Feb. 5, 1957 L. R. ZIFFERER 2,780,541

PROCESS FOR TREATING MOLTEN METALS

Filed April 9, 1954

Fig. 1.

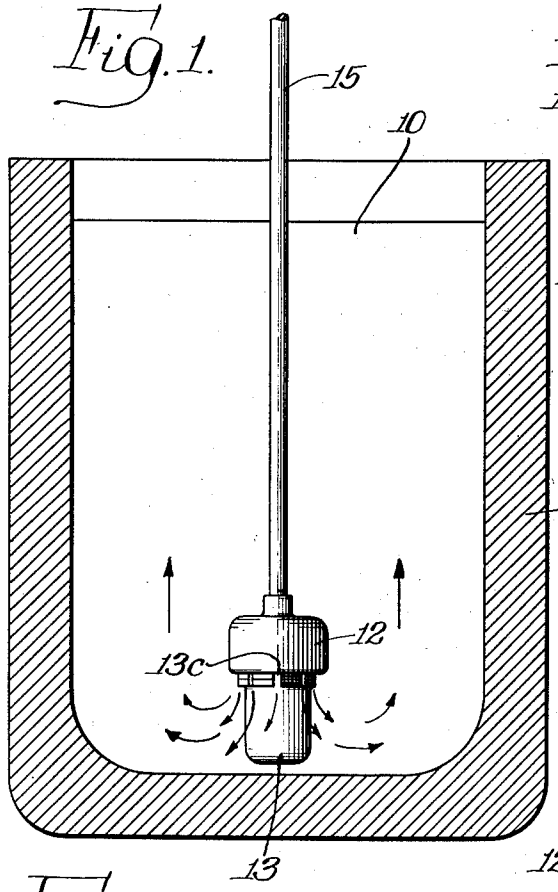


Fig. 3.

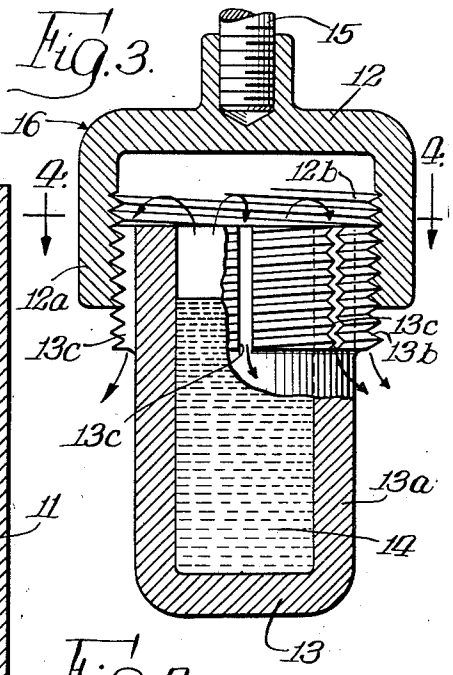


Fig. 4.

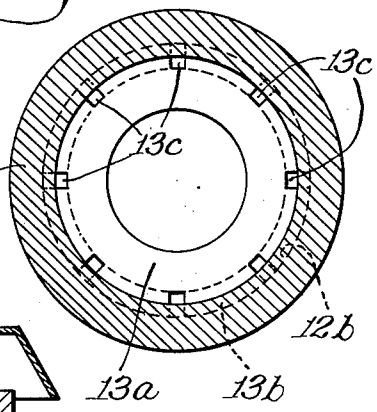
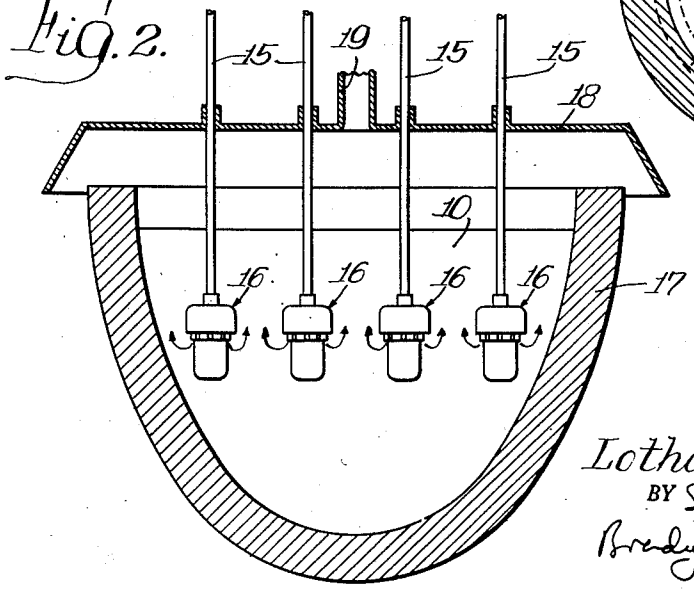


