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METHOD OF PROTECTING MAGNESIUM AND ITS ALLOYS AT ELEVATED TEMPERATURES

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The present invention relates to methods of preventing readily oxidizable metals, such as magnesium and its alloys, from combining with constituents of the air or other gases in contact with these metals, while in heated condition. One of the objects of my invention is to inhibit gases reactive to magnesium, such as air, nitrogen, carbon monoxide, carbon dioxide, sulphur dioxide, and the like or mixtures of the same, from combining with magnesium metal and its alloys. Another object of my invention is to inhibit detrimental attack upon magnesium and its alloys by gases in contact with the metal at elevated temperatures such as those employed in heat treating, hot working, and foundry operations, such as melting, alloying, die casting, and the like. Other objects and advantages will appear as the description proceeds.

As is well known, magnesium and alloys of the same containing preponderating amounts of magnesium, that is, containing more than 50 per cent of magnesium, react with oxygen or with nitrogen to form oxides and nitrides, respectively, when said metals are in heated condition. These reactions proceed with increasing rapidity the higher the temperature. This affinity of magnesium and its alloys, when in heated condition, for oxygen or nitrogen, greatly hampers any process of handling these metals in air at an elevated temperature. As the reactions above indicated take place, the heated metal becomes coated with an oxide-nitride film, or, if the metal is in molten condition, these reaction products may become intermixed with the metal and cause flaws in the castings, for instance, made therefrom.

Heretofore various methods have been proposed to prevent magnesium and its alloys from reacting with the constituents of the air while in highly heated condition, as in the case of a body of such metals in the molten state in preparation for casting. It has been proposed in United States Patent No. 906,820, when melting and pouring magnesium, to heat the metal to a temperature at which it becomes pasty and then, just before casting, to stir the contents of the melting pot so as to abstract heat from the pot walls and raise the pasty metal to a temperature at which it will be sufficiently fluid for pouring into the molds. While this method minimizes the amount of reaction products formed from the metal by contact with air during melting and pouring, it does not prevent oxidation completely enough to insure castings free from oxide inclusions. Other methods have been proposed and employed for protecting heated or molten magnesium from the air by displacing the contacting air with certain gases, such as carbon dioxide and sulphur dioxide, or by simply heating and melting in a vacuum. It has been proposed in United States Patent No. 1,540,867 to sprinkle sulphur on the molten metal to provide an atmosphere of sulphur vapor in contact therewith or in United States Patent No. 1,720,286 to employ sulphur in combination with a flux such as magnesium fluoride in contact with the metal, the flux protecting the metal from the tendency for sulphur to react with the same, while the sulphur above the flux on the metal generates sulphur vapor to provide a protective atmosphere. Gases such as carbon dioxide and sulphur dioxide cannot be relied upon alone to produce a protective atmosphere, due to the fact that magnesium will react with these gases according to the equations:—

$$CO_2+2Mg=2MgO+C$$
$$SO_2+2Mg=2MgO+S$$
$$SO_2+3Mg=2MgO+MgS$$

at temperatures encountered in foundry practice. Sulphur itself will react with molten magnesium at elevated temperatures, thus having the disadvantage of generating sulphide to contaminate the molten metal. Nitrogen alone for similar reasons cannot be advantageously employed as an inert protecting gas for molten magnesium. Hydrocarbon gases cannot be used alone as protective gases owing to their decomposition and formation of carbon when in contact with the heated metal. Fluxes may be employed advantageously in certain cases for

protecting molten metal at temperatures high enough to melt the fluxes so as to give an inert fluid covering over the metal. Fluxes of this type are well known and in general use.

I have found that in some processes of handling heated magnesium and its alloys, either in molten or solid condition, the presence of the aforementioned protective fluxes is undesirable. 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 metal, some flux may become entrained with the metal and thereby produce poor castings unless especial care is exercised and suitable apparatus be employed to make a complete separation of the flux from the metal before casting. If one or more of the above-mentioned gases, viz., air, nitrogen, carbon monoxide, carbon dioxide, or sulphur dioxide, are in contact with magnesium or its alloys at the temperatures employed in melting, pouring, or casting, some oxide or nitride, or both, is formed, which may contaminate the cast metal.

