May 17, 1966 N. P. GOSS ETAL 3,251,680

METHOD AND APPARATUS FOR TREATING STEELS

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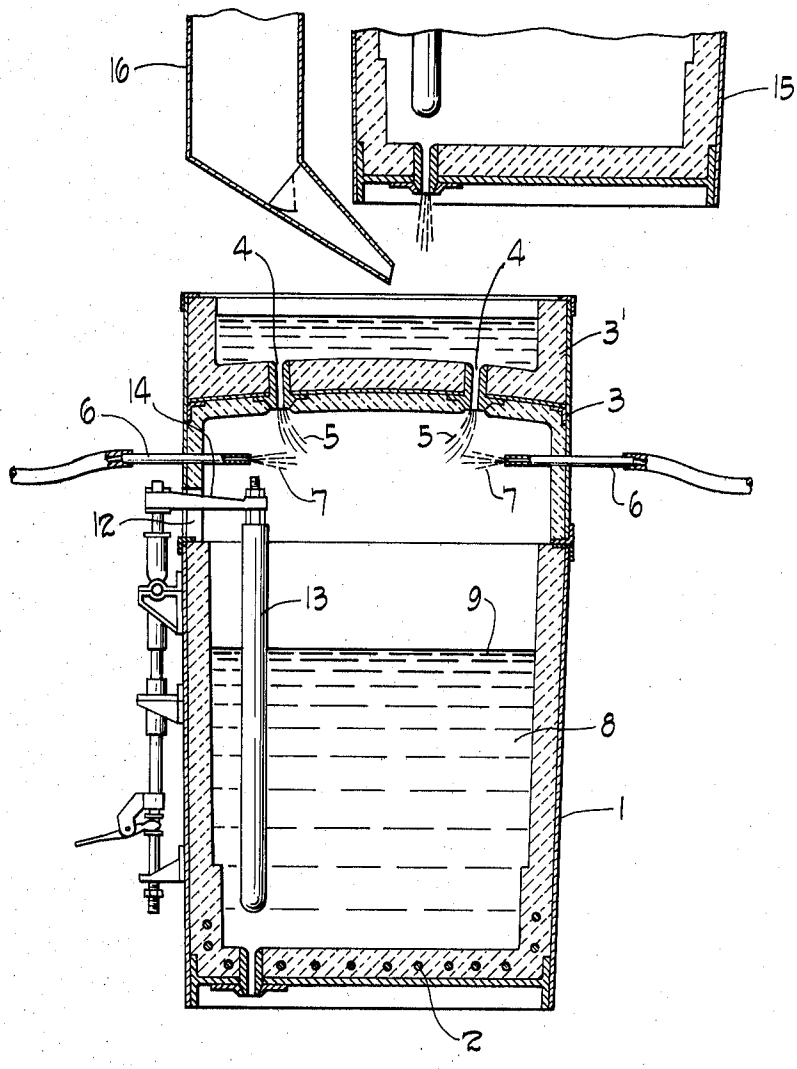


FIG. 1

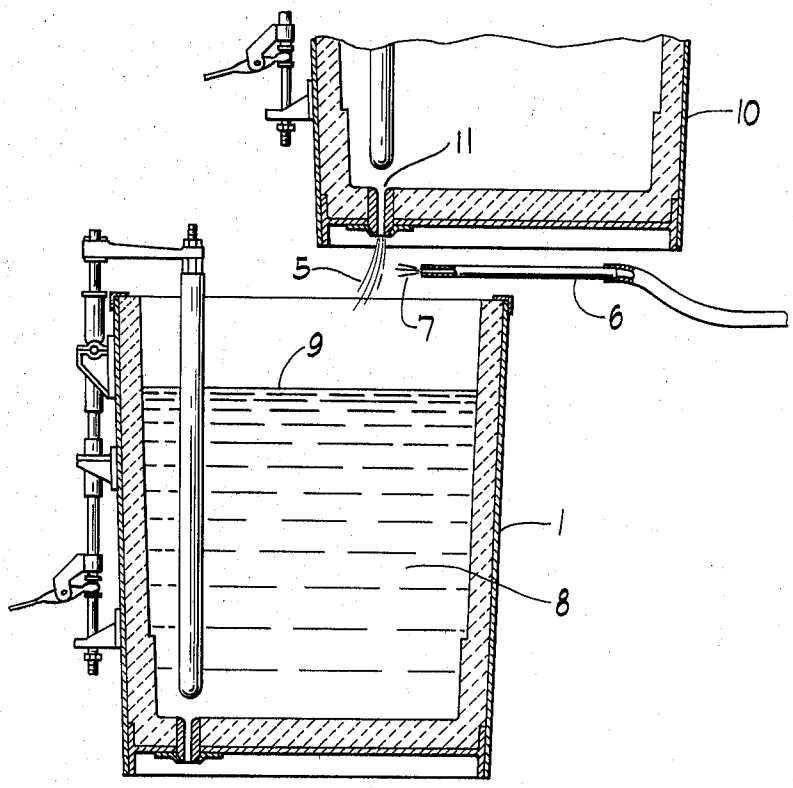
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Fig. 2



