Oct. 8, 1957 A. S. RUSSELL 2,809,107

METHOD OF DEGASSING MOLTEN METALS

Filed Dec. 22, 1953

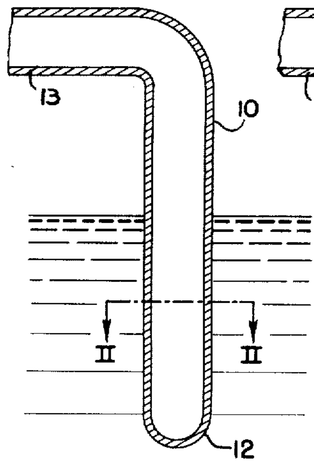

Fig. 1

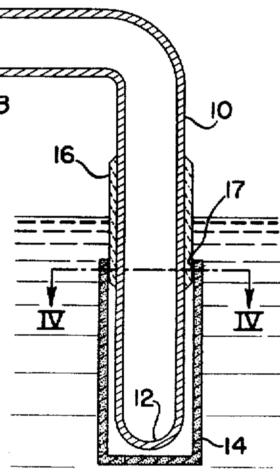

Fig. 3

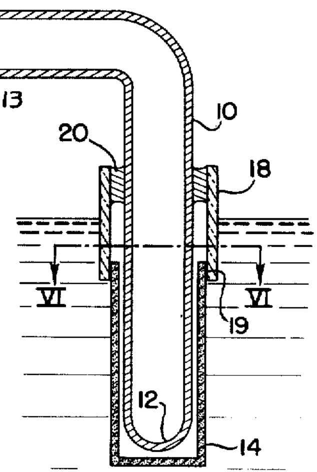

Fig. 5

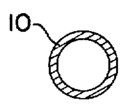

Fig. 2

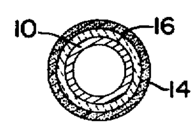

Fig. 4

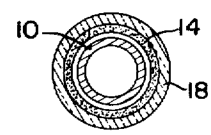

Fig. 6

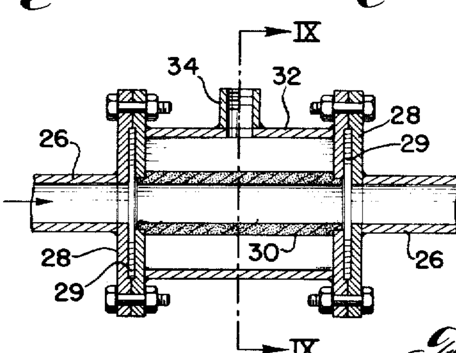

Fig. 8

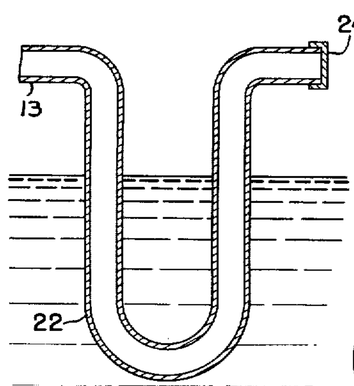

Fig. 7

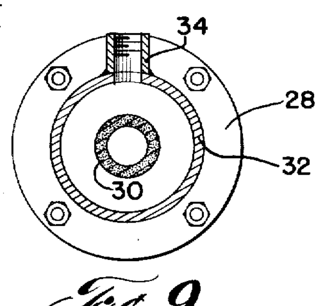

Fig. 9

INVENTOR.
ALLEN S. RUSSELL

BY George B. Todd
Attorney

United States Patent Office

2,809,107
Patented Oct. 8, 1957

1

2,809,107

METHOD OF DEGASSING MOLTEN METALS

Allen S. Russell, New Kensington, Pa., assignor to Aluminum Company of America, Pittsburgh, Pa., a corporation of Pennsylvania

Application December 22, 1953, Serial No. 399,791

10 Claims. (Cl. 75—67)

This invention relates to the removal of gases from liquid metals which contain or may be contaminated with dissolved or absorbed gases. In particular it relates to a degassing of or, if desired, measurement of the gas content of liquid aluminum, magnesium and the alloys in which these metals predominate.