Fig. 2.



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PROCESS FOR TREATING MOLTEN METALS

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10 Claims. (Cl. 75—130)

This invention relates to a method and apparatus for inoculating a first metal with a second metal.

When metals such as molten iron are treated with small amounts of another metal such as magnesium for the purpose of desulfurization and deoxidation of metal baths or for the production of spheroidal iron and the like, many problems are encountered. Thus, in the case of magnesium the metal itself is quite explosive when immersed in ferrous baths or otherwise confined, and great precautions are necessary to prevent accidental injury to the workmen and to the equipment. Furthermore, the methods previously used for this inoculating are wasteful of the metals used in the inoculation. This is an important factor in such materials as magnesium, cerium, and other expensive substances. It is also often difficult to secure a uniform treatment of the molten mass of metal so as to produce a satisfactory uniform product.

The methods and apparatus of this invention successfully solve these and other problems and provide for inoculating a mass of metal with a second metal in an inexpensive, safe and thorough manner. Furthermore, the present invention permits the highest possible percentage recovery of unused inoculant and carrier metal so that the entire invention is quite inexpensive to practice and is, therefore, applicable to the treatment of ductile iron and steel.

One of the features of this invention is to provide a method of inoculating a first metal with a second metal which comprises immersing an alloy of the second metal with a carrier metal into a molten mass of the first metal heated to a temperature above the boiling point of the second metal, the carrier metal having a melting point less than this temperature and a boiling point above this temperature, and maintaining this immersion during the inoculation of the first metal with the resulting vapors of the second metal, the percentage of the second metal in this alloy being sufficient to produce a vapor pressure in excess of the hydrostatic head pressure of the molten first metal at the point of maximum immersion.

Another feature of the invention is to provide an inoculating ladle for immersion in a molten mass of a first metal while the ladle contains a second metal having a boiling point less than the temperature of the first metal, comprising a container formed of separable parts and including at least one exit passage opening downwardly and extending from a point above the second metal within the container to prevent escape of the non-vaporous contents of the ladle.

Other features and advantages of the invention will be apparent in the following description of certain embodiments of the invention taken in conjunction with the accompanying drawings. Of the drawings:

Fig. 1 is a longitudinal sectional elevation showing one embodiment of the apparatus of this invention.

Fig. 2 is a view similar to Fig. 1, showing a second embodiment of the apparatus of this invention.

Fig. 3 is a longitudinal partial sectional elevation through one embodiment of the ladle of this invention, and

Fig. 4 is a transverse sectional elevation, taken substantially along line 4—4 of Fig. 3.

In the embodiment of the apparatus shown in Fig. 1, the molten first metal **10** is contained in a large cylinder **11** of the usual type adapted to withstand the temperature of the molten metal which may be iron.

In inoculating the molten first metal **10**, a container may be provided, with this container formed of a cover **12** provided with a depending substantially cylindrical side wall having on the inner surface thereof screw threads **12***b*. The container also includes a removable cup **13** having side walls **13***a* provided with screw threads **13***b*. The upper end of this cup **13** is received within the side wall **12***a* in a telescoping arrangement and the threads **12***b* and **13***b* cooperate to removably hold the cover and cup assembled.

