

Jan. 4, 1966

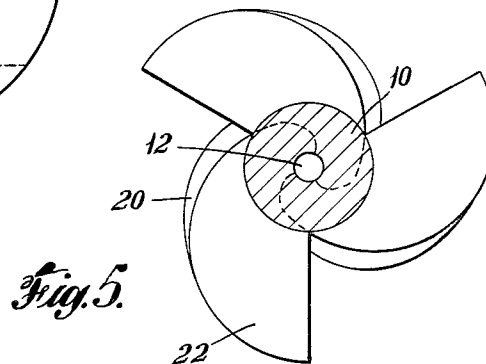
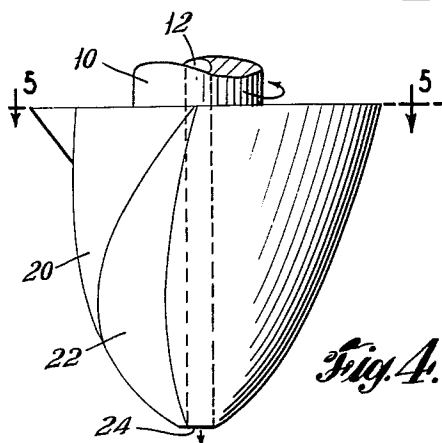
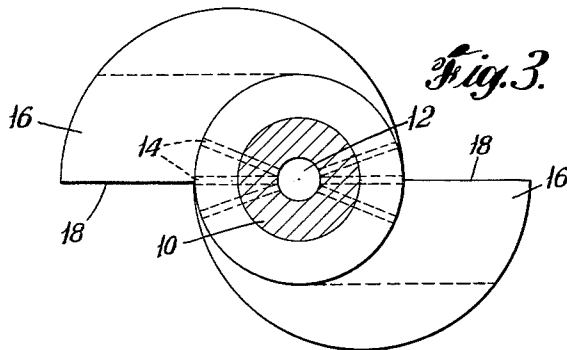
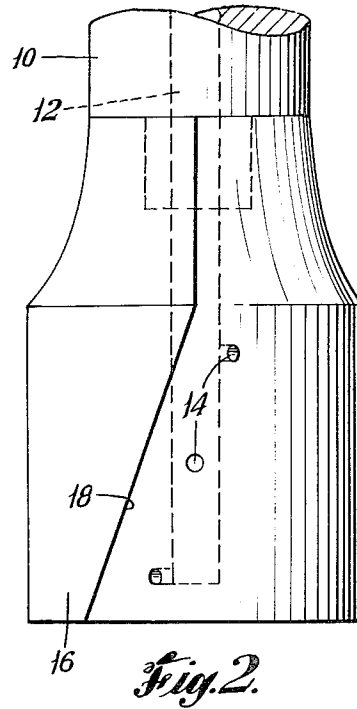
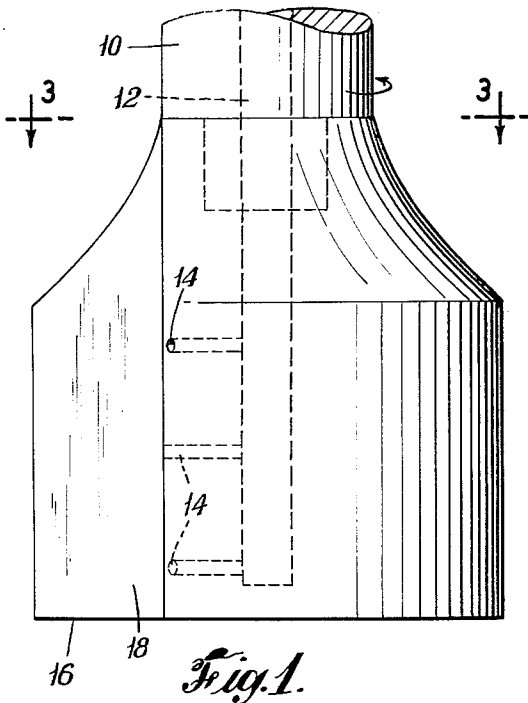
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3,227,547