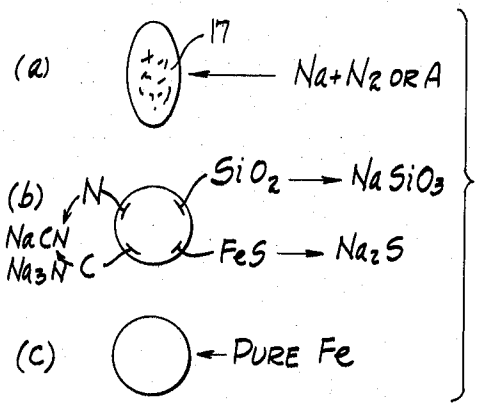


Fig. 3

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METHOD AND APPARATUS FOR TREATING STEELS

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10 Claims. (Cl. 75—59)

This invention relates to a train of steel-treating arrangements for removing non-metallic inclusions and for economically achieving desulphurization, deoxidation, degassing and composition control in order to purify steels.

A method of removing unmelted foreign matters included in the molten metal generally considered adoptable for industrial use is filtering. Those with different specific gravities from the metal may be removed by use of the centrifugal or centripetal force. There have been difficulties, however, preventing these methods from being satisfactorily adopted in removing foreign matters, such as non-metallic inclusions, etc., from the molten metal, and, therefore, they are not generally in use. The most usual method adopted for removing these impurities is to hold still after tapping the refined molten metal in the ladle sufficiently long to permit the inclusions to float up, provided that the pouring temperature of the molten metal and the operation of the stopper are not adversely affected. However, as is proved by Stokes' law, when the particles of these foreign matters are smaller than a certain size, they would remain in suspension and would not float up even if held still in the ladle for a considerable length of time, and would adversely affect the degree of purity of the steel. Steel-making engineers have recently come to fully recognize the fact that these minute inclusions affect adversely the quality of the steels particularly in relation to their kinds and usage, and hence the steel users also have come to demand purer and cleaner steels.

Although at the contact surface of the molten metal and the slag quick reaction takes place and the metal and the slag approach equilibrium instantaneously, it takes much longer time for the reaction to progress throughout the entire charge and come to equilibrium, for the reason that it must be accompanied by diffusion. The major portion of the non-metallic inclusions contained in the tap ladle is deoxidized products, which, if left undisturbed, would float to the surface and form slag. Some of them, however, are distributed in extremely small particles and are in a colloidal state.

This invention has been made to develop advantageous and unique method avoiding the aforementioned defects. In other words, the main feature of this invention is to disintegrate the stream of molten metal into numerous minute particles by means of a gaseous body or a body of gas containing addition agents, and to let these particles of molten metal pass through the layer of the slag.

The method of this invention may be applied profitably to all kinds of molten alloy with iron as their main ingredient. Application to steels with many element additions, such as to killed steels and semi-killed steels is especially advantageous.

This invention may be applied to every kind of molten metal stream, whatever be the case, as, for example, to that poured from the nozzle into casting molds or to similar molten metal stream or to metal stream being tapped from the molten metal in the furnace.

The pressure to be applied to the molten metal stream may be either increased or decreased in compliance with the particular needs of it, and thus to obtain advantageous conditions for improving yield, etc., by maximum stream disintegration.

The molten metal may be held in a ladle of an appropriate shape equipped with one or more nozzles, through which it may be re-poured.

