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ADDITIVE AGENT FOR FERROUS ALLOYS

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ABSTRACT OF THE DISCLOSURE

Method of producing vanadium and columbium alloy steels by adding to molten steel an addition agent containing an oxide of the alloying metal, an inorganic reducing agent, particularly silicon and aluminum, and lime. The amount of reducing agent employed is at least sufficient to reduce the oxide of the alloying metal to the corresponding metal, and the amount of lime is at least sufficient to combine with the oxide of the reducing agent which is produced to form a slag having a melting point below 1800° C.

In the manufacture of high strength, low alloy structural steels, and normal construction steels, significant amounts, e.g. up to 1.0 percent of vanadium and/or columbium, are utilized as alloying elements in order to improve the properties of the steels.

Until recently such alloying metals have been added in the form of ferro-alloys, such as ferrovanadium and ferrocolumbium. These ferro-alloys are usually added to steel in combination with an oxidizing agent, such as sodium nitrate, and a reducing agent, such as aluminum, which react exothermally in the molten steel to aid in the rapid solution of the ferro-alloys. Frequently the ferro-alloys of Cb and V are added to the furnace or the runner in the absence of such exothermic mixes, which mixes are used primarily in ladle additions of the alloys. Since these ferro-alloys comprise a substantial amount of iron, they are expensive to ship. In addition, their process of preparation, which generally involves aluminothermic reduction of the corresponding oxide, must be carefully carried out resulting in an expensive addition agent.

More recently there has been developed an addition agent comprising V_2C. This addition agent, which is described in U.S. Pat. No. 3,334,992, is prepared by reacting V_2O_3 in finely divided form with carbon at temperatures of 1200° to 1400° C. under vacuum conditions. Preparation of the addition agent is costly. Also, the presence of carbon in the addition agent limits its use to those steels in which a substantial amount of carbon can be tolerated.

It is an object of this invention to provide novel and inexpensive addition agents for use in the manufacture of steel.

Another object of this invention is to provide an improved method for alloying such metals as vanadium and columbium with steel.

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

According to this invention there is provided a novel addition agent for the production of steel comprising a mixture of (I) a metal oxide selected from the group

consisting of a vanadium oxide, a columbium oxide and mixtures thereof, (II) an inorganic reducing agent, and (III) lime. The reducing agent is present in the mixture in at least the stoichiometric amount to reduce the metal oxide to the corresponding metal. The quantity of lime should at least be sufficient to combine with the oxide of the reducing agent which is produced to form a slag having a melting point below about 1800° C. Preferred oxides are V_2O_5 and Cb_2O_5, and a preferred reducing agent is silicon.

The addition agents and methods of this invention are particularly useful in preparing high strength, low alloy steels, and constructional steels. Typical steels which may be produced utilizing the addition agents and methods of this invention are API 5XL Grades X–60 and X–65 steels for pipe, and ASTM A572 plate, bar and strip steel.

These steels may be prepared by introducing the addition agents of this invention to the molten steel, preferably before teeming, and separating the slag which is formed from the steel. Ordinarily the steels to which the addition agents are introduced will be at substantially elevated temperatures on the order of about 1450° to about 1650° C. and higher, at which temperatures there is rapid reaction between the oxide of vanadium or columbium and the reducing agent. By so doing, the columbium or vanadium metal are rapidly alloyed with the steel.

Metal oxides suitable for use in carrying out the present invention are the oxides of vanadium, such as V_2O_3, V_2O_4 and V_2O_5, and the oxide of columbium having the highest state of oxidation, normally Cb_2O_5. The lower oxides of columbium, such as Cb_2O_3 and Cb_2O_4 are difficult to produce. In addition, their reduction is only mildly exothermic, rendering solution of the resulting columbium metal difficult. Thus, these latter oxides of columbium are less desirable for use in the present invention. The preferred oxides are V_2O_5 and Cb_2O_5. Of course, depending upon the ultimate steel alloy desired, mixtures of the oxides of vanadium and columbium may be used.