DEGASSING MOLTEN METALS

Filed Nov. 24, 1961

3 Sheets-Sheet 1



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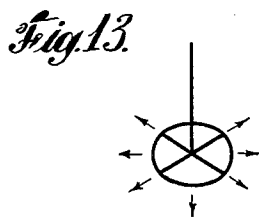
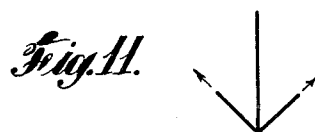
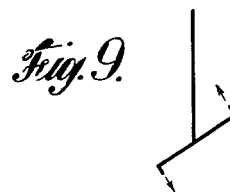
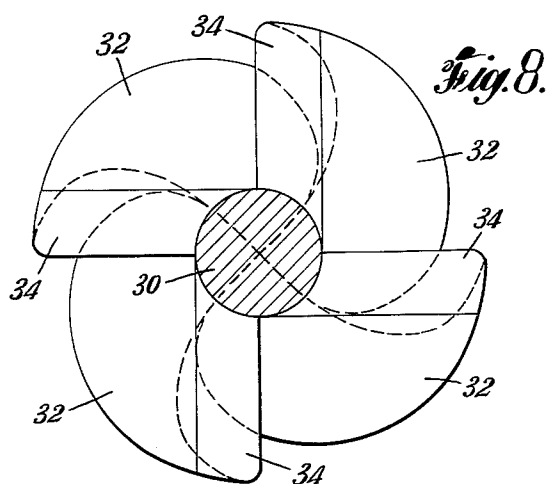
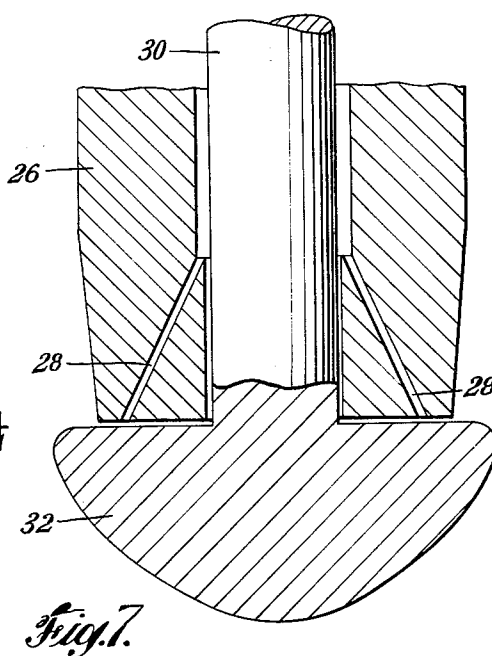
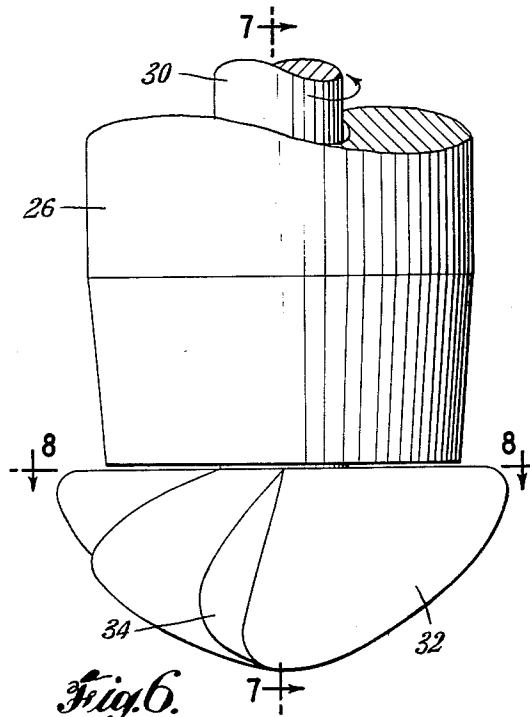
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3 Sheets-Sheet 2



