

Feb. 6, 1968

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3,367,646

APPARATUS FOR INJECTING METAL VAPORS INTO A MOLTEN METAL

Filed Feb. 23, 1965

Fig. 1

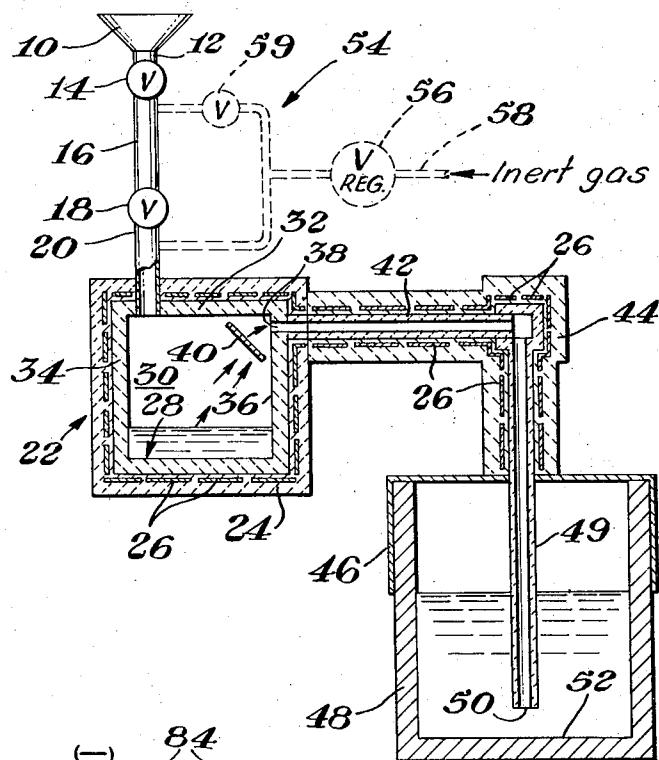
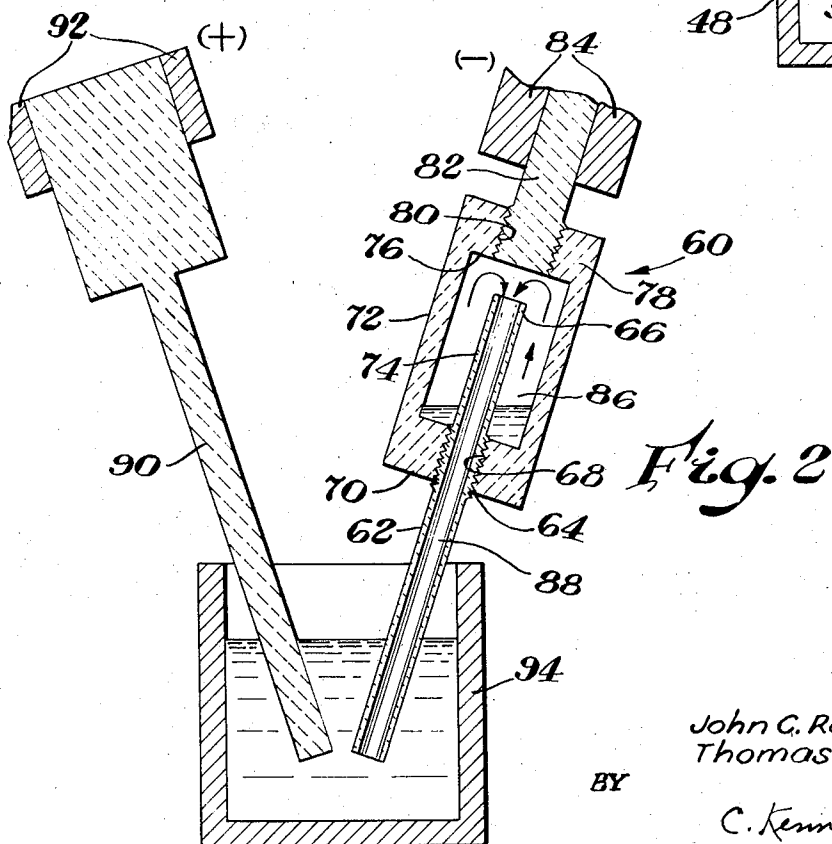


Fig. 2

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**APPARATUS FOR INJECTING METAL
VAPORS INTO A MOLTEN METAL**

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Filed Feb. 23, 1965, Ser. No. 434,461

1 Claim. (Cl. 266—34)

ABSTRACT OF THE DISCLOSURE

An apparatus for introducing a low boiling metal into a molten metal of higher boiling point which comprises a storage and metering chamber connected to a chambered furnace assembly, said furnace assembly communicating by means of a conduit with a metal holding vessel for a molten metal bath and the furnace assembly fitted with a baffle adjacent the junction of the furnace assembly and the conduit communicating with the metal holding vessel.