It is well known that liquid metals can and do absorb gas from the air, from solid bodies containing gas or generating it in contact with the molten metals and from reaction with water vapor in the air. The kind and amount of gas present depends upon the nature of the metal and the gaseous environment. For example, hydrogen is readily absorbed by aluminum, magnesium and their alloys as well as by iron, cobalt, silver, molybdenum and platinum, while oxygen in addition to hydrogen may be held by molten nickel or copper and nitrogen may be dissolved by titanium and zirconium. In steel making, the three gases, oxygen, hydrogen and nitrogen are of importance.

The absorption of gases in the metal is promoted by stirring or agitation which is incidental to the melting operation or transfer of metal to a container or to a mold. The use of wet or oily scrap, improperly dried working tools and molds, and reaction with moisture in the atmosphere above a melt also induce absorption of gas. In view of the variety of sources of gas in molten metal it usually happens that the cast metal product contains some gas and is adversely effected by the release of gas which occurs during freezing of the molten metal. While the presence of gas in the liquid metal may have no undesirable effect, this is not generally true of the solid metal. For example, voids are created in castings by gas bubbles, and blisters develop on the surface of rolled products such as sheet when subjected to an annealing treatment.

Various means of minimizing or preventing the introduction of gas into the molten metal have received a great deal of attention in the past and such expedients have been proposed as providing a slag or fused salt cover or melting under a vacuum or special atmosphere. Although these means are helpful in avoiding excessive gassing they are not wholly effective or they may be too costly or cumbersome for commercial use. As a result it is frequently necessary to degas a body of molten metal before it is poured into a mold. Such degassing has generally been accomplished through the introduction of another gas, which sweeps out the undesired gas or chemically combines with it to form a solid or fluid easily separated from the molten metal. In addition, solid materials have been employed which upon being submerged in the liquid metal form vapors which pass through the molten charge carrying the gas with them. Degassing treatments of this character are of course expensive and time consuming and they may yield objectionable fumes. Attempts to degas metals, such as aluminum, by subjecting them to treatment under a vacuum are not very effective if the oxide film which forms on the surface of the metal

2

is not ruptured because the oxide film itself impedes the escape of gas.

It is an object of this invention to provide an improved method for removing gas from molten metals containing gas and which is effective without the introduction of any substance to the melt.

Another object is to provide an improved method of degassing such light metals as aluminum and magnesium and their alloys by diffusion instead of by fluxing.

A further object is to provide a rapid method of measuring the gas content of liquid metal containing gas without freezing a sample of the melt.

Another object is to provide a novel form of apparatus for effecting a reduction in the gas content of molten metal.

My invention is based upon the discovery that gas can be extracted from liquid metal containing gas by causing the gas to diffuse through a membrane permeable to the gas but impervious to the passage therethrough of the liquid metal. The diffusion of gas through the membrane is produced by providing a vacuum or a greatly reduced gas pressure or concentration on the side of the membrane opposite to that in contact with the liquid metal as compared to the pressure or concentration of gas in the melt. This can be accomplished by employing a vessel or chamber having at least a portion of its walls composed of a membrane permeable to gas but not pervious to the passage of molten metal and evacuating or greatly reducing the gas pressure within the vessel or chamber. The gas extracted from the metal may be discharged into the atmosphere or passed into a gas measuring device if a determination of the gas content of the metal is desired.

