Patented Nov. 4, 1941 2,261,906

UNITED STATES PATENT OFFICE

2,261,906

METHOD OF ALLOYING MAGNESIUM WITH MANGANESE

Charles E. Nelson and George F. Gunn, Midland, Mich., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Michigan

No Drawing. Application April 25, 1941, Serial No. 390,366

6 Claims. (Cl. 75—168)

This invention relates to a method of alloying magnesium, or magnesium base alloys, with manganese. It relates in particular to a method wherein the magnesium is melted in the presence of a mixture of a reducible manganese compound and inorganic flux ingredients in such proportion that, after reaction between the magnesium and the manganese compound, the resulting flux has the desired fluxing characteristics.

It is standard practice to handle molten magnesium and molten magnesium base alloys in the presence of a flux consisting of a fused mixture of inorganic compounds, to prevent burning. The flux may be lighter than the alloy and form a crust over the surface of the molten metal, or it may be of such density that a part only of the flux remains over the metal as a film, the main body of the flux being beneath the metal. In some instances the flux is chosen for its ability to form a thin skin over a part of the metal, leaving a portion of the surface uncovered.

It is also well known practice to alloy magnesium with manganese by introducing an anhydrous reducible manganese compound into the molten magnesium. The commonest reducible manganese compound employed for alloying manganese with magnesium is manganous chloride. When manganous chloride is added to molten magnesium, or magnesium base alloy, there is an almost instantaneous reduction to metallic manganese, accompanied by the formation of magnesium chloride in amount equivalent to the chlorine introduced in the manganese chloride. The magnesium chloride so formed becomes part of the inorganic flux system, thereby changing the composition of the said system. The flux cannot, therefore, be re-used indefinitely in the same type of operation because of its changed composition, and, even in the same melt, it no longer serves its original function to the desired extent. When starting operation in a clean melting pot it is particularly undesirable to use as a flux a mixture already containing the magnesium analog of the manganese compound to be employed, though this has been standard practice.

It is, accordingly, among the objects of the present invention to provide a method of operation, particularly of initial operation, in which magnesium or a magnesium base alloy is melted in the presence of a reducible manganese compound together with inorganic flux ingredients, free from the magnesium analog of the manganese compound, in such proportion that, after reaction between the magnesium and the manganese compound, the resulting flux has the desired characteristics. Another object is to provide compositions of matter containing reducible manganese compounds, to be melted with magnesium or its alloys such that, after the manganese compound has reacted with the magnesium, there remains a flux having the desired characteristics.

It has now been found that the foregoing and related objects may be attained by initiating operation in a clean melting pot or other suitable alloying vessel employing a charge of magnesium or magnesium base alloy and a flux of inorganic compounds including a reducible manganese compound but free from the magnesium analog of said reducible manganese compound, the flux ingredients being in a suitable proportion as will be illustrated hereinafter, so that after reaction between the magnesium and the manganese compound there is formed a sufficient amount of the magnesium compound to contribute to the inorganic mixture the desired and well known fluxing characteristics normally sought in protective fluxes.

More specifically, the invention is a method of alloying magnesium or a magnesium base alloy with manganese, in which molten magnesium is to be protected with a final inorganic flux containing a particular magnesium compound, which comprises placing solid magnesium or magnesium base alloy in a clean melting vessel, in contact with an original flux (to give temporary protection) differing from the desired final flux by being free from significant amounts of the desired final magnesium compound and by containing the reducible manganese analog of the said magnesium compound desired in the final flux, in amount to yield the requisite amount of manganese and equivalent to the desired amount of said magnesium compound in the final flux, together with other flux ingredients in the proportion relative to one another in which they should appear in the final flux, and heating the magnesium and original flux at least to the melting point of the magnesium, thereby to reduce the manganese compound and to form an equivalent weight of its magnesium analog, producing the desired final flux and a manganese-containing magnesium alloy protected thereby.

The term "original flux" herein employed refers to the mixture of inorganic compounds including a reducible manganese compound initially charged into an empty and substantially

clean melting pot or equivalent vessel along with the magnesium or magnesium base alloy to which it is desired to add manganese as an alloying ingredients. The term "final flux" refers to the inorganic compound mixture present as flux after reaction between the magnesium and the manganese compound, and in the present specification it is understood that the final flux always contains the magnesium analog of the manganese compound employed in the original flux. The term "magnesium analog of the manganese compound employed" can best be defined by means of example: Thus, magnesium oxide is deemed to be the analog of manganous oxide, magnesium fluoride to be the analog of manganous fluoride, and magnesium chloride to be the analog of manganous chloride. In the following description and claims the term "magnesium" will be understood to include not only magnesium itself but also those alloys in which it predominates, generally referred to as magnesium base alloys.

