Patented Oct. 6, 1936

2,056,162

UNITED STATES PATENT OFFICE

2,056,162

PRODUCTION OF RUSTLESS IRON

William B. Arness, Baltimore, Md., assignor, by mesne assignments, to Rustless Iron and Steel Corporation, Baltimore, Md., a corporation of Delaware

No Drawing. Application April 9, 1934, Serial No. 719,810

7 Claims. (Cl. 75—22.5)

This application is a continuation in part of my United States Patent No. 1,954,400, issued April 10, 1934 and entitled Process of making rustless iron, and the invention relates to the production of rustless irons and steels, especially to the production of rustless irons.

Among the objects of my invention is the production of rustless irons and steels of required analyses of chromium, carbon (and desired supplementary additions of nickel, copper, molybdenum, silicon, manganese, aluminum, sulphur and the like), which are comparatively free of objectionable oxide inclusions, in a simple, efficient and economical manner, utilizing readily available and inexpensive raw materials and employing known and available furnacing and operating equipment.

The invention accordingly consists in the several steps and in the relation of each of the same to one or more of the others as described herein, and the scope of the application of which is indicated in the following claims.

As conducive to a clearer understanding of certain features of my invention it may be noted at this point that in heretofore known and/or used processes for the electric furnace production of rustless irons and steels (irons and steels analyzing approximately, 10% to 30% chromium, either with or without supplementary additions of nickel, copper, molybdenum, vanadium, tungsten, aluminum, silicon, manganese, sulphur and the like, with about .05% to about .15% carbon for the irons and about .15% to about 1.0% carbon for the steels and with the balance substantially iron), especially in the production of rustless iron, and particularly in those processes wherein chrome ore is employed as a substantial source of chromium as described and claimed in my copending application Serial Number 630,241, indicated above, great difficulty is experienced in achieving clean, sound metal free of oxide inclusions. This is particularly true where great quantities of chrome ore are employed, as in the production of rustless irons of the higher chromium contents, such as the 17%, 21% and 27% chromium grades.

The presence of unusually large quantities of oxide inclusions dispersed throughout the rustless iron or steel metal appreciably detracts from the corrosion-resisting properties. In addition, it appears that the presence of an abnormally high percentage of oxide inclusions is detrimental to the working characteristics of the metal, especially in such operations as rolling and forming.

It may be further noted that in the ordinary production of rustless irons and steels, and more particularly in the production of rustless iron, there is available as scrap metal about the melt shop and rolling mill approximately 20% of the tapped metal in ingot butts, crop ends and the like. Where metal is processed into bar stock there is then available a total of about 25% to 30% of the tapped metal as scrap. The total amount of scrap metal increases with the number of working or forming operations to which it is subjected and amounts to some 40% to 50% in the production of sheet and strip and may even amount to some 60% or 70% where the sheet or strip is further fabricated into various ultimate articles of manufacture, such as machine or burner parts, kitchen ware, automobile trim, architectural applications and the like.

In balanced manufacture, then, there is available for remelting purposes rustless iron and steel scrap amounting to approximately 25% to 50% of the tapped metal; the available rustless iron scrap ordinarily averaging about 35% of the tapped metal.

Accordingly, one of the outstanding objects of my invention is the efficient, practical and economical production of rustless iron and steel, especially rustless iron, of a desired analysis containing a minimum of objectionable oxide inclusions employing comparatively inexpensive and readily available raw materials in normally available proportions.

Referring now more particularly to the practice of my invention a suitable electric arc furnace, preferably a furnace of the direct arc type, employing carbon containing electrodes, such as the Heroult furnace, is prepared for the reception of a charge. For example, a six-ton Heroult furnace rated three-phase 25 cycles 2500 kv-a and 100 to 180 volts lined to a height somewhat above the slag line with chromite brick, and having side walls and roof of silica brick in accordance with standard practice, is preheated in any suitable manner.

In the production of a heat of rustless iron a charge of ingredients preferably comprising a proportion of rustless iron scrap ordinarily available as ingot butts, crop ends, scrap sheet, punchings, clippings and the like (usually amounting to some 25% to 50% of the amount of metal tapped over a period of time and marketed in the form of ingots, billets, sheet, strip and bar stock or the like), a maximum quantity of chrome ore to provide a cheap source of chromium and a minimum necessary quantity of ferrochrome of high carbon content (1% to 10%) to achieve

tapped metal of the desired chromium content comparatively free of undesirable oxide inclusions, together with an amount of an available oxide of iron, such as roll scale sufficient to remove and/or exclude carbon entering into the process, as from the furnace atmosphere and electrodes and the ferrochrome containing ingredients added, and such an amount of ordinary base iron or steel scrap as to complete the charge are melted down in the furnace previously prepared for the reception of the charge, as more particularly described above.