This invention relates to a novel apparatus and process for alloying minor proportions of relatively low-boiling metals into a molten metal and more particularly is concerned with a novel apparatus and process for introducing relatively low boiling metals into molten ferrous based melts. The present invention particularly is suitable for injecting vaporized alloying ingredients, e.g. magnesium, into molten cast iron to prepare ductile, i.e. nodular, cast iron.

Many alloys require the combination of relatively low-boiling alloying ingredients with a high boiling matrix metal. The introduction of low-boiling metals into molten ferrous based melts is widely practiced. However, the introduction of a readily vaporizable metal in the solid or liquid state into high-boiling metal charges is hazardous and dangerous because of the rapid, almost instantaneous volume expansion as the additive metal vaporizes. Such violently expelled metal vapors cause melt splattering and can pose both a fire hazard and toxicity problem. Additionally, there is little or no control of the amount of addition agent alloyed into the melt. Efficiencies as a rule are very low.

One means for adding low-boiling metals to molten iron is taught in U.S. Patent 2,678,266. In this patent an alloying ingredient is melted at a position remote from the iron and transferred to an injection device adjacent to and/or extending into the molten iron. At or near the point of injection into the molten iron, additional heat is applied to vaporize the alloying ingredient before it is finally forced or otherwise pressured from an external pressurizing force into the molten mass. The devices taught for use in performing this process are shown to require the use of inert gas as a pressurizing means both for moving the molten alloying ingredient into position for the vaporizing step and as a flow control agent.

Known art devices of the general type described in U.S. Patent 2,678,266 potentially can be extremely hazardous because of the possibility of mechanical failure. To illustrate, if temperature controls or gas pressure controls fail, there is a great possibility of injecting the alloying ingredient in the liquid state into the molten bath. The resulting sudden vaporization of the low-boiling alloying ingredient in the molten bath can be violent and explosive.

It is a principal object of the present invention to provide a novel apparatus and method of its use for safely introducing relatively low boiling metals into a metal bath which is molten at the boiling point of the low boiling metal.

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It is another object of the present invention to provide an apparatus and method for safely introducing vaporized alloying ingredients into molten iron without the use of extraneous pressurizing media.

It is also an object of the present invention to provide a novel process and apparatus for injecting a vaporized alloying ingredient, e.g. magnesium, into molten iron wherein controlled, non-violent reaction is achieved.

These and other objects and advantages of the present invention readily will become evident from the detailed description presented hereinafter when read in conjunction with the accompanying drawing.

In the drawing:

FIGURE 1 is a sectional schematic view of one embodiment of the apparatus of the present invention.

FIGURE 2 is a sectional schematic view of a second embodiment of the apparatus of the present invention.

In general, the process of the present invention comprises providing a low-boiling alloying metal or metal forming composition, heating said metal or composition to place the metal in the vapor state and introducing the metal vapors, under autogenous pressure, into a molten matrix metal having a boiling point higher than the low-boiling metal. This process readily is carried out by the apparatus of the present invention which comprises a metering unit for introducing a predetermined quantity of a relatively low-boiling metal into a vaporizing chamber or furnace. This vaporizing member is connected to a vessel for holding a higher boiling molten charge by means of conduit or other transfer means whereby vapors of low-boiling metal are introduced under autogenous pressure into a melt of the higher boiling metal.

