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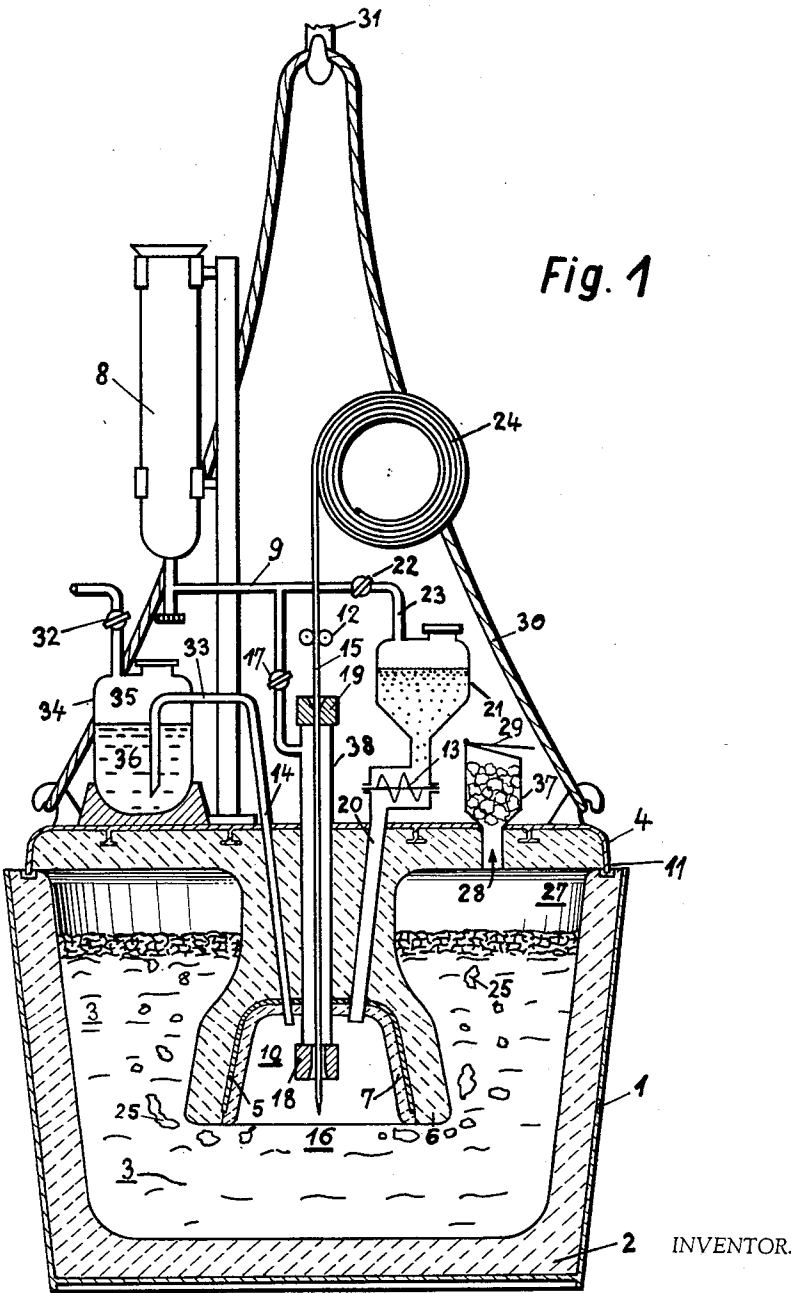
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DEVICE FOR TREATING METALLIC MELTS