The gaseous body, used to disintegrate such molten metal stream into numerous minute, highly dispersed particles comprises argon, hydrogen, nitrogen, sodium vapor, carbon monoxide, coke gas, carbon tetrachloride, and other compounds which are gasified at the temperature of usage, used either independently or in combination in accordance with the requirements of the specific operation. These gaseous bodies have the function of deoxidation prevention of oxidation, degassing, and gaseous ingredient addition, besides functioning as carrier media for other agents.

The gaseous body used in connection with the molten metal stream is regulated at proper speed, angle and quantity. As occasion may require, it may be used in confluence with the molten metal stream. In either case, it is used to create conditions conducive the disintegration of the molten metal stream into a system of highly dispersed minute particles.

The faster the speed of the current of gaseous body applied to the molten metal stream, the faster will be the disintegration process of the latter and the more highly will they be dispersed. For larger volume of the molten metal stream, the speed of the current and the volume of gaseous body may be increased. The angle of injection of the gaseous body into the molten metal stream is to be so arranged that the current of the gas may have the maximum relative speed against the movement of the molten metal stream. It is also desirable to arrange the angle so that the molten metal stream may spread out, and be highly dispersed into a system of uniform, minute, liquid particles.

It is desirable that the distribution of the disintegrated particles of the molten metal stream be uniform against the surface of the slag. For example, rather than injecting the gaseous body toward the center of the tap ladle, injection may be done so that it may rotate within the tap ladle creating a high speed rotation of air stream within it, and thus improve the effect of dispersion, while, at the same time, causing the rotation movement of the slag and molten metal to improve the effect of purification with the action of agitation. It is desirable to have the surface areas of disintegrated molten steel particles as large as possible. For this purpose, gaseous body is blown against the molten metal stream in order to disintegrate it into minute particles.

The disintegrated molten steel is further filtered through the layer of the slag, which is described below.

Injection is made, in accordance with the requirement, with pure gaseous body alone or gas mixed with deoxidizing, desulphurizing, purifying, heat generating, heat absorbing, degassing agents and ingredients addition, either separately or some or all of them together either in the form of solid or liquid. The injection of the aforesaid agents and ingredients addition may also be made separately. All such injections, moreover, are made into a closed or open box equipped with an exhaust for gas.

Effective results may be achieved by adding in advance the above-mentioned deoxidizing, desulphurizing, purifying, ingredients addition, and heat generating agents in the aforementioned ladle or re-poured vessel.

Slag, which is used to filter the molten metal under the method claimed by this invention, is made to form in the ladle or in the repoured vessel by adding the molten slag, or by transferring the slag melted in advance in another container, or may be formed on top of the molten metal by adding the slag-forming agent separately.

Disintegrated particles of the molten metal are filtered through this layer of the slag.

In carrying out the invention deoxidizing agents are added, such as hydrogen gas or metals such as Na, Mg, Si, Al, Ca, etc., or some or all of their compounds, as described before, to the re-poured vessel, molten metal stream, gaseous body for disintegration of the molten metal, or the ladle.

Especially if reducing gaseous body is used in order to disintegrate the molten metal, since the reducing agents may be added in the reducing atmosphere, good yield of reducing agents and effective deoxidation may be achieved.

Desulphurization agents used in this invention are fluorides such as NaF or CaF_2, chlorides, oxides such as CaO, and metals such as Mg, Ca, Na and Ce, either independently or in the form of a mixture, and may be added in the same manner as in the case of deoxidizing agents in order to attain effective desulphurization. Desulphurization may be made particularly effective when done within the reducing atmosphere as in the case of deoxidation.

The purifying agents to be used in connection with this invention are the aforementioned slag-forming agents, which are selected for better fluidity at operating temperature.

Slag-forming agents added by the aforementioned method (and the slag which is formed by adding the other addition agents) float up on top of the molten metal in the melted state and form the slag layer of predetermined required viscosity.

When the finely disintegrated particles of the molten steel pass through this slag layer, desulphurization is easily achieved; and, furthermore, because the chances of contact between non-metallic inclusions and the slag are increased, and since non-metallic inclusions combine with the slag, it functions at filtering mechanism, and non-metallic inclusions are removed effectively.

Another point of this invention is that although steels generally contain such harmful gases as hydrogen, nitrogen etc., these gases may easily be reduced by making the molten steel into the form of minute particles and at the same time reducing the partial pressure of the elements in the atmosphere.

The method covered by this invention, for the reason that it makes it possible to select and control the gas injection in turn makes the operation easy and effective.

