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METHOD OF ADDING MANGANESE TO ALUMINUM

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ABSTRACT OF THE DISCLOSURE

Manganese metal is added to molten aluminum in the form of a manganese body having thereon a coating containing a potassium fluoride and which forms a molten phase at the temperature of the molten aluminum. There is provided a novel manganese additive for this purpose comprising a body of manganese having the stated coating thereon, and there is also provided a method for making the additive comprising providing the stated coating on a body of manganese.

BACKGROUND OF THE INVENTION

Aluminum containing small amounts of manganese constitute a class of known alloys. For example, 3003 alloy contains 1¼% manganese (nominal) and has the high corrosion resistance of pure aluminum but a much higher strength. Aluminum alloys may contain much less manganese, down to about 0.1% manganese, such as the 5056 alloy. The addition of manganese metal to molten aluminum to provide final alloys of this type is generally prohibitive because of the extremely slow rate of dissolution thereof in the molten aluminum. Consequently, most manganese is added to molten aluminum, to provide the final alloy, in the form of a master aluminum-manganese alloy containing much higher (up to 30%) manganese contents. However, such master alloys are costly and/or inconvenient to produce and handle. Producers of the final alloy would prefer to add manganese itself, rather than a master alloy, if it weren't for the stated slow rate of dissolution.

It is the principal object of the present invention to provide a method for adding manganese to molten aluminum whereby the rate of solution of the manganese is markedly faster than heretofore.

It is another principal object of the present invention to provide a manganese metal additive for addition to molten aluminum which has a fast rate of dissolution in the molten aluminum.

It is a further principal object of the present invention to provide a method for making the aforesaid manganese metal additive.

Other objects will become apparent from a consideration of the following specification and claims.

The method of the present invention for adding manganese metal to molten aluminum to provide a manganese-containing aluminum alloy involves the improvement wherein the manganese metal added to the molten aluminum has thereon a coating containing a potassium fluoride and which forms a molten phase at the temperature of the molten aluminum. Preferably the coating contains at least one other chemically bound metal selected from the group consisting of sodium, aluminum, manganese, titanium and zirconium. The stated coating may be formed on the manganese by: (a) applying to the manganese a dispersion (solution or suspension) prepared by dispersing in water the required potassium-fluoride compound or compounds, followed by drying; or (b) applying to the manganese a melt prepared by melting the required potassium-fluoride compound or compounds, followed by solidification.

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The manganese metal additive of the present invention, hence, comprises a manganese body having thereon the stated coating and is prepared by providing on a manganese body the stated coating as by applying the required material in molten form or as a dispersion to the manganese body followed by solidification of the molten coating or drying of the dispersion.

As will be seen from the data hereinafter set forth, the manganese metal additive of the present invention, when added to molten aluminum, dissolves at a much more rapid rate than a similar body of manganese without the coating. The exact reason for this is not presently known; however, it may be theorized that the coating enhances wetting of the manganese surface by the molten aluminum, possibly either by virtue of the formation of the molten phase when added to the molten aluminum or by virtue of having attacked the manganese oxide film on the original manganese metal body, or both.

Referring to the manganese employed in accordance with the present invention, its method of preparation, whether by electrolysis or by pyrometallurgical reduction of ore, is not critical, although electrolytic manganese is preferred. The manganese body may be in the form of free powder, in the form of shaped bodies (e.g. briquets) formed from powder, in massive form as obtained by casting from molten manganese with or without subsequent crushing, in the form of chips (the form recovered by breaking electrolytic manganese away from the cathode onto which it was initially plated) or in the form of electrolytic manganese plated onto an aluminum cathode (that is, the manganese body may be an aluminum body, such as a sheet, having an electrolytic manganese deposit thereon). Since electrolytic manganese chips are highly satisfactory and economical, they represent the preferred form of manganese utilized in accordance with the present invention. In using electrolytic manganese it is preferred initially to remove adhering electrolyte as by washing or by a combination of suitable chemical treatment and washing.

