

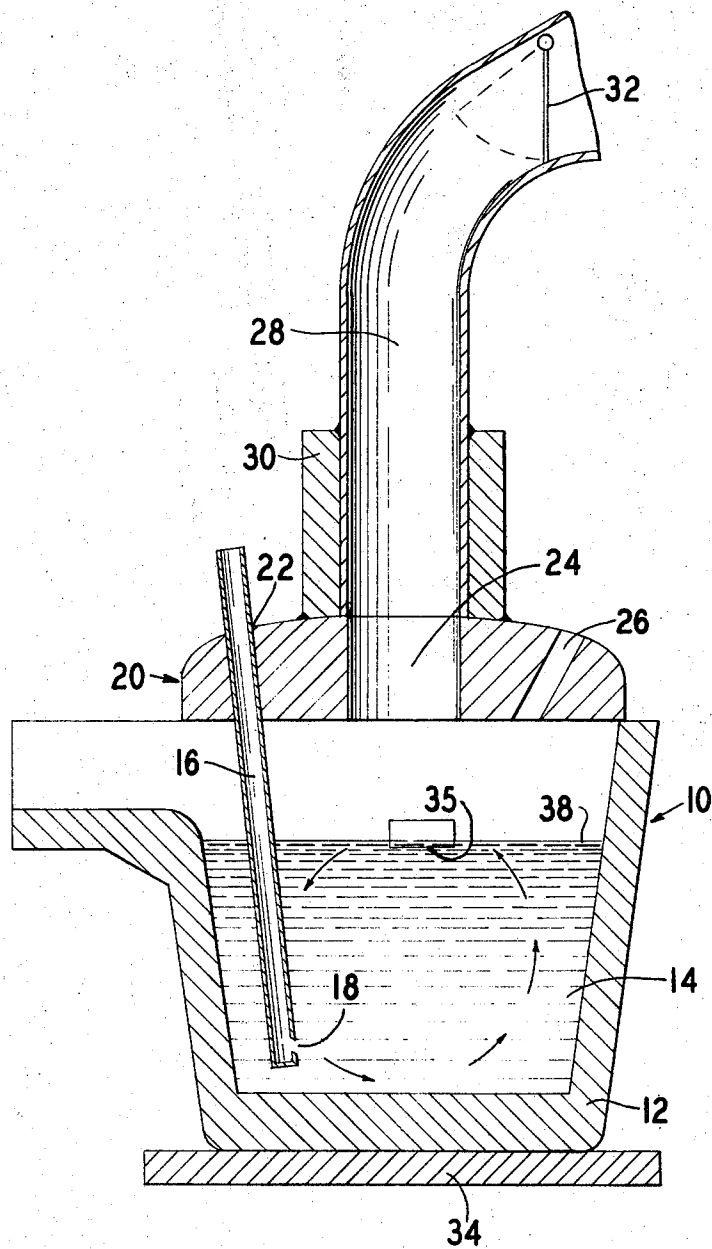
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ALLOY ADDITION PROCESS

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ALLOY ADDITION PROCESS

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8 Claims

ABSTRACT OF THE DISCLOSURE

A method for homogeneously intermixing a metal bath and a solid additive by means of gas agitation. A non-reactive gas is fed through a refractory tube at an angle into a molten bath to impart a rolling motion to the bath in a vertical plane. A solid material is then added to the bath and is evenly dispersed therein by the motion of the bath.

BACKGROUND OF THE INVENTION

Field of invention

This invention relates generally to a method of adding a solid material to a metal bath and more specifically to a method for homogeneously admixing and dissolving a solid additive and a metal bath by gas agitation.

Description of prior art

A wide variety of metallurgical processes involve the addition of a solid material to a molten metal. Carburization, desulfurization and the formation of alloys are just a few of many possible examples of such processes.

Invariably, some form of agitation is employed to stir the additive material into solution. One method of agitating the metal bath is achieved by introducing a non-reactive gas to cause a violent turbulence in the metal solvent. All too often, however, the turbulence is confined to a specific area of the metal bath and the additive is not properly dissolved or evenly dispersed. Furthermore, some additives such as magnesium react with certain metals to cause dangerous flaring and violent agitation is unacceptable in such circumstances.