As described hereinafter, this invention makes it possible to effectively purify the steel by deoxidation, desulphurization, degassing, removal of non-metallic inclusions, achieved either independently or simultaneously, by means of filtering the finely disintegrated particles of molten steel through the slag, and selecting and controlling the gaseous body used in order to disintegrate the molten steel into fine particles.

In other words, the addition gaseous body to be used as addition agents for the purposes of deoxidation, desulphurization, degassing and filtering, may be easily controlled and also addition agents can easily combine with gaseous body to give effective performances.

Furthermore, in this invention, for the reasons that the molten metal moves in the form of finely disintegrated form, addition ingredients can easily be mixed which makes it possible to easily attain uniform distribution of ingredients even with steels containing many addition ingredients.

In this invention, it may sometimes be desirable to agitate the molten metal contained in the ladle, and for this purpose any of the following methods may be used: electromagnetic induction agitation, placing the ladle on an eccentric turn-table, mechanical agitation, etc., depending upon the respective circumstances.

The molten metal thus processed by the methods covered in this invention is to be poured into the casting molds, etc., by operating the stopper.

This invention will be explained by citing an actual operational example.

The accompanying drawings show some of the apparatus that is used in connection with this invention. FIG. 1 is a cross section of an apparatus equipped with a tundish-type molten metal container above the ladle provided with an induction agitation device. FIG. 2 is a cross section of an ordinary ladle, equipped with a device to introduce the jet stream to be used for re-ladling in accordance with this invention. FIG. 3 is a diagram illustrating the effect of dispersing a molten stream of metal into droplets.

As shown in FIGS. 1 and 2, either a ladle **1** equipped with the coil **2** for inducting agitation, or the usual ladle without the coil **2** is used. FIG. **1** shows a ladle **1** covered with a shallow tundish-type molten metal container **3** and **3'** substantially the same diameter as the ladle **1** and with a single or a plurality of nozzles **4** at the bottom,

The invention is not limited to a particular location for these nozzles **4**.

The molten metal stream **5** in the tundish **3'** streams through the nozzle **4** of the molten metal container **3** and **3'** and then down to the ladle **1**. At this point, molten metal stream **5** is disintegrated into a cloud of fine particles by a gaseous body **7** jetted out from nozzles of pipes **6** equipped at the side of the molten metal container **3**.

On the other hand, either slag is placed in the ladle **1** in advance, or flux is mixed in the gaseous body projected through the pipes **6**.

The flux is melted and floats up above the molten metal **8** in the ladle **1** and forms a slag layer **9**. The disintegrated particles of the molten metal are filtered when passing through the layer of the slag **9** and non-metallic inclusions are removed.

The enclosure of the space within which the distintegration takes place by the cover **3**, such as explained in above, prevents oxidation of the finely disintegrated particles of molten metal.

To achieve such effect, neutral or reducible gas may be used as the gaseous body **7** so that the atmosphere within the ladle **1** may be easily controlled.

The injected gaseous body **7** is exhausted through a hole **12** cut through a portion of the lower part **3** of the molten metal container **3'**. This hole is positioned at the arm **14** used to attach the stopper **13** when the molten metal container **3'** is placed on top of the laddle **1**.

The molten metal may be introduced in a stream directly from a furnace (not shown) or from a ladle **15**. Apparatus **16** is provided for adding addition agents not introduced through the pipes **6**.

The molten metal is tapped from a 200-ton basic open-hearth furnace and pre-deoxidized. One hundred tons of the molten metal with the following chemical composition is poured into the laddle **15**:

	Percent
C	0.035
Si	0.32
Mn	0.29
P	0.008
S	0.014

Ferro-silicon is added to the molten metal within the molten metal container **3'** by means of the adding apparatus **16** raising its Si content to 1.2%.

The molten metal then is allowed to flow downward by natural gravity through 50 mm. nozzles **4** and argon gas is injected at the pressure of 5 kg./cm.^{2} through a 25 mm. inside diameter pipe to disintegrate the molten metal into fine particles.

