

[54] MANGANESE COMPOSITIONS

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[22] Filed: July 12, 1971

[21] Appl. No.: 161,876

[52] U.S. Cl. .... 75/134 M, 29/192

[51] Int. Cl. .... C22c 31/00

[58] Field of Search... 75/134 M, 138, 68, 44; 29/192

[56] References Cited

## UNITED STATES PATENTS

2,935,397	5/1960	Saunders et al. ....	75/44
3,591,369	7/1971	Tuthill .....	75/138
3,592,637	7/1971	Brown et al. ....	75/138

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## [57] ABSTRACT

A method, articles and compositions are described for the direct addition of manganese metal to molten aluminum, which provide more rapid dissolution of the manganese in the aluminum than has been possible heretofore. The manganese is added to the molten aluminum in powder form (minus 14 mesh) in intimate admixture with a flux capable of forming a molten phase at the temperature of the molten aluminum to which the mixture is added. The flux, which is employed in an amount from about 3 to about 10 percent by weight of the total manganese-flux composition, contains chlorides other than those of manganese, fluorides and mixtures of such chlorides and fluorides; the preferred flux being 40 percent sodium chloride, 40 percent potassium chloride and 20 percent cryolite ( $\text{Na}_3\text{AlF}_6$ ).

9 Claims, No Drawings

## MANGANESE COMPOSITIONS

## BACKGROUND OF THE INVENTION

Alloys of aluminum containing small amounts of manganese are widely known and used in the art and articles made from such alloys constitute a large proportion of all wrought aluminum products. Alloys of this type, other than so-called master alloys, generally contain no more than about 1½ percent of manganese by weight, although alloys containing up to 2 to 3 percent manganese may be useful for some purposes. Master alloys, which are intended to be dissolved in molten aluminum to make ordinary manganese containing aluminum alloys, may contain from about 4 to 30 percent manganese. As a rule, however, lesser amounts of manganese, i.e., from 1½ percent down to as little as about 0.01 percent are employed in commercial aluminum alloys. For example, type 3003 aluminum-manganese alloy, which contains from about 1.0 to 1½ percent manganese, retains the high corrosion resistance of pure aluminum, but has much greater strength than commercial pure aluminum and also exhibits excellent forming and welding properties which adapt it for use in a wide variety of applications, such as in aluminum foil and extruded shaped articles. Type 5056 manganese-aluminum alloy, which contains about 0.01 percent manganese, is a well known example of the low manganese alloys.

The direct addition of manganese metal to molten aluminum is difficult due to the fact that the melting point of manganese (1,245°C.) is much higher than the melting point of aluminum (660°C.). Moreover, the rate of dissolution of metallic manganese in molten aluminum is very slow. As might be expected, in general, the smaller the particle size of the manganese metal, the faster its rate of dissolution in aluminum. For example, manganese chips dissolve in molten aluminum more rapidly than larger lumps of the metal. Despite this observation it has not previously been feasible to pursue this advantage further with much smaller particles of manganese. This is due to the fact that when manganese in powder form is added to a bath of molten aluminum it floats on the surface and is sintered to a hard crust, with the result that much of the manganese is oxidized and fails to be recovered as manganese metal in the final alloy. For this reason powdered manganese has previously been added to molten aluminum chiefly in the form of briquettes formed from mixtures of powdered manganese with powdered aluminum. While such composite powdered manganese and aluminum briquettes have provided better results than powdered manganese alone they have not proven entirely satisfactory. Briquettes composed substantially entirely of manganese powder have been found entirely unsatisfactory since they do not dissolve in molten aluminum.

In view of the above the usual means of adding manganese metal to aluminum has been to prepare an aluminum-manganese master alloy containing from about 4 to 30 percent manganese by weight. Such master alloys have the advantage of dissolving relatively rapidly in molten aluminum and also provide homogeneous distribution of the manganese throughout the aluminum bath. Despite these advantages such master alloys have presented handling and storage problems for both users and producers and have the further dis-

advantage of being uneconomically high in cost. Therefore, a need has long existed for a simple, economical method for adding manganese metal directly to molten aluminum in such a way as to provide rapid dissolution of the manganese in the aluminum.