As stated, in accordance with the present invention, the manganese body is provided with a coating containing a potassium fluoride and which forms a molten phase at the temperature of the molten aluminum to which the coated manganese body is added. In general, the coating will form a molten phase at or below about 710° C. Since pure potassium fluoride (KF) melts well above this temperature, the coating will have present therein at least one other chemically bound element which serves to lower the melting point of the coating. Preferably such element is a metal selected from the group consisting of sodium, aluminum, manganese, titanium and zirconium.

The chemically bound metal may be combined with the potassium fluoride as a complex fluoride, such as a coating derived from potassium titanium fluoride, potassium zirconium fluoride, potassium aluminum fluoride, potassium manganese fluoride, or the like. Coatings derived from such complex fluorides may be provided by dispersing in water, or melting, the stated compounds themselves or by employing a mixture of compounds which result directly in such a complex. Furthermore, coatings, derived from such complex fluorides may be provided by employing a mixture of compounds which, at least partially through reaction with the manganese itself, result in such a complex potassium manganese fluoride in the coating.

On the other hand, the chemically bound metal may not be combined chemically with the potassium fluoride as a complex fluoride, but may be present as a compound in admixture with potassium fluoride so long as the coating forms the stated molten phase at the temperature of the molten aluminum. For example, a coating, formed on the manganese body by applying an aqueous solution of

potassium fluoride (KF) and hydrofluoric acid forms, in addition to the potassium fluoride (KF), a manganese compound, most likely manganese fluoride, as evidenced by reaction between the solution and the manganese surface. Likewise, a coating formed on the manganese body by applying an aqueous solution of potassium fluoride (KF) and sodium fluoride (NaF) most likely consists essentially of a mixture of these two fluorides.

The coating may be applied from aqueous dispersion (solution or suspension) or from a melt. When applied from a dispersion, the required material is added to water at a concentration which may vary widely and up to and beyond saturation, depending on the solubility of the particular material in water. To the extent the material is present beyond its solubility in water it is in the form of a suspension. Thus, the term "dispersion" as used herein is intended to apply to such suspensions as well as to solutions in which substantially no insoluble material is present. The dispersion is then applied to the manganese body, as by dipping the body therein, by mixing a plurality of manganese bodies (especially if finely-divided) with the dispersion, or spraying the dispersion onto the body, followed by drying. It is believed that some hydrolysis as well as some formation of HF (reactive with the manganese surface) results when complex fluorides, like potassium titanium fluoride, potassium zirconium fluoride and potassium manganese fluoride, are dissolved in water so that it is not believed that the resulting dried coating is necessarily in the form of the complex fluoride initially employed. In this connection it is possible to add potassium fluoride and either titanium fluoride, zirconium fluoride, or manganese fluoride, or combinations of these, to the water in proportions corresponding substantially in theory to the desired complex fluorides. Likewise, when the coating is applied as a melt, it is not believed that the resulting solidified coating is necessarily in the form of the original fluoride material before melting. Here again, the melt may be made by melting a mixture of potassium fluoride and either titanium fluoride, zirconium fluoride, or manganese fluoride, or combinations of these, in proportions corresponding substantially in theory to the desired complex fluoride.

The presently preferred coatings are those formed by applying, to the manganese body, an aqueous dispersion prepared by mixing with water: (a) potassium titanium fluoride; (b) potassium zirconium fluoride; (c) potassium manganese fluoride; (d) a combination of potassium fluoride and hydrofluoric acid; and (e) a combination of potassium fluoride, hydrofluoric acid and manganese fluoride. It is believed that these dispersions attack the manganese oxide film on the manganese body. As among the three mentioned complex fluorides, potassium titanium fluoride is especially preferred.

The coated manganese body, or more likely a number thereof depending on the size of the aluminum heat, is then added to molten aluminum. The amount added depends, of course, upon the particular alloy to be formed, and may range as low as about 0.1%, by weight, of manganese. While the present invention is particularly advantageous in preparing final alloys containing up to about 2% manganese, it is also applicable for utilization in the preparation of master alloys containing up to about 30% of manganese.

