

[54] METHOD OF IMPROVING THE PROPERTIES OF A FERROUS METAL IN THE MOLTEN STATE

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[*] Notice: The portion of the term of this patent subsequent to Dec. 16, 1986, has been disclaimed.

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Related U.S. Application Data

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[58] Field of Search75/45, 53, 58, 59

[56]

References Cited

UNITED STATES PATENTS

Table with 4 columns: Patent Number, Date, Inventor, and Reference Code. Includes entries for Bampfydle, Webbere, Spire, Spolders et al., and Karinthi et al.

FOREIGN PATENTS OR APPLICATIONS

Table with 4 columns: Patent Number, Date, Country, and Reference Code. Includes entries for Canada and Great Britain.

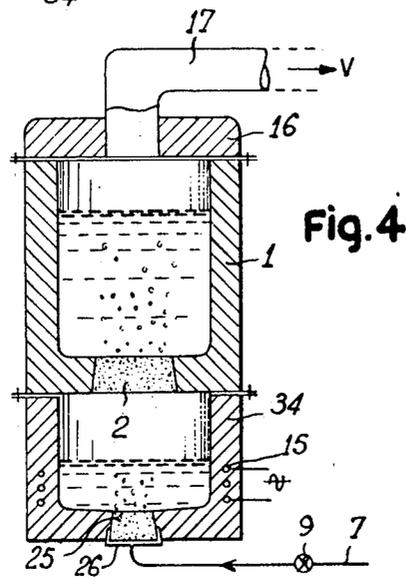
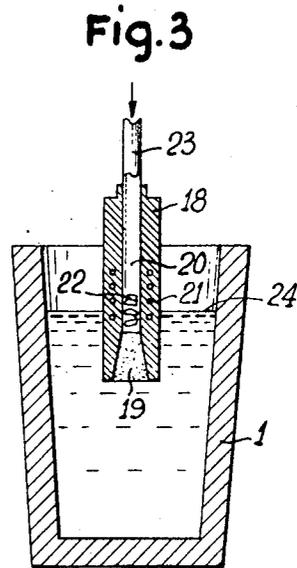
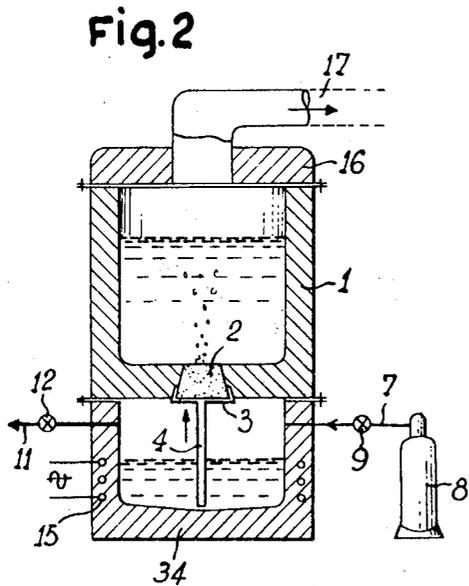
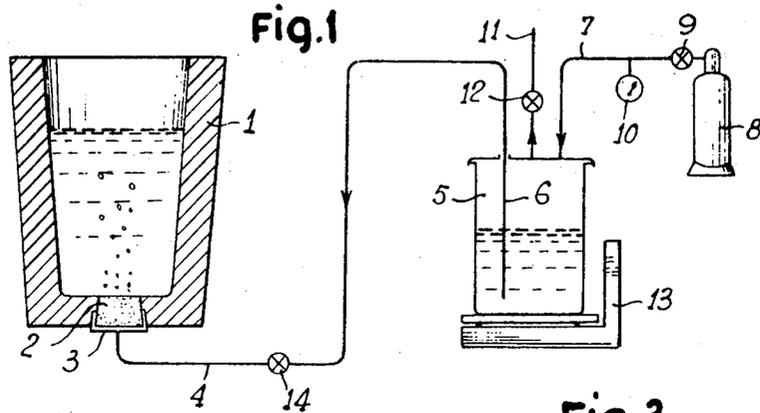
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[57]

ABSTRACT

A halogenated compound is brought in liquid phase into contact with a porous device which on its opposite side contacts molten ferrous metal. The halogenated liquid is forced by gas pressure through the porous device and into the molten metal. The halogen may be used to remove unwanted elements from the metal. The nonhalogen part of the compound may combine with elements dissolved in the metal or may itself dissolve in the metal.