Filed June 29, 1960

2 Sheets-Sheet 1



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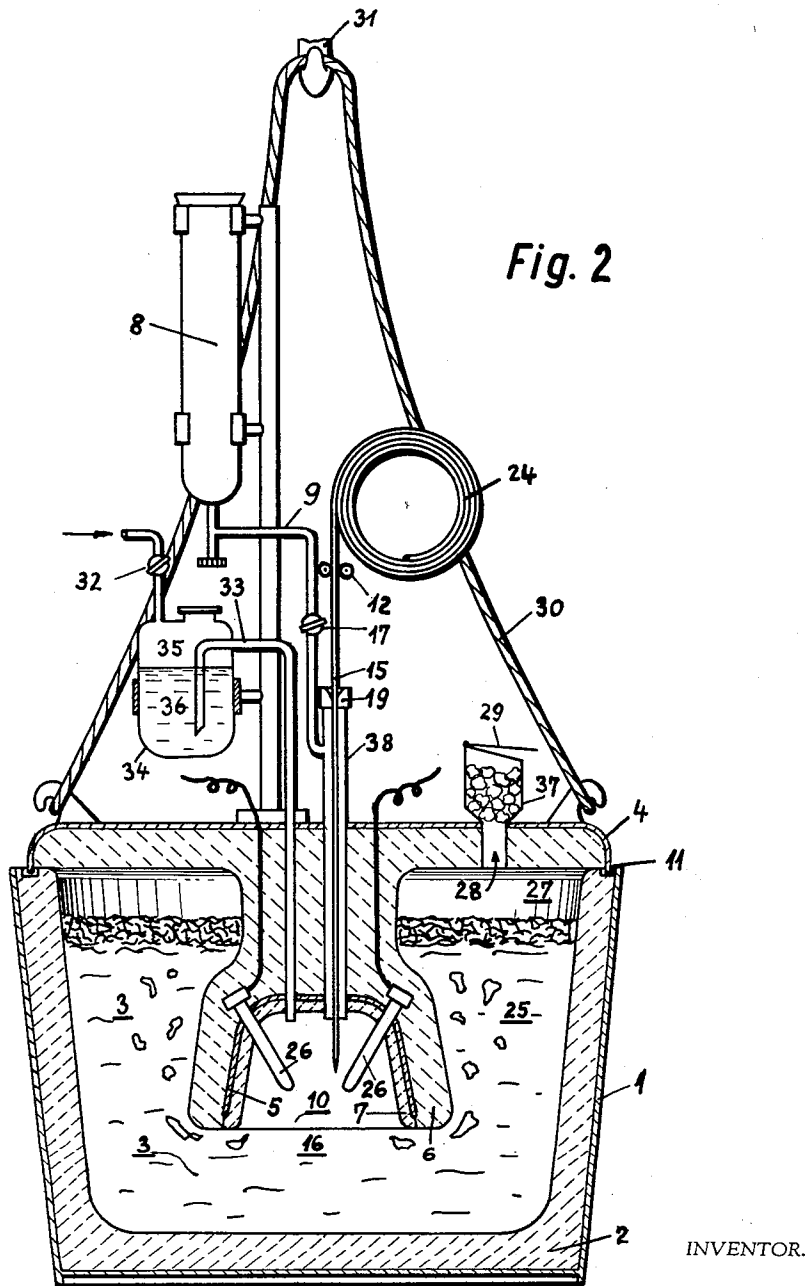
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DEVICE FOR TREATING METALLIC MELTS

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4 Claims. (Cl. 266—34)

The present invention relates to a method of and device for treating metallic melts for the purpose of degasification, desulphurization, dephosphorization or the formation of certain gas metallic compounds in such melts which affect the properties of solidification. The method according to the invention may also be employed for alloying with gas sensitive alloying elements.

Various methods have been developed during the last few years according to which attempts have been made with more or less success to react for instance magnesium with a melt. Thus, for instance, it has been suggested to introduce magnesium in form of a strand from the side of a casting ladle through the wall underneath the melt. Such method, however, has the drawback that the magnesium which directly contacts the steel melt when entering the ladle may be prevented from further entering the ladle by the contact with chilling steel.

According to another method, granulated or pulverous magnesium is together with a gas jet caused to act upon the melt in tiltable ladles while during the process a gas nozzle is arranged directly below the bath surface and after completed treatment the opening of the blow nozzle is again moved above the melt.

Attempts have furthermore been made to introduce magnesium directly into the melt by means of an immersed pipe, said magnesium being employed in this instance in granular or pulverous form.

To the above group of methods there pertain also such methods according to which magnesium together with calcium carbide and other substances is blown below the surface of the melt by means of so-called lance or twyer.

However, all of the above mentioned heretofore known methods have the drawback that they do not allow the formation of a proper magnesium vapor atmosphere which could react with the melt over a longer period of time. Quite to the contrary, with these methods, the magnesium entering the melt melts and evaporates in an explosion-like manner, and the vapor bubbles rise immediately in the melt whereby the reaction time of the magnesium vapor upon the melt will equal the rising speed of the magnesium vapor bubbles in the melt. This time, however, is generally very short and it is not possible within this short time to bring about other reactions according to which a vapor phase of for instance titanium tetrachloride will be able simultaneously or alternately with magnesium vapor to act upon the melt for a longer period of time.

