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[54] ALLOY ADDITIVE

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[58] **Field of Search** .. 75/122, 123 K, 123 L, 130 A, 75/128 E, 128 C

[56] **References Cited**

UNITED STATES PATENTS

2,485,760	10/1949	Millis et al.	75/123 CB
2,675,308	4/1954	Millis et al.	75/123

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[57] **ABSTRACT**

Addition agents containing controlled percentages of nickel, silicon, magnesium and iron are useful in the production of ferrous-base compositions, particularly ductile irons.

5 Claims, No Drawings

ALLOY ADDITIVE

The subject invention is addressed to ferrous metallurgy, and more particularly, to addition agents for incorporating magnesium in ferrous-base melts.

As is known, it is virtually the most conventional of metallurgical practices to innoculate or otherwise treat molten irons for purposes of deoxi- dation, desulfurization, degasification, modification of the as-cast morphological structures, etc. Magnesium has seen extensive use in this connection and has been largely used in the production of "ductile iron," i.e., cast iron in which at least part of the graphite is present in spheroidal form. This latter development, early described in U.S. Pat. No. 2,485,760 to Millis, Gagnebin & Pilling, significantly closed the gap between low-cost but brittle cast irons and the more expensive but less brittle steels.

In any case, over the years research has continued in respect of the development of improved procedures for introducing magnesium into a cast iron melt owing to its high degree of reactivity and propensity toward violent reactions. Too, in recent years increased emphasis has been and continues to be given to ecological considerations, namely, smoke emissions (attributable largely to evolved magnesium oxides). Since most approaches to the problem, as does the present, involve the production and use of addition agents, "crushability" of the additive as will be explained herein, also plays an important role. All these factors, in turn, focus attention on the economic picture.

In accordance with the present invention, it has been discovered that a hereinafter more fully described addition agent, provided that it is controlled to contain special and correlated percentages of magnesium, nickel, silicon and iron, results in a material having a unique "combination" of attributes, particularly for ductile iron production, including (i) relatively low reactivity with molten iron and thus low smoke emission, (ii) excellent magnesium recovery both in terms of preparation of the additive and in respect of the ferrous-base product produced, (iii) and good crushability such that excessive fines can be avoided, these obtaining (iv) with the simultaneous capability of using relatively low silicon levels and (v) relatively low cost. Prior art ductile iron addition agents have possessed one or more of these characteristics but, insofar as we are aware, none has combined all of them in one additive. Moreover, apart from ductile iron production, it is deemed that these novel addition agents also can be used in treating both wrought and cast low alloy steels, particularly in minimizing the difficulties occasioned by reason of the contaminant sulfur.

Generally speaking, the present invention contemplates addition agents containing about 3 to 5.5 percent magnesium, about 19 to 24 percent nickel, about 15 to 28 percent silicon and the balance essentially iron, the iron preferably being not less than 45 percent. Elements such as copper and manganese are not essential. Manganese need not exceed 2 or 3 percent although it can be as high as 12 percent

In carrying the invention into practice, should the magnesium be too low, e.g., 2 percent, the addition alloy is rendered too costly since a larger alloy addition would normally be required to produce a given magnesium level in a treated iron, notwithstanding a possibly higher magnesium recovery. On the other hand, based upon prior metallurgical principles it would be expected that as the magnesium is increased greater

would be the reactivity and larger would be the obnoxious emissions, (i.e., magnesium recovery and smoke generation would be expected to be roughly inversely proportional), this at the expense of smaller magnesium recoveries and higher cost. This need not be the case particularly if the nickel content is correlated with the magnesium percentage. Within the chemistry contemplated herein, nickel promotes an increase in magnesium solubility in the addition agent. And, accordingly, if sufficient nickel is present such that the magnesium is soluble or substantially so in the addition agent, less smoke emission is encountered and magnesium recovery is enhanced in treatment of, say, a ductile iron. While the magnesium level need not exceed 5.5 percent, it can be present up to 6 or 7 percent.

With further regard to the nickel content, it need not exceed 23.5 percent although up to about 25 percent can be present. And while it can be as low as 15 or 16 percent, particularly at the lowest magnesium levels, it is deemed that a range of 19.5 to 23.5 percent is most advantageous.

Concerning the element silicon, it should, at least in accordance herewith, be maintained at low levels. There is no significant reason why it should exceed about 30 or 32 percent; however, by keeping it below this level important commercial advantages are derived. For example, if in the production of ductile iron large quantities of silicon had to be added in the treatment and innoculation steps, then the silicon content of the ferrous melt would have to be kept low. However, this runs counter to desired commercial practice since it demands more careful selection of a base melt charge and would ostensibly occasion undue refractory wear. Too, excessive silicon detracts from a friable addition agent and tends to promote an unwanted amount of fines during crushing. These fines must be remelted. Thus, product yield is reduced and cost increased. A silicon range of 19 or 20 percent to 25 or 27 percent is quite satisfactory. Contributing to these desiderata is a low silicon (added) to magnesium (recovered) ratio. This ratio preferably does not exceed about 12:1 and is desirably less than about 10:1.