Magnesium ferrosilicon alloy having a uniform, homogeneous character is one example of an alloy which is difficult to produce. The difficulty is primarily due to the inherent disadvantages of the conventional methods employed by the industry for the production of this alloy. Ordinarily, the magnesium ferrosilicon is prepared by forming a molten bath of ferrosilicon and manually plunging a suitable quantity of rectangular magnesium ingots which have been removably attached to an iron bar into the molten bath. Each ingot is disengaged from the iron bar as it is submerged and dissolved in the bath. Another ingot is then inserted and the process continues until the necessary quantity has been added. Manual stirring of the bath is often a part of this "plunging" process and is used to provide the required agitation.

As can be readily appreciated, achieving product uniformity by this method is an arduous task. The admixed materials are sometimes undesirably segregated in the bath. Thus, when the material is poured from the ladle into the chills where it is to be formed into the end product, it is already non-uniform. It is not uncommon when employing this process to obtain a magnesium content of 12% at the top of a ladle and as low as 6% at the bottom.

There are additional problems associated with the aforementioned "plunging" process which have an adverse effect on the economical production of this important alloy. For example, high cost magnesium ingots of a particular shape are required to ensure success. Furthermore, uniform temperature control of the bath is difficult and more importantly the temperature which the bath must

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achieve is extremely high, thereby increasing magnesium fume losses. In addition, ladle skulling is a predominant source of concern.

SUMMARY OF THE INVENTION

It is a primary object of this invention to provide a method for dissolving and evenly dispersing a solid additive in a molten metal bath, which method is useful in a number of metallurgical processes.

It is a particular object of this invention to provide a method for efficiently producing a homogeneous magnesium ferrosilicon alloy.

Broadly, the method of the invention comprises passing a non-reactive gas at an angle into a molten metal for a time and at a rate sufficient to impart a rolling action to the bath in a vertical plane. A solid material, either in particulate or massive form, is then deposited on the surface of the bath and is caused to be dissolved and evenly dispersed by the rolling action.

More specifically, the process of the invention comprises introducing a metal bath into a ladle at a suitable molten temperature, placing a refractory tube into the bath, the tube being provided with a small opening near the end which is submerged, positioning the tube near a side wall of the ladle, directing the opening toward the center of the bath, maintaining the tube and/or the opening at an angle with the surface of the bath, passing a non-reactive gas such as nitrogen through the tube and into the bath at a rate which causes a rolling of the bath, and contacting the bath with a material such as magnesium, the continued rolling action dissolving the magnesium and causing it to be uniformly dispersed. The ladle is preferably provided with a cover during the process to further enhance the success of the operation since the cover shields the magnesium or other additive from oxygen and radiant heat losses, thereby permitting a higher additive recovery.

The tube which carries the gas to the bath must be properly positioned if the rolling action is to be achieved and if the process is to be most efficiently carried out. It has been discovered that best results are obtained when the tube is positioned nearer the bottom of the ladle than the surface of the bath and near an inside surface of the ladle. The opening which is drilled in the tube for the escape of gas preferably is as small as possible such as a diameter of between $\frac{1}{8}$ inch and $\frac{3}{4}$ inch to reduce the quantity of gas which is used during the process and to obtain the proper rolling motion. If an opening having too large a diameter is employed, the excess gas will tend to bubble the bath causing poor circulation thereof, and a costly amount of gas will be consumed. For proper operation, the tube or opening is set at an angle of preferably between 15° and 65° with respect to the uppermost surface of the bath and the gas flow must be directed to approximately the center of the ladle. In no event should the opening be set in a vertical position with respect to a horizontal bath surface since the rolling circulation would not be achieved. Gas flow rate is set such that a moderate rolling effect is created. The flow must not be so great as to cause significant splashing since this would have an unfavorable effect on additive recoveries and uniform dispersion would not be thereby accomplished, nor must it be so slow as to be ineffective.

The method of the invention will be more readily understood by referring to the drawing wherein the sole figure illustrates in cross section an apparatus which is suitably employed in the process of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In the drawing, a ladle 10 having an inner lining 12 of a suitable material such as carbon paste contains a

bath of molten metal 14. A tube 16, preferably composed of graphite, is positioned in the bath 14. The tube 16 is provided with an opening 18 through which a gas under pressure passing through the tube egresses into the bath. A cover 20 is placed over the ladle 10 and is provided with channels 22, 24, 26. As illustrated, channel 22 encloses tube 16 and provides partial support therefor, channel 24 permits passage of an additive material into bath 14 and the escape of gas from the ladle, and channel 26 is used to observe the temperature of the bath 14 with pyrometric means (not shown). A chute 28 is in communication with channel 24 and is rigidly supported by support column 30. A movable gate 32 is positioned at the uppermost portion of the chute 28. The entire assembly is conveniently placed on a scale 34 so that careful observation of the weight of the alloy or other material being processed may be carried out.