In an effort to extend the reaction time of the magnesium vapor over a longer period of time, it has been suggested to employ pressure ladles with pressure-tight lids adapted to withstand the high pressure of the magnesium vapor being formed. However, the employment of such ladles in the rough handling customary in foundries is rather cumbersome and in addition thereto is also dangerous.

It is, therefore, an object of the present invention to provide an improved method of treating metallic melts, which will overcome the above mentioned drawbacks.

It is another object of this invention to provide a method of and device for treating metallic melts which will make it possible with a relatively simple apparatus

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representing an entirety to carry out treatments in various treatment containers.

It is still another object of this invention to provide a method of treating metallic melts which will make it possible simultaneously to employ metal vapors which not only will have a deoxidizing effect upon the melt but will also be able to reduce niobium in its elementary form from niobium pentachloride.

These and other objects and advantages of the invention will appear more clearly from the following specification in connection with the accompanying drawings, in which:

FIG. 1 illustrates an apparatus partly in section according to the invention for carrying out the method of the present invention.

FIG. 2 shows a somewhat modified apparatus over FIG. 1, in which below the bell there is additionally provided a heating system in the form of an electric arc.

The above mentioned drawbacks of heretofore known methods and devices of the type involved have been overcome according to the present invention by immersing a bell in a liquid melt while maintaining in the interior of said bell during the introduction into the melt a protective gaseous atmosphere so that the melt cannot enter the interior of said bell. Furthermore, substances adapted to alloy with the melt, reacting therewith or substances adapted to produce vapors are brought into contact with the surface of the melt which surface is formed by the bell.

In this connection it has proved advantageous to feed certain substances, as for instance magnesium in the form of a strand, the feeding speed of which can be precisely controlled. If desired, the said certain substances may also be supplied in form of a pipe the interior of which is filled with reaction substances or alloying elements or reaction substances and alloying elements. When employing a strand composed of metals adapted to evaporate, it is possible so to control the feeding speed of said metals that only a slightly higher pressure of metal vapors with regard to the hydrostatic pressure of the melt will build up in the wall so that for instance the introduced calcium or magnesium will have sufficient time to react with the melt through the surface formed by the bell. By means of a protective gas, such as argon, which can be introduced into the interior of the bell during the process, the agitation and scavenging of the melt can be controlled in a manner similar to the control of the feeding speed of the evaporating metal strand. In this connection it should also be mentioned that the metal strand when being introduced by a bell will uniformly and quietly be evaporated. As a rule, the metal strand melts already prior to entering the melt, and the dripping melt of for instance magnesium, calcium, sodium, potassium, lithium, and other suitable treatment substances will produce below the bell a vapor atmosphere the discharge of which over the bell rim and the trickling through the melt can in a simple and safe manner be controlled by means of a feeding device.

It has furthermore proved advantageous to cause other substances, such as oxides, halogenides, fluorides, etc., to act upon the melt through the protective atmosphere of the bell. In this connection also such substances may be employed which when contacting the melt will form a vapor atmosphere, as for instance niobium-pentachloride, titanium-tetrachloride, or a mixture of oxides and halogenides. This process can at the same time be combined with corresponding metal vapors which act not only deoxidizing upon the melt but are also able to reduce for instance niobium from niobium-pentachloride to its elementary form.

The method according to the invention is particularly characterized and advantageous by and in view of these

possibilities. Furthermore, the method according to the invention also makes it possible with a relatively simple and a unit forming apparatus above the lid of the treating device, which latter can be deposited by a crane upon the treating container, to carry out treatments in various treatment containers.

The lid of the entire apparatus can be placed upon the container over a sand cup seal so that in the chamber below the lid the treated melt will be protected by a protective atmosphere against undesired gasification.

Referring now to the drawings in detail, the treatment container 1 is provided with a lining 2 of refractory material and is adapted to be filled with the melt 3 for instance a steel melt. After the container 1 has thus been filled, the treatment apparatus mounted on the lid 4 is lowered into the melt. The said treatment apparatus consists primarily of a bell 5 which is insulated by a lining 6 against attack by the melt. If desired, a protective layer 7 may also be provided on the inside of the bell 5.

