

## UNITED STATES PATENT OFFICE

2,639,232

ADDITION MATERIALS FOR IRON AND  
STEEL MANUFACTURE AND METHOD  
OF USE THEREOFJames C. Vignos, Canton, Ohio, assignor to Ohio  
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poration of OhioNo Drawing. Application October 19, 1951,  
Serial No. 252,210

14 Claims. (Cl. 75—130.5)

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This invention relates to an addition material and a method of using it in molten iron and steel and more particularly relates to a material and method for making chromium additions to molten steel.

In the manufacture of chromium-containing iron or steel it is the general practice to add the chromium to the molten bath in the furnace in the form of ferro-chromium. The most common form of ferro-chromium presently used is that known as "standard high carbon ferro-chrome" which contains about 65% to 70% chromium, 4% to 7% carbon and about 2% maximum silicon. In the manufacture of chromium steels in open hearth furnaces, the usual procedure is to work the carbon content of the molten steel bath down to the desired point then to "block" or "kill" the heat of steel and finally to add the ferro-chromium. If the chromium content of the steel is over 2%, it is frequently the practice to heat the ferro-chromium before adding it to the furnace in order to promote its solution and to prevent chilling of the bath. In any event, from 20 to 60 minutes are usually required to make chromium additions to the bath because the ferro-chromium has a high melting point and goes into the solution slowly. Moreover, due to the fact that chromium is reducing in its action recovery of chromium in the steel, depending, at least in part, upon the carbon content thereof, is low and varies generally from 70% to 85%.

The high melting point and low rate of solution of ferro-chromium alloys have also made it impossible in the past to make any appreciable additions of ferro-chromium or ferro-chromium-silicon directly to the ladle.

Various means have been proposed to overcome these difficulties and improve the recovery of the chromium added to the bath. For example, ferro-alloys of chromium containing silicon, manganese, aluminum or combinations of these elements have been suggested. However, they have not been the answer to the problem although some of the proposed alloys have been an improvement over the straight ferro-chrome alloys.

I have discovered a material suitable for making chromium additions to molten steel both in the furnace and in the ladle and a method of using it which substantially overcomes these difficulties of the prior art. I have found that the material of my invention may be added directly to the furnace or the ladle without producing a violent exothermic reaction and yet result in a clean steel, free from chromium segregation.

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I have discovered that ferro-chromium alloys comprising generally 5% to 70% chromium, up to 7% carbon, up to 50% silicon and the balance substantially iron in finely divided particles having a maximum size of about one-half inch and coated with a wetting agent will enter into solution in molten iron and steel at a greatly facilitated solution rate and will produce a higher and more economical recovery of the chromium. I have found a number of wetting agents which are suitable for coating the ferro-chrome alloy particles to produce the material of this invention. The wetting agents of this invention can consist of any material which will lower the surface tension of the molten slag or the metal to which the ferro-chrome is added. The preferred wetting agents for use in my invention are those which contain available free oxygen such as the alkali-metal nitrates, chlorates, peroxides, chromates, permanganates, the organic peroxide compounds such as urea peroxide, acetic peroxide and benzoyl peroxide. However, other wetting agents may be successfully used, for example, the alkali-metal salts of the halogens. I believe that these wetting agents promote the formation of an oxide film upon the surface of the ferro-alloy which oxide film in turn permits the molten metal to wet the exposed surfaces of the ferro-alloy and more readily dissolve it.

I have found that in order to obtain the maximum effectiveness of my invention the chromium-containing ferro-alloy must be crushed to a relatively finely divided state, i. e., below one-half inch and preferably below a maximum particle size of about one-quarter inch. The wetting agent may be applied to the ferro-chrome particles in any suitable manner as by spraying or immersing the particles in a water solution of the wetting agent and then removing the water by evaporation or by spraying or immersing the ferro-alloy particles in the molten wetting agent. The film of wetting agent which adheres to the chromium ferro-alloy particles may vary in amount and thickness depending upon the results desired, the wetting agent used and the particle size of the ferro-alloy. However, I have found that it is not desirable to have more than 5% of the wetting agent in any given mixture because the excess wetting agent is of no value in furthering the chromium-containing ferro-alloy addition. It is of course obvious that if the ferro-chromium particles as first treated are insufficiently coated after drying, the amount of wetting agent can be increased by repeating the process as I have already pointed out.

In order to show the effectiveness of the coated chromium-containing ferro-alloy of this invention several heats were made, some using standard chromium alone and others using the coated material of the present invention.

In Table I here below, a series of heats are tabulated using standard high carbon-ferro-chrome additions according to the practice of the prior art.