In operation, an additive such as magnesium is inserted into the chute 28 through gate 32 and passes through channel 24 in cover 20 and into bath 14. A non-reactive gas under pressure is fed into tube 16 and through opening 18. The gas causes the bath to roll in a vertical plane as illustrated by the arrows in the drawing and thereby aids in dissolving that portion of the solid magnesium 35 which is below the surface of the bath (about $\frac{1}{3}$ of its mass) and also provides equal distribution of the magnesium as it is dissolved. It will be appreciated that this type of agitation permits additives of any size or shape to be dropped on the surface 38 of the bath since it is quickly dissolved and dispersed throughout the bath and this is particularly important with respect to magnesium which heretofore had to be manually submerged in a ferrosilicon solution to avoid concentration of the magnesium near the surface and the subsequent volatilization and flaring that would occur.

The invention will now be more specifically described with respect to the processing of magnesium ferrosilicon alloy. In the preparation of this alloy, a ferrosilicon melt or bath is prepared by any convenient technique. For example, smelting quartz and steep scrap to obtain a 50% iron and 50% silicon melt is a commonly employed technique. The ferrosilicon bath is then transferred into a ladle of the type illustrated in the drawing at a temperature of about 1600° C.

Prior to the addition of the magnesium, a nonreactive gas such as argon, nitrogen or mixtures thereof is passed into the ferrosilicon bath at a suitable angle. The incoming gas exerts a pressure in the lower part of the bath in a direction so as to cause the bath to roll in a vertical plane toward the surface providing a continuously changing surface and a continuously changing melt in contact with the magnesium additive. This maintains at all times a dilute concentration of magnesium in the melt thereby avoiding volatilization of the magnesium and ensuring highly uniform magnesium distribution. The continued scrubbing action retards skull formation at the side of the ladle. Continued pressure from the gas stream causes a gentle rolling action which may be described as more than a ripple but less than significant splashing to exist at the surface of the bath as well as below the surface.

The magnesium material is added in an amount equal to about 3 to 10% by weight of the ferrosilicon melt. It may be of any size or shape when added, it having been determined that magnesium bodies having dimensions of 12 inches in diameter and 15 inches long may be added every 10-15 seconds until the desired quantity is achieved. It is to be emphasized, however, that when the process of the invention is used, magnesium bodies added need not be uniform in size and may be added in chunks of any size, which is a decided advantage in the processing of this alloy. When the magnesium is dropped onto the rolling surface of the ferrosilicon bath, about $\frac{1}{3}$ of the mass deposited submerges, is dissolved and evenly dispersed by the rolling action above and below the surface. The remainder of the magnesium is dissolved in several sec-

onds. When a sufficient quantity of magnesium has been added, the gas agitation may be continued for several minutes to continue mixing the alloy melt or it may be discontinued immediately. The molten alloy is then poured from the ladle into chills where it is solidified.

It will be appreciated that other materials may be added in small quantities to the bath in the process of the invention without adversely affecting the quality of the magnesium ferrosilicon alloy produced. For example, if a small percentage of calcium is desired in the final alloy, calcium silicon may be added in proper quantities after the magnesium is added. In this manner, a magnesium ferrosilicon alloy having $1\frac{1}{2}$ % calcium content was prepared according to the instant process.

It has been further discovered that the addition of 50 pounds of magnesium ferrosilicon fines to 8000 pounds of ferrosilicon bath lowers the temperature of the bath 10° C. Thus, lower bath temperatures may be achieved if desired by the addition of coolant materials without noticeably influencing the alloy homogeneity. In addition, after the magnesium is added, iron may be added in small quantities to reduce the level of silicon in the final alloy to a preferred percentage, such as 46-48%.

The following example is illustrative of the manner in which magnesium ferrosilicon alloy was made according to the teachings of this invention.