The term "membrane" as used herein refers to a rigid body which is permeable to gas but will not permit the molten metal to pass through it. The membrane should be thick enough to resist deformation by the molten metal in contact therewith yet thin enough to offer the least resistance to the passage of gas therethrough. Moreover, the membrane should be substantially inert toward the liquid metal, if subjected to repeated or continuous exposure to the molten metal. For example, it is appropriate to use steel in contact with molten magnesium but not aluminum since the former does not attack iron to any significant extent while the latter forms a brittle intermetallic compound with iron and eventually dissolves in the aluminum. Steel is very useful nevertheless where hydrogen is to be removed from the melt because that gas readily diffuses through iron at an elevated temperature, even if there are no microscopic pores or channels in the iron. In addition steel possesses a high strength which makes it possible to use thin sections for the membrane. In general, ferrous metal alloys may be employed for making membranes as well as such other metals as nickel and palladium if hydrogen is the principal gas to be diffused. If it is desirable to use steel or another metal which is attacked by the liquid metal a protective cover or coating should be provided as described below in greater detail. Where metals are to be degassed which have higher melting points than aluminum or magnesium or even in the treatment of these metals it may be desirable to use a more refractory material than a metal. Such substances as alumina, silicon nitride, beryllia, sillimanite, mullite, or zirconia may be employed if they are molded and fired to provide the necessary degree of permeability. Molded carbonaceous products made from powdered carbon or graphite are also useful. In addition, the combination of metals and ceramics known as "cermets" may be used if they have the requisite permeability and resistance to attack by the molten metals. It is also possible to construct the chamber of dissimilar materials joined to each other, one of which is permeable to gas and one which is not permeable, or to use the same material and render a portion of it permeable to gas. The latter condition may be established in a molded tube composed of very high purity alumina where one end is fired to make it impervious.

In order to cause gas to pass through the membrane it is necessary to provide a lower partial gas pressure on the side opposite to that in contact with the molten metal than exists in the molten metal. The gas within the metal exerts a certain pressure, commonly referred to as a partial pressure, which is proportional to the concentration of the gas. The diffused gas also has a partial pressure and it is the difference in partial pressures which causes diffusion to occur on the side of the membrane opposite to that in contact with the molten metal. Generally speaking, the total pressure should be below that of the atmosphere and for the best results, it should be below $1/100$ of an atmosphere which is equivalent to about 7.6 mm. of mercury. Since the rate of gas flow or diffusion through the membrane, as mentioned above, is governed by the difference in pressure and concentration of gas between the two sides of the membrane it is desirable to make the difference as great as possible. By establishing a high vacuum of less than 1 mm. mercury virtually no gas is present to decrease the net diffusion through the membrane.

In referring to the diffusion of gas through the membrane I offer no explanation of the mechanics of diffusion but I have found that by maintaining a difference in pressure on two sides of a permeable membrane gas can be removed from a gas-containing molten metal.

In addition to maintaining a pressure differential, it is generally advisable to maintain the molten metal at a temperature not far above the melting point if the gases are less soluble in a metal at a low temperature than at a high one. Aluminum, magnesium and other metals which react "exothermally" with a gas exhibit this property of increased solubility of gas with an increase in the temperature of the metal. In any event, the metal must be kept sufficiently hot to prevent substantially complete solidification.

For a better understanding of my method and the apparatus for carrying it out, reference is made to the accompanying drawings wherein:

Fig. 1 is a sectional elevation of a closed end steel tube;

Fig. 2 is a cross section of Fig. 1 on line II—II;

Fig. 3 is a sectional elevation of a closed end steel tube having the lower portion surrounded by a non-metallic protective jacket;

Fig. 4 is a cross section of Fig. 3 on line IV—IV;

Fig. 5 is a sectional elevation of a closed end steel tube having the lower portion surrounded by a protective jacket which is joined at its upper end to a ceramic thimble;

Fig. 6 is a cross section of Fig. 5 on line VI—VI;

Fig. 7 is a sectional elevation of a U-shaped tube;

Fig. 8 is an apparatus for the continuous degassing of a stream of molten metal, and

Fig. 9 is a cross section of Fig. 8 on line IX—IX.

Referring to the figures, Fig. 1 represents the degassing apparatus in its simplest form, namely, a steel tube **10** with a closed end **12** and a horizontal leg section **13** connected to an evacuating apparatus, not shown. In operating position the tube is partially immersed in a gas-containing liquid metal. The tube may be of circular shape as shown in Fig. 2, however, other shapes may be employed and, if desired, external fins may be provided to increase the area of contact with the liquid metal. The tube may consist of a single material such as steel, graphite or alumina or it may be composed in part of a gas permeable material joined to an impermeable material as described above.