Table I

| Heat No. | Type  | Pounds Ferro-Chrome Added | Residual Chrome | Chrome Added | Total Chrome | Final Chrome | Chrome Loss | Percent Loss |
|----------|-------|---------------------------|-----------------|--------------|--------------|--------------|-------------|--------------|
| A        | 8640  | 2,000                     | .18             | .53          | .71          | .62          | .09         | 16.98        |
| B        | 8620  | 1,850                     | .24             | .49          | .73          | .66          | .07         | 14.29        |
| C        | 8645  | 2,100                     | .18             | .57          | .75          | .60          | .15         | 26.32        |
| D        | 8620  | 2,000                     | .21             | .54          | .75          | .68          | .07         | 12.96        |
| E        | 8645  | 2,000                     | .24             | .53          | .77          | .66          | .11         | 20.75        |
| F        | 8617  | 1,300                     | .21             | .35          | .56          | .51          | .05         | 14.29        |
| G        | 8122  | 1,100                     | .15             | .30          | .45          | .40          | .05         | 16.67        |
| H        | 8620  | 2,100                     | .17             | .56          | .73          | .58          | .15         | 26.79        |
| I        | 8620  | 2,200                     | .12             | .62          | .74          | .63          | .11         | 17.74        |
| J        | 8617  | 1,700                     | .18             | .45          | .63          | .51          | .12         | 26.67        |
| K        | 94B17 | 600                       | .20             | .16          | .36          | .33          | .03         | 18.75        |

Reference to the above table will show that the average loss of chromium in making the above heats using standard high-ferro-chromium is about 19.3% which is in general agreement with average practice on this type of steel.

Several heats were then made in the same manner as those of Table I except that ferro-chrome-silicon twenty mesh down and eight mesh down coated with a wetting agent were added to the metal in the ladle. Heats Nos. 1, 2, and 3 were made by adding ferro-chromium-silicon twenty mesh and down coated with sodium nitrate. The analysis of the material was 53.57% chromium, 13.03% silicon, 4.64% carbon, 3.89% sodium nitrate and the balance substantially iron. Heats 4 and 5 were made by adding ferro-chromium-silicon twenty mesh and down coated with sodium nitrite. Analysis of the coated product was 53.25% chromium, 12.95% silicon, 4.60% carbon, 4.24% sodium nitrite and the balance substantially iron. Heat No. 6 was made by adding ferro-chromium-silicon eight mesh and down coated with sodium chlorate. Analysis of the finished product was 56.96% chromium, 13.40% silicon, 3.56% carbon, 3.20% sodium chlorate and the balance substantially iron. Heats 7 and 8 were made by adding ferro-chrome-silicon eight mesh and down coated with sodium nitrate. Analysis of the coated product was 56.12% chromium, 13.45% silicon, 3.87% carbon, 2.66% sodium nitrate.

Table II

| Heat No. | Type  | Pounds FeCrSi | Residual Chrome | Chrome Added | Total Chrome | Final Chrome | Chrome Loss | Percent Loss |
|----------|-------|---------------|-----------------|--------------|--------------|--------------|-------------|--------------|
| 1        | 8620  | 1,400         | .21             | .30          | .51          | .50          | .01         | 3.33         |
| 2        | 8620  | 2,000         | .21             | .44          | .65          | .63          | .02         | 4.55         |
| 3        | 8640  | 2,050         | .19             | .48          | .67          | .64          | .03         | 6.25         |
| 4        | 8620  | 1,800         | .25             | .40          | .65          | .66          | + .01       | +2.50        |
| 5        | 8650  | 1,750         | .25             | .36          | .61          | .60          | .01         | 2.78         |
| 6        | 94B40 | 650           | .20             | .14          | .34          | .33          | .01         | 7.14         |
| 7        | 8620  | 2,200         | .17             | .51          | .68          | .69          | + .01       | +1.96        |
| 8        | 8620  | 2,200         | .16             | .50          | .66          | .64          | .02         | 2.50         |

The average loss of chrome is about 2.76% which is approximately a saving of about 16.5% chromium over the standard practice illustrated in Table I, thus showing the effectiveness of the wetting agent in increasing the recovery of chromium. These heats passed all tests for segregation of chromium and were satisfactory in every respect. Grain size of the steels was

not affected by the additions nor was the inclusion count materially altered. The above examples show that it is possible by the use of the material of this invention to produce chrome steels in open hearth practice by the addition of crushed chromium-containing ferro-alloys to the ladle. This improvement, in addition to saving a large percentage of the chromium added, cuts the time of the heat in the furnace from 15

to 40 minutes, over the standard practice in the industry.