EXAMPLE

Molten ferrosilicon (50% iron and 50% silicon) in the amount of 8000 pounds was poured into a ladle and maintained at a temperature of about 1390° C. The ladle had dimensions of 4.5 feet upper diameter and 5 feet, 8 inches height and a volume of 67 cubic feet. A space of about 2 feet existed between the surface of the ferrosilicon bath and the top of the ladle. A graphite tube, 3 inches outside diameter and $\frac{3}{4}$ inch inside diameter, was positioned 6 inches from the bottom of the ladle and about 6 inches from the side wall measured at the bottom of the tube. The side wall of the tube was provided with an opening $\frac{1}{4}$ inch in diameter and the tube was positioned such that the opening formed an angle of 45° with respect to the surface of the bath and faced the bottom of the ladle. Nitrogen gas was passed through the tube and into the bath at a rate of 800 cubic feet per hour. The tube opening was directed toward the center of the ladle such that the gas caused a pressure in the bath which was initially in the direction of the bottom of the ladle near the tube but which was also transmitted across the center of the ladle in a vertical plane toward the surface portion diametrically opposite the tube. In this manner, the rolling motion hereinbefore described was generated. Magnesium bodies 12 inches in diameter and 15 inches long were added every 15 seconds until a total of about 800 pounds of magnesium had been added. The magnesium bodies were each quickly dissolved and evenly dispersed in the ferrosilicon. The alloy was then poured from the ladle into chills and solidified. The final alloy contained about 9% magnesium which was evenly dispersed throughout.

In order to test the effectiveness of the instant invention, five pound samples of molten alloy processed in accordance with the teachings of this invention were taken in cups as the alloy was being poured from the ladle into chills. The samples were taken each time the molten metal was being poured into a new chill, there being approximately four chills filled with each ladle. Another cup sample was taken as the last chill was being filled. Each cup was tested for magnesium content, by X-ray analysis, Table 1 sets forth the data obtained in these tests for 17 ladles of alloy. In addition, four ladles of molten magnesium ferrosilicon alloy prepared in accordance with the aforementioned "plunging" process were tested for magnesium content in the same manner, that is, five pound cup samples were taken from the molten alloy as it was.

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being poured into chills. Four cups were taken for each ladle, one cup each time the alloy was poured into a new chill. Table 2 sets forth the percent magnesium in each cup, the analysis again being made by X-ray.

TABLE 1

Cup	Percent magnesium							
	1	2	3	4	5	6	7	8
1.....	9.45	10.33	9.63	11.15	10.12	10.46	10.28	10.32
2.....	9.60	10.07	9.98	11.21	10.11	9.60	8.88	10.17
3.....	9.50	9.99	9.62	11.44	9.88	9.82	10.38	10.27
4.....	9.70	10.14	9.80	10.63	9.89	10.19	9.63	10.15
5.....	9.63	9.62	9.49	10.89	9.64	10.40	9.17	10.75
Range.....	0.25	0.71	0.49	0.81	0.48	0.86	1.50	0.60

Cup	Percent magnesium							
	10	11	12	13	*14	15	16	17
1.....	5.15	6.20	5.37	6.04	9.30	9.94	9.26	9.05
2.....	5.28	6.17	-----	6.10	9.42	9.85	9.38	9.14
3.....	5.46	6.20	5.75	5.92	9.47	10.27	9.15	9.15
4.....	5.22	6.40	5.24	5.68	9.44	9.95	9.13	8.89
5.....	4.56	5.82	5.49	5.91	6.19	10.20	9.27	9.04
Range.....	0.90	0.58	0.51	0.42	3.28	0.33	0.25	0.26

*Hole in graphite tube turned away from center of ladle.

TABLE 2.—“PLUNGING PROCESS”

Cup	Percent magnesium			
	1	2	3	4
1.....	10.82	10.12	12.41	9.93
2.....	10.90	10.99	11.33	9.71
3.....	8.48	10.90	9.97	7.26
4.....	6.55	8.28	6.58	6.14
Range.....	4.27	1.84	5.83	3.79

The tables clearly indicate that the alloy prepared in accordance with this invention exhibited a much greater homogeneity than when made by the prior “plunging” process.

Another improvement which is observed when the process of the invention is carried out is the reduction in the quantity of skull which forms in the ladle. When skull is formed, costly labor is needed to remove it from the walls of the ladle. The removed skull is not saleable and, therefore, must undergo further processing. With the instant process, superheated alloy in the center of the bath is constantly circulated along the wall of the ladle where the alloy usually freezes out, and therefore prevents the skull from forming.