3 Claims, 5 Drawing Figures



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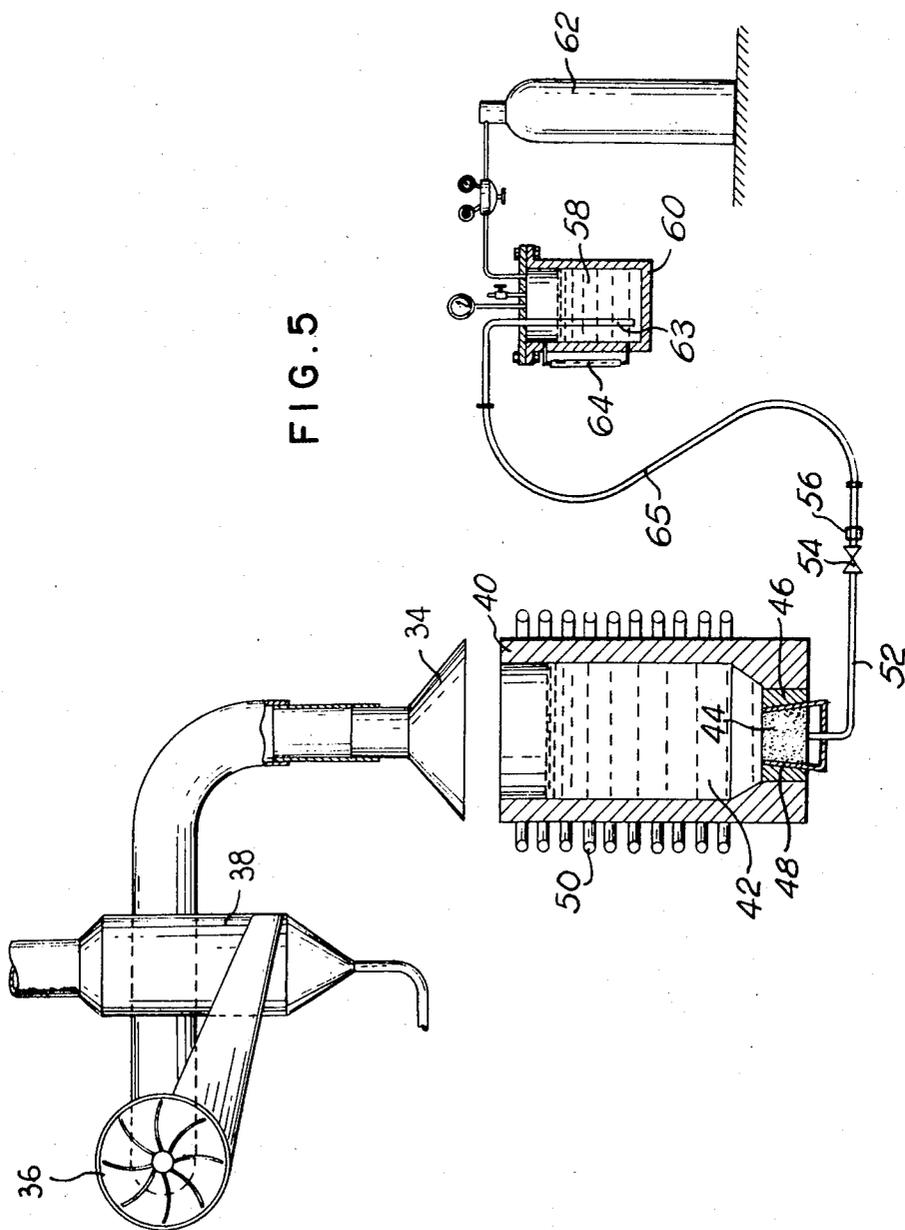


FIG. 5

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METHOD OF IMPROVING THE PROPERTIES OF A FERROUS METAL IN THE MOLTEN STATE

This application is a continuation-in-part of our copending application, Ser. No. 581,920, filed Sept. 26, 1966, now Pat. No. 3,484,232, Dec. 16, 1969.

This invention relates to a method of improving the properties of a steel or a cast iron by treating it in the molten condition.

The invention is characterized by the fact that there is injected into the molten metal, in the liquid or vapor state, mixed or not mixed with inert gas, through a permeable wall, a halogenated compound which is forced through said wall by gas pressure and which, having possibly decomposed on contact with the molten metal or in contact with a sufficiently hot portion of permeable wall, reacts chemically with the molten metal and improves the properties of the metal obtained, either by modifying its quality, or by modifying its composition.

