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METHOD OF CASTING MAGNESIUM

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The present invention relates to a method of casting magnesium and alloys thereof. One object of my invention is to permit casting such metals in water-bound or "green" sand molds and the like, whereby the metal is protected from attack by air or by the moisture in the mold. 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 magnesium but also alloys thereof in which the magnesium predominates.

The production of commercially acceptable castings of magnesium presents a problem which is unique in foundry practice due to the affinity for both oxygen and nitrogen which this metal possesses, especially at elevated temperatures. In the molten state, at temperatures employed in casting, the metal is capable of combining spontaneously with oxygen, which may be derived either from the air or from substances containing free or combined oxygen that are in contact with the metal, such as water or steam or other compounds in the molding material. The burning or oxidation of molten magnesium in an atmosphere of steam or in contact with water may be at times so violent as to approach explosiveness. Thus it is practically impossible to make a sound casting of magnesium in a simple water-bound mold of conventional type, such as is used for casting other metals.

Various methods have been proposed by which it is sought to overcome the tendency for water or other oxygen compounds in a mold to attack magnesium when cast therein. Heretofore, for example, it has been suggested to incorporate sulphur or boric acid in water-bound sand molds for casting magnesium to overcome the harmful effects of air or water vapor on the metal. However, these substances have proved to be not wholly satisfactory, inasmuch as when a sufficient amount of either sulphur or boric acid is added to the molding sand to prevent oxidation of a casting of relatively heavy section, the thin sections are liable to be pitted. On the other hand, if the amount of agent is reduced to a point where pitting of thin sections is reduced, heavier sections may be insufficiently protected from oxidation. Other types of protective agents, namely, ammonium fluoride and ammonium silicofluoride, have been proposed in United States Patent No. 1,825,242 to prevent the burning of magnesium when cast in water-bound molds, and at the same time to produce a corrosion-resistant film upon the surface of the casting. However, these sub-

stances are not wholly desirable, since, as the aforesaid patent disclosure shows, ammonium fluoride reacts with water in the molding sand and gives off ammonia, thus impoverishing the sand with respect to the agent and necessitating frequent readditions thereof to the sand. Furthermore, ammonium fluoride, and ammonium silicofluoride, as well, are stated to react with the sand, causing it to swell. It thus becomes necessary to replenish the sand with the protective agent or to provide with these agents other materials which will overcome the loss of ammonia and the swelling of the sand with the resulting distortion of the molds. Accordingly, the aforementioned patent proposes to reduce swelling and loss of ammonia by adding hydrofluoric acid or oxalic acid to the molding sand in addition to ammonium fluoride or silicofluoride. These materials, however, are undesirable inasmuch as hydrogen fluoride is especially corrosive, while oxalic acid is toxic.

Briefly stated, 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:—(1) oxidation, which may be due to attack by air, water vapor, or other oxygen compounds, or even by the sand itself; (2) the formation of pits and blowholes due to gas evolution when the molten metal is poured into the mold; (3) the formation of superficial coatings or films of a non-metallic nature on the surface of the castings which give them an unattractive appearance.

I have now discovered that certain new and improved agents which, when mixed with the molding material, possess the property of preventing oxidation of magnesium by steam generated in molds. These new agents do not become impoverished in their protective action even under the effect of heating the molding mixture in the course of casting. Moreover, difficulties previously encountered with former agents, owing to swelling of the sand mixture, do not exist with my new agents. They have the advantage also of exerting their protective action for longer periods of time and permit the production of clean castings of magnesium that are substantially free from pits, blowholes, or similar defects. The invention, then, consists in the method hereinafter more fully described and particularly pointed out in the claims.