At the same time the bell is lowered into the melt, a protective gas is introduced into the bell 5 from a gas source 8 through a conduit 9 so that the melt will be prevented from entering the chamber 10 of the bell 5.

When the bell 5 has been lowered deeply enough into the melt, preferably when the sand cup seal 11 is tight, the conveyor 12 for the metal strand 15 is made effective or the feeder worm 13 or the supply means for the liquid treating means 14. However, if desired, all of the said members may be made effective simultaneously. If, for instance, the metal strand 15 consists of metals which when entering the bell or when contacting the surface of the melt at 16 melt and evaporate, the supply of the protective gas for instance argon may be throttled partially or entirely by means of a throttle or valve 17 or the like. The metal strand 15 will pass through a nozzle 18 which does not contact the melt to be treated and which may advantageously consist of graphite and other substances adapted to withstand the vapor atmosphere in chamber 10. The metal strand will be passed from above through a seal 19 which latter will prevent the gas and vapor atmosphere from leaving the bell 5 in this direction. Independently of metal strand 15, it is possible by means of the feeder worm 13 through the feed line 20 to drop pieces of substances or to drop granulated material upon the surface 16 of the melt which are adapted to effect for instance a desulphurizing or dephosphorizing effect upon the melt and which will be followed up by further substances from the reservoir 21 dropping into the worm 13. By means of a valve 22 called for instance a shutoff valve, protective gas may be conveyed through conduit 23 into the reservoir 21.

Frequently it is desirable to treat the melt with a strand of sodium or sodium plus aluminum and other metals and alloys, i.e., alloys which when added while in contact with air would burn in an explosive-like manner, which alloys, however, introduced through the bell 5 will react with the melt in a quiet manner. Metal strand 15 will be unwound from a roller 24 as shown in the drawing. If alloys are involved which are easily attacked when surrounded by air, the roller 24 will be enclosed in a gas-tight housing (not shown in the drawing) inasmuch as any type of gas-tight housing will be suitable.

The vapors formed in chamber 10 of bell 5 will escape below the lower edge of the bell and will bubble through the melt 3 in form of smaller or larger bubbles 25 whereby an intensive agitation of the melt will be obtained. Slag reaction substances which are introduced into the melt through conduit 20 will be intensively agitated when passing and rising in the melt. In this connection, it is advantageous to add such substances to the melt which will neither easily melt nor evaporate so that no slag bridges will be able to form in the chamber 10 of bell 5. If desired, instead pulverous material may be added as for instance calcium oxide, which have a high melting point so that they will not compact, thereby like-

wise preventing the formation of slag bridges in the interior of the bell.

It is also possible by additional heating, for instance by means of a light arc created between the electrodes 26, to produce additional heat in the interior of bell 5.

In this connection, it should be noted that the electrodes will wear only very slightly because they are located in a reducing and almost absolutely oxygen-free protective gas or vapor atmosphere. The outlet nozzle 18 through which the metal strand 15 passes into the chamber 10, is advantageously made of graphite. As protective gas to be introduced into container 8, there may for instance be used argon. The high pressure or over-atmospheric pressure being built up in chamber 27 will escape through outlet conduit 28 adapted automatically to close by a lid 29 as soon as the said over-atmospheric pressure in chamber 27 subsides.

The entire apparatus may, for instance, be suspended on a crane hook 31 by means of a cable or rope 30. The valves 17, 22 and 32 may advantageously be designed as electromagnetic or pneumatic valves so that, if need should be, they could be remote controlled. The rollers 12 as well as worm 13 may be driven independently of each other by electric motors. In this connection, it has proved advantageous to employ electric motors coupled to a stepless transmission. The motors with corresponding transmission are not shown in the drawing. It is also possible by means of protective gas or vapor being discharged at 29 automatically to control the feeding speed of rollers 12 and feeder worm 13 as well as the shutoff valve 32. This control may, for instance, be effected in conformity with the opening angle of the lid 29.

The method according to the invention has the particular advantage that also liquid additions may be introduced into chamber 10 through supply line 33. For this purpose, not only liquid metals are suitable but also substances such as titanium tetrachloride, molten niobium, pentachloride and other substances. Thus, for instance, titanium tetrachloride not only is a first class degasification medium but the titanium freed during the reaction also forms an important alloy addition of high purity. The liquid additions are stored in container 34. When the shutoff valve 32 is opened, a pressure will build up in chamber 35 above liquid 36 as a result of which said liquid will rise in conduit 33 and thus enter chamber 10 of bell 5.