This injection enables use to be made of halogens, or elements combined therewith, or both, in a form easy to handle and often less onerous than when these reagents are used as in the prior art. In addition, the method of injection, which is easy to carry out, imparts great efficiency to the reagents because they are thereby finely distributed in the liquid metal.

The following uses of the method of the invention, which are merely nonlimitative examples, can be quoted:

A. Selective elimination or recovery of the manganese in cast iron intended in particular for the manufacture of cast iron comprising spheroidal graphite in a ferritic matrix, for example, by means of carbon tetrachloride, trichlorethylene, perchlorethylene, polyhalogenated derivatives of the hydrocarbons marketed under the name "FREONS," and lead dichloride. These reagents react through their halogens which combine with the manganese to give a volatile compound.

By way of example, a 100 kg. charge of a cast iron containing:

C	3.8%
Si	0.8%
Mn	0.85%
P	0.1%

was treated by blowing in liquid CCl_4 .

After blowing in 2.2 kg. of CCl_4 for 6 minutes, the manganese content was brought to 0.06 percent, the silicon content remaining unchanged. Thus, 93 percent of the initial manganese was eliminated.

B. Fixing the carbon, for example by means of titanium trichloride, titanium tetrachloride, zirconium tetrachloride and niobium pentachloride, particularly in stainless steels, extra-mild steels for sheet intended for enamelling, and in all ferrous metals in which this fixation is beneficial. These reagents react through their metal. It is known that certain ferrotitaniums, notably the conventional composition containing 30 percent of titanium, are difficult to dissolve in ferrous metals.

C. Incorporation of small quantities of an element to give increased efficiency, for example the addition of boron to steels by the introduction of boron trichloride.

D. Refining the grain of steel, for example by the introduction accompanied by increased yield, of niobium pentachloride in carbon steels for sheets having a high elastic limit and intended, for example, for use in the manufacture of pipes for carrying fluids under pressure; the niobium resulting from the decomposition of its chloride refines the grain of the steel.

The above-mentioned elimination of manganese is achieved by halogenation using inexpensive reagents and the method of introduction used gives a high yield on the part of the reagent because it is thereby finely distributed in the liquid metal. Furthermore, the recovery, from the fumes given off, of the manganese chloride, provides a valuable byproduct. This elimination generally calls for 1.3 to 5 kg. of chlorine per kg. of manganese to be removed: carbon tetrachloride, if this is used for the injection, contains 92 percent of chlorine. The recovery of the manganese can be carried out by bringing the vapor into contact with water which dissolves the manganese

chloride and iron chloride, the iron chloride being precipitated, then by subjecting the remaining solution to electrolysis, to obtain the manganese.

The incorporation of small quantities of an alloying element, using a compound which decomposes, has already been proposed. The compound in question was a metal carbonyl which is a costly reagent; furthermore, it would have been poorly utilized because it was proposed to introduce it through a single orifice which would have produced large bubbles. The present invention, on the other hand, permits the use of a relatively inexpensive reagent, and permits it to be employed very efficiently, in contrast to the conventional ferro-alloys, the yields from which are in the order of 60 percent.

Generally, the weight of reagent introduced does not exceed 1 percent of the weight of the metal treated.

The invention will again be described hereunder by reference to the attached drawing in which:

FIG. 1 represents the general arrangement of the treatment vessel and of the auxiliary vessel for introducing the reagent;

FIG. 2 shows a different embodiment of the same general arrangement;

FIG. 3 represents a variant in which the auxiliary vessel is in the form of a plunger tube having a permeable base;

FIG. 4 shows a variant of the equipment of FIG. 2, in which the reagent is vaporized before being introduced;

FIG. 5 is a view similar to FIG. 1 but showing apparatus for practicing another embodiment of the method of the present invention.

In FIG. 1 there is shown a vessel 1, the base of which is provided with a permeable plug 2. The rear portion of this plug is surrounded by a fluidtight envelope 3 connected by a pipe 4 to an auxiliary vessel 5 containing the halogenated compound to be forced into the plug. The pipe 4 passes into this vessel through a plunger tube 6. A pipe 7 connects the vessel 5 to a gas cylinder 8, provided with a control valve 9 and a manometer-flowmeter unit 10. The vessel 5 is further provided with a discharge pipe 11 fitted with a valve 12. Finally, the vessel 5 can be placed on a balance 13 so as to facilitate the measuring out of the liquid forced via the pipe 4 and control valve 14 through the porous plug.