## PRIOR ART

In Austrian Pat. No. 211,559, which issued on Oct. 25, 1960, it has been suggested that alloying materials such as manganese be introduced to light metal melts such as aluminum in the form of briquettes containing pulverized alloying materials in combination with the chlorides of the alloying material and other chlorides, with or without the addition of a fluoride. More specifically, the suggested briquettes would contain the pulverized alloying material in amounts equivalent to 8 to 10 times the total chloride content. For alloying manganese with a light metal the briquettes would contain about 80 percent manganese powder, about 10 percent manganous chloride and about 10 percent of other chlorides, preferably 5 percent sodium chloride and 5 percent potassium chloride. Optionally, a fluoride capable of dissolving the deoxidation products formed during alloying may also be employed. It is noted that manganous chloride is considered to be an essential ingredient of the briquettes suggested by the Austrian patent. Manganous chloride, being a hygroscopic material, tends to pick up sufficient moisture from the atmosphere to cause excessively violent agitation of the molten aluminum bath and is, therefore, difficult to employ on a commercial scale.

Our co-worker, Jordan P. Tuthill, in U.S. Pat. No. 3,591,369 issued July 13, 1971 has suggested the direct addition of manganese metal to molten aluminum in the form of a manganese body such as a chip having a coating containing a potassium fluoride which forms a molten phase at the temperature of the molten aluminum. Inasmuch as pure potassium fluoride melts above 710°C. the coating also contains at least one other chemically bound element which lowers the melting point of the coating and serves with the potassium and fluoride components to provide the molten phase. Such elements may be selected from the group consisting of sodium, aluminum, manganese, titanium and zirconium, which metals are preferably employed in the form of fluorides. While the Tuthill method and composition have proven successful, and represents a definite improvement over the prior art, it would, of course, be desirable to provide a method which would permit even more rapid dissolution of the manganese in the molten aluminum.

In view of the foregoing, it is apparent that despite significant advances in the art looking toward the direct addition of manganese to molten aluminum, a need remains for a method for accomplishing this result in a convenient and economical manner with improved rapidity of solution of the manganese in the molten aluminum and minimal loss of manganese.

It is, therefore, a principal object of the present invention to provide a method to meet this recognized need in the art.

More specifically, it is an object of the present invention to provide a method for the addition of manganese powder to molten aluminum with minimal loss of manganese due to oxidation of the powder and consequent high recovery of manganese metal in the final alloy.

It is another object of the invention to provide novel compositions and articles for the direct addition of manganese metal to molten aluminum, which provide hitherto unattainable rates of solution of manganese in the aluminum.

It is still another object of the invention to provide compositions and articles which accomplish the foregoing objects in a convenient, safe and economical manner.

#### BRIEF SUMMARY OF THE INVENTION

The present invention provides a method, articles and compositions for the direct addition of manganese metal to molten aluminum in such a way as to overcome the disadvantages of the methods of the prior art and provide previously unattainable rates of dissolution of the manganese in the molten aluminum. The method comprises the addition of powdered manganese-flux compositions to molten aluminum. The powdered manganese-flux compositions contain about 3 to 10 percent of flux by weight of the total compositions, the balance being essentially powdered manganese metal. The operable fluxes include those known to the art which contain chlorides and fluorides or mixtures thereof which are capable of forming a molten phase at or somewhat above the melting point of aluminum, i.e., at 660°C. up to about 710°C. The manganese-flux compositions are added to the molten aluminum bath in amounts to provide the desired concentration of manganese in the final alloy, e.g., from about 0.1 to 1.5 percent or up to 3 percent by weight of manganese in the aluminum alloy. Inasmuch as the manganese-flux compositions contain about 90 to 97 percent of manganese by weight, the amount of these compositions added to the aluminum is of about the same order of magnitude, although somewhat higher, (3 to 10 percent) than the percentage of manganese desired in the final alloy.