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DEGASSING MOLTEN METALS

Filed Nov. 24, 1961

3 Sheets-Sheet 3

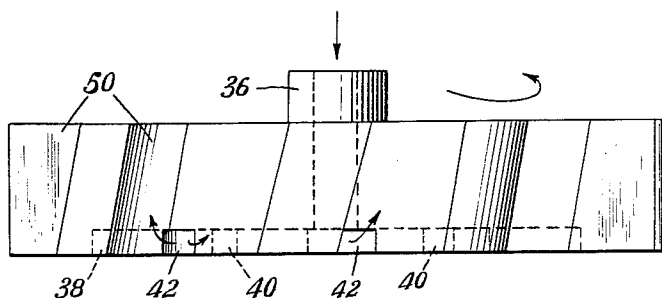


Fig. 14.

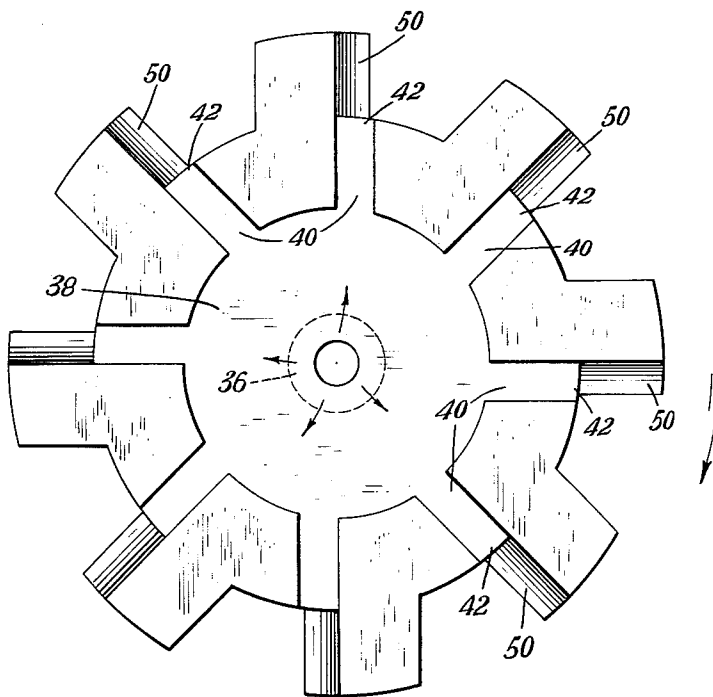


Fig. 15.

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3,227,547

DEGASSING MOLTEN METALS

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8 Claims. (Cl. 75—59)

The present invention relates to a method of degassing metallic melts and apparatus for accomplishing the same.

Several methods have been proposed for metal degassing all of which rely on the removal of the dissolved gases by decreasing the partial pressure of the gas in the atmosphere in contact with the melt. Such vacuum degassing and also degassing in environments of the inert gases of Group No. VIII of the Periodic Table have been practiced for some length of time for the removal of oxygen, carbon, hydrogen, and nitrogen.

The efficiency of degassing by these methods is controlled by two major variables; namely, environment-metal interfacial area and environment-metal contact time. In inert gas environments, 100 percent efficiency is attained when the desorbed gas present in the inert gas environment and removed with the inert gas environment is maintained in thermodynamic equilibrium with the melt. Under such circumstances degassing can be performed with the minimum amount of inert gas. This amount is governed by thermodynamics and can be calculated, for example, according to the equation put forth by W. Geller, in *Zeitschrift Für Metallkunde*, vol. 35, No. 11 (1943), pp. 213—217.

The minimum inert gas consumption, i.e., maximum efficiency, can be approached by providing a high specific interfacial area (surface-to-volume ratio) and sufficiently long contact time between the gas and the melt. Bubbling of gas through the melt is a means for providing high specific interfacial area and long contact time.

