United States Patent [19]

Church et al.

[11] **3,801,311**

[45] **Apr. 2, 1974**

[54] **METHOD OF INTRODUCING RARE EARTH METALS INTO ADDITION ALLOYS**

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[22] Filed: **Jan. 24, 1973**

[21] Appl. No.: **326,402**

[52] **U.S. Cl.** ..... **75/168 J**, 75/134 F, 75/135, 75/152, 75/168 R, 75/170

[51] **Int. Cl.** **C22c 19/00**, C22c 23/00

[58] **Field of Search** ..... 75/168 J, 168 R, 152, 170, 75/135, 134 N, 134 F

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[57] **ABSTRACT**

A method is provided for preparing alloys comprising nickel, magnesium and rare earth metals in which rare earth oxides are used as the source of the rare earth metals. The rare earth oxides are added to nickel-magnesium melts which contain at least about 35 percent magnesium. The resultant alloys may be tailored to produce alloys suitable for treating cast iron melts.

17 Claims, No Drawings

METHOD OF INTRODUCING RARE EARTH METALS INTO ADDITION ALLOYS

This invention relates to a method for introducing rare earth metals into nickel-magnesium alloys. More particularly it relates to a process for the production of nickel-magnesium-rare earth alloys which are especially useful in the manufacture of ductile iron.

It is well known to improve grahitic cast iron by adding magnesium and/or rare earth metals, for example cerium and its alloys, to molten cast iron to impart desired characteristics to the iron. These additions are advantageously introduced into the cast iron melt in the form of alloys with other metals. Nickel-based magnesium-rare earth alloys have been used successfully for this purpose. The nickel is extremely effective in moderating the reaction between magnesium and molten iron, and it is often a very useful constituent of the cast iron formed. Many alloys of this type have been proposed as addition alloys, in which the magnesium content varies from about 2 percent to about 35 percent. U.S. Pat. No. 3,030,205, for example, discloses the use of a nickel-based alloy containing about 25–35 percent magnesium and up to about 2 percent of a rare earth metal for addition to molten cast iron. Although nickel-magnesium alloys containing up to about 35 percent and even higher magnesium have been proposed as addition alloys to cast iron melts, currently the trend is to use alloys containing no more than about 20 percent magnesium, mainly because of the high reactivity and low magnesium recovery obtained with the higher magnesium alloys. The most commonly used source of rare earth metals in the preparation of such alloys is misch metal.

Misch metal is an alloy containing about 94 to 99 percent rare earth metal. The composition varies depending on the ore from which it is produced. Typically, it consists of 45–50 percent cerium, 22–25 percent lanthanum, and varying amounts of the other rare earths. It is prepared by electrolysis of fused rare earth chloride mixtures. The use of misch metal in the production of alloys has the disadvantage of being expensive, and it would be desirable to introduce the rare earth metals by direct chemical reduction of rare earth compounds such as the relatively low cost rare earth oxides.

Heretofore, it had been known that rare earth oxides could be used to produce silicon-based alloys which also contain magnesium. In fact, it is the silicon or a silicon alloy which is used as the reducing agent for the rare earth compounds in the preparation of such alloys. However, for certain applications it is highly desirable to have the alloy with a low silicon content or essentially free of silicon. Exemplary of such alloys are those nickel-magnesium rare earth alloys described above, which contain about 2–35 percent and preferably less than 20 percent magnesium. It is known that to be effective in certain applications, such as when used as additives in the production of ductile iron, the rare earth in the additive alloys must be present as the metal. However, when rare earth oxides are used in the preparation of the silicon-free nickel-magnesium alloys, the reduction of such oxides does not occur satisfactorily. Thus, heretofore, more expensive materials have been used in preparing the alloys.

Accordingly, it is an object of the present invention to provide a new method of producing nickel-magnesium rare earth alloys in which rare earth oxides can be used as the source of the rare earth metals.

Another object is to provide a new method of producing nickel-magnesium-rare earth alloys which are useful additives to ferrous melts, for example, in the production of ductile iron.

These and other objects will become apparent from the following description and illustrative examples.

SUMMARY OF THE INVENTION

It has now been found that nickel-magnesium-rare earth alloys can be produced efficiently and economically using rare earth oxides as the source of the rare earth metals when the melt to which the oxides are added contains greater than about 35 percent magnesium, the balance being essentially nickel. In the method of this invention, the magnesium reduces a high percentage of the rare earth oxide to cerium metal and other rare earth metals. Also, it has been found that the resultant alloys can be diluted to provide nickel-magnesium-rare earth alloys suitable for treating cast iron melts in the production of ductile iron.