More specifically, one embodiment of the apparatus as shown in FIGURE 1 comprises a hopper or other storage vessel 10 having a discharge outlet 12 in its bottom. This discharge outlet 12 communicates with a first valve 14. Valve 14 in turn communicates with a vertically positioned chamber 16 designed to hold a predetermined amount of material which chamber 16 communicates at its lower end with a second valve 18. Conveniently, chamber or vessel 16 can be made of a clear, transparent resinous material or glass and can be calibrated to show by column height in the chamber 16 equivalent amounts of different metals employed in the alloying process. Alternatively, chamber 16 can be of metal or other construction and can be calibrated by any of a variety of means as understood by one skilled in the art. Valve 18 communicates through a column or conduit 20, usually vertically disposed, with a furnace, or metal vaporizing, assembly 22.

Furnace assembly 22 comprises a jacket 24, ordinarily of a thermally insulating refractory material, having a plurality of electrical resistance heating elements 26 embedded therein which surround an inner shell 28. This shell 28 is inert to the metal being vaporized and is thermally conducting. Shell 28 defines a vessel 30 having a hollow interior. In operation, vessel 30 serves as a metal vaporization pot. As shown in the embodiment depicted in FIGURE 1, conduit 20 communicates with the vessel 30 through the top 32 near one side wall 34. The opposite side wall 36 of vessel 30 defines a passage 38 near its top. A baffle 40 is positioned near passage 38.

Passage 38 communicates in a vapor-tight relationship with one end of an L-shaped conduit 42. This conduit 42 has an outer shell 44 ordinarily of a refractory thermally insulating material, and contains a plurality of electric resistance heaters 26. The conduit 42 is fabricated of a material substantially inert to the vapors of the low melting metal and is thermally conducting.

The outer shell 44 of conduit 42 abuts, and ordinarily is joined or fastened to the cover 46 of a ladle or metal

holding pot 48. The leg 49 of conduit 42 opposite that communicating with vessel 30 passes through cover 46 thereby forming an injection tube and is of a length such that its end 50 is near the bottom 52 of metal holding pot 48.

For those metals which in the solid or molten state undergo detrimental oxidation from air, the apparatus can be fitted with a branched conduit assembly 54 containing a pressure regulator valve 56 and gas inlet tube 58 through which an inert gas can be introduced into the unit. Alternatively, valve 59 can be placed in the branch of the conduit assembly 54 communicating with the chamber 16, if desired so as to separately control the flow of inert gas to this chamber.

The operability of this embodiment readily can be understood from the following illustrative example.

Particulate magnesium, e.g. atomized pellets of from 20 to 150 mesh, are placed in the metal storage hopper or vessel 10, valves 14 and 18 being closed and chamber 16 being empty of metal. Valve 18 is opened and inert gas, e.g. substantially anhydrous argon, is passed through the branched conduit assembly 54 into the apparatus to flush out the vaporizing vessel 22 and metal vapor transfer conduit 42. The amount of gas employed ordinarily is just enough to provide a slight positive pressure in the system. Valve 18 is closed and valve 14 opened to introduce a predetermined quantity of the magnesium pellets into the chamber 16. Valve 14 is then closed and valve 18 opened whereupon the predetermined quantity of magnesium pellets is introduced into the vaporizing chamber 30. The resistance heaters 26 are actuated to heat and vaporize the magnesium. The inert gas flow is continued during the heating operation until the magnesium has become melted and starts to vaporize. As the magnesium vapor pressure builds up and the magnesium vapors under this autogenous pressure start to pass through conduit 42 and exit from the end 50 of the conduit under the surface of the molten ferrous bath, the flow of inert gas ordinarily is discontinued to minimize splashing in the iron-based melt. The baffle 40 in the vaporizing chamber 30 assures that no liquid metal splashes up into the conduit 42 at its junction with passage 38 of vessel 30. The process is continued until substantially all the magnesium has been vaporized and the vapors transferred to the ferrous based melt. Pressure regulator 56 is adjusted to provide a minimum of about 1 atmosphere of pressure. This assures that when the magnesium has been substantially completely vaporized a partial vacuum is not generated in the vaporizing vessel 30 and conduit 42 which could draw molten metal from the ladle 48 back up into the injection tube.