FIG. 2 represents a variant in which the auxiliary vessel 34 is attached to the treatment vessel 1 and is fixed in a fluidtight manner beneath the base of this latter vessel.

A forcer pipe is arranged in the form of a plunger tube 37 directed towards the base of the auxiliary vessel. As previously, this latter vessel is provided with a pressurizing pipe 7 connected to a gas cylinder 8, and with a discharge pipe 11. Finally, it is optionally provided with heating means represented symbolically by an electric coil 15. This could be a resistance or an inductance coil, or could even be replaced by a spiral steam pipe.

The halogenated compound can thus be loaded into the auxiliary vessel in the solid condition, then melts when it is to be forced up through the porous plug 2.

If need be, the halogenated compound could initially be contained, in the solid, liquid, or even gaseous state, in an ampul or a sealed cartridge fitted with a fusible plug or with a plug which could be broken by a magnetic hammer or any other equivalent means.

Optionally, the treatment vessel 1 is provided with a fluidtight cover 16 connected by piping 17 to a vacuum pump (not shown).

The injection equipment shown in FIG. 3 is in the form of a refractory plunger tube 18 closed by a porous plug 19. The tube 18 has in its axis a cavity 20 surrounded by a coil 21 intended to melt the halogenated compound 22 previously introduced in the solid condition into the cavity 20. This cavity is connected by a pipe 23 to a source of inert gas, not illustrated.

The tube 18 is plunged into the bath of metal to be treated, in such manner that its porous mouthpiece 19 is located below the surface 24 of the bath.

FIG. 4 shows a variation of the equipment of FIG. 2 in which the auxiliary vessel 34 is provided, at its base, with a porous plug fitted with a fluidtight envelope 26 connected to a gas pipe 7. This vessel is optionally provided with a heating coil 15. The bubbling of gas through the plug 25 and then through the halogenated reagent brought to the region of its boiling point entrains a certain quantity of this reagent in the diluted vapor state. This diluted vapor, together with the gas enters the metal bath through the permeable element 2 which separates the treatment vessel 1 and the auxiliary vessel 34. In this manner, the reagent passes into the metal in its gaseous form at its partial saturating vapor pressure at the temperature obtaining in the auxiliary vessel.

Another embodiment of the present invention is the treatment of ferrous metal by titanium chloride, generally titanium tetrachloride which is the most commercially available. Titanium deoxidizes steel and is an alloying element. It may happen that the major portion of the injected titanium chloride escapes from the molten metal bath without having reacted. This is a loss of reagent and, by virtue of the corrosive fumes which are emitted, an inconvenience.

It has been found that these drawbacks are nullified or greatly lessened when the treatment is effected in the presence of at least one element more avid for chlorine than titanium is, in the conditions prevailing in the metal being treated. Aluminum, manganese, chromium, vanadium, alkali metals and earth-alkaline metals are elements of this kind.

The element to be removed from the bath combines with the chlorine of the titanium chloride and liberates titanium. The chloride of the element separates from the ferrous metal bath in the form of slag or vapor; and thus the more or less complete elimination of metals such as aluminum and manganese is effected which otherwise would remain in the cast metal and whose content would be too great.

The titanium, having been introduced by very fine bubbles, is present initially in a highly dispersed condition. Therefore it functions as a very active deoxidant and distributes itself very homogeneously on a microscopic scale as an alloying element.

FIG. 5 shows an embodiment of apparatus for the practice of the method last described above. In FIG. 5, the treatment is carried out in an induction furnace 40, and comprises the injection of titanium tetrachloride in the steel bath 42. In the bottom of the furnace is disposed a fluid-permeable plug 44 which is sealed in place by a refractory cement 46 which expands somewhat on hardening. Plug 44 may for example be fired alumina or magnesia and is at least 100 mm. thick in the direction of fluid therethrough.

The lateral truncated conical surface of the fluid-permeable plug has been metallized with a spray gun projecting copper, and then has been force-fitted in a sheet steel sleeve 48, which latter is closed at its bottom so as to form, below the plug 44, a distribution chamber for titanium tetrachloride.

The layer of deposited copper and the steel sleeve are outside the region of highest field strength produced by the inductor 50 of the furnace, so that the value of the current induced in the coating and sleeve is reduced to an acceptable value.