The treatment time of a molten metallic bath should be kept to a minimum as determined by the tolerable heat losses of the molten metal and by economic process cycle considerations. Moreover, from a practical standpoint, the number of gas injection devices cannot be increased proportionally to the melt weight. These considerations lead to the conclusion that the inert gas has to be injected at relatively high flow rates.

Thus, in order to provide an efficient degassing process which utilizes inert gases, it was necessary to develop a process which provides a large specific surface area for the gas-metal interface and long gas contact times at high gas flow rates.

Accordingly, it is the main object of the present invention to provide a method and apparatus for the degassing of metallic melts by introducing into the melt a suitable gas at high flow rates commensurate with high degassing efficiency.

Other objectives are to provide a process and apparatus for dissolved gas removal utilizing inert gases in a process which obviates extensive splashing, and to provide an effective and efficient process utilizing gases for removing nitrogen, oxygen, hydrogen, and carbon from molten melts.

The process achieving the aforementioned objects comprises providing a supply of gas under pressure; conducting a confined stream of the gas into a body of molten metal below the normal surface of the metal; passing the gas through orifice means, the outlet of which is submerged in the molten metal; maintaining the flow rate of the confined stream of gas at a value greater than about 10 standard cubic feet per hour while simultaneously maintaining the cross sectional area of the confined gas stream at a value less than about 100 π square millimeters and essentially maintaining relative motion between the gas

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stream at its entrance into the body of metal and the molten metal greater than about 3 feet per second thereby producing a shear on the confined stream of gas at the point it emerges from the orifice means and enters the body of molten metal.

The maintenance of a relative velocity greater than about 3 feet per second in magnitude between the gas stream issuing from the orifice and the surrounding metal is critical to successful formation of bubbles in the present process. It is the shear generated by such relative velocity which causes formation of distinct, noncoalesced bubbles in the molten metal. The shear must be maintained at a magnitude greater than that resulting from the action of the aforementioned relative velocity between the gas stream injected into the melt and the melt itself (e.g. greater than 3 feet per second).

The shear can be generated by (1) moving the orifice in a stationary molten metal and/or (2) moving the metal and holding the orifice stationary and/or (3) moving both the orifice and the molten metallic bath.

The preferred embodiment of the present process includes, in addition to maintaining the hereinabove described shear, a step of impinging the bubbles formed by the hereinbefore described shearing mechanism on a solid moving surface. This step causes further subdivision of the bubbles.

In the drawings:

FIG. 1 is a plan view in elevation of one embodiment of apparatus according to the invention for carrying out the process;

FIG. 2 illustrates the apparatus of FIG. 1 after a 90° rotation about the longitudinal axis of the conduit; FIG. 3 is a view of a section taken at line 3—3 of FIG. 1;

FIG. 4 is a plan view in elevation of a second embodiment of the apparatus; FIG. 5 is a view of a section of the apparatus shown in FIG. 4 and taken at section 5—5 of FIG. 4.

FIG. 6 is a plan view in elevation of a third embodiment of apparatus; FIG. 7 is a view of a section taken at line 7—7 of FIG. 6; FIG. 8 is a full cross-section taken at line 8—8 of FIG. 6.

FIGS. 9—13 are views illustrating embodiments of various configurations of apparatus capable of injection of gas into a melt in various flow patterns.

FIG. 14 is a plan view in elevation of a ninth embodiment of apparatus; FIG. 15 is a bottom view of the apparatus illustrated by FIG. 14.

FIGS. 1—3, 6—8 and 14 and 15 illustrate embodiments of apparatus for producing both a shearing force on the gas stream at the point of exit from the orifice and a collision plane for further subdivision of the bubbles after formation by the shearing mechanism while simultaneously agitating the melt.

FIG. 1 is an illustration of an apparatus comprising a conduit 10 having a gas passageway 12 terminating at a closed end. Orifices 14 communicate through the side wall of conduit 10 between the passageway 12 and a surrounding molten metal. Two vanes 16, one of which is shown in FIGURE 1, are attached to the conduit near the orifices. The vane 16 has a leading plane 18 in working relationship to the orifices 14. The leading surface 18 is oriented to force metal flow generally downward past the orifices 14 thereby producing a shearing force on the gas streams during proper directional rotation of the orifices and leading plane about the longitudinal axis of the apparatus. In addition leading plane 18 acts as a collision plane for the bubbles formed at the orifices.

