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ALLOY ADDITION AGENT

Earle R. Saunders, Grand Island, N.Y., and Richard L. Pope, Old Greenwich, Conn., assignors to Union Carbide Corporation, a corporation of New York

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This invention relates to alloy addition mixtures, and more particularly concerns improved non-exothermic alloy mixtures for the incorporation of major amounts of alloying ingredients into low alloy steels during tapping.

In the production of low alloy steels, where alloying operations are necessary to impart special physical properties to the finished product, the improved and more uniform recoveries obtained from ladle additions compared with those obtained from additions made to the furnace using high-metallic oxide-containing slags have resulted in greater use of ladle addition agents. Since commercial open hearth furnaces are tapped in about five minutes, it is essential that these alloy agents be characterized by a rapid rate of solution. Otherwise the steel in the ladle will be non-uniform resulting in ingots of varying compositions. Additions of loose, finely comminuted alloys to achieve rapid solution result in low recoveries due to air oxidation at the surface of the steel.

In recent years exothermic ladle additions have been developed and used extensively. These products consist of crushed alloy, bonded into briquettes or larger aggregates, and contain chemicals which react to develop heat when the material is added to steel. The relatively small basic particle size of the alloy promotes rapid solution, and the chemical heat generated compensates in part for the chilling action resulting from solution of the alloy.

However, while satisfactory in most respects, certain disadvantages are attendant with the use of exothermic products for adding alloying ingredients to ferrous melts. The exothermic reaction will yield end products which contaminate the melt to some extent. For example, present exothermic commercial products contain sodium nitrate as the oxidant, which results in the generation of nitrogen gas as an end product, and the probability of contaminating the steel with this element. In addition, unless precise control of the balance between the reducing agent and the oxidant is maintained, some recovery of the silicon or aluminum normally employed to react with the nitrate may occur in steels in which an increase of these elements is often undesirable. Moreover, the reactants in exothermic products dilute the useful alloy content, resulting in a bulkier addition. Finally, these exothermic products are inherently more expensive than the base alloy.

A further problem arises when reactive metals such as aluminum are added to the steel melt. In order to compensate for loss of aluminum due to air oxidation, quantities beyond those required to deoxidize or alloy with the steel must be added. This practice results in the production of an excessive quantity of aluminum oxide, thereby increasing the likelihood of inclusions in the final product and substantially reducing the recovery of alloying aluminum. Air oxidation of aluminum is aided materially by its low density which causes it to float on the surface of the molten metal. Furthermore, tapping stream conditions vary widely from heat to heat, making it difficult to maintain the necessary close control of residual aluminum content.

The present invention aims to obviate the above difficulties and to secure alloy addition mixtures for steel melts and other uses which are efficient and economical to use for most low alloy steels of commercial interest.

It is, therefore, an important object of the present invention to provide an improved alloy addition mixture for adding alloy to a ferrous melt wherein a binder material is utilized to assist in promoting rapid solution.

Another object of the present invention is to provide an improved alloy additive and method of producing alloy steel in which reduced oxide inclusions are present in the resultant steel and alloy recovery is improved.

Another object of the present invention is to provide an improved alloy addition mixture for adding alloy to a ferrous melt having an improved rate of solution without resort to exothermic ingredients, thereby substantially minimizing the extent of undesirable contamination.

Other objects, features, and advantages of the present invention will be apparent from the following detailed description of a preferred embodiment thereof.

According to the invention, an organic binder material is utilized in a mixture comprising one or more alloy addition agents to attain an improved rate of solution comparable to that of exothermic addition agents heretofore produced for this purpose without the undesirable contaminating effects associated with such exothermic addition agents. Thus there is provided an addition mixture for a ferrous melt containing an aggregate of finely-divided alloy additive and a finely-divided organic binder therefor, the organic binder being readily combustible upon introduction of the mixture into the melt, and capable of developing gaseous reaction products, thereby causing agitation of the melt and promoting a rapid dissolution of the alloy additive. More particularly, there is provided a finely-divided alloy mixture consisting of 88 percent to 99.5 percent alloy mixture, and the remainder an organic binder which when dissolved in a steel melt, evolves gases for turbulently agitating the melt, thereby promoting the uniform dissolution therein of the alloy additive.

