Patented Sept. 4, 1934

1,972,317

UNITED STATES PATENT OFFICE

1,972,317

METHOD FOR INHIBITING THE OXIDATION OF READILY OXIDIZABLE METALS

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No Drawing. Application June 17, 1932, Serial No. 617,876

14 Claims. (Cl. 75—17)

The present invention relates to methods for inhibiting the oxidation of readily oxidizable metals, particularly magnesium, while maintained above the melting point thereof.

The term "oxidation" is used herein and in the appended claims to mean not only the reaction of oxygen with a readily oxidizable metal but also the chemical reaction of such metal with nitrogen, and/or carbon monoxide, carbon dioxide, sulphur dioxide, other gases which may be constituents of the atmosphere whereunder such metals are maintained in the molten condition. The term "magnesium" is used herein and in the appended claims to mean not only elemental magnesium but also alloys thereof wherein the magnesium content predominates.

It is well known that the surface of metals such as magnesium, aluminum, beryllium, etc., is oxidized readily by contact with gases of the atmosphere, particularly at temperatures above the melting point thereof. This fact renders difficult the operations of melting, alloying, transferring molten metal as by ladling, etc., thereby creating a problem for which numerous solutions have been proposed. For instance, it has been suggested to use a flux in combination with sulphur for inhibiting oxidation of the surfaces of magnesium during the foregoing operations. This suggestion has been reduced to practice with a fair degree of success, however, numerous difficulties inhere to such practice. For example, when making castings by ladling or otherwise transferring the molten metal from a melting pot in which a flux is used to protect the magnesium, some flux may become entrained with the metal and thereby produce castings containing flaws due to flux inclusions, unless especial care is exercised and suitable apparatus be employed to insure a complete separation of the flux from the magnesium before casting.

Thus, it has been found advantageous in the case of operating molten baths of such readily oxidizable metals, particularly in connection with die casting machines, to employ certain gases rather than a liquid flux, in order to inhibit oxidation of the metal by gases of the atmosphere, whereby the occurrence of flux inclusions in the castings is precluded. Accordingly, it has been proposed to displace the ordinary atmosphere in contact with the metals by a gas such as nitrogen, carbon dioxide, sulphur dioxide, etc. Similar atmospheres have been proposed for protecting the metal from oxidation during the melting, alloying, etc., thereof. However, in the case of magnesium, such gases can not be relied upon alone to produce a protective atmosphere, due to the fact that the magnesium will react therewith at temperatures above the melting point such as those encountered in the foregoing operations, whereby oxidation products are formed which may contaminate the metal.

It is therefore among the objects of the invention to provide a method whereby detrimental attack by atmospheric gases in contact with the surfaces of readily oxidizable metals while maintained in the molten condition is substantially inhibited; and further, to provide a method wherein suitable materials are employed so that contamination of the so-protected metal by the protective material is prevented. The present invention is not concerned with, nor do the claims cover, any step in which the inhibition of detrimental attack by atmospheric gases upon magnesium takes place within a casting mold. I have now found that the oxidation of readily oxidizable metals while maintained in the molten condition can be substantially inhibited by maintaining in the atmosphere in contact with the exposed surface thereof an oxidation inhibiting gas containing fluorine, either in elemental or combined form.

To the accomplishment of the foregoing and related ends, the invention, then, consists of the method hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail several modes of carrying out the invention, such disclosed modes illustrating, however, but several of various ways in which the principle of the invention may be used.

The hereinbefore mentioned protective gaseous mixture containing fluorine, which is to be maintained in contact with the exposed surface of the readily oxidizable metal, may contain the fluorine as: (1) the elemental gas, or (2) combined with another element or elements to form a compound having a boiling, sublimation, or decomposition point below about 750° C., preferably below about 400° C.; either with or without the presence of a diluent gas or gases, such as air.

Among the elements which may be employed in the preparation of fluorine-containing compounds suitable for use in practicing my invention are the following: antimony, arsenic, bismuth, boron, bromine, carbon, chlorine, hydrogen, iodine, nitrogen, oxygen, phosphorous, silicon, sulphur, tin and titanium.

The following table shows some groups of compounds which are illustrative of the type of compounds produced by combinations of the foregoing elements with fluorine, which compounds I have found can be utilized in creating a protective atmosphere for inhibiting the oxidation of readily oxidizable metals. The table shows combinations of fluorine with one, two, three, and four other elements, respectively.