The following examples illustrate the practice of the invention but are not to be construed as limiting.

Example 1

Magnesium is melted in a clean pot, i. e., one containing no flux remaining from previous operations, in the presence of an original flux consisting of

	Per cent
Manganous chloride	38
Potassium chloride	48
Calcium fluoride	5
Barium chloride	9

When the magnesium reaches the melting point it reacts instantly with the manganous chloride liberating an equivalent amount of magnesium chloride. The so-formed manganese-containing alloy floats on the main body of flux with but a thin film of flux over its surface. The final flux has the approximate composition

	Per cent
Potassium chloride	53
Calcium fluoride	5
Barium chloride	10
Magnesium chloride	32

The foregoing final fluxing composition is one which has long been used satisfactorily for the protection of molten magnesium and its alloys.

Example 2

In a clean melting pot was placed a magnesium-aluminum alloy containing more than the desired amount of iron as an impurity. This alloy was melted in the presence of an original flux containing sufficient manganese compound to settle the iron and to alloy with the magnesium. The original flux employed consisted of

	Per cent
Manganous chloride	72
Potassium chloride	23
Calcium fluoride	2.5
Barium chloride	2.5

The iron was settled in the customary manner and the final flux had fluxing characteristics very similar to those of the final flux described with respect to Example 1, though containing somewhat more magnesium chloride and less potassium chloride, having an approximate analysis of

	Per cent
Potassium chloride	28
Calcium fluoride	3
Barium chloride	3
Magnesium chloride	66

Example 3

In a manner similar to that described in the preceding examples magnesium was melted with an original flux consisting of

	Per cent
Manganous chloride	64
Sodium chloride	36

in quantity sufficient to produce 1 per cent of manganese based on the weight of the magnesium present. The final flux, consisting of

	Per cent
Sodium chloride	44
Magnesium chloride	56

is a well known flux for magnesium metals and behaved in its normal manner, settling to the bottom of the vessel but leaving a film of flux over the top of the molten metal.

Example 4

A mass of magnesium was placed in a clean melting pot along with a small amount of an original flux consisting of

	Per cent
Manganous chloride	70
Calcium fluoride	15
Magnesium oxide	15

The final flux, after the reaction between the manganous chloride and the magnesium, was of the "crucible type" forming a crust over the top of the molten metal which protected the metal during the ensuing pouring operation. It had an approximate analysis of

	Per cent
Calcium fluoride	18
Magnesium oxide	18
Magnesium chloride	54

Another original flux which has been found to give a satisfactory final flux with normal flux characteristics is one consisting of

	Per cent
Manganous chloride	30
Potassium chloride	35
Lithium chloride	30
Potassium fluoride	5

The corresponding final flux is

	Per cent
Magnesium chloride	25
Potassium chloride	38
Lithium chloride	32
Potassium fluoride	5

Another suitable original flux is

	Per cent
Potassium chloride	15
Lithium chloride	15
Potassium fluoride	10
Manganous oxide	60

The corresponding final flux is

	Per cent
Potassium chloride	20
Lithium chloride	20
Potassium fluoride	14
Magnesium oxide	46

A fluid final flux is obtained when using as the original flux a mixture of

	Per cent
Calcium chloride	50
Calcium fluoride	10
Barium fluoride	20
Manganous fluoride	20

The final flux is

	Per cent
Calcium chloride	54
Calcium fluoride	11
Barium fluoride	21
Magnesium fluoride	14

The foregoing examples have illustrated original flux compositions wherein the manganese compound has been manganous chloride, manganous fluoride, and manganous oxide. The resulting final fluxes have been of various types representing the range of fluxing properties desired for the different types of high temperature operations normally carried out on molten magnesium and its alloys. Numerous other original fluxes may be made up, according to the invention, in a proportion to yield known and desired final fluxes. The manner in which this may be done will be understood readily by a skilled chemist or metallurgist from the description herein contained.

It is observed that the present invention is necessarily limited to an operation where the melting vessel contains no residual fluxing ingredients from previous operations at the time the magnesium and herein described type of original flux are introduced.

The invention is of particular advantage where small total amounts of flux, e. g. 15 per cent or less, are employed with large amounts of metal, since in such cases, if the reducible manganese compound were added to the metal through any of the customary final fluxes, the amount of magnesium compound formed normally adds to the flux system enough magnesium compound to alter materially the fusion characteristics of the flux. When, however, the manganese compound is added in an original flux of the herein described type this flux gives adequate protection until the metal is melted, at which time it promptly reacts with the manganese compound, liberating enough magnesium compound to give to the inorganic flux mixture well recognized fluxing characteristics.

