United States Patent Office 3,272,623 Patented Sept. 13, 1966

3,272,623

INOCULATING ALLOYS CONSISTING OF Si-Al-Ca-Ba-Mn-Zr-Fe

Walter Crafts, Niagara Falls, N.Y., and Peter F. Wieser, Cleveland, Ohio, assignors to Union Carbide Corporation, a corporation of New York

No Drawing. Filed Oct. 28, 1963, Ser. No. 319,505
8 Claims. (Cl. 75—134)

The present invention relates to addition alloys for use in the manufacture of cast iron. More particularly, the present invention relates to addition alloys for reducing chill depth in iron castings which addition alloys can be used without the formation of interfering amounts of slag or dross.

The inoculation of cast iron with alloy additions for the purpose of avoiding the formation of iron carbide during solidification has been practiced for many years. The intent in using alloy additions is to minimize the hard chilled surface in rapidly cooled parts of castings and to minimize the formation of undesirable undercooled microstructures of fine graphite and associated soft ferrite, to thus provide uniformity of hardness, higher strength, and improved wear resistance in the cast iron.

Various alloy addition agents have been used as inoculants in attempts to achieve the aforementioned benefits, and it is recognized that effective inoculation is a nucleating mechanism that produces a change in microstructure and properties in cast iron that are disproportionately large in relation to the change made in the chemical composition of the cast iron. One family of commonly used inoculants is based on ferrosilicon in combination with other alloying elements. Silicon itself has a softening effect on the cast iron, whether it is added during melting or pust prior to solidification. This effect of silicon generally is considered to result from an alloying effect that is more or less proportional to the amount present in the cast iron and not to result from the nucleating effect of an inoculant. This relation is described in the Metals Handbook, 8th Edition, pp. 349–365 and 379–394, American Society for Metals, 1961.

Silicon alloys containing various other elements to improve the inoculation of cast iron have been used for many years as noted in the above-mentioned articles.

However, it has been found that with the presently known addition agents, the use of alloy constituents which are generally considered beneficial as regards inoculation, cause various undesirable effects in use which substantially offset any advantages obtained. For example, presently known inoculating agents in the form of ferrosilicon alloyed with other elements have low rates of dissolution and also tend to produce increased amounts of slag or dross when the constituents of the inoculating agent are oxidized, very often with the retention of slag in the solidified castings which causes surface defects and porosity.

It has been discovered, however, as part of the present invention, that by closely controlling the constituents in addition agents, it is possible to achieve highly effective inoculation while avoiding the aforementioned difficulties associated with the formation of slag and dross.

Accordingly, it is an object of this invention to provide an alloy addition agent which will effectively inoculate molten iron to produce a cast iron of reduced chill depth with uniform structure and properties.

It is another object to provide an alloy addition agent which will dissolve rapidly in molten iron.

A further object is to provide an alloy addition agent which will dissolve in molten iron without excessive formation of slag, such slag as is formed being refractory and readily removable from the surface of the iron bath prior to casting.

Other objects will be apparent from the following description and claims.

An addition agent in accordance with the present invention is an alloy of silicon, aluminum, calcium, and barium, manganese and zirconium.

It has been discovered, as part of the present invention, that by including all of the foregoing elements in the composition of an alloy addition agent, and by closely controlling the amounts of the respective elements, undesirable dross and slag conditions can be avoided while at the same time substantially improved chill reduction is provided.

In order to achieve the full benefits of the invention, the composition of the alloy addition agent in weight percent must be within the range

Silicon	35–85
Aluminum	0.5–1.5
Calcium	0.5–4.0
Barium	0.5–4.0
Manganese	2–7
Zirconium	2–7
Iron	Balance

A preferred range for the alloy addition agent of the present invention is:

Silicon	60–65
Aluminum	.75–1.25
Calcium	1–2.5
Barium	2–3
Manganese	5–7
Zirconium	5–7
Iron	Balance

A particularly effective range for providing a very high chill reduction while practically eliminating the slag and dross problem is:

Silicon	61–66
Aluminum	0.5–1
Calcium	1–2.5
Barium	1–2
Manganese	4–6
Zirconium	2–3
Iron	Balance

In order to illustrate the effect of various alloy additions, a system of evaluating reduction in chill depth in cast irons and other properties was developed and used in the testing of various specimens.