FIGURES 4, 5 and 9—13 illustrate embodiments of the present apparatus whereby only a shearing force is pro-

duced during normal operation in conjunction with agitation of the melt.

FIGURE 4 comprises an apparatus with a vane 20 having a curved leading surface 22 with the gas orifice 24 located to inject the gas stream in the surrounding melt generally along the longitudinal axis of rotation of the apparatus. The curved leading surface, during rotation of the apparatus, cause metal to flow tangentially past the orifice to produce tangential shear on the gas stream in addition to stirring the melt. There is no collision surface in FIG. 4.

The apparatus shown in FIG. 7 comprises a stationary tube 26 serving as a housing for the rotating shaft 30 and having several gas orifices 28 communicating between the molten metal bath and the inner passageway of the stationary tube 26. A loose fitting shaft 30 extends through the passageway of stationary tube 26 terminating in four vanes 32. The vanes 32 have a leading surface 34 conforming in shape to one another and positioned closely adjacent the end wall of the tube 26. As the shaft 30 rotates, the vanes 32 sweep molten metal past the orifices 28 to produce a shearing force on the gas stream existing from the orifices 28. Leading surface 34 is also a collision surface.

As shown in FIGS. 14 and 15, a depressed section 38 provides a passageway for gas communication between conduit 36, through depressed sections 33 and grooves 40, and the orifices 42. The gas is restricted in the depressed sections from above and on the sides by the apparatus itself and from below by the surrounding molten metal to form a gas passageway in the depressed sections. The leading edges 50 of vanes are also a collision plane for the bubbles formed by the shear mechanism.

In all of the figures it will be noted that the apparatus are adapted to perform at least two functions; namely, (1) directing the gas stream and causing passage of molten metal past the orifice so as to cause a resulting shearing force to act on the gas stream and (2) dispersing the bubbles throughout the melt. The embodiments of apparatus in FIGS. 1-3, 6-8, 14 and 15 perform the above two functions and in addition provide a collision surface for further subdivision of the bubbles.

In the present process the gas introducing apparatus may be held motionless and the metal may be stirred by such devices as rotating crucibles by magnetic stirring techniques. Similarly, the present invention can be practiced in a stationary molten metallic bath by imparting movement to the orifice and/or the conduit to cause a resulting shearing force by the metal bath on the gas stream emerging from the orifice. Dispersion in this particular arrangement is caused by movement of the orifice. In the same manner and subject to the critical shearing force restriction both orifice and molten bath may be in motion.

The bubble size produced by the apparatus of this invention is less than about 10 mm. in diameter. The upper limit of the bubble size is dictated by two considerations. The first consideration is maintenance of a large specific interfacial area between the metal and the gas in contact with the metal. Small bubbles provide an extremely large metal surface area per unit amount of gas introduced into the melt. For example, one standard cubic foot of inert gas will be exposed to about 610 square feet of molten metal surface if an approximately spherical bubble of about 3 mm. in diameter is injected into the melt. The second consideration concerning bubble size is that with small bubbles excessive splashing can be avoided.

Commensurate with attainment of optimum bubble size, the orifices must have a diameter of less than about 20 millimeters (cross-sectional area= 100π mm.²), and preferably less than about 8 millimeters (cross-sectional area= 16π mm.²). When multiple orifices are used in the apparatus it is necessary that they be spaced, center to center, at a distance greater than the diameter of the

bubbles being produced. This effectively prevents coalescence of the bubbles at the orifice.

Dispersion of the bubbles throughout the melt aids in obtaining optimum contact time between the bubbles and the melt. Generally, the moving molten metal must impart a force on the bubbles at an angle with the buoyancy force acting on the bubble substantially greater than 0 degrees and up to 180 degrees. This may be effected, for example, by employing the rotating vanes shown in FIGURES 1, 4, 6, and 14, by moving the molten metal in a rotating crucible and/or by employing magnetic stirring means.