The powdered manganese-flux additives may be handled in any suitable way for introduction to the molten aluminum. For example, a measured quantity of the additive may simply be added to the aluminum bath manually, or a conventional vibratory feeder may be used to drop the particulate material into the bath. For added convenience, the powdered additive may be enclosed in a suitable consumable container for addition to the aluminum bath, e.g., a bag or envelope of aluminum foil, paper or a moisture proof laminate such as polyethylene-aluminum foil-Kraft paper may be used. In another, but less preferred embodiment of the invention, the manganese-flux powder additive may be formed into briquettes by conventional procedures and added in that form. While good results may be obtained in this way, it has been found that addition of the new compositions in free flowing powder form provides more rapid dissolution of the manganese in the aluminum than in the compacted powder form of the briquettes, probably due to the presence of a binder.

While the invention is especially useful for adding manganese directly to the molten aluminum to provide alloys containing from about 0.1 to 1.5 percent or up to 3 percent by weight of manganese, it may also be used to produce master aluminum alloys containing from 4 to 30 percent of manganese by appropriate adjustment of the amounts of the new additive compositions or articles added to the aluminum bath, i.e., from somewhat more than 4 to somewhat more than 30 per-

cent by weight of the additive, depending on the concentration of manganese in the additive.

#### DETAILED DESCRIPTION OF THE INVENTION

The manganese employed in the additive compositions of the present invention may be derived from any known source according to known techniques, such as by the pyrometallurgical reduction of ore, or by electrolysis. Electrolytic manganese is preferred, however. The manganese metal is reduced to the form of a free-flowing powder by known grinding techniques. When using electrolytic manganese, such as chips of the metal formed by breaking manganese away from the cathode on which it has been plated, it is preferred to remove any adherent electrolyte by washing, suitable chemical treatment, or both.

The powdered manganese-flux additive compositions of the invention may be formed by simply mixing the powdered manganese and dry flux materials in conventional mixing apparatus to obtain a dry, free-flowing powder. It is not essential, however, that the flux be in powder form and if desired the powdered manganese may be incorporated in a cake of agglomerated or fused flux.

While the particle size of the manganese powder may vary widely, it is preferred that it be essentially minus 14 mesh, and primarily plus 100 mesh. By this it is meant that substantially all of the manganese particles will pass through a standard 14 mesh screen and be retained on a standard 100 mesh screen. While it is, of course, desirable that the particle size of the manganese metal be relatively fine, i.e., minus about 14 mesh, in order to promote rapid dissolution in the molten aluminum, it is preferred that no more than about 20 percent by weight of manganese particles be minus 100 mesh, in order to prevent undue losses of manganese in the final alloy due to oxidation of such fines. The distribution of particle sizes within the stated range is not critical and various distributions of particle sizes within the above ranges have been found to be entirely suitable. For example, specific powdered manganese additives have been tested containing manganese particles of (1) substantially all minus 30 mesh and plus 100 mesh; (2) substantially all minus 30 mesh and smaller; and (3) substantially all minus 20 mesh and smaller, all mixed with about 10 percent by weight of flux based on the total additive compositions.

The amount of flux required for best results depends to some extent upon the particle size of the manganese powder employed; the finer the manganese powder, the more flux required to prevent its oxidation. In general, if the particle size of the manganese powder is in the range from about minus 14 mesh to plus 100 mesh, or minus 14 mesh and smaller with no more than about 20 percent minus 100 mesh, about 3 to about 10 percent of flux, by weight of the total additive compositions is employed. From these general considerations, those skilled in the art will be able to select an appropriate flux concentration within the about 3 to about 10 percent range, or at somewhat lower or higher concentration levels for larger or smaller mesh manganese particles, respectively.

The fluxes, as noted above, are chlorides or fluorides, or mixed chlorides and fluorides, and which are capable of forming a molten phase at the temperature of the molten aluminum to which the manganese-flux compositions are added in order to aid in the wetting of the

manganese particles by the aluminum and thus facilitate solution of the manganese in the aluminum. Suitable fluxes include those described in the Tuthill U.S.