The steel tube **10** shown in Figs. 3 and 4 is adapted to be used in molten metals which attack iron, for example, aluminum and aluminum base alloys. To prevent such attack, a graphite jacket **14** completely surrounds the lower portion of the tube which is immersed in the liquid metal and the jacket is fitted to or bonded at **17** to a gas impermeable coating **16** on the tube immediately above the jacketed area. Although it is generally desirable to allow some space between the jacket and the tube, this is not always essential. The impermeable coating may consist of a vitreous enamel or alumina or other metallic or non-metallic substances which can be bonded to the tube and which can also be fitted or sealed to the jacket. The joint between the coating and jacket need be only tight enough to prevent seepage of a metal therethrough. By providing this type of coating on the area of the tube in the region of the liquid metal-air interface no diffusion of gas is permitted through this area. This is of particular importance if the apparatus is employed for measuring the gas content of the liquid metal as well as degassing the same.

The jacket **14** may consist of graphite or any similar material which is inert and impervious to the liquid metal and yet is permeable to gas. Ceramic or refractory materials such as alumina, silicon nitride, beryllia, sillimanite, mullite, and zirconia may be substituted for the graphite if desired. In any case, the pores of the body should be sufficiently small to prevent entrance of molten metal therein. It has been found that graphite of ordinary grade has a sufficiently small pore size to prevent intrusion of molten aluminum into the body under atmospheric pressure.

An alternate construction which prevents diffusion of gas into the tube immediately above the metal bath level is illustrated in Figs. 5 and 6. In place of the enamel or ceramic coating **16** there is provided a thimble **18** spaced from tube **10**. The thimble is tightly fitted or sealed at **19** to graphite jacket **14** and it is also sealed at **20** to tube **10**. The thimble should consist of a ceramic or refractory material which is impermeable to gas. As to the sealing substance **20** it may be either metallic or nonmetallic and must necessarily be impermeable to the flow of gas. A frozen metal seal has been found to be quite satisfactory for this purpose.

In order to provide a greater area of membrane to be exposed to the liquid metal than provided by a straight tube shown in the preceding figures the tube may be bent into a U-shape as shown in Fig. 7 or it may be in coiled form. In Fig. 7 U-tube **22** has a horizontal leg section **3** connected to an evacuating apparatus while the other leg is capped at **24**. If desired, both legs of the U-shaped tube may be connected to a vacuum pump.

To continuously treat a stream of metal the apparatus shown in Figs. 8 and 9 is useful. Here a pipe **26**, employed to transfer liquid metal, has a section replaced by a degassing unit composed of a gas permeable graphite cylinder **30** surrounded by a metal shell **32** which is evacuated through the opening in nipple **34**. The unit may be bolted to pipe flanges **28** and the joint sealed at **29** by means of frozen metal initially deriver from the stream of metal passing through the tube. To increase the area of contact between the molten metal and the gas permeable tube internal fins may be provided within the tube. To affect the desired degassing of the stream of metal attention must be given to the volume and rate of flow. This is a matter which can be readily ascertained upon test in any given instance. In some instances it may be desirable to provide heat to the unit to prevent freezing of the metal, especially if the metal moves slowly.

In using the above-described closed end tubes to degas a liquid metal containing gas the tube is immersed in the liquid metal to a sufficient depth to submerge all or a substantial portion of the permeable membrane and then the tube is evacuated. To avoid freezing of molten metal around or in the device, it may be desirable to preheat it before bringing it in contact with the molten metal. The degassing operation may be continued as long as desired either to degas the melt as nearly as possible or to reduce the gas content to a predetermined value. To insure most effective degassing, it is recommended that the metal container be covered and thus minimize access of air to the melt. Also, it is advisable to prevent any oxide films from accumulating on the membrane which would interfere with the diffusion of gas. If such films do collect on the membrane and reduce the flow of gas, they should be removed, of course. In degassing the light metals aluminum, magnesium and the alloys in which they predominate the metal bath is held at a temperature of 1250 to 1400° F. It is to be understood that although degassing may be accomplished solely by use of my device, it may be advantageously employed in conjunction with the other degassing treatments where the gas content is not reduced to a desired low point.