The vanes of the apparatus further aid in the production of a high gas-metal interfacial area by providing a collision plane for the newly formed gas bubbles at the orifices. Upon collision with the planes the bubbles are further subdivided thereby increasing the effective gas-metal interfacial area. This is the preferred method for bubble dispersion.

In employing the rotating vanes, the usual known criteria for mixing should be observed, i.e. vortex formation in the melt should be avoided. This can be accomplished by submerging the rotating vanes off-center into the vessel containing the melt (i.e. eccentric) and maintaining the axis of the rotating vanes at a slight angle from the vertical. The proper degree of eccentricity of the axis of rotation of the vanes varies with the particular vessel employed and is usually determined empirically.

Moreover, in employing rotating vanes, it has been found that for optimum gas bubble dispersion throughout the melt, the gas injector-to-vessel diameter ratio should be maintained between about .15 and .30. At a ratio less than .15 inconveniently high peripheral velocities were required to achieve good gas dispersion, and no significant improvements in gas dispersion were observed if the ratio was greater than .30. For the purpose of determining this ratio, the gas injector diameter is taken as the largest distance between two diametrically opposite points of the gas-injecting device. In non-cylindrical vessels the shortest dimension across the vessels is taken as the effective diameter.

Degassing molten metals requires large quantities of sparging gas as is evident from the theoretical requirements dictated by the equation given above. For instance, to remove nitrogen from iron-base alloys by sparging with argon, the gas requirements are of the order of about 100 to 600 standard cubic feet per ton of metal. Similarly, to remove hydrogen, about 50 to 300 standard cubic feet of gas per ton of metal are required.

The time of treatment and so the gas flow rate is determined mainly by the heat losses from the molten bath. The gas injection devices of this invention are capable of gas flow-rates of the order of about 10 to 1000 standard cubic feet per hour per device while producing the above described gas dispersion. The present process contemplates the use of a gas-flow rate of greater than about 10 standard cubic feet per hour.

Suitable gases for use in the degassing methods of this invention are those which remain relatively insoluble in the molten metal during the treatment. Such gases are exemplified by argon, xenon, neon, helium, krypton, and the like. Moreover, reactive gases such as nitrogen, can also be applied if their presence is not deleterious to the physical properties of the finished metal. In addition the present invention may be utilized to treat molten metals with other reactive gases such as oxygen or chlorine.

The following embodiments serve to illustrate the present invention.

Six short tons of steel are degassed in a 5 x 5 ft. ladle. The injection device consists of two spinning nozzles submerged into the melt 2 feet apart from each other. The sparger heads, of a design similar to that presented in FIGURE 1, were rotated at 860 r.p.m. The peripheral velocity of the orifices was 15 ft./sec. Argon was introduced as sparging gas at a rate of 40 s.c.f.m. Degassing

was completed after 25 minutes. The nitrogen content of the steel had decreased from 0.035 wt. percent to 20 p.p.m. The oxygen and hydrogen content of the treated steel was less than 10 p.p.m.

Fifty short tons of steel were degassed in a spinning crucible. The crucible measured 8½ ft. tall with a 3 foot inside diameter at the top. Argon was fed at a rate of 270 s.c.f.m. through a central tube in a stationary sparger disk measuring 34 inches in diameter and having orifices drilled around the periphery of the disk. The distance between the orifices and the crucible wall was approximately one inch and the peripheral velocity was maintained at about 10 ft./sec. The crucible was rotated at 67 r.p.m. for 30 minutes after which degassing was completed. The original nitrogen content of 0.035 wt. percent had been reduced to 20 p.p.m. and the oxygen and hydrogen content had been reduced to less than 10 p.p.m.

Since it is extremely difficult to observe and measure bubble size and contact time in opaque melts, the several tests were performed in water to gather this information.

Replacing molten steel by water for testing the performance of rotating nozzles is justified since the factors determining the size and the retention time of gas bubbles are similar in both fluids.