The cup **13** is intended to hold an alloy **14** of the inoculant second metal, with this second metal having a boiling point less than the temperature of the molten first metal **10**. This alloy **14** also contains a carrier metal having a melting point less than the temperature of the molten first metal **10** and a boiling point greater than this temperature. The alloy is introduced as a solid into the cup **13**, the cover **12** is then fastened on the cup and the entire assembly is lowered by means of a handle **15** into the molten mass of the first metal **10**. The heat of this first metal causes the alloy to melt, as is shown in Fig. 3. In order to permit the vapors of the relatively low boiling second metal in the alloy **15** to escape and thus inoculate the first metal **10**, at least one exit passage is provided in the container opening downwardly and extending from a point above the second metal **14** within the cup **13** to prevent escape of the non-vaporous contents of the ladle or container into the molten first metal **10**. In the embodiment shown, the exit passage is formed of a plurality of grooves **13***c* arranged longitudinally in the outer surface of the upper portion of the cup **13**. These grooves provide passages for the escape of the vapors of the second metal in the alloy **14** in the manner shown by the arrows in Figs. 1 and 3. These escaping vapors serve to inoculate the first metal **10** with the second metal of the alloy **14**. The carrier metal of the alloy, having a boiling point greater than the temperature of the molten first metal, does not escape in any substantial quantities but remains in the cup **13** and can be recovered for later use.

In Fig. 2 there is illustrated an embodiment in which a plurality of ladles **16** are used for the simultaneous inoculation of a large quantity of a first metal **10** in a large container **17**. In this embodiment, the container **17** may contain between 200 and 300 tons of molten metal such as iron and is of the type embodied in the transfer ladles used to transport molten pig iron from the blast furnace to the open hearth furnace.

In this second embodiment each of the ladles or containers **16** are provided with a handle **15** arranged substantially parallel to each other and extending upwardly with these handles passing through and attached to a hood **18** provided with a stack **19** for the escape of noxious gases. Here the entire assembly of handles **15**, the containers **16** and hood **18** is raised and lowered as a unit. Various types of raising and lowering apparatus may be employed with this embodiment of the invention, and such apparatus is well known to those skilled in the art.

The ladle or container **16** may be made of any heat resisting material such as graphite, refractory materials, carbon, silicon carbide and the like.

When the container **16** is immersed in the molten first metal **10**, which may be molten iron, heat from the first metal flowing through the wall of the container raises

the temperature of the alloy. As both the inoculant or second metal and the carrier metal in the alloy have melting points below the temperature of the first metal **10**, the alloy melts and begins to superheat. As soon as the boiling point of the second metal in the alloy is reached, fractional distillation occurs with the second metal vaporizing and passing through the exit passages **13***c* and into the molten first metal **10**. The temperature of this distillation depends upon the percentage of each metal in the alloy **14**. Thus, the vapors emitted from the container will be composed of all the metals in the alloy in a proportion consistent with or depending upon the vapor pressure of the constituent metals and the percentage of each metal in the alloy. Where the alloy is a preferred magnesium-aluminum alloy, the difference in vapor pressure between magnesium and aluminum is so great that practically no aluminum escapes as a vapor. Where the alloy is one of magnesium-cerium-aluminum, both magnesium and cerium have a substantial vapor pressure at the temperature of molten iron so that while both of these elements escape as vapors substantially all the aluminum is retained. By regulating the magnesium content and cerium content in the alloy, a definite quantity of cerium vapor and magnesium vapor are caused to pass into the molten first metal. This latter alloy is quite important as cerium plays an important role in the production of ductile or nodular iron.

During the immersion of the container in the molten first metal, which may be molten iron, heat flows from this molten first metal through the walls of a container into the alloy within the container. This first melts the inoculant second metal and then raises its vapor pressure so that when the vapor pressure is sufficiently great these vapors escape from the container and pass into the molten first metal **10**. This pressure, called the release pressure, is equal to the atmospheric pressure plus the hydrostatic head pressure due to the depth of metal above the container. The heat transfer equation may be expressed as follows:

$$\frac{dq}{dt}=\frac{KA}{S}(T_2-T_1)$$

where:

q=B. t. u. of heat.
K=a constant depending upon the material of the container **16**, B. t. u./sec./ft.^{3}/° F.
S=thickness of the container in feet.
A=mean area of container.
T_2=temperature of first metal **10**, ° F.
T_1=alloy temperature at "release" pressure, ° F.
t=time, seconds.