An example of the degassing of an aluminum melt will serve to illustrate my invention. In this case a closed end graphite tube was employed which was sealed to an iron tube leading to a vacuum pump. The iron tube extended down over a portion of the graphite tube below the sealed joint in order to limit diffusion of gas to the graphite tube when immersed in the molten metal. Although the iron tube was satisfactory for this test it would not have lasted upon extended exposure to the liquid aluminum. The aluminum was of a purity commonly used for electrical conductor purposes containing a total of not over 0.4% of copper, iron and silicon impurities. An 1100 g. charge of metal was melted, heated to a temperature of 700° C. and held at that temperature during the period of testing. The melt was saturated with hydrogen by bubbling the gas through it. When saturated with hydrogen at 700° C. aluminum is considered to contain 1 ml. of the gas per 100 g. of metal. By saturating the melt, a known base was obtained from which determinations could be made. The 2½" exposed length of the ⅜" O. D. graphite tube was inserted in the gassed melt to a depth of about 4 inches so that the lower end of the protective iron tube sheath was also immersed in the molten metal. After the tube had attained the temperature of the melt it was evacuated to a pressure less than 0.01 mm. of mercury. The initial gas content of the metal was determined by freezing a 44 g. sample under 50 mm. of mercury pressure, and measuring its density. The sample was found to have a density of 1.8 g./ml. The initial flow of gas from the tube was measured at the rate of 0.20 ml./min. After 43 minutes of the degassing treatment a sample of the metal had a density of 2.6 g./ml. after freezing under 50 mm. of mercury pressure. The increase in density shows that the metal has lost gas in the treatment.

In another test involving removal of gas from molten magnesium, a 540 g. melt of commercial purity metal was prepared. A conventional type of cover flux was used to protect the melt. The metal was heated to 800° C. and was saturated with hydrogen by bubbling the gas through the molten charge. At 800° C. molten magnesium is considered to dissolve 28 ml. of hydrogen per 100 g. of metal. Gas removal was effected by inserting a closed end steel tube into the melt to a depth of about 3 inches and evacuating the tube. The amount of gas diffused through the tube was measured at intervals and the rate of removal determined. When the degassing operation began immediately after saturation of the melt with hydrogen the rate of removal was 0.77 ml./min. At this rate complete degassing could be obtained in 196 minutes. However, as gas removal progressed the rate became lower for after 125 minutes of degassing the removal rate had dropped to 0.46 ml./min. This means that if complete removal of gas were to be attempted under these conditions and with this apparatus, a long degassing treatment would be required. As a practical matter it is not usually necessary to remove the last traces of gas in commercial operations and therefore a shorter treatment would suffice than might be indicated by calculations.

Although the apparatus and method have been described in terms of degassing a melt it will be appreciated that they may also be used for measuring the gas content if the apparatus is connected to a measuring device. Such devices are well known in the art and need not be described here.

Having thus described my invention, I claim:

1. The method of removing dissolved hydrogen from molten metal by diffusion comprising bring the molten hydrogen-containing metal into intimate association with a solid membrane which is permeable to the passage of said hydrogen by diffusion but which is impervious to the passage of molten metal therethrough and which is heated through association with the molten metal, and causing said hydrogen to diffuse through said membrane.

2. The method of removing dissolved hydrogen from molten metal by diffusion comprising bringing the molten hydrogen-containing metal into intimate association with a solid membrane which is permeable to the passage of said hydrogen by diffusion but is impervious to the passage of molten metal therethrough and which is heated through association with said molten metal and causing said hydrogen to diffuse through said membrane by maintaining a lower hydrogen pressure on the side of the membrane opposite to that in contact with the molten metal than the hydrogen pressure is said molten metal.

3. The method of removing dissolved hydrogen from molten metal by diffusion comprising bringing the molten hydrogen-containing metal into intimate association with a solid membrane which is permeable to the passage of said hydrogen by diffusion but is impervious to the passage of molten metal therethrough and which is heated through association with said molten metal and causing said hydrogen to diffuse through said membrane, said metal being under atmospheric pressure and the pressure on the side of the membrane opposite to that in contact with the molten metal being less than 1/100 of an atmosphere.