Although the subject material results in greater chilling of the bath, this increase is not objectionable for alloy additions less than 1.5 percent, which constitutes the field of primary interest in ladle additions. This is to be distinguished from the prior practice of introducing major amounts of alloying material in the furnace prior to tapping.

The alloy addition agent or non-exothermic addition mixture of the invention may comprise any desired constituents for alloying with the metal bath, for example, ferrous or non-ferrous alloys, low melting metals such as aluminum, or refractory metals such as chromium, manganese, vanadium, zirconium, tungsten, titanium and columbium. When aluminum is incorporated into a melt as an alloying component, it may comprise from 20 percent to 70 percent of the addition mixture while at least one other alloying agent other than aluminum may be present in a similar range.

As a second important use of aluminum, it is occasionally desirable to provide in the total alloy additive an amount of aluminum sufficient to effect deoxidation of the melt. A familiar example would be the production of a steel for deep-drawing applications. When used in this connection, up to approximately 5 pounds of aluminum per ton of steel is added for deoxidation purposes. The amount required depends upon the carbon content of the melt, which in turn governs the oxygen in the steel. Tapping conditions must also be considered. The end requirement is to obtain .02 percent to .07 percent residual aluminum in the steel.

A third important use of aluminum arises when adding highly reactive metals such as titanium and zirconium.

For example, part of the titanium reacts with oxygen to form TiO_2 a highly refractory substance, which inhibits the rate of solution of the remaining Ti. To avoid this condition, and to improve the rate of solution, it has been found desirable to incorporate fluxing materials such as CaF_2 and aluminum to form Al_2O_3 in the addition mixture of the invention. When used in this manner, aluminum may be present in quantities up to 5 percent.

It should be understood that the above three uses of aluminum are given merely as examples. They are not mutually exclusive and may be combined as desired. Aluminum may be added as an alloying ingredient, for example, and also be present in additional quantities for deoxidation.

The binder material to be used in the alloy addition mixture of the invention may comprise an organic binder which is substantially non-oxidizing in nature and which generates gases when the mixture is added to molten steel. By making use of such a non-oxidizing binder, oxidation of the alloy before entering into solution is prevented. In the process of the invention, the development of gaseous reaction products causes a desirable agitation of the bath, promoting solution and uniform distribution of the alloy. Examples of suitable binders which may be used in the practice of the invention are wood rosins and higher melting derivatives thereof, as well as synthetic and natural resins which will not cake during storage. Rosins that may be suitably applied in the practice of the invention are usually constituted of abietic acid ($C_{20}H_{30}O_2$), and complexes thereof. Binder materials that are most desirable are those which will not introduce impurities into the melt, will decompose at temperatures above approximately 75° C., and are substantially non-oxidizing. A thermoplastic resinous binder material of this character is marketed under the trade-mark "Corex." The "Corex" binder material is recovered from the refining of wood rosin. It is insoluble in petroleum naphtha, soluble in alcohols, and partially soluble in coal tar solvents.

The composition of the alloy addition mixture of the invention may be varied over a considerable range without impairing its properties. Because of this, the non-exothermic addition mixture of the invention is applicable to a variety of steel-making procedures practices in different steel mills. For example, in its broadest aspect, a substantial percentage of useable alloy additives may be efficiently incorporated in a steel melt when the composition of the addition mixture is within the following range:

	Broad, percent	Narrow, percent
Alloy additive	88 to 99.5	95 to 99
Binder	0.5 to 7	1 to 3
CaF_2	0 to 10	0 to 3
Al (exclusive of alloying Al)	0 to 5	0 to 3

The addition mixture of the invention may be loosely packed in suitable containers to facilitate the handling thereof in either the shipping or storage stages or in administering it to a steel melt. To do this, each of the additive ingredients is first comminuted so as to pass through screen mesh openings of ¼ inch or less. A more desirable range of particle size is one wherein the alloying material is at least capable of passing through a 20 mesh screen (.833 mm. openings), the preferred size being inversely related to the density of the alloying ingredient. The ingredients are then well mixed and bonded as by baking the mixture in a suitable can at a low heat. The heating period is maintained for a period sufficient to melt the binder and cohere the particles so that upon cooling, a bonded mass is obtained.

