the molten steel (13) at a preselected rate of speed.

FIG. 1.

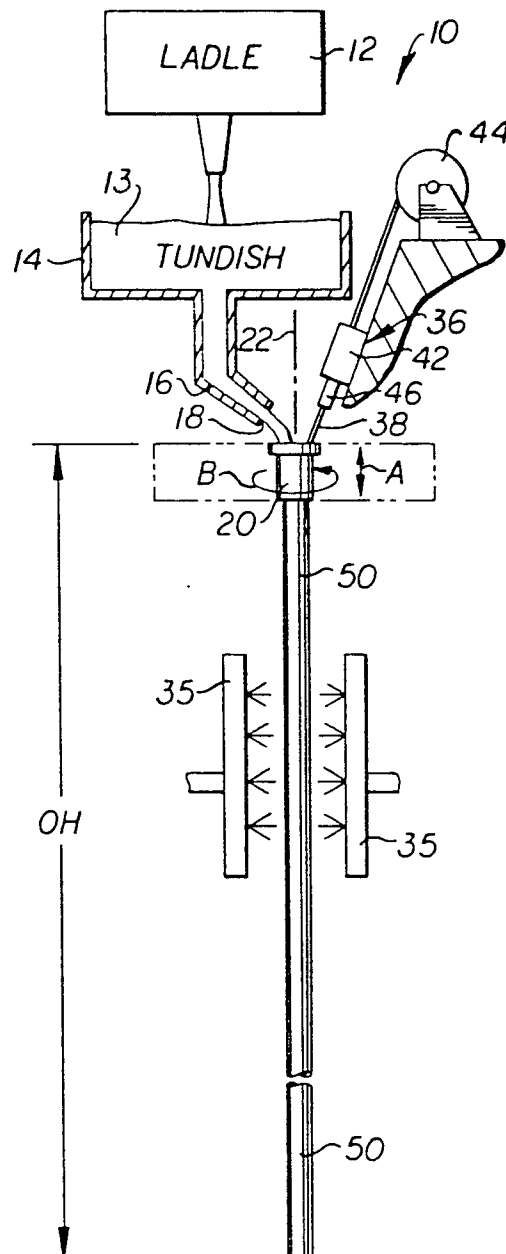
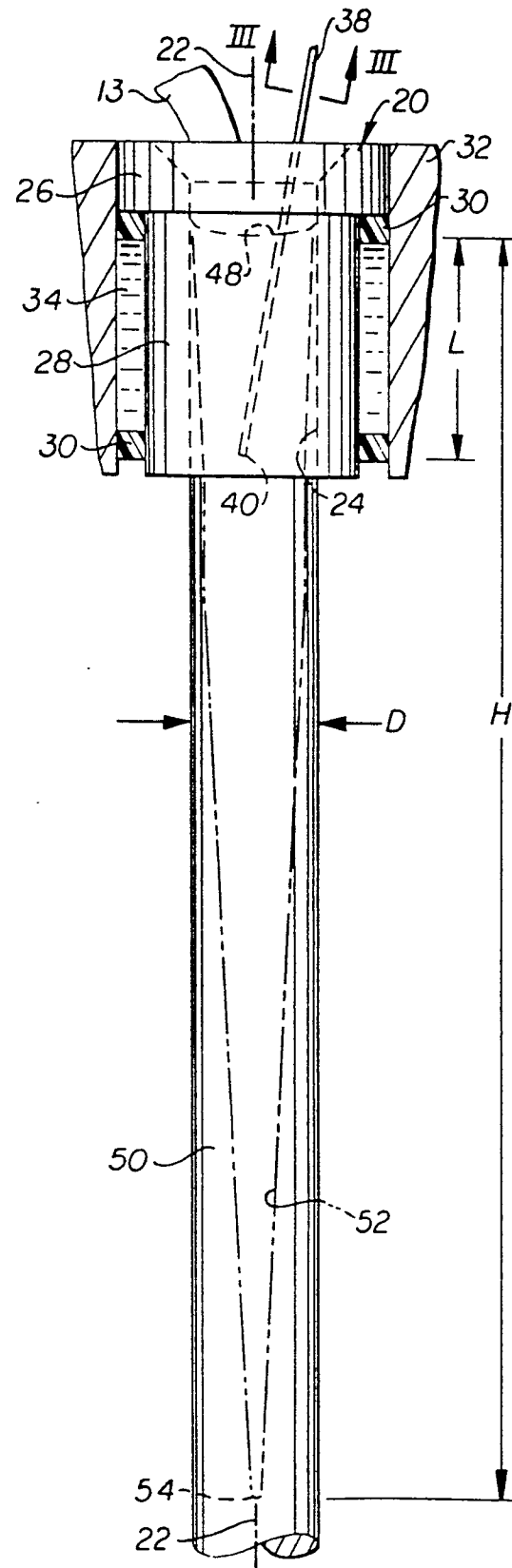


FIG. 2.