The steel addition agents of this invention contain a reducing agent which reacts with the oxide of vanadium or columbium to provide metallic vanadium or columbium which alloys with the steel. Any of the several well known reducing agents for such metal oxides may be used. Typical reducing agents are aluminum, silicon, and certain alloys, such as ferrosilicon, calcium silicon and ferrosilicon aluminum. The preferred reducing agent is silicon, which forms a calcium silicate slag during the process.

A third essential constituent of the addition agents is lime, i.e. hydratable lime or quicklime. Any of the well-known types of lime, such as high calcium limes whose magnesium content generally runs approximately 2% or less but may run as high as 5–10%; the high magnesium limes obtainable from dolomite which contain approximately 40% magnesium oxide, and limes whose magnesium content lies between those of the high calcium and high magnesium limes, may be used.

The three essential constituents, i.e. the oxide of vanadium or columbium, the reducing agent and lime are mixed together in finely divided form. To obtain the desired mixture, the individual constituents, preferably, are first reduced to minus 20 mesh by down and then uniformly blended.

The amount of reducing agent present should be sufficient to reduce all of the oxide of vanadium or columbium to the corresponding metal. Preferably, the amount of reducing agent exceeds the stoichiometric amount required for the reduction by a small amount, but not by more than about 110 percent, by weight, of stoichiometric.

The lime reacts with the oxide of the reducing agent which is produced in the redox system to form a slag which has a melting point below about 1800° C., and preferably below about 1600° C. The quantity of lime used will depend upon the particular reducing agent employed. For example, where the reducing agent employed is aluminum, the quantity of lime present in the addition agent should be such as to produce a slag whose composition ranges substantially from $CaAl_2O_4$

$(CaO \cdot Al_2O_3)$

to $Ca_3Al_2O_6$ $(3CaO \cdot Al_2O_3)$. Where the reducing agent is silicon, the amount of lime employed should provide a slag whose composition ranges substantially from $CaSi_2O_3$ $(CaO \cdot 2SiO_2)$ to Ca_3SiO_5 $(3CaO \cdot SiO_2)$. Preferably, the quantity of lime employed provides, in the case of aluminum, a slag whose composition is substantially $Ca_{12}Al_7O_{33}$ $(12CaO \cdot 7Al_2O_3)$ and, in the case of silicon, a slag whose composition is substantially $CaSiO_3$ $(CaO \cdot SiO_2)$. Where the preferred reducing agent, silicon, is used, it is particularly preferred that the quantity of lime be such as to form a slag comprising wollastonite ($CaSiO_3$) which has a melting point of approximately 1544° C.

The addition agents of this invention may be added to steel in the form of a powder, preferably tightly packed, or as briquettes formed by compressing the dry powder. The briquettes may be of any suitable shape, such as square, cylindrical, spherical, etc. The major dimension of such briquettes preferably does not exceed about 3 inches in order to obtain a rapid oxidation-reduction reaction and solution of the reduced metal in the steel.

The quantity of addition agent which is added to a ferrous alloy generally will be sufficient to provide from about 0.10 to about 1 percent, by weight, of the alloying metal, vanadium or columbium, in the ferrous alloy.

The following examples are illustrative of the invention and are not intended to limit the scope thereof.

EXAMPLE I

A mix was prepared containing 100.5 parts by weight of vanadium pentoxide (99.79% V_2O_5) sized 20 mesh by down, 43.75 parts of silicon metal (96.16% Si) sized 20 mesh by down, and 77.5 parts of lime sized 20 mesh by down. This mix was compressed into cylindrical briquettes having a length of approximately 2" to 3" and a diameter of approximately ¾".