The following data will help serve as illustrative of the instant invention.

A number of addition alloys, both within and without the invention, were prepared as follows: electrolytic nickel, ferromanganese (when used) and iron were melted together (about 3 percent carbon was added in Alloy 1 to lower the melting temperature) and small amounts of FeSi were added as required to keep the baths deoxidized and quiet. To assure complete solution of the elements the melts were heated to about 2850° F. and then cooled to about 2600°F. whereupon the remainder of the silicon was added.

The baths were then cooled to a temperature (about 2350°F.) near the freezing point and the magnesium was added either in the form of pure magnesium sticks or 50 Ni-50 Mg master alloy. The alloys were cast into small truncated cone-shaped pig molds (1, 2 and 5 lb. sizes) and subsquently crushed to provide generally uniform equiaxed shaped pieces of roughly ½ to ¼ inch in diameter.

Often overlooked is the magnesium recovery in simply producing the addition agent, the emphasis usually being accorded to magnesium retention in the final ferrous base melt to be produced. However, this is an important adjunct to cost and therefore "magnesium addition agent recovery" was determined for most instances (Table I).

Addition alloy No. 1, Table I, was added to molten ferrous base nominally of 3.4 percent C, 2 percent Si, .45 percent Mn, Bal. Fe, prepared using pig iron, Armco iron, ferro-manganese and ferrosilicon, and heated to 2,800°F. The above-described magnesium addition alloy (enough to provide approximately 0.05 percent Mg to the bath) was placed in a cavity in the bottom of a specially lined treatment ladle (100 lb. melts treated except Alloy 1 which was 30 lbs.) and the cavity was covered in the case of Alloy 1 with a ⅛ inch thick steel plate weighing 0.6 lb. A cover crushed FeSi (50—50) equal to about 1 percent by weight of the bath was used for the remining addition agents. The iron melt was tapped into the ladle at 2,800°F. On the basis that smoke emissions were relatively proportional to flare, which in retrospect is seemingly reasonably true for very high nickel (93–95 percent) addition agents, a camera was used to photographically judge the amount of smoke emmision. In this instance, during tapping into the ladle a still camera was opened and when all visible sign of reaction ceased, the shutter was closed. After the reaction, a chill slug was poured for chemical analysis of magnesium. The bath was poured into a second ladle and innoculated with 0.5 percent S: as standard foundry grade ferrosilicon containing about 85 percent Si. A second chill slug was anaylzed for magnesium.

Because it was thought that the flare test was not sufficiently accurate for smoke generation in the more reactive agents, a different smoke test was devised for the remaining alloys (and also a repeat of Alloy No. 1). A Staplex Hi-Volume Air Sampler was used to sample a portion of the smoke drawn off through an exhaust vent. The exhaust hood was placed to encompass practically all the generated smoke, the exhaust being sampled at a distance of 20 feet from the ladle. A fraction of the air and likely a similar proportion of the MgO smoke was drawn through the sampler by a small fan. The soke was collected on a filter which was weighed both before and after test. The weigh gain was taken as the measurement of smoke emitted. Since clogging of the filter occurred in the more reactive alloys, a corection factor, $S_2=S_1(2F_0/F_0+F_1)$, was used to compensafe for the drop in air flow rate through the sampler. S_2 represents the corrected weight gain, S_1 the measured weight gain, and F_0 and F_1, respectively, correspond to the air flow from the smoke tester before and after test.

Various addition agent compositions are given in Table I below together with the percent magnesium recovery in preparing the same. It will be noted that a high magnesium recovery was obtained in most instances. However, magnesium recovery was low in respect of Alloys A, B, and C (alloys outside the invention) due largely, it is believed, to low nickel levels.