1.850 tons of slag forming agents in powder form with the following composition is placed in the ladle **1** in advance:

	Percent
CaO	52
SiO_2	14
MgO	5
Al_2O_3	7
CaF_2	22

The slag is thus made to float up on top of the molten metal, while the finely disintegrated particles of molten metal react and are purified by being filtered by the above-mentioned slag. The final composition of the molten metal is found to be as follows:

	Percent
C	0.033
Si	1.32
Mn	0.30
P	0.008
S	0.009

The ratio of desulphurization has been found to be 45% and the non-metallic inclusions have been found to show the following reduction in comparison to the steel not treated by the method of this invention:

	Percent
SiO_2	Approximately 65
Al_2O_3	Approximately 45

Since the gas is injected under pressure and contains in said gaseous streams other agents such as sodium, magnesium, silicon, calcium, cerium, lithium, sodium or calcium fluoride, and so forth intimate mixing is achieved between these agents and the highly dispersed stream of metal. Reaction will therefore occur very rapidly due to the high increase of internal surface. These conditions favor high rate of reaction and will be completed even before the dispersed particles reach the filter slag. It is well known that due to surface tensions inclusion within the liquid particle will tend to be squeezed to the surface so will the other impurities. The purification of the particles occur in the atmosphere filled with sodium vapor for example or the like and it will pass through the highly reactive filter slag thereby rubbing off the inclusion and so forth.

This invention may also be practiced by using the apparatus shown in FIG. 2, using a ladle **10** with a nozzle **11** discharging into the ladle **1**.

Also, in case re-ladling is to be performed, by using the molten metal container of the tundish-type **3** and **3'** as shown in FIG. 1, the same effect as performing re-ladling twice may be attained by performing the re-ladling only once, thus contributing to the simplification of the operations. The molten metal **8** in the casing ladle **1** can easily be made of uniform composition by adding the addition alloys to its surface in the container **3'** by means of the adding apparatus **16**.

The induction coil **2** may be used also for heating the ladle **1** and maintaining the metal **8** molten in case any reaction tends to be endothermic.

It will be understood that in the usual metal smelting process air or oxygen is introduced for the purpose of removing impurities such as carbon, silicon or phosphorus; but after a point the effectiveness of the process diminishes because of the small portion of impurities left and oxides remaining in the metal become objectionable. The efficiency of the present invention in removing such oxide inclusions and also sulphides is illustrated in FIG. 3. As shown in FIG. 3*a*, each droplet of molten metal as it issues from the nozzle **4** of FIG. 1 tends to be an elongated form. However, since the molten metal has been very finely dispersed into minute droplets the surface tension of the droplet quickly causes each droplet to assume spherical form as illustrated in FIG. 3*b*. Finely dispersed or colloidal inclusions or "dirt" **17** which are originally in the interior of the droplet are squeezed to the surface as shown in FIG. 3*b* by surface tension. They therefore come into direct contact with the reducing agents introduced through the pipes **6** and issuing as the finely dispersed particles in the gaseous spray **7**.

If sodium vapor is used as the reducing agent, the effect is illustrated in FIG. 3*b*. The silicon dioxide is reduced by the sodium vapor to $NaSiO_3$, F_2S is reduced to Na_2S, nitrides and carbides are reduced to NaCN and excess nitride are reduced to Na_3N so that as is shown in FIG. 3*c* a droplet of pure iron emerges and falls into the ladle **1**. These reactions take place very rapidly because the droplets are very minute. The reducing agent is introduced in very finely divided form. Even when materials other than sodium are used as the reducing agent the reducing agents are very quickly molten by their contact with the molten steel because they are in such finely divided form and action takes place quickly.

The sodium may be introduced by self-generated pressure from sodium tanks which are heated to vaporize the sodium and injected through the nozzles **6**. Sodium vapor may also be injected together with nitrogen or argon or carbon monoxide, hydrogen or other reducing or inert gas. Magnesium, calcium or cerium may be used in the same manner as sodium. Since nitrogen is cheaper than argon nitrogen may be employed instead of argon, the excess nitrogen merely being removed as sodiumnitride. It is significant that all the reaction products of sodium remain vaporous so that they do not introduce impurities into the molten steel in the ladle **1**.

The method described produces the highest possible dispersion of the molten steel. This tremendously increases the effective internal surface of the molten metal by breaking it up into countless particles and by bringing the impurities to the surface of each of these particles so that the area over which the chemical reaction of purification and reduction may take place is tremendously increased, thus making the reaction substantially instantaneous and taking place while the droplets are drifting downward and before they have coalesced into the molten mass **8**.