The briquettes were added to Armco ingot iron in an induction furnace and protected by an atmosphere of an inert gas. The iron had the following composition prior to addition of the briquettes:

TABLE I

Constituent:	Weight percent
Carbon	0.012
Manganese	0.017
Phosphorous	0.005
Sulphur	0.025
Silicon	Trace
Iron	Remainder

After addition of the briquettes, the resulting alloy composition contained approximately 0.026–0.029%, by weight, of vanadium (determined by wet chemistry) and 0.031% vanadium (spectrographic determination). The slag formed on top of the steel consisted mainly of wollastonite ($CaSiO_3$).

EXAMPLE II

A mix was prepared containing 145 pounds of columbium pentoxide (98% Cb_2O_5) sized 30 mesh by down, 43.75 pounds of silicon metal (96.16% Si) sized 200 mesh by down, and 77.5 pounds of lime sized 20 mesh by down. This mix may be formed into briquettes and employed in the same manner as that of Example I to provide a ferrous alloy containing approximately 0.03% columbium.

The mesh sizes referred to in the foregoing description are U.S. series.

Various modifications of the invention as described above will be apparent to those skilled in the art. Hence, it will be understood that the invention is not limited to the foregoing description except as it is defined in the appended claims.

What is claimed:

1. A method for producing vanadium and columbium alloy steels which comprises adding to molten steel an addition agent comprising a mixture of (I) a metal oxide selected from the group consisting of a vanadium oxide, a columbium oxide and mixtures thereof, (II) an inorganic reducing agent, and (III) lime, said reducing agent being at least the stoichiometric amount to reduce said metal oxide to the corresponding metal, and said lime being at least the amount required to combine with the oxide of said reducing agent to form a slag having a melting point below about 1800° C., and separating the resulting alloy steel from said slag, the amount of addition agent added to the molten steel being sufficient to provide a steel alloy containing from about 0.01 to about 1.0 percent, by weight, of said alloying metal.

2. The method according to claim 1 in which said reducing agent comprises silicon.

3. The method according to claim 1 in which said metal oxide comprises V_2O_5.

4. The method according to claim 1 in which said metal oxide comprises Cb_2O_5.

5. The method according to claim 1 in which said mixture is added to molten steel in the form of a briquette.

6. A method for producing vanadium alloy steel which comprises adding to molten steel an addition agent comprising a mixture of (I) a vanadium oxide selected from the group consisting of V_2O_3, V_2O_4 and V_2O_5 and mixtures thereof, (II) an inorganic reducing agent selected from the group consisting of aluminum, silicon, ferrosilicon and calcium silicon, and (III) lime, said reducing agent being at least the stoichiometric amount to reduce said metal oxide to vanadium metal but not exceeding about 110 percent, by weight, of stoichiometric, and said lime being at least the amount required to combine with the oxide of said reducing agent to form a slag having a melting point below about 1800° C., and separating the resulting vanadium-bearing alloy steel from said slag, the amount of addition agent added to the molten steel being sufficient to provide a steel alloy containing from about 0.01 to about 1.0 percent, by weight, of vanadium.

7. The method according to claim 6 in which said reducing agent is silicon and said lime is approximately the stoichometric amount to combine with the oxide of said reducing agent to form a slag having the approximate composition of wollastonite.

8. The method according to claim 7 in which said addition agent is in the form of a briquette.

9. A method for producing columbium alloy steel which comprises adding to molten steel an addition agent comprising a mixture of (I) Cb_2O_5, (II) an inorganic reducing agent, and (III) lime, said reducing agent being at least the stoichiometric amount to reduce said metal oxide to columbium metal but not exceeding about 110 percent, by weight, of stoichiometric, and said lime being at least the amount required to combine with the oxide of said reducing agent to form a slag having a melting

point below about 1800° C., and separating the resulting columbium-bearing alloy steel from said slag, the amount of addition agent added to the molten steel being sufficient to provide a steel alloy containing from about 0.01 to about 1.0 percent, by weight, of columbium.

10. The method according to claim **9** in which said reducing agent is silicon and said lime is approximately the stoichiometric amount to combine with the oxide of said reducing agent to form a slag having the approximate composition of wollastonite.

11. The method according to claim **10** in which said addition agent is in the form of a briquette.

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