BRIEF DESCRIPTION OF PREFERRED EMBODIMENTS

The initial melt to which the rare earth oxide is added to produce an alloy, preferably contains about 40 or 50 percent to about 80 percent magnesium, the balance being essentially nickel. The optimum nickel-magnesium melt compositions contain about 50 to 70 percent magnesium, the balance essentially nickel. As indicated above, melts containing less than about 35 percent are essentially ineffective for the reduction of the rare earth oxides. Cerium recovery in melts containing about 50 to 80 percent magnesium may be as high as 50 percent and even higher. The use of magnesium concentrations much higher than 80 percent is impractical, as will be obvious to those skilled in the art.

Known processes may be used for preparing the alloys using the rare earth oxides, provided the magnesium content of the melt is controlled in accordance with this invention. For example, the nickel-magnesium-rare earth metal alloys of this invention may be produced by melting nickel and carbon, adjusting the molten bath to about 2,450°F., and then adding magnesium to the nickel melt, in an amount to provide a concentration greater than about 35 percent either by thrusting magnesium ingots into the bath or pouring the molten nickel over magnesium ingots held in a ladle. Alternatively, a nickel-magnesium melt may be made by reacting molten magnesium with particulate nickel, preferably in the form of reduced nickel oxide containing about 90 percent nickel (by weight) to form a molten alloy containing, for example, about 50 percent magnesium and the balance essentially nickel, while maintaining the bath temperature in the range of about 1,300°F. to 1,500°F., i.e., at bath temperatures not exceeding the melting point of magnesium by more than 300°F. In the preparation of this melt, it is desirable to maintain a flux over the surface of the magnesium bath. A flux composed of equal parts of anhydrous magnesium chloride and calcium chloride fluidized with a small amount of sodium chloride is satisfactory. Regardless of the method of preparing the nickel-magnesium melt to which the rare earth oxides are added, it is important that the melt be heated suffi-

ciently above the liquidus temperature to provide a fluid bath. In the fluid bath a homogeneous mixture of the components can be effected and the reduction of the oxides takes place rapidly.

Generally, the desired rare earth metal content of the nickel-magnesium alloys will depend on the ultimate use. For use in producing suitable cast iron, for example, the required rare earth content depends not only on the amount of rare earth metal that must be retained in the ultimate product, but also on the magnesium content of the alloy. By way of example, where it is desirable to produce a cast iron product having a magnesium content of 0.03 to 0.07 percent and a cerium content of 0.003 to 0.007 percent the additive alloy will suitably have a magnesium: cerium ratio of about 25 to 30:1. It will be noted that while the magnesium recovery in the final ferrous alloy may be about 50 percent, the cerium recovery will be much higher. Generally, suitable alloys may be prepared — using oxides of rare earth metals as the source of such metals, in accordance with this invention — which have a ratio of magnesium:rare earth metal down to about 10:1, corresponding to a magnesium:cerium ratio of about 20:1. It will be appreciated, of course, that the proportion of magnesium to rare earth metal in the alloy can be much higher, e.g., 15:1 or 20:1 or even higher, depending on the alloy desired, which in turn depends on the ultimate use. In a preferred embodiment of this invention the magnesium:rare earth metal ratio is about 15:1 to about 10:1.

It is a further aspect of this invention that the nickel-magnesium-rare earth metal alloy resulting from the reduction of rare earth oxides may be used as a precursor to produce alloys used in the manufacture of various ferrous metal alloys. Alloys which have been satisfactorily employed for the purpose of introducing magnesium and rare earth metals into cast iron melts in the production of ductile iron include a wide variety of nickel-magnesium alloys. As indicated previously, however, the trend has been to use alloys containing less than about 35 percent, and preferably no more than about 20 percent magnesium.

To prepare such addition alloys, the nickel-magnesium-rare earth alloys of high magnesium and rare earth metal content, prepared as described above, are diluted as required, for example, by the addition of nickel.

It will be appreciated that elements other than nickel, magnesium and rare earth metals may be present in addition alloys depending on the use of the ultimate product. For example, additives to cast iron melts may contain up to about 10 percent iron, up to about 20 percent copper, up to about 10 percent manganese, up to about 2 percent carbon and up to about 2 percent phosphorus, or a combination thereof. Thus various elements may be present in the additive alloy without otherwise affecting the concept disclosed herein, viz., that the rare earth oxides may be used as the source of the rare earths in preparing the nickel-magnesium-rare earth metal alloys so long as the initial melt contains at least about 35 percent magnesium. The other elements which may be present may be introduced, for example, in the initial melts or in the dilution melts. Further, the rare earth metal content of the alloy may be increased at any stage as the more expensive misch metal.