To be effective deoxidizers must have a strong affinity for oxygen, and the reaction products formed should be completely insoluble in the molten steel. The ideal deoxidizer would not only be insoluble, but be in the gaseous state, in the molten steel. In other words, it would form a vapor; when the deoxidizer combines with the various oxides in the molten bath. Aluminum while being an effective deoxidizer, forms an oxide, Al_2O_3 which fails to be entirely removed, since it forms a solid at the temperature of liquid steel. Some of the Al_2O_3 remains in the bath as finely dispersed particles of Al_2O_3, which are detrimental, in the solid steel, reducing its impact strength, ductility etc. and adversly effecting many other physical properties.

On the other hand, sodium is even more potent as a deoxidizer of steel. It also forms an oxide Na_2O which remains in vapor form at the temperature of liquid steel. In other words it will not contaminate the steel bath with finely dispersed particles, as in the case of aluminum, but will pass from the bath as a gaseous oxide. This is also a rapid reaction. Such oxides in the bath as SiO_2, Al_2O_3, Cr_2O_3, MnO, FeO, etc. which contact the Na_2O as it passes through bath will form highly fluid particles, which will coalesce, and rise from the bath, and if they remain in the steel are of a type which are far less detrimental than the Al_2O_3. No one has heretofore worked out a satisfactory way to inject sodium into the bath safely and effectively and by a low cost practical method. This has now been achieved, by injection with argon, CO, nitrogen, H_2 or even the self-injection of Na vapor.

While the invention has been described as embodied in concrete form and as operating in a specific manner in accordance with the provisions of the patent statutes, it should be understood that the invention is not limited thereto, since various modifications will suggest themselves to those skilled in the art without departing from the spirit of the invention.

What is claimed is:

1. The method of removing inclusions from molten steel which comprises the steps of forming a plurality of streams of molten metal and projecting inert gas thereagainst to disintegrate the streams of metal into particles and allowing the particles to descend through a filter composed of approximately 52% CaO, 14% SiO_2, 5% MgO, 7% Al_2O_3 and 22% CaF for scrubbing out undesirable inclusions.

2. The method of claim 1 wherein the dispersion and filtering are carried out in an enclosed chamber for forming a highly dispersed cloud of metal and preventing air from contacting the cloud of metal.

3. A method of purifying molten steel which comprises the steps of forming a plurality of streams of molten metal and projecting gas thereagainst to disintegrate the streams of metal into minute particles, said gas including a metallic reducing agent which is in the form of a vapor at the temperature of molten steel.

4. The method of claim 3 wherein the metallic reducing agent is selected from the group consisting of sodium, and cerium.

5. The method of claim 3 wherein the reducing gaseous metal is mixed with a gas selected from the group consisting of argon, nitrogen, carbon monoxide and hydrogen.

6. The method of purifying a metal which comprises the steps of forming a stream of molten metal, confining sodium, raising the temperature of the sodium to the temperature of gasification, releasing gasified sodium in a confined path transverse to the molten metal stream and thereby projecting a stream of gaseous sodium reducing agent against the stream of molten metal to disintegrate the stream of metal into particles and expose the surfaces of the particles to reducing action.

7. The method of purifying molten steel which comprises the steps of forming the molten steel into a plurality of fine descending streams of molten metal, melting sodium in argon, atomizing the sodium in said argon and projecting a jet of argon and atomized sodium against each stream of molten metal to disintegrate the streams of metal into minute particles.

8. In combination, a ladle, a shallow tundish type cover therefor forming a shallow molten metal bath container having a plurality of metal outlet nozzles therein of approximately 50 mm. diameter for directing a plurality of fine streams of molten metal into the ladle.

9. A steel treating apparatus comprising a ladle with a closed chamber above the ladle and equipped with a gas exhaust at the lower portion of the chamber, with a plurality of metal outlet nozzles for the molten metal to flow down through the bottom portion of the upper chamber, and a plurality of spaced gas injection nozzles at a level below the nozzles for molten metal, said gas injection nozzles serving for injection of a gaseous body directed to the molten metal from a plurality of sides within the closed chamber.

10. The method of purifying molten steel which comprises the steps of forming the molten steel into a plurality of fine descending streams of molten metal, projecting a jet of argon against each stream of molten metal to distintegrate the streams of metal into minute particles, and carrying fluid sodium in said argon jets against each stream of molten metal to make intimate contact and promote reaction with the minute particles of metal.

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