Surface tension and gravity forces (buoyancy) do not appear to play a significant role in the mechanism of bubble formation at the conditions preferred for metal degassing (high gas flow rate). The disintegration of the gas jet or gas pockets formed on the orifice is governed mainly by inertial and viscous forces. The resultant force acting between the moving orifice (or gas body) and the liquid is, therefore, some function of the Reynold's number

$$Re = \frac{Dv\zeta}{\mu}$$

The liquid enters the relationship by its kinematic viscosity only. Water at 20° C. has about the same kinematic viscosity as molten iron at 1550° C. as shown by the following:

$$\text{Water at } 20^{\circ} \text{ C.: } \nu = \frac{\mu}{\zeta} = \frac{10^{-2}}{0.998} = 1.00 \times 10^{-2}$$

$$\text{Iron at } 1550^{\circ} \text{ C.: } \nu = \frac{\mu}{\zeta} = \frac{6.7 \times 10^{-2}}{7.21} = 0.93 \times 10^{-2}$$

Therefore, according to the similarity law of fluid dynamics, a nozzle spun in molten iron will produce bubbles of roughly the same size as in water at the same speed of rotation and geometry of container and bubble forming apparatus.

With respect to the contact time, the velocity of the rising bubbles may be split into two velocity vectors. One of these has a direction corresponding to the motion imparted by the agitated liquid, and the other is directed vertically upward and is governed by the same buoyancy force as if in a stagnant bath. Both of these vectors, and hence, the resultant velocity, are very similar in water and in molten iron. The forced motion of the gas bubbles is similar because the flow of the stirred metal is dynamically similar to that of water at the same stirring conditions.

The velocity of rising gas bubbles larger than 1 mm. in radius is determined by the equation:

$$v = 1.35 \sqrt{\frac{T}{r}}$$

where v is the bubble rising velocity in cm./sec., r is the bubble (spherical) radius in cm., and T is equal to

$$\frac{\text{surface tension in cm.}^3/\text{sec.}^2}{\text{density}}$$

The bubble velocities of gas bubbles in water at about 20° C. and in molten iron at about 1550° C. were found to be of the same order of magnitude.

In summary, it may be concluded that molten iron can be reliably characterized by means of water with respect to bubble size and retention time at our metal degassing conditions.

The following examples illustrate how contact time can be prolonged by moving the orifice, in this instance rotating the orifice about a central axis.

A glass tank (dimensions: 50 cm. x 26 cm. x 40 cm.) was filled with approximately 43.6 liters of water. Air was supplied through a rotary seal into glass nozzles which were rotated at speeds of about 600, 1000, and 1500 r.p.m. The number of revolutions was measured by means of a stroboscope and the bubble pattern was photographed. The nozzles had about 1 mm. orifices and were of the configurations shown in FIGURES 9, 10, 11, 12, and 13 of the attached drawing. The orifice-to-rotational-axis distance was 50 millimeters on each model. The nozzle-immersion depth varied between 172 and 185 millimeters and in runs utilizing the configurations of FIGURES 9, 10 and 11 a uniform gas flow rate of 180 s.c.f.h. was used and with the configuration of FIGURES 12 and 13 a uniform gas flow rate of 60 s.c.f.h. was used.

The experimental results are summarized as follows:

(a) When the nozzles were stationary, irregularly shaped gas pockets of about 15 to 30 millimeters were formed and the liquid surface boiled violently;

(b) When the nozzles were rotated, spherical bubbles of 1 to 3 millimeter diameter were formed. It was found that the bubble size did not vary considerably with the speed of rotation between 600 and 1500 r.p.m., nor with the type of nozzle. The bubble size was also insensitive to the gas flow rate through the orifice, in the range investigated. The liquid surface was free from splashing and the tiny bubbles collapsed without significantly disturbing the surface;

(c) The bubbles were remarkably uniformly sized;