1	2	3	4
HF	NH_4F	$(NH_4)_3TiF_7$	
BF_3	HBF_4	NH_4BF_4	$C_6H_5N_2BF_4$.
SiF_4	H_2SiF_6	$(NH_4)_2SiF_6$	$C_6H_5SO_3F$.
SbF_4	$HSbF_6$	$(NOF)SbF_5$	
SF_6	SO_2F_2	SO_3HF	NH_4SO_3F.
IF_5	CCl_2F_2	$P(NH_2)_2F_3$	$C_7H_7SO_3F$.
PF_5	PSF_3	NH_4PF_6	$P(NH_2)_2SF$.
NF_3	NH_4FHF	$(NH_3)_3(SbF_4)_3$	

The selection of the proper compound to be utilized in the production of a protective atmosphere for use during the effecting of a particular melting, alloying, or similar operation will depend principally upon the temperature above which the metal is maintained during such operation. Thus, the compound selected should have a boiling, sublimation, or decomposition point below the temperature at which the metal is to be maintained in any particular operation. Beyond the foregoing stipulation the points of cost, toxicity, ease of application, etc. will largely govern the selection in any case.

The application of the compound to the exposed surface of the metal may be made in various ways. For instance, in a melting operation carried out in a closed melting pot, if the compound selected is a solid at room temperatures, a protective atmosphere can be formed over the surface of the metal by dropping, dusting, or otherwise placing at suitable intervals of time, small quantities of the solid substance upon the surface thereof, or upon a hot surface immediately out of contact with the metal; or by subliming the substance with or without a diluent gas such as air, nitrogen, etc., and passing the so-formed gas over the surface of the metal to be protected. In the event that the compound selected is gaseous at ordinary temperatures it can be stored in containers, under pressure if desired, and passed with or without a diluent gas over the surface of the metal to be protected. In transferring molten magnesium in a ladle from a melting pot to a mold into which it is to be poured, it has been found sufficient to place one or more small cakes or lumps of one of the compounds, such as ammonium borofluoride, ammonium fluophosphate, etc., on the surface of the metal in the ladle, whereby a protective atmosphere is formed thereover and oxidation of the metal substantially inhibited during the interval while it is being transported to and poured into the mold.

Other suitable methods of application will readily appear to those skilled in the art of foundry practice.

As an example of the results which may be obtained in practicing my invention, I will now describe the protection of magnesium from oxidation during a melting operation, employing various compounds for producing the protective atmosphere.

The apparatus employed consisted of an oil-fired, tilting-type, covered melting pot holding on an average about 250 pounds of molten magnesium. The pot was equipped with a mechanical feeding device which permitted between about .5 and 2 grams per minute of a solid fluorine-containing compound to fall upon the surface of the metal in the pot. In an 8 hour period about 1600 pounds of magnesium was melted and poured from the pot at various intervals of time in about 150 pound lots. A total quantity of 675 grams (24 ounces) of ammonium borofluoride (NH_4BF_4) was used in protecting the aforesaid 1600 pounds of magnesium. No appreciable burning or oxidation of the metal was observed during the entire melting and pouring operation. Normal ammonium fluoride (NH_4F) was substituted for the borofluoride compound with satisfactory results, as was the commercial ammonium fluoride, i. e. ammonium bi-fluoride ($NH_4F.HF$). Similar protection to the metal was obtained by passing boron trifluoride (BF_3) gas thereover, and a successful run was made using silicon tetrafluoride (SiF_4) gas as a protective atmosphere. Dichlorodifluoromethane (CCl_2F_2) was also used with good results, as was hydrogen fluoride (HF). Various other similar compounds, e. g. ammonium fluophosphate, were tested with excellent results.

To illustrate further the superior effectiveness of my method of inhibiting the oxidation of magnesium the following experiment was performed:—

About 175 pounds of a magnesium alloy containing 93.7 per cent by weight of magnesium, 6.0 per cent of aluminum, and 0.3 per cent of manganese was melted in the hereinbefore described melting pot and maintained in the molten condition at a temperature between about 700° and 760° C. (1292°–1400° F.) for 15 hours. Ammonium borofluoride was fed on to the surface of the metal throughout the 15 hour period at the rate of about 1 gram per minute. In all, 900 grams (2 pounds) of the fluorine compound was used. During the entire period a very satisfactory degree of protection against oxidation was afforded the metal, and the properties of specimens cast therefrom at the end of the experiment were well within the normal range of properties of the alloy.

It is especially to be noted that air was present at all times in the atmosphere over the metal during the foregoing examples which show the facile manner in which compounds containing fluorine may be applied to the exposed surfaces of magnesium in order to produce a protective atmosphere thereover.

While I have set forth a number of compounds which may be utilized in carrying out my invention I prefer to employ one or more of the following compounds:—ammonium borofluoride, ammonium silicofluoride, ammonium bi-fluoride and ammonium fluophosphate, or the gases evolved therefrom upon heating thereof. All of the foregoing compounds have a boiling, sublimation, or decomposition point below 400° C., and the gases evolved therefrom upon heating can be readily commingled with the atmosphere in contact with the surfaces of magnesium at elevated temperatures thereby inhibiting oxidation thereof.