During the inoculation the generation of magnesium vapor cools the inside of the container and keeps it at a temperature of T_1 ° F. This temperature is related to the release pressure of the second metal for a given composition of the alloy. As the second metal boils off, however, the composition of the alloy is changing to one poorer in the second metal. Thus, as the molarity or percentage composition of the magnesium drops, higher temperatures are required in the alloy to maintain the release pressure. This is a consequence of Rauolt's Law. As T_1 rises the factor, T_2-T_1, in the heat flow equation diminishes and the rate at which the vapors are generated likewise diminishes.

The system comes to equilibrium when T_2 equals T_1. At this temperature pure magnesium, for example, has a high vapor pressure when subjected to the temperature of the molten iron. The vapor pressure of the magnesium in the alloy solution, however, is approximately proportional to its molarity. Therefore, for a composition in the alloy of 10% magnesium and 90% aluminum, the approximately 10 atmospheres pressure which would exist for pure magnesium when T_2 equals T_1 is reduced to one atmosphere. This means that at a molarity of 0.1 and a temperature in the alloy equal to the temperature of the molten iron, the system has reached equilibrium and the magnesium vapor ceases to evolve.

When the container is slowly withdrawn, the decreasing hydrostatic pressure causes a lowering of the release pressure so that vapors are again generated even when the alloy has apparently been exhausted at the initial immersion depth. These vapors continue until the release pressure due to the molarity of the magnesium is again at equilibrium with the atmospheric pressure plus the new reduced hydrostatic pressure. Thus, it is greatly preferred that the container be withdrawn slowly from the bath in order to prevent evolved magnesium being ejected violently into the atmosphere with resulting waste and excessive pyrotechnics.

The vapor pressure of magnesium, for example, as a function of temperature can readily be calculated by the use of the Clapeyron Equation. In this instance, the equation may be expressed as follows:

$$\log P=\frac{-H}{4.575\,T}+B$$

where:

P=absolute pressure, atmospheres
T=degrees absolute, ° K.
B=5.158
H=32,520

From the use of this equation, the following vapor pressures of substantially pure magnesium as a function of temperature and degrees F. is obtained:

T ° F.:	Pressure (Atmos.)
2400	4.95
2450	5.74
2500	6.82
2550	8.02
2600	9.42
2650	10.86
2700	12.82
2750	14.82
2800	17.1
2850	19.63
2900	23.34
2950	25.4

These vapor pressures are, of course, absolute and the pressures above atmospheric is obtained by subtracting one.

The vapor pressure is, of course, dependent upon the molar percentage of the inoculating second metal in the alloy. Thus, if the alloy contains 0.25 molar percentage of magnesium and the temperature of the molten first metal is 2700° F. the maximum possible pressure above atmospheric pressure is approximately 2.25 atmospheres, calculated as $(13\times0.25)-1$. Similar tables may, of course, be worked out for other inoculants, where metals other than magnesium are calculated.

As the vapor pressure is dependent upon the molar percentage of the magnesium or other inoculant metal, the system is quite safe as even if the container were to break, the maximum instantaneous pressure developed by dumping the alloy into the molten first metal would be relatively small. This is true because the heat capacity of the carrier metal would slow down the attainment of the temperature of the molten first metal. This would cause a substantial time lapse during which the second metal, such as magnesium, would boil away and be relatively non-explosive before an excessively high temperature was reached. On reaching this temperature of the molten first metal, the alloy would contain considerably less magnesium so that the maximum vapor pressure would be greatly reduced. The carrier metal, which is preferably aluminum, is easily recovered. Thus, the carrier metal plus any remaining portion of the inoculant second metal remaining in the ladle or container **16** upon

completion of one treatment may be removed, melted and mixed with more of the inoculant second metal to form a new alloy for the next treatment in the manner specified. Thus, practically none of the metals in the alloy are wasted.