4. The method of removing dissolved hydrogen from molten light metal of the class consisting of aluminum and magnesium and the alloys in which these metals predominate comprising bringing the molten hydrogen-containing light metal into intimate association with a solid membrane which is permeable to the passage of said hydrogen by diffusion but which is impervious to the passage of molten metal therethrough and which is heated through association with said molten metal, and causing said hydrogen to diffuse through said membrane, said molten metal being under atmospheric pressure and the partial pressure of the hydrogen on the side of the membrane opposite to that in contact with the molten metal being less than the partial pressure of the hydrogen within said molten metal.

5. The method of removing dissolved hydrogen from molten metal by diffusion comprising partially immersing a closed end solid tube in said molten hydrogen-containing metal, said tube having at least a portion of that part of the tube which is immersed in the molten metal composed of a membrane diffusively permeable to hydrogen, causing the hydrogen to diffuse through said membrane by maintaining a lower partial hydrogen pressure within the tube than the partial pressure of hydrogen within the molten metal and removing the diffused hydrogen from the interior of said tube.

6. The method of removing dissolved hydrogen from molten metal by diffusion comprising partially immersing a closed end metal tube in said molten hydrogen-containing metal, said metal tube having a melting point above that of the molten metal and having at least a portion of that part of the tube which is immersed in the molten metal composed of a metal diffusively permeable to hydrogen, causing said hydrogen to diffuse through said permeable portion of the tube by maintaining a lower partial hydrogen pressure inside the tube than the partial

pressure of hydrogen within the molten metal and removing the diffused hydrogen from the interior of the tube.

7. A device for removing dissolved hydrogen from molten metal and adapted to be at least partially immersed in the molten metal comprising a tubular metal member closed at one end having at least a portion of that part of the tube which is to be immersed composed of a metal which is diffusively permeable to hydrogen but impervious to the passage of molten metal therethrough and connected to means for evacuating the interior of said tube and removing the hydrogen which has diffused through the tube wall.

8. A device for removing dissolved hydrogen from molten metal which is adapted to be partially immersed in the molten metal, said device comprising a closed end tubular assembly composed of a closed end inner metal tube and an outer graphite jacket surrounding at least the closed end portion of the metal tube, said inner tube consisting of a metal diffusively permeable to hydrogen in at least that portion which constitutes the closed end and the immediately adjoining wall section, said jacket being sealed to the inner metal tube at the open end of the jacket whereby air and molten metal are excluded from any space between the metal tube and jacket during operation of the device, said device being connected to means for evacuating the interior of the metal tube and removing the hydrogen which has diffused through the metal tube wall.

9. The method of removing dissolved hydrogen from a stream of molten metal by diffusion while the metal is in motion comprising passing said stream of metal over a solid membrane which is permeable to the passage of

hydrogen by diffusion but which is impervious to the passage of molten metal therethrough and which is heated through association with the molten metal, and causing said hydrogen to diffuse through said membrane from said moving metal by maintaining a lower partial hydrogen pressure on the side of the membrane opposite to that in contact with the molten metal than the hydrogen pressure in said molten metal.

10. A device for removing dissolved hydrogen from a moving body of molten metal comprising a tubular member having solid walls and open at both ends, said walls being diffusively permeable to hydrogen but impervious to the passage of molten metal therethrough, said tubular member being connected to means for continuously supplying molten metal thereto and receiving degassed metal therefrom, and a gas tight shell spaced from said tubular member and completely surrounding it, said shell being connected to means for evacuating the space between said shell and said member and removing the hydrogen which has diffused through the walls of said member from said moving body of molten metal.

References Cited in the file of this patent

UNITED STATES PATENTS

957,058	Hixon	May 3, 1910
2,263,549	Peyches	Nov. 18, 1941
2,752,233	Peyches	June 26, 1956

OTHER REFERENCES

Thompson et al.: AIMME Trans., vol. 25, pages 253, 254, 300. Publ. 1937.