The effectiveness of the present invention wherein organic binder material is employed to compact aggregates of finely divided alloy additives will be described for simplicity in connection with the addition of elemental manganese and aluminum and of ferroalloys of chromium and manganese, although it is to be understood that the invention is not limited thereto, but is susceptible of application with various other metals, alloys and ferroalloys.

EXAMPLE I

A sufficient quantity of alloy material consisting of finely divided electrolytic manganese bonded with about 1.8 percent wood rosin was added to a 100 pound bath of molten steel to raise the manganese content of the steel 1 percent, the bath being at a temperature of about 1600° C. The material dissolved in about 13 seconds and a temperature drop of about 11° C. was recorded. Analysis showed 91 percent recovery of the manganese in the steel.

EXAMPLE II

A mixture of 98.5 percent of 20 mesh ferrotitanium alloy and 1.5 percent rosin was added to a 100 pound bath of molten steel. The metal dissolved in approximately 2 minutes and 45 seconds. In similar tests employing CaF_2 and/or aluminum for fluxing purposes, the solution times were markedly reduced as shown in the following test data:

Composition, Percent				Solution Rate, Seconds
FeTi	Rosin	CaF_2	Al	
93.2	1.8	3	2	31 to 35
93.5	1.5	5	-----	39

EXAMPLE III

Medium-carbon ferromanganese was comminuted to pass through a 20 mesh screen (.833 mm. openings) and aluminum to pass through a 5 mesh screen (3.96 mm. openings). A mixture was formed using 61 percent ferromanganese, 34 percent aluminum, 3 percent CaF_2, and 2 percent wood rosin. The ingredients were bonded by baking the mixture in a suitable can at low heat so that, upon cooling, a bonded mass was obtained. This mixture was then used as an additive in small scale tests. The following table indicates the great improvement in the recovery of aluminum and manganese over the recoveries obtained in prior commercial practice.

	By Normal Commercial Practice	By Small Scale Tests Using The Present Invention
	Percent	*Percent*
Al Recovery	Approx. 25	52.5
Mn Recovery	75–85	90.0

EXAMPLE IV

Medium-carbon ferromanganese was comminuted to pass through a 20 mesh screen (.833 mm. openings) and aluminum to pass through a 5 mesh screen (3.96 mm. openings). A mixture was formed using 73 percent ferromanganese, 25 percent aluminum, and 2 percent wood rosin. The ingredients were bonded by baking the mixture in a siutable can at low heat so that, upon cooling, a bonded mass was obtained. This mixture was then used as an additive in small scale tests. The

following table indicates the improved recovery of aluminum and manganese.

	By Normal Commercial Practice	By Small Scale Tests Using The Present Invention
	Percent	*Percent*
Al Recovery	Approx. 25	45
Mn Recovery	75–85	Approx. 100

Analysis of the steel samples produced in accordance with the present invention indicated that the number of oxide inclusions contained therein was at the low end of the range encountered in ingots produced by normal commercial practice.

In order to further indicate the scope of the present invention, the following Table I sets forth the results of typical heats wherein approximately 1 percent manganese or chromium was added to each of three 100 lb. steel heats to determine the rate of solution and temperature drop. In each instance, the alloying ingredient in the form of a ferroalloy, was comminuted to below 20 mesh size and bonded with about 1.5 percent of a thermoplastic resin derived from wood rosin. The bonded mixture was added as pieces 1 inch by ¼ inch. The information contained in Table I compares favorably with the approximate temperature drop of about 11° C. and a solution time of from 25 seconds to 30 seconds which characterizes exothermic pellets when employed in similar tests.