The use of aluminum as a carrier is much simpler and less expensive than carriers now being used. This is true because aluminum may be alloyed with the relatively low-boiling inoculant second metal at a lower temperature, which may be approximately between 1100 and 1200° F.

In the case of the magnesium-cerium-aluminum alloy, the aluminum functions only as a carrier. By the proper adjustment of the percentages of each component, an exact ratio can be maintained in the manner explained in detail above between aluminum and the magnesium and cerium which is evolved. In this case, the residue at the end of the treatment will contain some cerium and some magnesium in a relatively large mass of aluminum carrier. This residue may then be used in re-alloy. The melted alloy is cast into weighed ingots and these ingots are again readily loaded into the container. Thus, with the unused metals, which in the case of cerium and other such metals are quite expensive, no waste is encountered.

Although aluminum is preferred as a carrier metal, other carrier elements such as lead, tin, antimony, bismuth and the like may be used. The preferred carriers for use in inoculating molten iron preferably have melting points not greater than about 1400° F. and high boiling points which are preferably about 3000° F. or more.

Having described my invention as related to the embodiments shown in the accompanying drawings, it is my intention that the invention be not limited by any of the details of description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

I claim:

1. The method of inoculating a first metal with a second metal which comprises immersing an alloy of said second metal with a carrier metal into a molten mass of the first metal heated to a temperature above the boiling point of said second metal, the carrier metal having a melting temperature less than said temperature and a boiling temperature greater than said temperature, and maintaining said immersion during the inoculation of the first metal with the resulting vapors of said second metal while preventing substantial mingling of said carrier metal with said molten mass of said first metal, the percentage of said second metal in the alloy being sufficient to produce a vapor pressure in excess of the hydrostatic head of said molten first metal at the point of maximum immersion.

2. The method of claim 1 wherein said first metal is iron.

3. The method of claim 1 wherein said second metal is magnesium.

4. The method of claim 1 wherein said carrier metal is aluminum.

5. The method of inoculating a first metal with a second metal which comprises immersing a compound including said second metal from which the second metal is freed by thermal action into a molten mass of the first metal heated to a temperature sufficient to maintain said thermal action, the second metal having a boiling point below said temperature and the remaining product from said composition having vaporizing temperatures above said temperature, and maintaining said immersion during the inoculation of the first metal with the resulting vapors of said second metal while preventing substantial mingling of said carrier metal with said molten mass of said first metal, said second metal having a vapor pressure in excess of the hydrostatic head of the molten first metal at the point of maximum immersion.

6. The method of claim 5 wherein said first metal is iron.

7. The method of claim 5 wherein said second metal is magnesium.

8. The method of inoculating a molten metallic mass with magnesium which comprises immersing into said mass a mixture including magnesium sulfide and calcium carbide, the temperature of said mass being sufficient to cause a reaction between said sulfide and carbide to generate metallic magnesium, calcium sulfide and carbon and said temperature being above the boiling temperature of said magnesium, and maintaining said immersion during the inoculation while preventing substantial mingling of said calcium sulfide and carbon with said molten mass.

9. The method of inoculating a molten metallic mass with magnesium which comprises immersing into said mass a mixture including magnesium oxide and calcium carbide, the temperature of said mass being sufficient to cause a reaction between the oxide and carbide to generate metallic magnesium, calcium oxide and carbon and said temperature being above the boiling temperature of said magnesium, and maintaining said immersion during the inoculation while preventing substantial mingling of said calcium oxide and carbon with said molten mass.

10. The method of inoculating a molten metallic mass with magnesium which comprises immersing into said mass a material including Mg_3N_2, the temperature of said mass being sufficient to cause thermal decomposition of said nitride compound to generate metallic magnesium and nitrogen and said temperature being above the boiling temperature of said magnesium, and maintaining said immersion during the inoculation while venting said nitrogen.

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