The coating in large part forms slag, although, in the case of coatings derived from the complex potassium titanium and zirconium fluorides, some of the titanium and/or zirconium may dissolve in the aluminum. Since these materials are beneficial, as being well known grain refiners, their presence may provide an additional incidental benefit from the present invention.

The present invention will be more readily understood from a consideration of the following specific examples which are given for the purpose of illustration only and are not to be considered as limiting the scope of the invention in any way. The manganese bodies of each of the

examples were tested for rate of dissolution of manganese in molten aluminum by adding 31.25 parts, by weight, of manganese body to about 2469 parts, by weight, of molten aluminum at 1375° F. Analytical samples were drawn from each melt at various time intervals over a period of 84 minutes for determination of solution rate curves. Values for the times required to dissolve 25%, 50%, 75% and 90% of the added manganese were taken from these curves and are set forth in Table I which follows.

EXAMPLES 1-A THROUGH 1-F

(1-A) Electrolytic manganese chips ranging in size from about ¼" for the smallest dimension up to about ¾" for the largest dimension (the electrolytic manganese had previously been dipped, at room temperature, in an approximately 1% aqueous solution of potassium dichromate, washed with water and dried) were placed in a wire screen basket and dipped, at 80-90° C., in an aqueous solution prepared by dissolving potassium zirconium fluoride (K_2ZrF_6) in water to saturation at that temperature. The chips were then dried in warm air. The values set forth in Table I are average from two different samples.

(1-B) Electrolytic manganese chips prepared as in 1-A but dipped, at 80-90° C., in an aqueous solution prepared by dissolving potassium titanium fluoride (K_2TiF_6) in water to saturation at their temperature, instead of in the solution prepared from potassium zirconium fluoride.

(1-C) Electrolytic manganese chips prepared as in 1-A but dipped, at room temperature, in an aqueous solution prepared by adding 35 g. of potassium fluoride (KF) and 63 ml. of 48% hydrofluoric acid to 937 ml. of water, instead of in the solution prepared from potassium zirconium fluoride.

(1-D) Electrolytic manganese chips prepared as in 1-A but dipped, at room temperature, in an aqueous solution prepared by dissolving 41 g. of sodium fluoride and 84.5 g. of potassium fluoride (KF) in a liter of water, instead of in the solution prepared from potassium zirconium fluoride.

(1-E) Electrolytic manganese chips prepared as in 1-A but dipped, at about 800° C., in a melt prepared by heating potassium zirconium fluoride (K_2ZrF_6), instead of in the solution prepared by dissolving potassium zirconium fluoride in water.

(1-F) Electrolytic chips as in 1-A, 1-B, 1-C, 1-D and 1-E but without any treatment with the fluoride solution or melt. In Table I the values are averages from 17 different samples.

EXAMPLES 2-A AND 2-B

(2-A) Electrolytic manganese following removal from the electrolytic cell was simply washed with water, removed from the cathode, heated to 1500-1800° F. to remove hydrogen and graded into chips having the dimensions of the chips in Example 1. The chips were then dipped, at 80-90° C., in an aqueous solution prepared by dissolving potassium zirconium fluoride in water to saturation at that temperature. The chips were then dried in warm air.

(2-B) Electrolytic manganese chips as in 2-A but without treatment with the fluoride solution. In Table I the values given are averages from four different samples.

EXAMPLES 3-A AND 3-B

(3-A) Electrolytic manganese was deposited on both sides of an aluminum sheet about 0.020" thick, until a layer of manganese about ⅛" thick was formed on each side. The resulting "sandwich" was removed from the cell, dipped in an approximately 1% aqueous solution of potassium dichromate, washed with water and dried. Pieces approximately ⅜" x ½" were cut from the sandwich, and the pieces were dipped, at 80-90° C., in an aqueous solution prepared by dissolving potassium zirconium fluoride in water to saturation at that temperature. The pieces were then dried in warm air.

(3-B) Pieces prepared as in 3-A, but without treatment with the fluoride solution. In Table I the values are averages from two different samples.