TABLE I

Alloy	Ni	Si	Mg	Fe	Other	Recovery Magnesium
1	21.5	30.2	1	31.6	11.8Mn	93
2	22.5	24.6	3.35	bal.	—	67
3	21.7	27.0	3.81	bal.	—	76
4	23.8	29.2	3.4	bal.	—	68
5	18.2	24.3	3.66	bal.	—	61
6	22.1	21.6	3.64	bal.	—	72
7	22.1	30.8	4.50	bal.	—	57
8	24.4	16.2	3.70	bal.	—	62

TABLE I-Continued

Alloy	Ni	Si	Mg	Fe	Other	Recovery Magnesium
9	21.6	17.4	4.41	bal.	—	55
10	24.2	23.0	6.41	bal.	—	
11	24.5	23.4	6.24	bal.	—	78
12	24.3	30.1	5.10	bal.	—	85
13	20.9	20.2	3.04	bal.	9.64Mn	63
14	19.7	29.9	3.85	bal.	9.60Mn	80
A	10.8	25.6	1.21	bal.	—	20
B	10.9	30.6	0.61	bal.	9.27Mn	13
C	14.9	26.3	2.11	bal.	—	35
D	94	—	4.5	bal.	1.5C	—
E	—	40	5.5	bal.	—	—

The data obtained using the above agents are reported in Table II, the ductile iron base melt nominally having contained about 3.6 percent C, 1.7 percent Si, 0.4 percent Mn, balance iron and impurities.

TABLE II

Alloy	Ni	Si	Mg	% Mg Recovered	Si/Mg	Weight Gain, S_2
1	22	30	4	71	10.65	0.41
2	23	25	3.35	62	12.0	0.185
3	22	27	3.8	62	11.4	0.19
4	24	29	3.4	70	12.2	0.20
5	18	24	3.66	48	13.7	0.19
6	22	22	3.6	60	10.0	0.23
7	22	31	3.5	70	9.9	0.29
8	24	16	3.7	70	6.2	0.27
9	22	17	4.4	66	5.9	0.31
10	24	23	6.4	70	5.1	0.38
11	25	23	6.24	70	5.3	0.43
12	24	30	5.1	60	9.8	0.37
13	—	—	—	—	—	—
14	—	—	—	—	—	—
A	11	26	1.2	72	29.9	0.09
C	15	26	2.1	66	18.6	0.14
D	94	—	4.5	95	0	0.10
E	—	40	5.5	44	16.5	1.00

NOTE: The percentages of Ni, Si and Mg are rounded off in Table II.

Concerning the alloys beyond the invention, Alloys A, C, D, and E, either the S_2 factor, the Si/Mg ratio or cost left something to be desired. As to the alloys within the invention, a number of them had a desirably low smoke emission factor, S_2, of not more than 0.4, a magnesium recovery of 60 percent or more, and a Si/Mg ratio below about 12. The photograph flare test for Alloy No. 1 indicated the alloy to be less reactive than a number of commercially available additives, although it was difficult to quantitatively determine the result. It is considered that a higher nickel content would have proven beneficial for alloys such as Alloy No. 5 (Mg recovery 48 percent) as evident from Alloy No. 6 (Mg recovery 60 percent). Lowering the magnesium level of Alloy No. 5 would also have likely been helpful. An addition agent containing 19.5 percent to 23.5 percent nickel, 20 to 27 percent silicon, 4 to 5.5 percent magnesium is deemed particularly beneficial.

As will be understood by those skilled in the art, in referring to the iron content as constituting the "balance" or "initially the balance" of the addition agents contemplated herein other consituents can be present in amounts which do not adversely affect the basic characteristics of the additives. In this connection, elements such as calcium, cerium, rare earth metals, carbon, cobalt, etc., can be present though they need not exceed up to 1 percent calcium, up to 1 percent cerium, up to 1 percent of other rare earths, up to 1 percent carbon, up to 2 percent cobalt, etc. Copper, if any, preferably does not exceed about 1 percent or 2 percent, since it is a pearlite stablizizer and can deleteriously affect graphite shape.

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

We claim:

1. A composition of matter particularly adapted for use as an additon agent to ferrous molten baths and consisting of by weight from about 3 to 5.5 percent magnesium, about 19 to 24 percent nickel, about 15 to 28 percent silicon and the balance essentially iron, said composition being characterized by relatively low reactivity and low smoke emission as a consequence of having been introduced into a molten ferrous body, excellent magnesium recovery not only in respect of the ferrous base product produced but also in terms of recovery as a result of the preparation of the composition per se, and also good crushability such that excessive fines are avoided.

2. A composition of matter in accordance with claim 1 in which a substantial portion of the magnesium is soluble in the composition.

3. A compostiion of matter in accordance with claim 2 containing 19.5 to 23.5 percent nickel, 20 to 27 percent silicon, and 4 to 5.5 percent magnesium.

4. A composition of matter in accordance with claim 1 containing at least 45 percent iron.

5. A composition of matter particularly adapted for use as an addition agent to ferrous molten baths and consisting of by weight from about 3 percent to about 7 percent magnesium, about 15 to 25 percent nickel, about 15 to 30 percent silicon, up to 12 percent manganese, up to 1 percent of calcium, up to 1 percent cerium, up to 1 percent rare earth metal, up to 1 percent carbon, up to 2 percent cobalt, up to about 2 percent copper and the balance essentially iron.

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