75 percent and 95 percent dissolution of manganese were then read from these curves, and set forth in Table I below.

TABLE I

Type Mn Added	Time in Minutes Required to Reach % Mn Dissolved			
	25	50	75	95
Mn Powder + 9.1% flux**	1.25	1.50	1.70	5.00
32 Hr. Electrolytic Mn Chips	6.75	17.50	40.50	*
16 Hr. Electrolytic Mn Chips	4.75	11.25	23.50	*
32 Hr. Electrolytic Mn Chips Coated with $K_2TiF_6$	3.50	7.50	13.50	22.25
16 Hr. Electrolytic Mn Chips Coated with $K_2TiF_6$	1.50	2.75	4.25	9.50

\* Did not reach 95% dissolved during the 84 minute test.

\*\* The manganese powder was substantially all minus 30 mesh and plus 100 mesh and the flux consisted of 40% KCl, 40% NaCl and 20% cryolite.

Pat. No. 3,591,369 issued July 13, 1971, the disclosure of which is incorporated herein by reference. As noted in that application, potassium fluoride which is an excellent flux, has a melting point of about 710°C. and, therefore, when it is desired to alloy aluminum at a temperature below 710°C., but above the melting point of aluminum (660°C.) it is necessary to lower the melting point of the potassium fluoride by the addition of another chemically bound element. Suitable materials for this purpose include the chlorides and fluorides of sodium, aluminum, titanium and zirconium, and manganese fluoride. Manganous chloride is not desirable in a flux for aiding the dissolution of manganese in molten aluminum since, due to its hygroscopic nature, it normally carries with it sufficient moisture to cause unacceptably violent agitation of the molten aluminum bath. The chemical identity of the flux is not critical so long as it is capable of forming a molten phase at the temperature of the aluminum bath and also serves to aid in the wetting of the manganese particles by molten aluminum. Suitable fluxes include  $MgF_2$ ,  $K_2ZrF_6$ ,  $KF$ ,  $AlF_3$ ,  $LiF$ ,  $ZrF_4$ ,  $KCl$ ,  $LiCl$ ,  $MgCl_2$ ,  $ZrCl_4$  and mixtures of these salts. While  $K_2TiF_6$  is a particularly suitable flux it is more expensive than the preferred flux of the invention, which consists of a mixture of KCl, NaCl and cryolite. An especially preferred flux consists of 40% KCl, 40% NaCl and 20 percent cryolite ( $Na_3AlF_6$ ).

The invention will now be described in greater detail in relation to the relative rates of solution of manganese metal in molten aluminum attainable with the method, articles and compositions of the invention as compared with those of the prior art.

#### EXAMPLE 1

A series of laboratory experiments were carried out in which various manganese-containing additives were introduced to a bath of molten aluminum maintained at 746°C. (1,375°F); the amount of manganese in each additive being equivalent to 1.25 percent of the weight of the molten aluminum bath. Analytical samples were withdrawn from the molten aluminum bath at various intervals until 95 percent of the manganese was dissolved or until a maximum time of 84 minutes. These samples were analyzed for manganese dissolved in the aluminum bath and the calculated values of the percentage of the manganese in each additive which had dissolved were plotted against time. The time in minutes for each sample to reach 25 percent, 50 percent,

It is apparent from the foregoing Table I that while the manganese chips coated with  $K_2TiF_6$  according to the invention of the Tuthill method referred to above dissolve in the molten aluminum much more rapidly than uncoated manganese chips, the manganese powder-flux additive of the present invention is markedly superior to both the coated and uncoated chips in the rate of solution of manganese metal in the molten aluminum.

#### EXAMPLE 2

In order to evaluate the manganese powder-flux articles and compositions of the present invention with respect to those of the prior art, a series of tests were carried out according to the following general procedure.