(d) At higher r.p.m., the bubble distribution was better. The bubble distribution depended mainly on the stirring characteristics of the nozzle as indicated by results with the configurations of FIGURES 10 and 11. In FIGURE 10, the gas flow was directed downward, and in FIGURE 11, upward. However, using the configuration of FIGURE 10 at 1500 r.p.m., the boundary of the cloud of bubbles appeared 20 mm. higher than the tip of the gas jet produced with the nozzle held stationary. In the case of the configuration of FIGURE 11, the bubble cloud boundary moved downward by 20 mm. (relative to the tip of the orifice), indicating that in this case, the water was pulled downward directed stirring action similar to that produced in the apparatus of FIGURE 6 and the tank was filled with a cloud of bubbles down to the bottom (the nozzle-to-bottom distance was about 155 mm.);

(e) The bubble contact times for the configuration of FIGURE 12 were calculated as a function of r.p.m. These data are presented in Table I.

Table I.—Contact time as a function of speed of rotation

Speed of Rotation, r.p.m. -----	0	600	1,000	1,500
Contact time, t , in millise./cm.	30	74	144	157
Contact time as a multiple of t at 0 r.p.m.	1.0	2.5	4.8	5.2

From the space-shown data and discussion it is readily apparent that the present invention has great utility in gas treatment of molten metals.

What is claimed is:

1. A process for forming and dispersing a multitude of gas bubbles less than 10 millimeters in diameter within a body of molten metal comprising;

(a) providing a supply of gas under pressure;

(b) conducting a confined stream of said gas into said body of said molten metal below the normal surface of said molten metal;

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- (c) passing said gas through orifice means, the outlet of which is submerged in said body of said molten metal;
- (d) maintaining the flow rate of said confined stream of said gas at a value greater than about 10 standard cubic feet per hour and simultaneously maintaining the cross-sectional area of said confined stream of gas at the outlet of said orifice means at a value less than about 100π square millimeters and;
- (e) essentially maintaining relative motion between said confined stream of gas at the outlet of said orifice means and said molten metal of greater than about 3 feet per second thereby producing a shear on said confined stream of gas at the outlet of said orifice means.
2. A process in accordance with claim 1 wherein the bubbles formed from the confined stream of gas are contacted with a moving surface to further subdivide said bubbles.
3. A process in accordance with claim 1 wherein a plurality of orifice means are employed each of which is spaced at a minimum distance slightly greater than the size of bubbles being formed.
4. A process in accordance with claim 1 wherein
- (a) the molten body of metal is stationary and;
- (b) said orifice means is a moving orifice means; the velocity vector of said moving orifice means essentially forming an angle greater than 0 degrees and less than 180 degrees with the velocity vector of said confined stream of gas at the point of exit from the outlet of said moving orifice.
5. A process in accordance with claim 1 wherein
- (a) said orifice means is stationary orifice and;
- (b) said body of metal is a moving molten body of metal; the velocity vector of said moving molten body of metal at said orifice means essentially forming an angle greater than 0 degrees and less than 180 degrees with the velocity vector of said confined stream of gas at the point of exit from the outlet of said stationary orifice means and said metal impart-

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- ing a force on said bubbles at an angle substantially greater than 0 degrees and up to 180 degrees with the buoyancy force acting on said bubbles.
6. A process in accordance with claim 1 wherein
- (a) said orifice means is a moving orifice means and;
- (b) said molten body of metal is a moving molten body of metal; the resultant velocity vector of said moving orifice means and said moving body of molten metal at the outlet of said orifice means essentially forming an angle greater than 0 degrees and less than 180 degrees with the velocity vector of said confined stream of gas at the point of exit from the outlet of said moving orifice means and said metal imparting a force on said bubbles at an angle substantially greater than 0 degrees and up to 180 degrees with the buoyancy force acting on said bubble.
7. A process in accordance with claim 1 wherein said shear velocity vector ranges from about 3 feet per second to about 30 feet per second.
8. A process in accordance with claim 1 wherein said gas is at least one selected from the group consisting of argon, xenon, neon, helium, nitrogen and krypton.

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