A conduit 52, provided with a valve 54 and with a detachable coupling 56, brings the titanium chloride in liquid phase and under pressure into the distribution chamber and extends up to the fluid-permeable plug which it supports. However, the conduit 52 is traversed by lateral openings (not shown) through its end within the distribution chamber thereby to supply the distribution chamber with titanium chloride. The titanium tetrachloride then vaporizes in the body of the plug 44.

The titanium tetrachloride 58 which is to be injected is disposed in a container 60 and is placed under pressure by an inert gas such as argon from a cylinder 62. A sight level 64 permits viewing the liquid level in container 60.

A plunger tube 63 permits liquid titanium tetrachloride under pressure to flow to the distribution chamber by means of a flexible conduit 65 and then through conduit 52. From the distribution chamber, it passes through plug 44 from which it

escapes in the form of a multitude of very fine bubbles, into the metal bath.

As described above, the chlorine of the tetrachloride combines with certain elements and the resulting chlorides escape from the bath as fumes or slag. Such fumes, captured by a hood 34, are removed by a ventilator 36 and dust is removed from them in a cyclone 38.

When, as in the illustrated embodiment, the metal bath is open to the air, it is desirable to avoid oxidation of the titanium which is produced by the reduction of the tetrachloride. This is achieved when the bath contains aluminum. The aluminum thus plays several roles: it reduces the oxidation of the formed titanium; it fixes the chlorine of the titanium tetrachloride; and it may also alloy with the steel. The initial aluminum content of the bath may in general be greater than 0.5 percent so that all or most of the titanium introduced as chloride will be retained in the treated metal.

Vanadium can also reduce titanium oxide and serve as an alloying element, in addition to performing a chlorine-fixing function.

Manganese, which is almost always present, is desirably partially eliminated. Its content may be reduced to less than 0.05 percent if desired.

Chromium can also preferentially fix the chlorine.

Along with the titanium tetrachloride, sodium can also be introduced, for example, by pumping liquid sodium through a porous plug; or calcium can be introduced, for example by bubbling through the metal bath an inert gas in which is suspended a powdered calcium alloy. Sodium and calcium fix the chlorine of the titanium tetrachloride and the oxygen of the ferrous bath. Other alkali metals or alkaline earth metals may also be used.

The flow rate of injected tetrachloride is generally between 0.6 and 2.3 grams per minute per square centimeter of the surface of the porous plug which is in contact with the bath. Under these circumstances, and with a weight of steel bath of the order of 175 kg., the following results have been attained, the figures being in weight percent except where otherwise indicated:

Total TiCl ₄ , in kg.	14.0	6.67	65.4
Initial Ti	0.057	0.045	0.080
Final Ti	0.410	0.153	1.53
Ti retention (%)	100	64	89
Initial Al	0.580	0.150	3.25
Final Al	0.465	0.073	1.15
Initial Mn	1.36	0.010	0.86
Final Mn	0.93	0.005	0.28

The metal treated according to the present invention generally contains, in its finally solidified condition, 5 to 15 p.p.m. of chlorine. If it is desired to avoid this retention, then the metal can be treated in the liquid condition by a small addition of calcium alloy once the introduction of titanium tetrachloride is completed.

The process according to the present invention permits the production of steel of good characteristics, ingots suitable for vacuum refining, and maraging steels. It can be used in connection with other ferrous metals, for example, castings. It may be practiced in manners other than those described, for example in an argon atmosphere, which makes aluminum unnecessary as a protecting material, or in an unheated vessel.

Having described our invention, we claim:

1. A method for improving the properties of a ferrous metal, comprising establishing a bath of molten ferrous metal to be treated, and forcing titanium chloride through a fluid-permeable wall and into the bath, said bath containing an element fixing chlorine with more avidity than titanium in the conditions prevailing in the bath of the ferrous metal, said element being a member selected from the group consisting of aluminum, chromium, vanadium, alkali metal and alkaline earth metal.

2. A method as claimed in claim 1, said titanium chloride being titanium tetrachloride.

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3. A method for improving the properties of a ferrous metal, comprising establishing a bath of molten ferrous metal to be treated, contacting liquid titanium chloride with a face of a fluid-permeable wall another face of which contacts the molten ferrous metal bath and forcing said titanium chloride through said fluid-permeable wall into the bath, said bath con-

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taining an element fixing chlorine with more avidity than titanium in the conditions prevailing in the bath of the ferrous metal, said element being a member selected from the group consisting of aluminum, chromium, vanadium, alkali metal and alkaline-earth metal.

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