In the testing two common types of base irons were employed. One having an average carbon equivalent ($CE=C_{tot.}+\frac{1}{3}(Si+P)$) of 4% and characterized as a "soft" iron (C=3.3%, Si=2%, Mn=0.8%, S=0.12%) and a second having an average carbon equivalent of 3.5% characterized as a "hard" iron (C=2.9%, Si=1.6%, Mn=0.7%, S=0.1%).

Both types of iron were used in the preparation of test specimens and were prepared by melting a charge of pig and Armco iron with minor additions of other elements as required to produce the desired composition, in an induction furnace with a basic lining, forming a heat of about 100 pounds weight. More particularly, in preparing the specimens, the primary charge of a major portion of the pig iron and all of the Armco iron were placed in the furnace, heated, and when substantially melted, the remaining pig iron and minor elements were added. The bath was deoxidized with silicon, deslagged, and the remainder of the required silicon added. Any remaining slag was removed, and the temperature was adjusted to 1500° C. The power input to the furnace was such as to maintain the bath at about 1500° C. (measured by immersion thermocouple) throughout the subsequent tapping operations.

A weighed quantity of the molten iron was tapped into a clay-lined graphite ladle, which had been preheated to a red heat in a gas-fired furnace. An inoculating alloy was added to the tapped molten iron, and the metal was stirred with a steel rod. When the temperature dropped to within the range of 1320 to 1350° C., the molten metal was cast into test specimens which were a standard 1.2-inch diameter by 21-inch long arbitration bar, and an ASTM Type 4c chill test bar.

Additional taps of molten metal were separately treated with different inoculants and cast in the same manner, to provide additional test specimens. Also, additional taps were processed in the same manner but not treated with any inoculant and thus served as a standard for subsequent comparative measurements. The amount by weight of addition alloy added in each instance was controlled to provide an addition of 0.1 to 0.3 percent silicon to the cast iron. For twenty pound taps, the amount of addition alloy was on the average, about 0.06 lb.

Specimens of "soft" and "hard" irons prepared in the foregoing manner were tested and observed as regards chill depth, rate of solution and dross-forming behavior. The chill depth, i.e. the white iron structure produced in the castings as a result of rapid solidification, was measured in accordance with standard practice.

In rating the effectiveness of the inoculants in controlling chill depth, the following formula was used:

$$\text{Percent Reduction in Chill Depth} = \left(\frac{\text{Chill depth of base iron-chill depth of inoculated iron}}{\text{chill depth of base iron}}\right) \times 100$$

The solution rate and dross-forming characteristics of the various addition alloys tested were also evaluated using the following standards:

Rate of solution

Scale

1 Almost instantaneous solution as typified by ferrosilicon pure enough to have virtually no inoculating effect.

2 Moderately fast with perceptible solution time of less than 30 seconds.

3 Slower than 2 but fast enough to dissolve within about one minute.

4 Slower than 3 and questionable whether complete solution is reached after one minute.

5 Incomplete solution after one minute or more.

Dross-forming characteristics

Scale

A Virtually no dross, as in the case of ferrosilicon pure enough to have practically no inoculating effect.

B Light dross that may require skimming but does not usually result in defective castings.

C Dross that usually requires skimming to avoid defective castings.

D Heavy dross that requires extensive and continued skimming; sound castings are produced with difficulty.

Refractoriness of dross

Scale

S Stiff and coagulating, covering less than 25% of metal surface.

L Liquid, covering less than 25% of metal surface.