In the embodiment depicted in FIGURE 2, a graphite electrode assembly 60 is fabricated which comprises an elongated hollow, tubular member 62. This member 62 has a threaded portion 64 near one end 66. The tubular member 62 is attached, by mating threads in a passage 68 substantially in the center of the bottom 70, to an open top cylindrical body member 72 having an internal chamber of diameter greater than tubular member 62. The shorter section 74 of tubular member 62 beyond threads 64 is of such a length that the end 66 of the tube is contained within cylindrical member 72. Preferably, the end 66 of tubular member 62 extends to within a relatively short distance from the inner face 76 of the top 78 of cylindrical member 72. The top 78 of cylindrical member 72 is fitted, by means of a mating thread assembly 80, with a solid graphite member 82 having a conventional clamping and electrode connector assembly 84. When assembled, the graphite electrode assembly 60 provides a reservoir or chamber 86 within cylindrical member 72. This communicates with through passage 88 in tubular member 62. A second solid graphite electrode 90 having a conventional clamping and electrode connector assembly 92 also is provided.

For use in accordance with the present novel method,

a low boiling metal additive is placed in the reservoir 86 of cylindrical member 72. The assembled graphite electrodes are positioned in a molten, higher boiling metal bath contained in a ladle, crucible or other metal holding pot 94. The electrodes are placed in the ladle so as to make electrical contact through the molten metal bath. An electrical current is applied whereby the hollow electrode becomes a resistance heater. This vaporizes the low boiling metal in the reservoir 86 which under autogenous pressure forces the metal vapors into the molten metal bath.

These depicted embodiments of the apparatus are not meant to be limiting but merely serve to illustrate the present invention.

The materials of construction to be used are those which are substantially inert to the metals being handled, have the requisite strength, electrical and thermal properties for use at the operating conditions and which are not appreciably detrimentally degraded at these conditions. Conveniently, graphite is used as a construction material for those surfaces contacted by the liquid and vapor states of the low-boiling metal additive, although other construction materials inert to these materials and having requisite thermal conductivity characteristics can be employed.

Relatively low-boiling alloying metals which can be added in the present process include, for example, magnesium, sodium, zinc, tellurium, selenium, cadmium, lithium, calcium, potassium, cesium, mercury and barium. These can be readily introduced into higher boiling metals such as, for example, iron, copper, aluminum, etc. The present invention is particularly suitable for controllably and without violence introducing magnesium into ferrous based melts. The production of ductile, i.e. nodular cast iron by adding magnesium to grey cast iron is a particularly useful application of the present invention.

The low-boiling additive metals for use in the present invention can be in any form whereby they can be metered or added in controlled amounts to the vaporizing reservoir. Conveniently, spherical pellets, as produced by atomization, are employed. Such pellets, of a fairly uniform size range, provide both ready feed by gravity flow as well as lend themselves to weight-volume equivalent calibrations of the feed chamber. With feed sources other than shown in the depicted embodiments employing pre-weighed batches, weigh-beam mechanisms or other weight controlling feed devices, the particle size and shape of the additive metal is of no concern or problem. Irregular chunks, scrap, chips, powders, and molten charges can be fed into the vaporizing chamber.

Additionally, if desired, metal producing compositions, such as mixtures of aluminum and magnesium oxide, aluminum carbide and dolomite, aluminum-calcium carbide-magnesium oxide and the like, e.g. all of which upon heating generate magnesium can be introduced in a predetermined amount into the vaporizing chamber. As the heating takes place, magnesium is generated in situ and subsequently transferred as vapors into the higher boiling melt.

The following examples will serve to further illustrate the present invention but are not meant to limit it thereto.

Example 1

About 1600 grams of a cast iron having the following composition (carbon, 3.2-3.5 wt. percent; manganese, 0.2-0.35 wt. percent; silicon, 1.5-1.9 wt. percent; phosphorus, 0.025-0.03 wt. percent; sulfur, 0.004-0.008 wt. percent); balance iron was melted in a zircon induction furnace crucible about 2½ inches in diameter and 4 inches deep. The crucible was heated by a 6-kilowatt high frequency converter. When the melt reached a predetermined temperature of between 2750 to 2780° F., as determined by an optical pyrometer, a metal vapor injection apparatus of the same general design as depicted in FIGURE 2 was positioned in the ferrous melt. This vapor