Table I

Percent Composition of Ferroalloy Addition				Maximum Mesh Size of Ferro-alloy Component	Time For Solution, Seconds	Temperature Drop, ° C.
Mn	Cr	C	Si			
81.31	Nil	1.42	0.81	20	17	18
81.31	Nil	1.42	0.81	20	18	21
Nil	68.4	5.50	1.32	20	21	22

Further evaluation of these addition agents were made by laboratory heats in which manganese alloy additions were added to 800 pound steel melts during tapping at 1650° C. into a ladle, in amounts sufficient to raise the manganese content 1.45 percent. Temperature drops of about 100° C. were recorded. These temperature drops represent the total chill effect of the alloy addition plus the loss of heat by ladle chill and exposure of the steel to air during tapping. Solution times of about 20 seconds were recorded in each instance and manganese recoveries of about 98 percent were achieved. In similar tests using similar manganese alloy additions but in the form of commercial exothermic mixtures, a temperature drop of about 90° C. and manganese recoveries of about 95 percent were recorded. Analysis of the steel produced by the exothermic addition method also indicated nitrogen pick-up as high as 0.007 percent, whereas the nitrogen pick-up using the non-exothermic addition agent of the invention ranged from zero to about 0.003 percent. Analysis of the steel produced by each type of addition showed that excellent distribution of the manganese was achieved throughout the steel, despite the very short tapping times of about 30 seconds.

From the above it will be seen that the alloy additions of the invention represent simpler and more efficient aggregates with respect to economy, uniformity of alloy distribution throughout the melt, and good recovery, with no risk of contaminating the steel. The present non-exothermic alloy addition, when introduced into a steel heat, dissolves remarkably fast, and does not unduly chill the melt.

This application is a continuation-in-part of copending application Serial No. 621,209, filed November 9, 1956, by E. R. Saunders and R. L. Pope and entitled "Ferroalloy Addition Agent."

It will be understood that modifications and variations may be effected without departing from the spirit and scope of the present invention.

What is claimed is:

1. An addition agent to a molten metal bath for alloying metals consisting of an aggregate 88 percent to 99.5 percent of finely-divided alloying materials, 0.5 percent to 12 percent of at least one finely-divided organic binder selected from the group consisting of abietic acid, complexes thereof, and wood rosins, up to 10 percent of a fluxing agent and up to 5 percent aluminum.

2. An addition agent to a molten metal bath for alloying metals consisting of an aggregate 95 percent to 99 percent of finely-divided alloying materials, 1 percent to 3 percent of at least one finely-divided organic binder selected from the group consisting of abietic acid, complexes thereof, and wood rosins, up to 3 percent of a fluxing agent and up to 3 percent aluminum.

3. A ferromanganese-base alloy addition agent consisting of an aggregate 88 percent to 99.5 of finely-divided ferromanganese alloy and 0.5 to 12 percent of a finely-divided wood rosin binder.

4. A nonexothermic ferrochromium-base alloy addition agent consisting of an aggregate 88 percent to 99.5 percent of finely-divided ferrochromium alloy and 0.5 percent to 12 percent of a finely-divided wood rosin binder.

5. A ferrotitanium-base alloy addition agent consisting of an aggregate of 88 percent to 99.5 percent of finely-divided ferrotitanium, up to 10 percent calcium fluoride, up to 5 percent aluminum, and 0.5 percent to 7 percent of a wood rosin binder.

6. A nonexothermic alloy addition agent to a molten steel bath for alloying metals consisting of comminuted aluminum in an amount up to at least 70 percent by weight of said addition agent, at least one comminuted alloy addition agent other than aluminum, and at least one organic binder selected from the group consisting of abietic acid, complexes thereof, and wood rosins.

7. A nonexothermic alloy addition agent to a molten steel bath for alloying metals consisting of, by weight, 20 percent to 70 percent comminuted aluminum, 20 percent to 70 percent of an alloying agent other than aluminum, up to 5 percent fluxing agent, and 1 percent to 5 percent of a wood rosin binder.

8. A nonexothermic alloy addition agent to a molten steel bath for alloying metals consisting of, by weight, 20 percent to 70 percent comminuted aluminum, 20 percent to 70 percent medium-carbon ferro-manganese, up to 5 percent fluxing agent, and 1 percent to 5 percent of a wood rosin binder.

9. A method of forming a nonexothermic ladle addition agent consisting of alloying material for a molten steel bath which comprises providing finely-dividing alloying material having particle sizes capable of passing through 20-mesh screen and being retained on a 200-mesh screen; admixing with said alloying material at least one similarly sized organic binder selected from the group consisting of abietic acid, complexes thereof; wood rosins; and bonding the mix by baking at a low temperature.

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