It is also possible to heat container 34 by means of additional heating means (not shown in the drawing). The gases and vapors leaving the melt 3 and escaping through passage 28 are passed through a filter 37 which may be filled with a suitable filter material such as for instance coke or calcium oxide. This feature is actually relatively spoken much larger than shown in the diagrammatic drawing of FIG. 1.

This bell method also has particular advantages in connection with the entry of such metallic alloy elements into the melt which are sensitive against the influence of gases, as for instance lithium, niobium, zirconium and others. It will be appreciated that during the entry of such metallic elements a high reducing metal vapor atmosphere will be maintained to high advantage in the chamber 10 of the bell. The reducing atmosphere may then be created by means of the strand 15 while the alloy material will be added through conduit 20. It is, of course, also possible to proceed in the inverse manner.

As will be evident from the above, the method according to the invention thus affords universal possibilities for processing a metal melt inasmuch as it makes possible not only the degasification of the melt but also permits by means of a precisely controlled addition of titanium chloride, niobium pentachloride and other halogenides or chemical compounds of similar metals to produce a precisely controlled design of crystallization nuclei in the melt. The bell will make it possible, without vacuum or gas-tight seal, to carry out processes which are particu-

larly sensitive with regard to air or other atmospheric gases. Thus, for instance, a magnesium treatment may be effected in a carbon oxide or nitrogen enriched atmosphere in a completely different manner than will be the case in an atmosphere forming under such bell and practically free from carbon oxide, nitrogen and other undesired gases. On the other hand, it will be possible in the chamber 10 below bell 5 to introduce a precisely measured quantity of nitrogen or hydrogen when it is intended to form certain nuclei forming enclosures in the melt. Such reactions forming crystallization nuclei are extremely sensitive and can be obtained only through a precisely controlled and precisely adjusted atmosphere. It is in particular this finding which gave birth to the method according to the present invention which method affords metallurgists considerably more possibilities than is the case with other methods according to which for instance by means of a lance or twyer magnesium grit is introduced into the melt. The method according to the invention may be carried out by means of an apparatus which does not require that the melt to be treated has to be enclosed in a vacuum or gas-tight container. The reaction chamber 10 which has to be absolutely sealed with regard to the outer atmosphere is obtained in a relatively simple manner by means of the above mentioned bell immersed into the melt.

It may be added that through the various inlets of the bell, for instance liquid columbium chloride (CbCl_5), titanium chloride (TiCl_4) and carbon tetrachloride (CCl_4) may be introduced.

The pressure conditions in the bell and in the various containers are as follows:

In the bell approximately 4.2 p.s.i. (0.3 atmosphere above atmospheric pressure)

In the solid substance container at least 4.2 p.s.i. (0.3 atmosphere above atmospheric pressure)

In the liquid container at least 7.0 p.s.i. (0.5 atmosphere above atmospheric pressure)

In the wire introducing pipe at least 5.6 p.s.i. (0.4 atmosphere above atmospheric pressure)

The voltage in the electrodes 26 in FIG. 2 may be approximately 100 volts, but may also vary therefrom to a considerable extent.

There will now be set forth a specific example of treating a melt with a treatment bell according to the present invention.

Example

For purposes of preparing a stainless steel Type AISI 347 (SAE 30347) the following steps were taken:

From the container 35 preheated to approximately 250° C. liquid columbium tetrachloride (CbCl_5) was by means of compressed air pressed through conduit 33, 14 into the treatment chamber 10. (Instead of compressed air, also argon might have been used.) The CbCl_5 produced a degasification of the melt. For purposes of aiding the degasification process, simultaneously or subsequently magnesium wire forming coil 24 was introduced into the melt by means of a variable transporting device 12. The melt became strongly deoxidized while at the same time magnesium reacted with CbCl_5 to thereby produce metallic columbium in statu nascendi. The MgCl produced during this process will pass in vapor form through the melt and will effect therein a stirring and degasification. Through opening 20, further columbium granulars are conveyed from container 21 into the melt until the desired alloy content has reached equilibrium with the carbon content.