In order to give those skilled in the art a better understanding of the invention, the following examples are given. It will be understood, however, that these examples are only illustrative and not intended to limit the invention. All percentages given herein are by weight.

EXAMPLE I

This example illustrates the preparation of a nickel-magnesium rare earth alloy in accordance with this invention.

In Test A, a commercial mixture of rare earth oxides (containing about 45–50 percent cerium, 32–34 percent lanthanum, 13–14 percent neodymium, 4–5 percent praseodymium and less than about 1 percent each of other rare metals) is added to a nickel-magnesium melt to provide a mixture consisting (by weight) of approximately 44 percent nickel, 50 percent magnesium and 6 percent rare earth oxide. The magnesium is melted first in an induction furnace under a flux of magnesium chloride, calcium chloride and sodium chloride. Nickel oxide powder is added to the magnesium melt at 1,400°F. When the melt is in a state of a fluid bath, the rare earth oxide mixture is added and reaction occurs rapidly to produce a bath consisting of 52 percent magnesium, 2 percent cerium, 1.8 percent other rare earths, and the balance nickel. This bath is cast into ingot form.

EXAMPLE II

This example shows that the rare earth in the alloy prepared in accordance with this invention is actually in a form suitable for use in the production of ductile iron.

In Test B, carbon and nickel are melted and heated to 2,800°F., the melt is then cooled to 2,300°F., and sufficient nickel-magnesium-rare earth alloy of Example I is added to produce ingots containing 14.7 percent magnesium, 0.34 percent cerium, and the balance essentially nickel. (No carbon analysis was obtained.)

This diluted alloy is used to treat an iron melt of the following nominal composition:

Weight Percent			
C	Mn	Si	Fe
3.6	0.6	2.4	Bal.

To determine whether cerium is present in the alloy, the magnesium addition to the iron melt is intentionally made below the concentration required to obtain a 100 percent spheroidal structure. It is known that such melt will contain some flake graphite. If cerium is present as the metal, however, it will instead contain some vermicular graphite.

In Tests C and D, the diluted alloy of Test B is added to the iron melt in an amount of 0.27 percent. On examination, both of the resulting irons contain 85 percent spheroidal graphite and the balance vermicular graphite, indicating the cerium is present in usable form in the treatment alloy.

EXAMPLE III

This example illustrates that a nickel-magnesium alloy containing 15 percent magnesium, i.e., having a magnesium content comparable to the treatment alloy prepared in Example II, is not effective for reducing the rare earth oxides to the metal.

In Test E approximately 3 percent of rare earth oxide commercial mixture, described in Example I, containing about 50 percent cerium is added at about 2,450°F. to a melt of 15.8 percent magnesium, 82.7 percent nickel, and 1.6 percent carbon. The melt is maintained at about 2,450°F. After adding the rare earth oxide mixture, a loose powdery material formed on top of the melt which could not be stirred in to the bath. Analysis of the solidified melt shows only 0.07 percent cerium (Mg:Ce = >200:1) is obtained. Thus the nickel-magnesium melt containing only 15 percent magnesium is not an effective reductant for the rare earth oxides.

EXAMPLE IV

A series of alloys are prepared utilizing various concentrations of magnesium in nickel-magnesium melts. The method of preparing the alloys is similar to that described in Examples I and II. The compositions of the original melt before addition of REO (rare earth oxide) and the composition of the final melt after addition of REO were determined, the cerium content and rare earth content being determined by gravimetric analysis and the rare earth content other than cerium being the difference. The Table below shows a tabulation of data obtained in connection with these alloys and the alloys prepared in Examples I, II and III.

From the results tabulated in the Table it can be seen that for initial melts containing over about 40 percent magnesium, the cerium recovery is greater than 25 percent. Where the initial melt contains about 50–80 percent magnesium the cerium recovery in most instances is 49 percent and higher. Where the magnesium content was about 15 percent and 30 percent the cerium recovery is very low.

