Patented Feb. 21, 1933 1,898,437

UNITED STATES PATENT OFFICE

JOHN A. GANN, JAMES B. REID, AND HANS A. REIMERS, OF MIDLAND, MICHIGAN, ASSIGNORS TO THE DOW CHEMICAL COMPANY, OF MIDLAND, MICHIGAN, A CORPORATION OF MICHIGAN

METHOD FOR CASTING READILY OXIDIZABLE METALS SUCH AS MAGNESIUM AND ALLOYS THEREOF

No Drawing. Application filed May 4, 1932. Serial No. 609,262.

The present invention relates to methods of casting readily oxidizable metals, particularly magnesium and alloys thereof wherein the magnesium content predominates. One object of the present invention is to permit casting such metals in moist or "green" sand molds and the like, whereby the metal is protected from attack by air or by the steam generated in the mold when the hot metal is poured. Another object of our invention is to produce castings of the aforementioned metals the surface of which has a good appearance and is substantially free from burned spots, pits, or other defects which result from casting such metals in ordinary water-bound molds. Other objects and advantages will appear as the description proceeds.

For convenience, the term "magnesium" is used herein and in the appended claims to mean not only pure magnesium but also alloys of the same in which the magnesium content predominates.

The casting of magnesium presents a problem which is unique in commercial foundry practice due to the great affinity for oxygen this metal possesses at elevated temperatures. In the molten state at the temperatures employed in casting, the metal is capable of combining spontaneously with oxygen, which may be derived either from the atmosphere or from substances containing oxygen that are in contact with the metal, such as water or steam or other oxygen compounds in the molding material. Thus it is practically impossible to make a sound casting of magnesium in a conventional type of mold in which the molding material has been rendered moldable with water, inasmuch as the steam generated from the water in the mold material by the hot metal produces an atmosphere in which magnesium oxidizes rapidly and may even cause the metal to ignite and burn so long as oxygen or oxygen-containing substances have access to it.

Various casting methods have been developed to overcome the tendency for the water or other oxygen compounds in the mold to attack the magnesium. Heretofore, for example, magnesium has been cast in water-bound sand molds in which the sand of said molds has been mixed with an oxidation inhibitor, such as sulphur or boric acid, so as to prevent chemical attack or burning of the magnesium in the steam atmosphere generated by the hot metal in contact with moist molding sand. In United States Patent No. 1,825,242, other types of volatile agents, viz., ammonium hydro-fluoride and ammonium-silico-fluoride, have been described as being able to prevent the burning of magnesium in water-bound molds and also to produce a corrosion-resistant film upon the surface of the casting. These complex ammonium fluorides, when employed as oxidation inhibitors, have the peculiar disadvantage in that they react with sand, forming various compounds therewith so that the mixture of sand with said agents soon loses the property of inhibiting attack upon the metal by the water in the mold. Furthermore, the admixture of the aforesaid fluorides with molding sand causes the sand to swell and interferes with the forming of molds therewith. It has been suggested to allow the sand mixture to stand for a period of time before use in order to permit the swelling to complete itself before the sand molds are made. The tendency for these substances to decompose and liberate ammonia, especially on being heated during the casting process, also results in rapid impoverishment of the molding mixture with respect to the agent added, thus necessitating frequent re-addition of the same. These agents in the molding sand also produce on the surface of castings made therein an adherent coating which detracts from the appearance of the casting. Furthermore, while the addition of the proper amount of one of the aforementioned agents to the molding sand prevents oxidation of a casting of uniform cross section, with other types of castings having an irregular or non-uniform cross section it often happens that, when sufficient of the agent is added to provide protection of the heavy portions of the casting, the thin sections become pitted; or, if a smaller quantity of said agents is employed so as to prevent pitting of the thin

sections, the heavy sections are inadequately protected from oxidation.