My invention is based upon the discovery that the direct addition compounds, formed by combining a fluorine-containing acid with an or-

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ganic base, when mixed with water-tempered foundry sand, not only overcome the tendency for magnesium castings to be oxidized by the steam generated in the mold, but also permit making castings of both relatively heavy and light section substantially without pitting, blowholes, or similar flaws, and of commercially acceptable appearance. Moreover, there appears to be no detrimental reaction between my new agents and moisture or the sand, so that sand molds formed from water-tempered foundry sand containing my new agents do not swell nor become rapidly impoverished with respect to the protective substance. Molding sand treated with my new agents, therefore, may be used repeatedly owing to their greater stability and permanence without readdition of protective agent, thus reducing the cost of casting.

Organic compounds that are sufficiently basic to form direct addition compounds with fluorine-containing acids to employ in the molding material are characterized by possessing a nitrogen-containing radical of one of the following types, namely:—amines, $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, in which R may be an alkyl or aryl group; hydroxylamines, $-\text{NHOH}$; hydrazines, $-\text{NHNH}_2$; and azo compounds, $-\text{N}:\text{NH}$. Among the various fluorine-containing acids which may be combined with such organic bases are the following:—hydrofluoric acid, HF ; borofluohydric acid, HBF_4 ; hydrofluosilicic acid, H_2SiF_6 ; hexafluorophosphoric acid, HPF_6 ; difluorophosphoric acid, HPO_2F_2 ; monofluorophosphoric acid, $\text{H}_2\text{PO}_3\text{F}$; and fluosulphonic acid, HSO_3F . Examples of the direct addition compounds, suitable for use according to my invention, which may be obtained by combining an organic base of one of the aforementioned types with a fluorine-containing acid are the following:—methyl amine hydrofluoride, $\text{CH}_3\text{NH}_2\text{HF}$; dimethyl amine hydrofluoride, $\text{CH}_3\text{NHCH}_3\text{HF}$; trimethyl amine hydrofluoride, $\text{CH}_3\text{NCH}_3\text{CH}_3\text{HF}$; aniline hydrofluosilicate, $(\text{C}_6\text{H}_5\text{NH}_2)_2\text{H}_2\text{SiF}_6$; ethyl hydroxyl amine hydrofluoborate, $\text{C}_2\text{H}_5\text{NHOH}.\text{HBF}_4$; phenyl hydrazine hydrofluosulphonate, $\text{C}_6\text{H}_5\text{NHNH}_2.\text{HSO}_3\text{F}$; azobenzene hydrodifluorophosphate, $\text{C}_{12}\text{H}_{10}\text{N}_2.\text{HPO}_2\text{F}_2$. It is to be understood that the invention is not necessarily limited to the use of the above-mentioned direct addition compounds of an organic base and a fluorine-containing acid shown by way of illustrative examples inasmuch as other direct addition compounds than those shown may be formed from the various organic bases and fluorine-containing acids aforementioned and employed in accordance with my invention.

In carrying my invention into effect I mix with the water-tempered molding material one or more of the direct addition compounds of the type described in amount which may be varied according to the size of the casting and nature of the molding material, and then form the mixture into a mold. In making large castings it is preferable to employ a greater proportion of the agent or compound than when relatively small castings are made. Normally the foundry molding material may be intimately mixed with from 0.5 to 10 per cent by weight of any one of the compounds aforementioned, although usually about 3 to 6 per cent is satisfactory. Mixtures of two or more of these substances may be employed, the sum of which preferably does not exceed about 10 per cent. For castings having relatively thin sections from 2 to 5 per cent of the agent may be sufficient, while for the average run of castings approximately 4 per cent of

same may be used. It is understood, however, that the quantity of one or more of such agents employed in a given case is a matter of judgment, governed more or less by the size and character of the casting.

Naturally the effectiveness of any agent for use as hereinbefore described varies with the permeability of the molding material, it being somewhat greater with sand of high permeability than with those of relatively low permeability. The molding material should, therefore, be sufficiently open or permeable to permit the free escape out of the mold of gases which are formed by contact with the hot metal as it is poured. In general, I 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 are described in the Bulletin "Testing and Grading Foundry Sand" published by The American Foundryman's Association, March, 1931.