EXAMPLES 4-A AND 4-B

(4-A) Electrolytic manganese was deposited on both sides of an aluminum sheet as in Example 3 and the resulting sandwich, upon removal from the cell, was held for 10 minutes and then washed with water, without treatment with the dichromate solution, and dried. Pieces were then cut from the sandwich as in Example 3 and the pieces were dipped, at 80-90° C., in an aqueous solution prepared by dissolving potassium zirconium fluoride in water to saturation at that temperature. The pieces were then dried in warm air.

(4-B) Pieces prepared as in 4-A, but without treatment with the fluoride solution. In Table I the values are averages from two different samples.

EXAMPLES 5-A AND 5-B

(5-A) Electrolytic manganese chips were prepared as in Example 1 but with only washing of the electrolytic manganese with water and drying and without treatment with potassium dichromate. The chips were dipped, at 80-90° C., in a solution prepared by dissolving potassium zirconium fluoride in water to saturation at that temperature. The chips were then dried in warm air.

(5-B) Chips were prepared as in 5-A but without treatment with the fluoride solution. In Table I the values are averages from four different samples.

The times required (in minutes) to dissolve various percentages of the manganese added to the molten aluminum are set forth in the following Table I:

TABLE I

Example	Treated with fluoride	Time in minutes to reach percent dissolved:			
		25%	50%	75%	90%
1-A	Yes	2	5	8	15
1-B	Yes	2.5	5	9.5	14.5
1-C	Yes	2.5	5.5	11	23
1-D	Yes	2.6	7.5	14	20.5
1-E	Yes	2.5	6	12	20
1-F	No	6.5	17.5	41	76
2-A	Yes	2	7	20	70
2-B	No	5	19	54	(1)
3-A	Yes	2	4.5	7.5	13.5
3-B	No	7.5	21.5	47	83
4-A	Yes	7	17	34	60
4-B	No	27	67	84+	(1)
5-A	Yes	4.5	10.5	20	33
5-B	No	13.5	38	83	(1)

¹ Didn't reach 90% during time of test, 84 minutes.

In the foregoing examples wherein the manganese is pretreated with a solution of potassium dichromate, sodium dichromate may be substituted therefor.

In connection with Example 1-C, repeated use of the solution by dipping manganese chips therein, with progressive (but not complete) depletion of hydrofluoric acid by reaction with the manganese producing increased man-

ganese values in the solution, showed similar results in providing faster dissolution of the so-treated manganese chips in molten aluminum.

Modification is possible in particular materials used as well as in techniques employed without departing from the scope of the invention.

What is claimed is:

1. In the addition of manganese metal to molten aluminum to provide a manganese-containing aluminum alloy, the improvement wherein the manganese metal added to the molten aluminum has thereon a coating containing a potassium fluoride and which forms a molten phase at the temperature of the molten aluminum.

2. The method of claim 1 wherein said manganese metal is electrolytic manganese.

3. The method of claim 2 wherein said electrolytic manganese is electrolytic manganese chips.

4. The method of claim 2 wherein said electrolytic manganese is in the form of manganese plated onto an aluminum body.

5. The method of claim 1 wherein said coating contains at least one other chemically bound element serving, with the potassium and fluoride components, to provide said molten phase.

6. The method of claim 5 wherein said element is a metal selected from the group consisting of sodium, aluminum, manganese, titanium and zirconium.

7. The method of claim 6 wherein said coating is formed by applying to said manganese an aqueous dispersion prepared by mixing with water at least one complex potassium fluoride selected from the group consisting of potassium manganese fluoride, potassium titanium fluoride and potassium zirconium fluoride.

8. The method of claim 7 wherein said complex potassium fluoride comprises potassium titanium fluoride.

9. The method of claim 6 wherein said coating is formed by applying to said manganese an aqueous solution of potassium fluoride and hydrofluoric acid.

10. The method of claim 6 wherein said coating is formed by applying to said manganese an aqueous solution of potassium fluoride, hydrofluoric acid and manganese fluoride.

11. The method of claim 6 wherein said coating is formed by applying to said manganese an aqueous solution of potassium fluoride and sodium fluoride.

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