#### Solution Rate Test Procedure

Aluminum (400 lbs.) is melted in an iron pot, heated to 746°C. and maintained at that temperature throughout the test procedure. Any dross present on the surface of the molten aluminum is removed by skimming. The samples of manganese-containing additives are added directly to the molten aluminum. Powder mixtures were enclosed in a polyethylene-aluminum foil-Kraft paper bag and the entire bag dropped into the aluminum bath. Briquetted mixtures were removed from the trilaminated bags and added to the aluminum bath with a shovel. The briquettes are made by mixing 10 ml of "Acrysol G-110" (an ammonium polyacrylate solution available from Rohm and Haas) as a binder in 20 ml of water with the bulk (2,551.8 to 2,807 g.) of the mixture to be briquetted and compressing the resulting material into briquettes at 15,000 psi. The mixed or briquetted products are immediately sealed in polyethylene-aluminum foil-Kraft paper bags to prevent those which are hygroscopic from picking up water from the atmosphere. After addition of each sample of additive to the molten aluminum bath 0.2 lb. samples of liquid metal are removed from the bath at the end of 1, 3, 6, 9, 14, 19, 24 and 34 minute intervals. The samples are then analyzed for manganese content by X-ray fluorescence according to known techniques and the percentage of dissolved manganese in the bath is calculated according to the formula:  $X(I) = (C(I) \cdot (A + M - I \cdot S) + S \cdot Cl) / M$   
 $I$  = sample number  
 $X(I)$  = percent dissolved of the  $I$ th sample  
 $C(I)$  = percent Mn of the  $I$ th sample  
 $A$  = weight of Al

M = weight of Mn

S = weight of the liquid metal sample

Cl = sum of the manganese for all samples up to and including the Ith sample

\* = multiplication

All of the samples tested contained 2296.6 g of manganese, substantially all of which passed a 30 mesh screen but was retained on a 100 mesh screen. All of the samples employed a flux containing 102.1 g of KCl, 102.1 g of NaCl and 51.0 g of cryolite ( $\text{Na}_3\text{AlF}_6$ ) for a total 255.2 g which is 10 percent by weight of the manganese-KCl-NaCl-cryolite mixture. The proportions of KCl:NaCl:cryolite in this flux are 40 percent; 40 percent; 20 percent, respectively. Some of the compositions also contained 255.2 g of  $\text{MnCl}_2$  as recommended by the Austrian patent referred to above. Some of the compositions were briquetted as described above while some were used in the form of the free-flowing powders. Inasmuch as the degree of agitation is a factor in the dissolution of manganese in molten aluminum, the effect of this factor was also evaluated by stirring some of the samples and not stirring others. The samples tested are listed by identifying code number and described in table II below.

TABLE II

Sample	Charges and Variables $\text{MnCl}_2$		Stirred
		Briquetted	
44 A	yes	yes	no
B	no	no	no
45 A	yes	no	no
B	no	yes	no
46 A	no	no	no
B	no	yes	no
47 A	yes	no	no
B	yes	yes	no
48 A	yes	no	yes
B	no	no	yes
49 A	no	yes	yes
B	yes	yes	yes

The percentage of the original manganese content of each additive sample of table II dissolved in the molten aluminum bath at the end of specified time periods during the test procedure is set forth in table III below.

Table III

Sample	Percentage of Manganese Content of Additive Dissolved in Molten Aluminum Bath							
	Time in Minutes							
	1	3	6	9	14	19	24	34
44 A	44.0	66.4	68.0	69.6	71.2	73.6	74.4	71.2
B	3.2	9.6	12.0	12.0	13.6	15.2	17.6	19.2
45 A	24.0	50.4	56.0	57.6	58.4	61.6	63.2	62.4
B	11.2	14.4	16.0	16.8	17.6	20.0	20.8	21.6
46 A	3.2	5.6	7.2	6.4	8.8	9.6	10.4	12.0
B	8.0	17.6	19.2	19.2	21.6	22.4	22.4	22.4
47 A	44.8	52.0	57.6	57.6	56.8	58.4	58.4	60.0
B	50.4	68.8	70.4	73.6	71.2	71.2	70.4	76.8
48 A	17.6	77.6	83.2	84.8	82.4	84.0	83.2	83.2
B	3.2	100.0	100.0	100.0	100.0	103.2	99.2	100.0
49 A	8.0	86.4	93.6	95.2	96.0	95.2	97.6	95.2
B	55.2	72.8	76.0	73.6	74.4	74.4	74.4	78.6