The problem encountered in satisfactorily casting magnesium in temporary water-bound molds involves overcoming the detrimental effect of one or more of the following factors, namely; (1) oxidation (burning), which may be due to attack by the air, attack by water vapor, or attack by oxygen compounds in the sand or by the sand itself; (2) the formation of pits and blowholes; (3) the formation of superficial coatings or films of a non-metallic nature on the surface of the castings which give them a rough, discolored or otherwise unattractive appearance.

We have discovered that the aforementioned difficulties may be practically overcome by employing certain new and improved agents for incorporating in molding sand, which are more stable and permanent than the compounds aforementioned, do not cause swelling of the molding sand, and do not produce an unsightly surface on the casting. We have found, for instance, that we may produce castings having a surface finish which is clean and bright and which is also smooth and free from imperfections, such as pitting and blowholes, when the sand is treated with our new agents.

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

Our invention is based upon the discovery of the fact that hydrogen fluoride in aqueous solution, when added to a permeable foundry sand in which enough water is present to render the sand moldable, permits casting magnesium without detrimental attack upon the metal by steam generated in the mold. However, since hydrogen fluoride, when so employed, attacks the sand more or less rapidly, the quantity of the same which is present as such becomes diminished after a time to a point where the amount may be inadequate to prevent oxidation of the metal. We have discovered that we may overcome this disadvantage by mixing with the molding sand certain metallic salts of hydrogen fluoride which are of low volatility and are not quickly displaced from the sand when in use. The salts which we have found applicable in the sand mixture with hydrogen fluoride, or which may be substituted for it, are the simple binary fluorides of aluminum (AlF_3), antimony (SbF_3), calcium, chromium (CrF_3), iron (FeF_3), lithium, zinc, bismuth, or mixtures of these salts. Also, it has been discovered that, when employing relatively small amounts of the aforementioned metallic fluorides, certain other salts or acid salts may be advantageously employed to replace a part or all of the hydrogen fluoride. For example, potassium acid sulphate ($KHSO_4$) in conjunction with these metallic fluorides effectively inhibits burning or oxidation. The principle of our invention consists in providing a strongly acidified moist atmosphere in contact with the hot metal within the mold at the time of casting, which atmosphere is developed by the heat of the cast metal and slightly attacks the surface of the casting, and prevents the formation of magnesium oxide films thereon. Thus, by our improved method the surface of the casting presents a clean and bright appearance and is free from pitting. These new agents are much less volatile than ammonium salts and are retained in the sand for long periods of time, thus permitting numerous castings to be made without renewal of the agent.

Suitable procedures to follow for casting magnesium according to our invention are given in the following examples in which an open or permeable type of foundry sand was employed.

Example 1

To foundry sand was added 2 per cent of hydrogen fluoride and the whole thoroughly mixed and tempered with water. Castings of magnesium alloys poured in molds made of this mixture were free from flaws and possessed a clean surface with metallic luster.

Example 2

Foundry molding sand was thoroughly mixed with about 5 per cent of antimony fluoride and tempered with water, then formed into a mold. Castings obtained from such molds were sound and of clean appearance. The fluorides of chromium, zinc, bismuth, etc., employed in similar manner gave equally good castings.

Example 3

A molding sand was thoroughly mixed with about 5 per cent of finely powdered calcium fluoride and about 3 per cent of potassium acid sulphate and the mixture tempered with water. Castings poured in molds employing this molding mixture were free from flaws.

Example 4

A similar molding sand was thoroughly mixed with about 5 per cent of aluminum fluoride and 2 per cent of hydrogen fluoride, tempered with water and then formed into a mold. The casting obtained from this mold was clean and free from flaws.

The amount of such agents or mixtures

thereof which may be employed varies with the type of casting to be made and with the nature of the molding material. In making large castings it is preferable to employ a greater proportion of inhibitor than when relatively small castings are made. Normally the foundry molding material may be intimately mixed with from 1 to 10 per cent by weight of any one of the simple binary metallic fluorides aforementioned, or with hydrogen fluoride in amount from 0.5 to 3.0 per cent. Mixtures of two or more of these substances may be employed, the sum of which need not exceed about 15 per cent, with or without up to 6 per cent of potassium acid sulphate. For castings having relatively thin sections, smaller amounts than the maximum stated may be used, preferably from 3 to 7 per cent of at least one of the binary fluorides or from 0.5 to 3.0 per cent of hydrogen fluoride, while for medium section castings approximately 5 per cent of the same may be used, with or without up to 6 per cent of potassium acid sulphate. It is to be understood, however, that the quantity of one or more of such agents employed in a given case is to be governed by the size and character of the casting. When adding hydrogen fluoride to the molding mixture it is convenient to use commercial aqueous solutions of the same.