V Viscous-fluid, covering virtually 100% of metal surface.

The following Table I sets forth data obtained in the preparing and testing of cast specimens in the manner hereinbefore described and also data obtained as a result of field tests.

TABLE I

	Test Specimen	Additional Alloy			Percent Ba	Percent Mn	Percent Zr	Percent Fe	Percent Si added to Cast Iron		Percent Chill Reduction		Rate of Sol.	Dross
		Percent Si	Percent Al	Percent Ca					Soft Iron	Hard Iron	Soft Iron	Hard Iron		
I	12/W-961	63	1	3.5	2.5	6	6	Bal.	.15	.3	100	96	3	CS
II	42/SZ-51	66	0.62	2.13	1.55	5.6	3	Bal.	0.2		98		3	BS
III	36/SZ-51	63	0.5	1.10	1.23	4	2.28	Bal.	0.2		98		2–3	BS
IV	SMZ	63	1	3.5		~6	~6	Bal.	0.2		72		3	CV
V	19/SZ-51	66	0.9	5.2	1.25			Bal.	0.2				4	CV
VI	2/W-647	65	1.5	10	5			Bal.	0.15	0.3	85	91	5	DS
VII	1/W-646	65	1.5	15				Bal.	0.15		66		5	DV
VIII	15/W-881	75	1	2.5	5			Bal.	0.15		74		3	DS
IX	15/W-880	75	1	2.5	2.5			Bal.	0.15		88		3	CS
X	4/SZ-51	75	<0.4	<0.5	<0.5			Bal.	0.2		72		1	AL
XI	90408	65.9	0.73	4.15		4.79	6.04	Bal.						DV
XII	19SZ-51	66.8	0.90	5.2	1.25			Bal.						DV
XIII	5/SZ-51	77	0.5	0.5	1.03			Bal.	0.2		97		1	BL
XIV	2/W-647	65	1.5	10	5			Bal.		0.3		91	5	DS
XV	12-A/887	63	1	3.5	5	6	6	Bal.	0.15		100	91	4	DS
XVI	3B/W-958	65	1	3.5	5	10		Bal.	0.2		96		4	DS
XVII	10/W-885	63	1	3.5	5	6	3	Bal.	0.15	0.3	99	96	3	DS

As can be seen from the data of Table I, the first three additional agents, which are in accordance with the present invention, provide the most desirable combinations of properties. For example, the chill reduction is greater than 95% in each case, the solution times are 1 minute or less, and the dross is essentially non-interferring.

On the other hand, the other addition agents shown in the table, which are not in accordance with the present invention provide a combination of lesser chill reduction and generally undesirable dross formation and solution times.

It is to be particularly noted that Tests XIII, XIV, XV, XVI, and XVII shown in Table I illustrate the criticality of the compositional ranges of the present invention by showing that alloy addition agents which are effective in reducing chill depth do not necessarily have suitable solution times or dross forming characteristics.

In addition to the aforedescribed tests, various comparative field tests were conducted using the addition agents listed below.

FIELD TEST ADDITION AGENTS

A	(SQ-29)	64.8 Si	0.8 Al	1.5 Ca	2.8 Ba	6.3 Mn	5.3 Zr	Bal.	Fe
B	(4SZ2-51)	61.1 Si	0.55 Al	2.13 Ca	1.55 Ba	5.65 Mn	2.82 Zr	Bal.	Fe
C		62 Si	1.0 Al	3.5 Ca		6 Mn	6 Zr	Bal.	Fe.
D	(90408)	65.9 Si	0.73 Al	4.15 Ca		4.79 Mn	6.04 Zr	Bal.	Fe
E	(19SZ-51)	66.8 Si	0.96 Al	5.20 Ca				Bal.	Fe

As can be seen addition agents A and B are in accordance with the present invention while addition agents C, D and E are not.