It has been found especially advantageous in the case of operating molten baths of such readily oxidizable metals, in connection with die casting machines, to employ gases rather than liquid fluxes for protecting the metal from the atmosphere, so as to preclude the occurrence of flux inclusions in the castings.

I am aware that the rare gases of the atmosphere, namely, helium, neon, argon, krypton, or xenon could be employed singly or as mixtures to great advantage as a non-reactive atmosphere for magnesium and its alloys since it is well known that these gases do not form any chemical compounds with other elements. However, the great expense and unavailability of the rare gases above-mentioned preclude their use as protective atmospheres.

I have discovered a gaseous atmosphere which may be employed in contact with heated magnesium and its alloys at temperatures as high as those encountered in foundry practice, that inhibits the formation of detrimental reaction products and obviates the need for employing fluxes.

My invention is based upon the discovery of the fact that carbon bisulphide inhibits reactions between magnesium or its alloys, in heated condition, and certain gases, when in contact therewith. Some of the gases on which carbon bisulphide has been found to exert an inhibiting effect on their tendency to combine with, or be decomposed by, these metals at temperatures as high as those encountered in foundry practice, include nitrogen, carbon monoxide, carbon dioxide, sulphur dioxide, or mixtures of these gases. Accordingly, the protective gaseous mixtures which come within the scope of my invention contain a gas normally reactive to heated magnesium, but unreactive to carbon bisulphide, such as nitrogen, carbon monoxide, carbon dioxide, sulphur dioxide, and the like or mixtures of said gases, together with carbon bisulphide.

A gas mixture which I have found well adapted to accomplish the protection required in handling heated magnesium and its alloys may be generated by treating air according to a process hereinafter described. In treating air to obtain nitrogen for use in my method of protection I may burn therein any one of the substances sulphur, hydrogen, coal, coke, or the like, so as to remove the oxygen. The products of combustion are then passed through a scrubber to remove substantially all the water, carbon dioxide, or sulphur dioxide, as the case may be, thus leaving a more or less pure nitrogen gas free from oxygen. Carbon bisulphide is added to the nitrogen, prepared as above or otherwise obtained, to form the gaseous mixture to be employed as the protective gas. In some cases it may not be desirable to remove the carbon dioxide or sulphur dioxide in the scrubber since the tendency for these gases to react with magnesium is inhibited when mixed with carbon bisulphide vapor.

The relative amount of carbon bisulphide in the protective gas mixtures is capable of considerable variation, since compositions containing up to as much as 50 per cent by volume of carbon bisulphide, or more, are effective. Preferably the gaseous mixture may contain from 1 to 10 per cent by volume of carbon bisulphide when nitrogen is employed, while somewhat larger amounts of carbon bisulphide may be used with the other gases, viz., carbon monoxide, carbon dioxide, sulphur dioxide, or mixtures of these gases.

The manner of the application of my novel protective atmosphere depends upon the nature of the operations involving the metals to be protected. To protect a body of molten magnesium or magnesium base alloy in a melting pot, for example, it is sufficient to provide means to direct the protective atmosphere into contact with the surface of the molten metal so as to prevent thereby the access of air to the same. This may be accomplished by providing the melting pot with a cover having a more or less restricted opening through which molten metal may be added or removed and another opening through which a stream of the protecting gases may be supplied continually, or in any other convenient manner. Where the container of the molten metal is part of a die casting machine, such as the type employing a goose-neck submerged in the body of the molten metal, the protective atmosphere may be directed over the surface of the

molten metal, around the goose-neck outlet and through the mold operating in connection therewith so as to provide protection for both the metal in the melting pot and in the mold during the filling operation and solidification of metal therein. In operating equipment such as above indicated, a convenient method of determining when a suitable concentration of carbon bisulphide is present in the gaseous mixture may be based upon maintaining a flow of liquid carbon bisulphide into the gas stream led to the metal surface sufficient to produce the characteristic flame of burning carbon bisulphide vapor at the openings in the equipment where the gas mixture comes in contact with the air. The maintenance of enough carbon bisulphide in the protective gas mixtures to give the characteristic flame is an advantage also, when carbon monoxide is employed, as it insures the complete burning of this gas to carbon dioxide.