Naturally the effectiveness of any oxidation inhibitor for use as hereinbefore described varies with the permeability of the sand, being somewhat greater with sands of high permeability than with those of relatively low permeability. The molding sand should, therefore, be sufficiently open or permeable to permit of free escape of gases out of the mold, which are formed by contact with the hot metal as it is poured into the mold. In general we have found that a permeability factor of 30 or more gives satisfactory results, although in many cases good results may be obtained with sands of somewhat lower permeability. The definition of the term "permeability" as used herein and the method of measuring its numerical value is described in the bulletin "Testing and Grading Foundry Sands", published by the American Foundrymen's Association, March 1931.

While we have described our invention more particularly in terms of molding sand having in admixture therewith one or more of the agents above specified, our invention is not necessarily limited thereto, inasmuch as these agents are effective as oxidation inhibitors when used in mold facings or in solution sprayed upon the inner surface of the mold or upon baked cores, or the surface of the mold parts coming in contact with the molten metal may be dusted or otherwise coated with the aforementioned substances. The use of our new agents, furthermore, is not necessarily limited to molds made from sand since other moldable materials such as graphite, pulverized carbon, coke, and the like, may be substituted for the sand.

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

We therefore particularly point out and distinctly claim as our invention:—

1. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and a relatively small amount of a substance selected from the group consisting of aluminum fluoride, antimony fluoride, (SbF_3), calcium fluoride, chromium fluoride (CrF_3), iron fluoride (FeF_3), zinc fluoride, bismuth fluoride, hydrogen fluoride, forming said mixture into a mold, and casting magnesium therein.

2. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and a relatively small amount of at least one of the substances selected from the group consisting of aluminum fluoride, antimony fluoride (SbF_3), calcium fluoride, chromium fluoride (CrF_3), iron fluoride (FeF_3), zinc fluoride, bismuth fluoride, hydrogen fluoride, forming said mixture into a mold, and casting magnesium therein.

3. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and from 1 to 10 per cent of at least one of the substances selected from the group consisting of aluminum fluoride, antimony fluoride (SbF_3), calcium fluoride, chromium fluoride (CrF_3), iron fluoride (FeF_3), zinc fluoride, bismuth fluoride, hydrogen fluoride, forming said mixture into a mold, and casting magnesium therein.

4. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and from 1 to 10 per cent of at least one of the substances selected from the group consisting of aluminum fluoride, antimony fluoride (SbF_3), calcium fluoride, chromium fluoride (CrF_3), iron fluoride (FeF_3), zinc fluoride, bismuth fluoride, hydrogen fluoride, and up to 6 per cent of potassium acid sulphate, forming said mixture into a mold, and casting magnesium therein.

5. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and from 1 to 10 per cent of at least one of the substances selected from the group consisting of aluminum fluoride, antimony fluoride (SbF_3), calcium fluoride, chromium fluoride (CrF_3), iron fluoride (FeF_3), zinc

fluoride, bismuth fluoride, and from 0.5 to 3 per cent of hydrogen fluoride, forming said mixture into a mold, and casting magnesium therein.

6. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and from 1 to 10 per cent of at least one of the substances selected from the group consisting of aluminum fluoride, antimony fluoride (SbF_3), calcium fluoride, chromium fluoride (CrF_3), iron fluoride (FeF_3), zinc fluoride, bismuth fluoride, and from 0.5 to 3 per cent of hydrogen fluoride and up to 6 per cent of potassium acid sulphate, forming said mixture into a mold, and casting magnesium therein.

7. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and from 3 to 7 per cent of at least one of the substances selected from the group consisting of aluminum fluoride, antimony fluoride (SbF_3), calcium fluoride, chromium fluoride (CrF_3), iron fluoride (FeF_3), zinc fluoride, bismuth fluoride, forming said mixture into a mold, and casting magnesium therein.

8. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and from 3 to 7 per cent of at least one of the substances selected from the group consisting of aluminum fluoride, antimony fluoride (SbF_3), calcium fluoride, chromium fluoride (CrF_3), iron fluoride (FeF_3), zinc fluoride, bismuth fluoride, hydrogen fluoride, and up to 6 per cent of potassium acid sulphate, forming said mixture into a mold, and casting magnesium therein.

9. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and from 3 to 7 per cent of at least one of the substances selected from the group consisting of aluminum fluoride, antimony fluoride (SbF_3), calcium fluoride, chromium fluoride (CrF_3), iron fluoride (FeF_3), zinc fluoride, bismuth fluoride, and from 0.5 to 3 per cent of hydrogen fluoride, forming said mixture into a mold, and casting magnesium therein.

10. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and from 3 to 7 per cent of at least one of the substances selected from the group consisting of aluminum fluoride, antimony fluoride (SbF_3), calcium fluoride, chromium fluoride (CrF_3), iron fluoride (FeF_3), zinc fluoride, bismuth fluoride, and from 0.5 to 3 per cent of hydrogen fluoride and up to 6 per cent of potassium acid sulphate, the total amount of the said substances added to the sand not materially exceeding 15 per cent, forming said mixture into a mold, and casting magnesium therein.

11. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and from 3 to 7 per cent of at least one of the substances selected from the group consisting of aluminum fluoride, antimony fluoride (SbF_3), calcium fluoride, cromium fluoride (CrF_3), iron fluoride (FeF_3), zinc fluoride, bismuth fluoride, and from 0.5 to 3 per cent of hydrogen fluoride and up to 6 per cent of potassium acid sulphate, forming said mixture into a mold, and casting magnesium therein.

12. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and from 1 to 10 per cent of aluminium fluoride, from 1 to 10 per cent of antimony fluoride, and from 0.5 to 3 per cent of hydrogen fluoride, tempering the mixture with water, forming said mixture into a mold, and casting magnesium therein.

13. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and from 1 to 10 per cent of aluminium fluoride and from 1 to 10 per cent of antimony fluoride, tempering the mixture with water, forming said mixture into a mold, and casting magnesium therein.

14. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand from 1 to 10 per cent of aluminium fluoride and from 0.5 to 3 per cent of hydrogen fluoride, tempering the mixture with water, forming said mixture into a mold, and casting magnesium therein.

15. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and from 1 to 10 per cent of antimony fluoride and from 0.5 to 3 per cent of hydrogen fluoride, tempering the mixture with water, forming said mixture into a mold, and casting magnesium therein.

16. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and from 3 to 7 per cent of aluminum fluoride, tempering the mixture with water, forming said mixture into a mold, and casting magnesium therein.

17. The method of casting magnesium and alloys thereof in sand molds which comprises forming an intimate mixture of foundry sand and from 3 to 7 per cent of antimony fluoride, tempering the mixture with water, forming said mixture into a mold, and casting magnesium therein.

18. The method of casting magnesium and alloys thereof in temporary molds which comprises forming an intimate mixture of

molding material and a relatively small amount of a metallic fluoride characterized by a melting point lying between approximately 289° and 843° C., forming said mixture into a mold, and casting magnesium therein.

19. The method of casting magnesium and alloys thereof in temporary water-bound molds which comprises forming an intimate mixture of molding material and a relatively small amount of one of the fluorides selected from the group consisting of aluminum fluoride, antimony fluoride, chromium fluoride, iron fluoride, bismuth fluoride, forming said mixture into a mold, and casting magnesium therein.

Signed by us this 29 day of April, 1932.

JOHN A. GANN.
JAMES B. REID.
HANS A. REIMERS.