Further analyzing the results of this series of tests, the percentages of manganese recovery, i.e., percent of manganese from the additive found in the samples of liquid aluminum alloy, by each of the variables  $\text{MnCl}_2$  present or not, powder or briquette, and stirred or not stirred, are set forth in table IV below.

Table IV

		Percent Manganese Recovery by Variable $\text{MnCl}_2$ — Powder — Briquette-Stirring	
		Powder	Briquette
A. No Stirring	$\text{MnCl}_2$	62.4	71.2
	No	60.0	76.8
	$\text{MnCl}_2$	19.2	21.6
B. Stirring	$\text{MnCl}_2$	12.0	22.4
	No	83.2	77.6
	$\text{MnCl}_2$	100.0	95.2

It was observed that all of the samples containing  $\text{MnCl}_2$  caused such violent agitation of the bath of molten aluminum that molten metal actually bubbled out of the pot. While this bubbling aided in raising the solution rate of manganese in the unstirred melts due to the stirring action of the bubbling, such violent bubbling would not be acceptable in commercial practice. The powdered manganese-flux compositions of the present invention, on the other hand, did not agitate the melt significantly. The stirred melts containing  $\text{MnCl}_2$  showed little improvement over the unstirred melts also containing  $\text{MnCl}_2$ .

It is apparent that the usual commercial practice of stirring the melt is necessary with the articles and compositions of the invention. It is noted, however, that with stirring, the briquetted articles of the invention were superior to the briquetted  $\text{MnCl}_2$  — containing articles of the prior art, since they achieved 95.2 percent manganese recovery as compared to only 77.6% recovery for the  $\text{MnCl}_2$ -containing articles.

The best results, however were achieved by the preferred free-flowing powder manganese-flux compositions of the invention which achieved 100 percent manganese recovery as compared to only 83.2% recovery for such compositions also containing  $\text{MnCl}_2$ . It is clear, therefore, that  $\text{MnCl}_2$  is detrimental to the recovery of manganese metal in aluminum alloys and that its use also presents safety hazards.

While the invention has been described in conjunction with certain specific embodiments it is to be understood that these are merely illustrative of others which will be apparent to those skilled in the art.

What is claimed:

1. A composition consisting essentially of about 90 to 97 percent of finely particulate manganese metal and about 3 to 10 percent of a non-hygroscopic metal salt flux, based on the weight of the total composition, substantially all of said manganese metal being minus 14

mesh and said flux forming a molten phase at the temperature of molten aluminum to which said composition is added.

2. A composition according to claim 1 wherein the flux melts at a temperature in the range from about 660° C. to about 710° C.

3. A composition according to claim 2 wherein the manganese metal is substantially all minus 30 mesh.

4. A composition according to claim 3 wherein not more than about 20 percent of the manganese metal is minus 100 mesh.

5. A composition according to claim 3 wherein the manganese metal is substantially all plus 100 mesh.

6. A composition according to claim 1 wherein the flux consists essentially of materials selected from the group consisting of metal chlorides other than manganese chlorides, metal fluorides, and mixtures of said

chlorides and fluorides.

7. A composition according to claim 6 wherein said metal chlorides are selected from the group consisting of the chlorides of sodium, potassium, aluminum, titanium, and zirconium, and said metal fluorides are selected from the group consisting of the fluorides of sodium, potassium, aluminum, titanium, zirconium and manganese.

8. A composition according to claim 1 wherein said flux is a mixture of sodium chloride, potassium chloride and cryolite.

9. A composition according to claim 1 wherein said flux contains about 40 percent sodium chloride, about 40 percent potassium chloride and about 20 percent cryolite.

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