1. A method of alloying magnesium with manganese, in which molten magnesium is to be protected with a final inorganic flux containing a magnesium compound, which comprises placing solid magnesium in a clean melting vessel, in contact with an original flux differing from the desired final flux by being free of significant amounts of the desired final magnesium compound and by containing the reducible manganese analog of the magnesium compound desired in the final flux, in amount to yield the requisite amount of manganese, and equivalent to the desired amount of analogous magnesium compound in the final flux, together with other flux ingredients in the proportion relative to one another in which they should appear in the final flux, and heating the magnesium and original flux at least to the melting point of the magnesium, thereby to reduce the manganese compound and to form an equivalent weight of its magnesium analog, producing the desired final flux and a manganese-containing magnesium alloy protected thereby.

2. A method of alloying magnesium with manganese, in which molten magnesium is to be protected with a final inorganic flux containing magnesium chloride, which comprises placing solid magnesium in a clean melting vessel, in contact with an original flux differing from the desired final flux by being free from significant amounts of magnesium chloride and by containing manganese chloride in amount to yield the requisite amount of manganese, and equivalent to the desired amount of magnesium chloride in the final flux, together with other flux ingredients in the proportion relative to one another in which they should appear in the final flux, and heating the magnesium and original flux at least to the melting point of the magnesium, thereby to reduce the manganese chloride and to form an equivalent weight of magnesium chloride, producing the desired final flux and a manganese-containing magnesium alloy protected thereby.

3. A method of alloying magnesium with manganese, in which molten magnesium is to be protected with a final inorganic flux containing magnesium fluoride, which comprises placing solid magnesium in a clean melting vessel, in contact with an original flux differing from the desired final flux by being free from significant amounts of magnesium fluoride and by containing manganese fluoride in amount to yield the requisite amount of manganese, and equivalent to the desired amount of magnesium fluoride in the final flux, together with other flux ingredients in the proportion relative to one another in which they should appear in the final flux, and heating the magnesium and original flux at least to the melting point of the magnesium, thereby to reduce the manganese fluoride and to form an equivalent weight of magnesium fluoride, producing the desired final flux and a manganese-containing magnesium alloy protected thereby.

4. A method of alloying magnesium with manganese, in which molten magnesium is to be protected with a final inorganic flux containing magnesium oxide, which comprises placing solid magnesium in a clean melting vessel, in contact with an original flux differing from the desired final flux by being free from significant amounts of magnesium oxide and by containing manganese oxide in amount to yield the requisite amount of manganese, and equivalent to the desired amount of magnesium oxide in the final flux, together with other flux ingredients in the proportion relative to one another in which they should appear in the final flux, and heating the magnesium and original flux at least to the melting point of the magnesium, thereby to reduce the manganese oxide and to form an equivalent weight of magnesium oxide, producing the desired final flux and a manganese-containing magnesium alloy protected thereby.

5. A method of alloying magnesium with manganese, in which molten magnesium is to be protected with a final flux consisting of about 53 per cent potassium chloride, about 5 per cent calcium fluoride, about 10 per cent barium chloride, and about 32 per cent magnesium chloride, which comprises placing solid magnesium in a clean melting vessel, in contact with an original flux consisting of about 48 per cent potassium chloride, about 5 per cent calcium fluoride, about 9 per cent barium chloride, and about 38 per cent manganous chloride, and heating the magnesium and original flux at least to the melting point of the magnesium, thereby to reduce the manganous chloride and to form an equivalent weight

of magnesium chloride, producing the desired final flux and a magnesium-manganese alloy protected thereby.

6. A method of alloying magnesium with manganese, in which molten magnesium is to be protected with a final flux consisting of about 54 per cent calcium chloride, about 11 per cent calcium fluoride, about 21 per cent barium fluoride, and about 14 per cent magnesium fluoride, which comprises placing solid magnesium in a clean melting vessel, in contact with an original flux consisting of about 50 per cent calcium chloride, about 10 per cent calcium fluoride, about 20 per cent barium fluoride, and about 20 per cent manganous fluoride, and heating the magnesium and original flux at least to the melting point of the magnesium, thereby to reduce the manganous fluoride and to form an equivalent weight of magnesium fluoride, producing the desired final flux and a magnesium-manganese alloy protected thereby.

CHARLES E. NELSON.
GEORGE F. GUNN.