The great advantage consists in that the addition of columbium is effected from a protective gas atmosphere into a degasified melt. With non-degasified melts, always a portion of the added columbium reacts with the nitrogen or with the oxygen of the melt or the atmosphere of the furnace which depending on the melting condition

will be more or less prevalent in every melt or furnace atmosphere.

With the heretofore customary methods of introducing columbium into the melt, there will always form more or less large quantities of harmful non-metallic enclosures which reduce the physical properties of the material, especially of the grain boundary.

With a titanium stabilized steel such as stainless steel AISI 321 (SAE 30321), instead of CbCl_5 always TiCl_4 is employed which is liquid at ordinary temperature so that the heating of container 35 will become superfluous.

It is, of course, to be understood that the present invention is, by no means, limited to the specific method and apparatus described in the above description but also comprises any modifications within the scope of the appended claims.

What I claim is:

1. In an apparatus for treating metallic melts: a vessel for receiving and containing the metallic melt to be treated, a bell-shaped member enclosing a cavity opening towards the bottom of said vessel and positioned beneath the level of the melt in the vessel, the interior of said cavity being substantially unobstructed and having a refractory lining, at least two conduits leading into the cavity in said bell-shaped member above the liquid level therein of the melt, positive feeding means for feeding material through at least one of said conduits into the cavity in said member for reaction with the melt, at least one of said conduits being adapted for supplying a protective gas into the cavity in said member, a source of gas under pressure connected to said one conduit, and means for maintaining pressure on the gas sufficient to prevent melt from entering said bell-shaped member to thereby establish a secondary level in the melt where the said material comes in contact with the melt and in the presence of the said gas.

2. In an apparatus for treating metallic melts: a vessel for receiving and containing the metallic melt to be treated, a bell-shaped member enclosing a cavity opening towards the bottom of said vessel and positioned beneath the level of the melt in the vessel, the interior of said cavity being substantially unobstructed and having a refractory lining, at least two conduits leading into the cavity in said bell-shaped member above the liquid level therein of the melt, positive feeding means for feeding material through at least one of said conduits into the cavity in said member for reaction with the melt, at least one of said conduits being adapted for supplying a protective gas into the cavity in said member, the said means associated with the said conduit through which reaction material is fed to the cavity of said bell-shaped member comprising means for feeding strand-like material through said one conduit toward the said cavity in the bell-shaped member, a source of gas under pressure connected to said one conduit, and means for maintaining pressure on the gas sufficient to prevent melt from entering said bell-shaped member to thereby establish a secondary level in the melt where the said material comes in contact with the melt and in the presence of the said gas.

3. In an apparatus for treating metallic melts: a vessel for receiving and containing a metallic melt to be treated, a bell-shaped member enclosing a cavity opening downwardly, the interior of said cavity being substantially unobstructed and being lined with refractory material and positioned below the level of the melt in the vessel, at least two conduits leading into said cavity and positioned above the level of the melt within the cavity, positive feeding means for feeding reaction material through at least one of said conduits into said cavity, means for supplying a protective gas under pressure through at least one of said conduits into said cavity, and means connected with said cavity operable for limiting the maximum pressure that can be developed therein to about that pressure necessary to prevent melt from entering said cavity to any substantial degree thereby to establish a second level of the melt be-

low the upper level thereof in said vessel and at which second level said material comes in contact with said melt and in the presence of said gas.

4. In an apparatus for the treatment of metallic melts: a vessel for receiving and containing the melt being treated, a lid sealingly engaging said vessel, a bell-shaped member enclosing a cavity, said member opening downwardly and being connected by a neck having a thickness less than the outer diameter of said bell-shaped member, to the underneath side of said lid and positioned below the level of the liquid melt in the vessel, said bell-shaped member having walls diverging outwardly throughout the entire length thereof, having the cavity thereof lined with refractory material and having the interior thereof substantially unobstructed, at least two conduits leading into the cavity of said bell-shaped member and positioned above the level of the liquid melt within said cavity, positive feeding means for feeding strand-like material through one of said conduits to the said cavity, a source of gas under pressure connected to at least one of said conduits for supplying a shielding gas to said cavity, and said cavity being of a substantial size, a device operable for limiting the pressure that can be developed in said cavity to a predetermined value, and means connecting said device to said cavity, said predetermined value of the pressure on

said gas being about that which will prevent melt from entering said cavity to any substantial degree whereby a secondary level is created in the melt and at which secondary level the said material contacts the melt and in the presence of said gas.

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