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injection apparatus consisted of two spaced apart graphite electrodes which made electrical contact through the molten iron. An amount of magnesium granules (about 12 mesh, U.S. Standard Sieve) to provide a predetermined calculated residual magnesium concentration in the iron product were placed in the hollow chamber of one of the electrodes which also was fitted with a vapor conduit as depicted. A direct current power supply (from an electric welding apparatus) was connected to the electrodes to complete the circuit. This power supply was activated and adjusted to supply about 640 amperes current at about 15 volts. After about 1 to 2 minutes magnesium vapor began feeding into the melt as observed visually from melt activity. The alloying continued in an active but not violent manner. Some flaring of magnesium was observed, but there was no explosion or melt splattering as occurs when liquid or solid magnesium is introduced into ferrous melts. When no further alloying activity was visible, the power was shut off to the two-electrode metal vaporizing apparatus and the vaporizer removed from the furnace. About 0.5 weight percent, on basis of total charge, of 85 percent ferrosilicon was rabbled into the melt and the iron tapped into a shell mold.

The resulting castings were examined microscopically and found to contain graphite only in a compacted, spheroidal form. The product was analyzed for residual magnesium by emission spectroscopy.

The results of a number of different runs are presented in Table I.

TABLE I

Run No.	Melt Temp., °F.	Injection Period, Sec.	Mg. Input ¹ Wt. percent of Total Melt	Mg. Residual in Pdt., Wt. percent.	Mg. Recovery, percent
1-----	2,750	70	.1865	.02	10.7
2-----	2,750	65	.1255	.024	19.1
3-----	2,750	134	.1223	.021	17.17
4-----	2,750	68	.1872	.022	11.75

¹ Based on total amount of pellets placed in reservoir of vaporizer.

Example 2

A vapor injection apparatus of the same design as and operating in the same manner as that described in Example 1, but scaled up for use in a 20 kilowatt furnace, was used to introduce magnesium into a similar cast iron melt.

For these studies, a 26 pound ferrous melt was employed. The graphite electrode vaporizer assembly was positioned in the melt such that the bottom tips of the electrodes were near the bottom of the melt. Magnesium pellets (about 12 mesh, U.S. Standard Sieve) were placed in the reservoir of the electrode vaporizer apparatus and introduced as vapors into the melt. The so-treated melts were cast into a shell mold.

The injection of magnesium vapor proceeded smoothly but actively. No violent pyrotechnics were observed and no melt splattering occurred.

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Table II summarizes the results of a number of different runs carried out with this apparatus.

TABLE II

Run No.	Melt Temp., °F.	Injection Period, Sec.	Mg. Input Wt. percent of Iron Melt	Mg. Residual in Pdt., Wt. percent.	Mg. Recovery, percent
1-----	2,760	95	0.024	0.011	45.5
2-----	2,760	107	0.050	0.017	34.1
3-----	2,710	107	0.050	0.016	31.75
4-----	2,760	103	0.065	0.018	27.7

In a manner similar to that described for the foregoing examples, calcium, sodium, selenium, zinc, tellurium, cadmium, lithium, potassium, cesium, mercury, barium and the like relatively low boiling metals can be readily introduced in the vapor state into iron, ferrous based compositions, copper, aluminum and the like higher boiling metals which are in the molten state.

Various modifications can be made in the present invention without departing from the spirit or scope thereof for it is understood that we limit ourselves only as defined in the appended claims.

We claim:

1. An apparatus for introducing a low boiling metal into a molten metal having a boiling point higher than that of said low boiling metal which comprises;
 - a storage and metering chamber for containing said low boiling metal in a solid form, said chamber communicating with a chambered furnace assembly wherein said low boiling metal is vaporized, said furnace assembly communicating by means of a conduit with a metal holding vessel for a molten metal bath, the length and shape of said conduit being such that its end is near the bottom of said metal holding vessel, said conduit serving to transport vapors of said low boiling metal from said furnace assembly to said metal holding vessel such that said vapors exit from the end of said conduit under the surface of a molten higher boiling metal in said holding vessel, and
 - a baffle, said baffle positioned in the chamber of said furnace assembly adjacent the junction of said furnace assembly and said conduit communicating with said metal holding vessel, said baffle serving to restrain the liquid form of said low boiling metal from splashing into said conduit.

References Cited

UNITED STATES PATENTS

1,315,208	9/1919	Burr	75—135 X
2,594,972	4/1952	Muehlenkamp	13—23 X
2,678,266	5/1954	Zifferer	75—130
3,271,132	9/1966	Groves	75—68

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