In another series of tests, sixteen batches of magnesium ferrosilicon alloy containing 9% of magnesium which was prepared by the method of the invention at an additive temperature of between 1370° C. and 1400° C. left an average skull residue in the ladle of 77 pounds per batch. Eleven batches of 5% magnesium alloy prepared in the same manner at an additive temperature of 1350° C. left a skull residue of 75 pounds per batch. Both average skull values are well below the values obtained by the “plunging” process.

The temperature at which the magnesium can be successfully added has been lowered significantly in the process of the invention. Normally, a temperature of 1500° C. is required for the ferrosilicon bath when the “plunging” process is employed whereas a bath temperature of about 1370° C.—1390° C. for a 9% magnesium alloy and about 1340° C.—1350° C. for a 5% magnesium alloy is all that is required in the instant process. The probable reason for this important effect is the fact that there is less temperature differential in the ladle due to the total agitation provided by the gas.

From the foregoing, it will be appreciated that the pro-

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cess of the invention is efficient and economical and provides more uniform magnesium ferrosilicon alloy than heretofore was capable with prior art processes. In addition, the process of the invention permits various materials to be added to a ferrosilicon bath solution to alter the alloy mixture or to cool the bath. Such additions were not possible with prior art processes because of difficulty of dispersion of the added materials.

While the invention has been described in detail with respect to a specific alloy, it will be appreciated that it is applicable to a wide variety of metallurgical processes such as desulfurizing, carburizing and the like. For example, the process was employed to desulfurize 700 pounds of pig iron. Calcium carbide in an amount of 1½% by weight of the iron was added after gas agitation in accordance with the aforementioned teachings was applied, and the carbide was evenly dispersed in the iron. The sulfur content of the iron was reduced from 0.11% to less than 0.03%, using the process of the invention. In addition, other alloys such as ferroaluminum silicon or strontium silicon and many others may also be effectively produced by this method.

What is claimed is:

1. A process for the addition of a solid material to a molten bath of metal, comprising

- placing the molten metal bath in a ladle;
- directing a stream of non-reactive gas into said bath in a downward direction at an angle with the surface of the bath, said gas being provided at a rate and in a direction toward the center of the bath which is sufficient to impart a rolling movement in a vertical plane to a substantial portion of said bath; and
- depositing a solid material on the surface of said bath, said rolling motion of the bath causing said solid material to be dissolved and dispersed throughout said bath whereby a homogeneous mixture is achieved.

2. A process for the addition of a solid material to a molten bath of metal, comprising

- placing the molten metal bath in a ladle;
- submerging a portion of a tube in said bath, said tube having an opening in that portion which is submerged, said opening being positioned at an angle with respect to the surface of said bath and being maintained at a bath level nearer the bottom of said ladle than said surface of said bath;
- positioning said submerged portion of said tube proximate a side wall of said ladle and directing said opening toward the center of said bath;
- passing a non-reactive gas through said tube and said opening into said bath at a rate sufficient to impart a rolling movement in a vertical plane to a substantial portion of said bath, and
- depositing a solid material on the surface of said bath, said rolling motion of the bath causing said solid material to be dissolved and to be dispersed throughout said bath whereby a homogeneous mixture is achieved.

3. The process of claim 2 wherein said opening is positioned at an angle of between 15° and 65° with respect to the surface of said bath.

4. The process of claim 3 wherein said solid material is magnesium and said bath is composed of ferrosilicon.

5. The process of claim 3 wherein said tube is graphite and said opening in said tube is between ⅛ inch and ¾ inch in diameter.

6. The process of claim 4 wherein said magnesium is added in an amount of about 5% by weight of said ferrosilicon bath and the temperature of said bath during said process is between 1340° C. and 1350° C.

7. The process of claim 4 wherein said magnesium is added in an amount of about 9% by weight of said ferrosilicon bath and the temperature of said bath during said process is between 1370° C. and 1390° C.

8. The process of claim 3 wherein said solid additive

material is calcium carbide and said bath is composed of iron.

References Cited

UNITED STATES PATENTS

2,853,376	9/1958	Blanc et al.	75—59 X
3,058,822	10/1962	Volianik	75—129 X
3,333,954	8/1967	Dawson	75—129

FOREIGN PATENTS

760,561 10/1956 Great Britain 266—34

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