TABLE

Approx. comp. of original bath (weight percent)					Melt practice*	Percent REO addition	Final melt comp. after REO addition (percent)							Approx. percent Co added as REO	Percent Ce recovery
Mg	Ni	C	P	Fe			Mg	Ni	C	Ce	Other RE	P	Fe		
15.8	82.7	1.6	----	----	A	3.6	16.7	Bal.	~1.5	0.07	N.a.	N.a.	N.a.	1.80	4
30.0	70.0	----	----	----	A	3.8	32.7	Bal.	~1.5	<0.05	<0.05	N.a.	N.a.	1.90	**<3
37.8	60.3	1.9	----	----	A	4.1	34.6	Bal.	1.57	0.15	0.28	N.a.	N.a.	2.05	7
43.2	54.8	2.0	----	----	A	4.7	40.7	Bal.	1.17	0.64	0.63	N.a.	N.a.	2.35	27
53.5	42.4	----	1.1	3.0	B	6.0	50.0	Bal.	N.a.	1.46	1.76	0.23	N.a.	3.00	49
55.8	44.2	----	----	----	B	6.9	52.0	Bal.	N.a.	2.00	1.80	N.a.	N.a.	3.45	58
56.0	44.0	----	----	----	B	6.3	49.8	Bal.	N.a.	1.97	2.28	N.a.	N.a.	3.15	62
67.0	33.0	----	----	----	B	7.4	64.9	Bal.	N.a.	2.49	2.35	N.a.	N.a.	3.70	67
70.0	30.0	----	----	----	B	7.4	68.9	Bal.	N.a.	1.04	1.29	N.a.	N.a.	3.70	28
78.3	21.7	----	----	----	B	8.6	67.7	Bal.	N.a.	2.77	3.38	N.a.	N.a.	4.30	64
100	----	----	----	----	B	12.0	Bal.	N.a.	N.a.	1.75	2.35	N.a.	N.a.	6.0	29

*Melt practice:
A—Melt Ni and C, add Mg starting at 2,450° F., add REO at a temperature as close to the melting point of the bath as possible. Carbon is added in melt practice A to lower the melting temperature of the Ni.
B—Melt Mg and flux ($MgCl_2$, CaCl and NaCl), at 1,400° F. shut power off and slowly add Ni oxide powder. Add REO at an appropriate temperature.
**Cerium content considered too low to warrant analysis. The ratio of Mg:Ce is >600:1.
N.a.=not analyzed.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are to be within the purview and scope of the invention and appended claims.

We claim:

1. In a process for the production of alloys comprised of nickel, magnesium and a rare earth metal, wherein the rare earth is introduced into a silicon-free melt comprised of nickel and magnesium, the improvement comprising adding a rare earth oxide to the melt, said melt containing at least about 35 percent magnesium.

2. A process of claim **1** wherein the melt consists essentially of about 40 percent to about 80 percent magnesium and the balance nickel.

3. A process of claim **2** wherein the melt contains about 50 percent to 70 percent magnesium.

4. A process of claim **1** wherein the rare earth oxide is added to the melt in sufficient amount to provide an alloy having a magnesium to rare earth metal ratio of down to about 10:1.

5. A process of claim **4** wherein a sufficient amount of rare earth oxide is added to the melt to provide a magnesium to rare earth metal ratio of 15:1 to 10:1.

6. A process of claim **1** wherein a mixture of rare earth oxides is added to the melt.

7. A process of claim **6** wherein the mixture of rare earth oxides contains at least about 45 percent cerium oxide.

8. A process of preparing an addition alloy especially suitable for treating a cast iron melt to produce ductile iron, said alloy being comprised of nickel, magnesium and a rare earth metal, and containing about 2 to about 35 percent magnesium, comprising

a. forming an initial melt comprised of nickel and magnesium, said magnesium being present in the melt in an amount at least greater than about 35 percent, and said melt being essentially free of silicon;

b. adding a rare earth oxide to the melt to form a first alloy comprised of nickel, magnesium, and a rare earth metal; and

c. diluting the resulting first alloy to form a second alloy comprised of nickel, magnesium, and a rare earth metal, said diluted addition alloy containing about 2 to about 35 percent magnesium.

9. A process of claim **8** wherein the initial melt to which the rare earth oxide is added consists essentially of about 40 percent to about 80 percent magnesium and the balance nickel.

10. A process of claim **10** wherein the initial melt contains about 50 percent to 70 percent magnesium.

11. A process of claim **8** wherein the rare earth oxide is added to the initial melt in sufficient amount to provide an alloy having a magnesium to rare earth metal ratio down to about 10:1.

12. A process of claim **11** wherein the rare earth oxide is added to the initial melt in sufficient amount to provide a magnesium to rare earth nickel ratio of about 15:1 to 10:1.

13. A process of claim **12** wherein a mixture of rare earth oxides is added to the melt.

14. A process of claim **13** wherein the mixture of rare

earth oxides contains at least about 45 percent cerium oxide.

15. A process of claim **8** wherein the initial melt containing nickel and magnesium is heated to a temperature sufficiently above the liquidus temperature to provide a fluid bath and the rare earth oxide is added to the fluid bath.

16. A process of claim **8** wherein the resultant first alloy is diluted with an additive selected from nickel, iron, carbon, copper, manganese, phosphorus, or a combination thereof.

17. A process of claim **16** wherein the diluted addition contains a maximum of about 20 percent magnesium.

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