In the first of the field tests the addition agents B, D and E were separately used in the amount of about five pounds per 2500 pounds of cupola iron. The additions were made during tapping of the iron into identical foundry ladles. Motion pictures were taken of the dross floating on the surface of the iron in order to obtain a comparison of the type and quantity of the dross resulting from the various additions.

In the use of addition agent B of this invention the results were substantially the same as for Test Specimen 42/SZ–51 as noted in Table I. The average coverage of the metal surface was 18% using addition agent B and the dross was dry or easily skimmed.

Addition agents D and E each resulted in a DV type dross and the average metal coverage for each was about 80%.

In a further field test, using addition agents A and C, five pounds of addition alloy were added per ton of cupola iron. The use of addition agent A resulted in a relatively small amount of "dry" dross and about a 19% improvement in chill reduction as compared to the results obtained using addition agent C.

In another test, adding two pounds of addition alloy per 800 pounds of cupola iron, addition agent A provided about a 37% improvement in chill reduction as compared to the results obtained using addition agent C.

In still another test, about 1.5 pounds of addition alloy were added in the ladle to 900 pounds of cast iron, the treated iron being held in the ladle for about 8 minutes before pouring. The chill depth in castings from the metal treated with addition agent A was 7 mm. as compared to 12 mm. for the same castings from metal treated with addition agent C.

In all of the foregoing field tests, the dross resulting from the use of addition agent A was substantially drier and in substantially smaller amounts as compared to the dross resulting from the use of addition agent C.

What is claimed is:

1. An addition alloy for use in the manufacture of cast iron consisting essentially of about 35 to about 85% silicon, about 0.5 to about 1.5% aluminum, about 0.5 to about 4% calcium, about 0.5 to about 4% barium, about 2 to about 7% manganese, about 2 to about 7% zirconium, balance iron.

2. An addition alloy for use in the manufacture of cast iron consisting essentially of about 60 to about 65% silicon, about 0.75 to about 1.25% aluminum, about 1 to about 2.5% calcium, about 2 to about 3% barium, about 5 to about 7% manganese, about 5 to about 7% zirconium, balance iron.

3. An addition alloy for use in the manufacture of cast iron consisting essentially of about 63 to about 66% silicon, about 0.5% to about 1% aluminum, about 1 to about 2.5% calcium, about 1 to about 2% barium, about 4 to about 6% manganese, about 2 to about 3% zirconium, balance iron.

4. An addition alloy for use in the manufacture of cast iron consisting essentially of about 63% silicon, about 1% aluminum, about 3.5% calcium, about 2.5% barium, about 6% manganese, about 6% zirconium, balance iron.

5. An addition alloy for use in the manufacture of cast iron consisting essentially of about 66% silicon, about 0.6% aluminum, about 2.1% calcium, about 1.6% barium, about 5.6% manganese, about 3% zirconium, balance iron.

6. An addition alloy for use in the manufacture of cast iron consisting essentially of about 63% silicon, about 0.5% aluminum, about 1.1% calcium, about 1.2% barium, about 4% manganese, about 2% zirconium, balance iron.

7. An addition alloy for use in the manufacture of cast iron consisting essentially of about 65% silicon, about 0.8% aluminum, about 1.5% calcium, about 2.8% barium, about 6.3% manganese, about 5.3% zirconium, balance iron.

8. An addition alloy for use in the manufacture of cast iron consisting essentially of about 61% silicon, about 0.6% aluminum, about 2.1% calcium, about 1.6% barium, about 5.7% manganese, about 2.8% zirconium, balance iron.

References Cited by the Examiner

UNITED STATES PATENTS

2,767,084	10/1956	Chandler	75—134
2,810,639	10/1957	Kessler	75—134 X
2,950,187	8/1960	Ototani	75—124 X
3,137,570	6/1964	Mickelson	75—124
3,215,525	11/1965	Sprankle	75—134

HYLAND BIZOT, *Primary Examiner.*

R. O. DEAN, *Assistant Examiner.*