A feature of the invention lies in the fact that a relatively small concentration of fluorine, or fluorine-containing gases evolved from a fluorine compound, in the air or other atmosphere in contact with the surface of molten magnesium suffices to inhibit oxidation of the metal and to prevent ignition thereof. In other words, the action of the protective compound is not to produce a blanketing layer of gas in contact with the surface of the molten metal which excludes oxidizing gases from contact therewith, but merely to provide a low concentration of the protective fluorine compound in the normal atmosphere surrounding the metal, the presence of which serves to inhibit oxidation of the metal by the gases of the normal atmosphere.

Throughout the specification and in the appended claims the term "molten condition" as applied to the condition of a metal, means that the temperature of the metal is maintained above the melting point thereof in the range normally encountered in the foundry operations of melting, alloying, etc., e. g. for magnesium the foregoing range is between about 600° and 900° C. (1112°–1650° F.).

My improved method for inhibiting the oxidation of magnesium and other readily oxidizable metals while maintained in the molten condition, by adding a relatively small amount of a fluorine compound to the container for the molten metal, has the following advantages:—(1) fully satisfactory protection from detrimental attack by gases of the atmosphere is obtained; (2) possible inclusions of the protective compound in the metal are prevented; (3) the ease with which the protective atmosphere can be produced and applied to the metal; and, (4) the low cost incident to protecting such metals from oxidation.

Other modes of applying the principle of my invention may be employed instead of those explained, change being made as regards the method herein disclosed, provided the means stated by any of the following claims or the equivalent of such stated means be employed.

I therefore particularly point out and distinctly claim as my invention:—

1. The method of inhibiting the oxidation of molten magnesium which comprises maintaining a fluorine-containing atmosphere in contact with the surfaces of said magnesium.

2. The method of inhibiting the oxidation of molten magnesium which comprises maintaining in the atmosphere in contact with the surface of said magnesium a compound consisting of fluorine with one or more elements from the group consisting of antimony, arsenic, bismuth, boron, bromine, carbon, chlorine, hydrogen, iodine, nitrogen, oxygen, phosphorous, silicon, sulphur, tin and titanium.

3. In melting magnesium, the step which consists in maintaining a fluorine-containing atmosphere in the container wherein said magnesium is being melted.

4. The method of inhibiting the oxidation of molten magnesium which comprises heating a fluorine-containing compound having a boiling, sublimation, or decomposition point below 750° C. to produce a fluorine-containing gas, and commingling the gas evolved therefrom with the atmosphere in contact with the said magnesium.

5. The method of inhibiting the oxidation of molten magnesium which comprises heating a fluorine-containing compound having a boiling, sublimation, or decomposition point below 400° C. to produce a fluorine-containing gas, and commingling the gas evolved therefrom with the atmosphere in contact with the said magnesium.

6. In a method of inhibiting the oxidation of molten magnesium, in a container therefor, the step which consists in adding to said container a relatively small amount of a fluorine compound capable of evolving a fluorine-containing gas at the temperature of the molten metal.

7. In a method of inhibiting the oxidation of magnesium, while maintained in the molten condition in a container therefor, the step which consists in adding to said container successive small portions of a compound selected from the group consisting of ammonium borofluoride, ammonium silicofluoride, ammonium bi-fluoride and ammonium fluophosphate.

8. The method of inhibiting the oxidation of magnesium during the handling thereof in the molten condition which consists in placing upon the surface of the said molten magnesium a compound selected from the group consisting of ammonium borofluoride, ammonium silicofluoride, ammonium bi-fluoride and ammonium fluophosphate.

9. The method of inhibiting the oxidation of magnesium while maintained in the molten condition which comprises so placing a compound selected from the group consisting of ammonium borofluoride, ammonium silicofluoride, ammonium bi-fluoride and ammonium fluophosphate, that said compound is heated by the said magnesium and the gases evolved therefrom commingled with the atmosphere in contact with the surfaces of said magnesium.

10. The method which comprises melting magnesium in a container therefor, adding to said container successive portions of a fluorine compound having a boiling, sublimation, or decomposition point below 400° C., transferring the molten metal from the container to a ladle containing a small amount of the said fluorine compound, and pouring the molten metal from the ladle.

11. The method which comprises melting magnesium in a container therefor and adding to said container a relatively small amount of a fluorine compound having a boiling, sublimation, or decomposition point below 400° C.

12. The method which comprises melting magnesium in a container therefor and adding to said container a relatively small amount of a fluorine compound selected from the group consisting of ammonium borofluoride, ammonium silicofluoride, ammonium bi-fluoride and ammonium fluophosphate.

13. In a method of transferring molten magnesium in a ladle the step which consists in adding to said ladle a relatively small amount of a fluorine compound having a boiling, sublimation, or decomposition point below 400° C.

14. The method which comprises transferring molten magnesium to a ladle, adding to said ladle a relatively small amount of a fluorine compound selected from the group consisting of ammonium borofluoride, ammonium silicofluoride, ammonium bi-fluoride and ammonium fluophosphate, and pouring the molten metal from the ladle.

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