While I have described the application of the principle of my invention more specifically in connection with a method of protecting magnesium and its alloys in the molten state, such as are encountered in foundry practice, it is to be understood that the method may be employed in connection with the above-mentioned metals in solid state. For example, during heat treatment or other process in which the said metals are heated below the melting point and up to temperatures at which oxide-nitride films are formed, I may advantageously employ my gas mixture containing carbon bisulphide vapor for the working atmosphere instead of air or other gases.

Other modes of applying the principle of my invention may be employed instead of those explained, change being made as regards the process 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 protecting magnesuim or its alloys while in heated condition, which comprises maintaining in contact with the surface of the metal a gaseous mixture of carbon bisulphide vapor and at least one of the gases selected from the group consisting of nitrogen, carbon monoxide, carbon dioxide, sulphur dioxide.

2. The method of protecting magnesium or its alloys while in heated condition, which comprises maintaining in contact with the surface of the metal a gaseous mixture of carbon bisulphide vapor and nitrogen.

3. The method of protecting magnesium or its alloys while in heated condition, which comprises maintaining in contact with the surface of the metal a gaseous mixture of carbon bisulphide vapor and carbon dioxide.

4. The method of protecting magnesium or its alloys while in heated condition, which comprises maintaining in contact with the surface of the metal a gaseous mixture of carbon bisulphide vapor and sulphur dioxide.

5. The method of producing a protective atmosphere for magnesium and its alloys in heated condition, which comprises adding carbon bisulphide to at least one of the gases selected from the group consisting of nitrogen, carbon monoxide, carbon dioxide, sulphur dioxide.

6. A method of protecting a molten bath of magnesium or its alloys, which comprises directing upon the surface of the molten metal a stream of a gaseous mixture of carbon bisulphide vapor and at least one of the gases selected from the group consisting of nitrogen, carbon monoxide, carbon dioxide, sulphur dioxide.

7. A method of protecting a molten bath of magnesium or its alloys, which comprises directing upon the surface of the molten metal a stream of a gaseous mixture of carbon bisulphide vapor and nitrogen.

8. A method of protecting a molten bath of magnesium or its alloys, which comprises directing upon the surface of the molten metal a stream of a gaseous mixture of carbon bisulphide vapor and carbon dioxide.

9. A method of protecting a molten bath of magnesium or its alloys, which comprises directing upon the surface of the molten metal a stream of a gaseous mixture of carbon bisulphide vapor and sulphur dioxide.

10. A method of protecting magnesium or its alloys in the solid state at temperatures up to the melting point thereof, which comprises heating the solid metal in an atmosphere composed of a gaseous mixture of carbon bisulphide vapor and at least one of the gases selected from the group consisting of nitrogen, carbon monoxide, carbon dioxide, sulphur dioxide.

11. A method of protecting magnesium or its alloys in the solid state at temperatures up to the melting point thereof, which comprises heating the solid metal in an atmosphere composed of a gaseous mixture of carbon bisulphide vapor and nitrogen.

12. A method of protecting magnesium or its alloys in the solid state at temperatures up to the melting point thereof, which comprises heating the solid metal in an atmosphere composed of a gaseous mixture of carbon bisulphide vapor and carbon dioxide.

13. A method of protecting magnesium or its alloys in the solid state at temperatures up to the melting point thereof, which comprises heating the solid metal in an atmosphere composed of a gaseous mixture of carbon bisulphide vapor and sulphur dioxide.

14. As a new product, a gas to be used

as an inert atmosphere in contact with magnesium and its alloys in heated condition, comprising a mixture of carbon bisulphide and at least one of the gases selected from the group consisting of nitrogen, carbon monoxide, carbon dioxide, sulphur dioxide.

15. As a new product, a gas to be used as an inert atmosphere in contact with magnesium and its alloys in heated condition, comprising a mixture of carbon bisulphide and nitrogen.

16. As a new product, a gas to be used as an inert atmosphere in contact with magnesium and its alloys in heated condition, comprising a mixture of carbon bisulphide and carbon dioxide.

Signed by me this 19 day of March, 1932.

EDWIN O. BARSTOW.