While I have described a preferred embodiment and practice of my invention, it will be understood that it may be otherwise embodied within the scope of the following claims.

I claim:

1. An addition material for making chromium additions to a bath of molten steel comprising a mixture of finely divided particles of a high chromium-containing ferro-alloy coated with a wetting agent not exceeding about 5% of the mixture.

2. An addition material for making chromium additions to a bath of molten steel comprising a mixture of particles of a high chromium-containing ferro-alloy having a maximum particle size of about one-half inch coated with not exceeding about 5% of a wetting agent.

3. An addition material for making chromium additions to a bath of molten steel comprising a mixture of finely divided particles of a high chromium-containing ferro-alloy having a maximum particle size of about one-quarter inch coated with not exceeding about 5% of a wetting agent.

4. An addition material for making chromium additions to a bath of molten steel comprising a mixture of finely divided particles of a high chromium-containing ferro-alloy coated with not exceeding about 5% of a wetting agent capable

of promoting the formation of an oxide film on the particle surface.

5. An addition material for making chromium additions to a bath of molten steel comprising a mixture of particles of a high chromium-containing ferro-alloy having a maximum particle size of about one-half inch coated with not exceeding about 5% of a wetting agent capable of

promoting the formation of an oxide film on the particle surface.

6. An addition material for making chromium additions to a bath of molten steel comprising a mixture of finely divided particles of a high chromium-containing ferro-alloy having a maximum particle size of about one-quarter inch coated with not exceeding about 5% of a wetting agent capable of promoting the formation of an oxide film on the particle surface.

7. An addition material for making chromium additions to a bath of molten steel comprising a mixture of finely divided particles of a high chromium-containing ferro-alloy coated with not exceeding about 5% of a wetting agent of the group consisting of alkali nitrates, nitrites, chlorates, peroxides, chromates, permanganates, the organic peroxide compounds and alkali-metal salts of the halogens.

8. An addition material for making chromium additions to a bath of molten steel comprising a mixture of particles of a high chromium-containing ferro-alloy having a maximum particle size of about one-half inch coated with not exceeding about 5% of a wetting agent of the group consisting of alkali nitrates, nitrites, chlorates, peroxides, chromates, permanganates, organic peroxide compounds and alkali-metal salts of the halogens.

9. An addition material for making chromium additions to a bath of molten steel comprising a mixture of finely divided particles of a high chromium-containing ferro-alloy having a maximum particle size of about one-quarter inch coated with not exceeding about 5% of a wetting agent of the group consisting of alkali nitrates, nitrites, chlorates, peroxides, chromates, permanganates, the organic peroxide compounds and alkali-metal salts of the halogens.

10. An addition material for making chromium additions to a bath of molten steel comprising a mixture of particles of ferro-alloy comprising 5% to 70% chromium, up to 7% carbon, up to 50% silicon and the balance substantially iron, said particles being coated with not exceeding about 5% of a wetting agent.

11. An addition material for making chromium additions to a bath of molten steel comprising a mixture of particles of ferro-alloy comprising 5% to 70% chromium, up to 7% carbon,

up to 50% silicon and the balance substantially iron, said particles being coated with not exceeding about 5% of a wetting agent of the group consisting of alkali nitrate, nitrites, chlorates, peroxides, chromates, permanganates, the organic peroxide compounds and alkali-metal salts of the halogens.

12. The method of adding chromium to molten iron and steel which comprises coating finely divided particles of a high chromium-containing ferro-alloy with a film of wetting agent which will permit the chromium ferro-alloy to be wetted by the molten metal and adding the coated finely divided particles of high chromium-containing ferro-alloy to the molten metal whereby the particles of ferro-alloy are substantially immediately wetted by the molten metal and go into solution therein.

13. The method of adding chromium to molten iron and steel which comprises coating particles of a high chromium-containing ferro-alloy having a maximum particle size of about one-half inch with a film of wetting agent which will permit the chromium ferro-alloy to be wetted by the molten metal, said wetting agent making up not more than 5% of the resulting composition and adding the coated particles of ferro-alloy to the molten metal whereby the particles of ferro-alloy are substantially immediately wetted by the molten metal and enter into the solution therein.

14. The method of adding chromium to molten iron and steel which comprises coating particles of a high chromium-containing ferro-alloy whose maximum particle size is about one-half inch with a film of wetting agent of the group consisting of alkali nitrates, nitrites, chlorates, peroxides, chromates, permanganates, the organic peroxide compounds and alkali salts of the halogens and adding coated particles of ferro-alloy to the molten metal whereby they are substantially immediately wetted by the molten metal and enter into the solution therein.

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