212

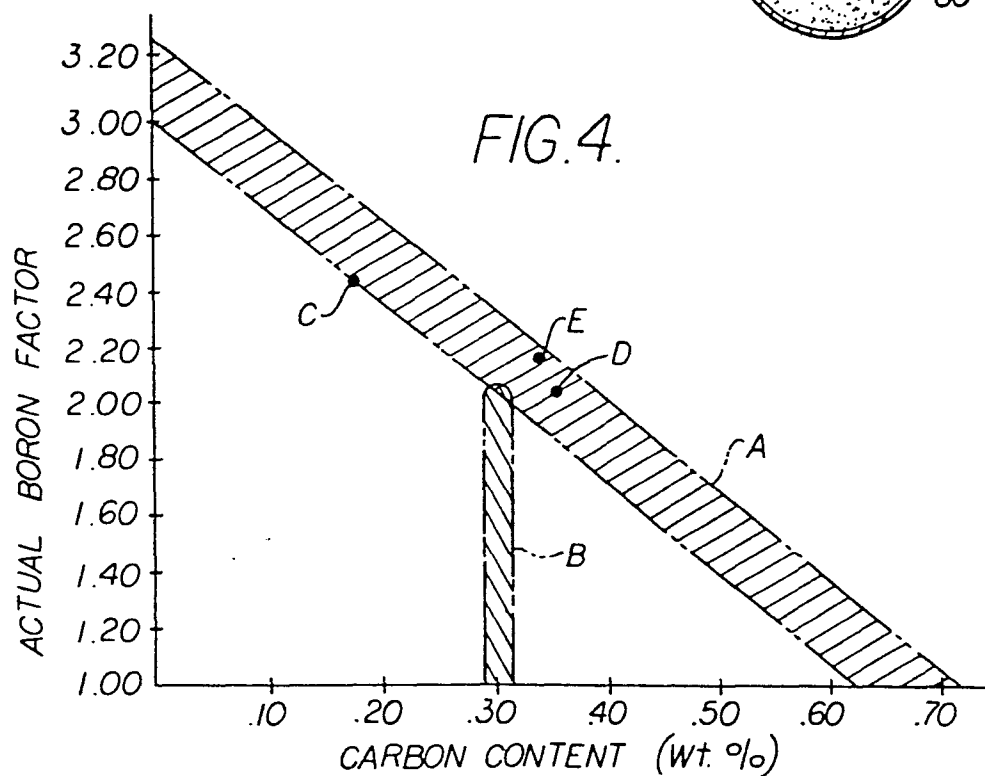
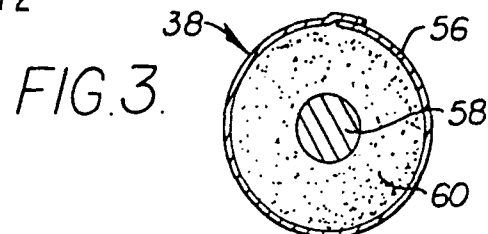


FIG. 5.

ADDITIVE RATIO BY WEIGHT

ROD NO.	TITANIUM*	BORON*	ALUMINUM**	VANADIUM*	COLUMBIUM*
NO. 1	58	1			
NO. 2	58	1	29		
NO. 3	75	1			
NO. 4	75	1	46		
NO. 5	42	1	32	29	
NO. 6	28	1	9	24	
NO. 7	28	1	9		23

* ADDED AS FERROTITANIUM, FERROBORON, FERROVANADIUM,
AND FERROCOLUMBIUM PARTICULATE MATERIAL.

** ADDED AS A SOLID WIRE.

0034469



European Patent
Office

EUROPEAN SEARCH REPORT

Application number

EP 81 30 0574.1

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	DE - A1 - 2 519 275 (NIPPON STEEL CORP.) * claims 1, 8 *	1,6	B 22 D 11/10 B 22 D 1/00 C 21 C 7/00
	& US - A - 4 047 556 --		
	DE - A1 - 2 810 537 (OLIN CORP.) * claims 1, 3 *	1,6	
	--		
A	DE - B2 - 2 017 660 (VOEST) * claim *	1	
	& GB - A - 1 296 271 --		TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
A	DE - A1 - 2 830 411 (HÜTTENES-ALBERTUS CHEMISCHE WERKE) * claim 1 *	1	B 22 D 11/00 B 22 D 1/00 C 21 C 7/00
	--		
A	DE - A1 - 2 810 797 (CATERPILLAR TRAC- TOR CO.) * claims 1, 2 *	1	
	& FR - A1 - 2 384 029 & GB - A - 1 558 333 --		
A	US - A - 4 134 196 (HITACHI CABLE LTD.) * fig. 1 to 3 *	1	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
A,D	US - A - 3 921 700 (CATERPILLAR TRAC- TOR CO.) * fig. 1, 2 *	1	
	& DE - A1 - 2 531 573 ----		
X The present search report has been drawn up for all claims			& member of the same patent family corresponding document
Place of search: Berlin		Date of completion of the search 05-05-1981	Examiner GOLDSCHMIDT