By way of illustrating a suitable mode of carrying out my invention, I made an intimate mixture of water-tempered foundry sand having a permeability factor of about 30 and about 3 per cent of aniline hydrofluosilicate, and formed the mixture into a mold. Then I poured into the mold a magnesium alloy consisting of approximately 6 per cent of aluminum, 0.2 per cent of manganese, the balance being magnesium, at a temperature between 1300° and 1375° F. The surface of the resulting casting was free from pits, blowholes, and oxidized areas. No further superficial treatment was required to render the casting suitable for use. In similar manner I made a mold from water-tempered foundry sand containing about 3 per cent of aniline hydrofluoride, and poured therein a magnesium alloy at a temperature between 1300° and 1375° F. The resulting casting was substantially free from oxidized areas and pitting and of commercially acceptable appearance.

While I have described my invention more particularly in terms of a water-tempered molding sand having in admixture therewith one or more of the agents above specified, my invention is not necessarily limited thereto inasmuch as these agents are effective to prevent oxidation or other defects in casting magnesium when used in mold facings or in solution sprayed upon the inner surface of the mold. For example mold facings may be made from foundry sand with which is mixed one or more of my new agents, and the mixture applied to the pattern in the usual manner. A suitable method of coating the mold cavity or core pieces is to form a solution or suspension of one or more of my new agents, preferably in a non-aqueous liquid such as carbon tetrachloride, and then spray or otherwise apply the mixture to the mold parts which come into contact with the metal. The use of my new agents, furthermore, is not necessarily limited to molds made from sand since other moldable materials, such as graphite, pulverized carbon, coke, cinders, or the like, may be substituted for the sand.

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

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

1. The method of casting magnesium and alloys thereof in temporary molds which comprises incorporating in the molding material a direct addition compound of an organic nitrogen base and a fluorine-containing acid, forming a mold of the mixture and casting the metal in the mold.
2. The method of casting magnesium and alloys thereof in temporary molds which comprises incorporating in the molding material a direct addition compound formed from an organic amine and a fluorine-containing acid selected from the group consisting of hydrofluoric acid, borofluohydric acid, hydrofluosilicic acid, hexafluophosphoric acid, monofluophosphoric acid, difluophosphoric acid, fluosulphonic acid, forming a mold of the mixture and casting the metal in the mold.
3. The method of casting magnesium and alloys thereof in temporary molds which comprises incorporating in the molding material a direct addition compound formed from a primary aromatic amine and a fluorine-containing acid selected from the group consisting of hydrofluoric acid, borofluohydric acid, hydrofluosilicic acid, hexafluophosphoric acid, monofluophosphoric acid, difluophosphoric acid, fluosulphonic acid, forming a mold of the mixture and casting the metal in the mold.
4. The method of casting magnesium and alloys thereof in temporary molds which comprises

incorporating in the molding material a direct addition compound formed from an aliphatic amine and a fluorine-containing acid selected from the group consisting of hydrofluoric acid, borofluohydric acid, hydrofluosilicic acid, hexafluophosphoric acid, monofluophosphoric acid, difluophosphoric acid, fluosulphonic acid, forming a mold of the mixture and casting the metal in the mold.

5. The method of casting magnesium and alloys thereof in temporary molds which comprises incorporating in foundry sand aniline hydrofluosilicate, forming a mold of the mixture and casting the metal in the mold.

6. The method of casting magnesium and alloys thereof in temporary molds which comprises incorporating in foundry sand methylamine hydrofluoride, forming a mold of the mixture and casting the metal in the mold.

7. The method of casting magnesium and alloys thereof in temporary molds which comprises incorporating in foundry sand aniline hydrofluoborate, forming a mold of the mixture and casting the metal in the mold.

8. In casting magnesium and alloys thereof, the step which consists in casting metal in a sand mold in which is incorporated, at least for the parts adjacent to the metal cast therein, a direct organic addition compound of an organic nitrogen base and a fluorine-containing acid.

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