As illustrative of the practice of my invention, in the production of a nine-ton heat of metal to a specification, for example, of 16% to 18% chromium, less than .12% carbon, less than .50% each of manganese and silicon and with sulphur and phosphorus each less than .030%, 6,700 pounds of rustless iron scrap having an average analysis of about 17.5% chromium, .10% carbon, with the usual percentages of silicon, manganese, sulphur and phosphorus, and the balance substantially iron, 1,700 pounds of high carbon ferrochrome analyzing approximately, 70% chromium, 5% carbon and the balance substantially iron, 2,000 pounds of chrome ore analyzing approximately, 48% chromium oxide (Cr_2O_3), together with 3,000 pounds of roll scale and 7,000 pounds of base low carbon steel scrap are charged into the furnace. Alternating current electrical energy is supplied the furnace and the charge of ingredients begins to melt down, first forming individual pools of ferrous metal containing carbon and chromium immediately beneath the furnace electrodes which merge into a single pool or bath that grows as the application of power continues.

Under the action of the intense heat of the electric furnace arcs the melting charge of ingredients soon forms a bath of ferrous metal containing large quantities of chromium and appreciable quantities of carbon, as indicated above, and an overlying blanket of slag rich in the oxides of iron and chromium.

The strongly oxidizing character of the slag blanket overlying the bath of metal is effective in oxidizing the carbon supplied the metal by the base scrap, the rustless iron scrap and the ferrochrome, as well as the carbon coming from the furnace electrodes. The presence of fairly large quantities of carbon as supplied by the high carbon ferrochrome, is apparently effective, either by virtue of the vigor of the reaction with the iron oxide and the resulting circulation of the metal or because of some action not wholly understood, in achieving a type of oxidation, or distribution of oxidation reaction, which renders the metal more amenable to refinement or cleansing in subsequent stages of the process.

The oxidation of carbon from the metal is greatly accelerated and rendered effective in achieving a commercially practicable process by conducting the melting operation at a high melt-down temperature.

While no reliable method is known to me for precisely determining the temperature of the metal immediately beneath the slag blanket, it is estimated that this temperature is approximately 3100° F. to 3250° F., which is some 150° F. to 300° F. higher than the temperatures ordinarily employed in the usual electric steel making practices. For convenience I designate this temperature as a temperature of superheat.

The oxidation of chromium from the molten metal, normally incidental to the oxidation of carbon, is materially lessened by the inhibiting effect of the large quantities of chromium initially present in the slag; the tendency toward chromium oxidation being greatly lessened by the initially high balance between the molten chromium oxide in the slag and the chromium oxides dissolved in the metal. In this manner certain savings are realized in materials and labor required to recover chromium from the slag, as more particularly described hereinafter.

After the initial charge of ingredients is completely melted down samples taken from the bath for chemical analysis indicate that the carbon content is several points below the permissible maximum value. For the example given, the carbon content amounts to about .07%; the corresponding chromium content of the metal is about 10% to 12%.

At this stage of the process, there are available in the slag great quantities of iron and chromium in the form of oxides of these metals, although much of the iron oxide in the slag has been lost during the melt-down-oxidation period in removing and/or excluding carbon from the melting metal, and in the oxidation of chromium incidental to the oxidation of carbon, as more particularly indicated above. To render the process commercially feasible these metals are substantially completely recovered from the slag in a subsequent reducing period where an amount of, preferably, a non-carbonaceous reducing agent, such as ferrosilicon, chemically in excess of the oxides of iron and chromium contained in the slag, is charged onto the slag overlying the molten bath of metal. For the illustrative heat of metal indicated above, a substantially complete recovery of iron and chromium from the slag is achieved by almost continuously charging onto the slag successive batches of 75% grade ferrosilicon in a total amount of about 1,950 pounds.

To minimize the silicon contamination of the metal during this stage of the process despite the use of an excess of silicon, and to generally improve the efficiency of the reducing action, burnt lime in an amount of from 3 to 5 times the total silicon content of the ferrosilicon is charged along with the reducing agent. Conveniently, the burnt lime is thoroughly mixed with the reducing agent on the floor of the melt-shop prior to charging and the reducing agent and burnt lime are then charged as a mixture from time to time as furnace conditions permit. The use of this large quantity of burnt lime assures the maintenance of a basic slag condition during the reducing stage of the process and effectively prevents silicon contamination of the metal, despite the presence of a required excess of silicon, by the formation of a series of calcium silicates, which are among the most stable components of the slag, by virtue of the reaction of the basic lime with the acid silicates resulting from the reduction of the reducible oxides of the slag by the silicon reducing agent, all as more particularly described in my recently granted Patent No. 1,932,252 of October 24, 1933 and entitled Process of producing alloys.

An additional quantity of chrome ore (1,600 pounds for the illustrative example given) is conveniently charged along with the ferrosilicon and the lime in corresponding successive batches. The addition of chrome ore at this stage of the process permits the use of a maximum quantity of this cheap source of chromium (a feature particularly important in the production of rustless irons and steels of the higher chromium grades—

21% to 27%) while maintaining a manageable volume of slag within the furnace throughout both the melt-down-oxidation period and the subsequent reducing period with a minimum submersion of the furnace electrodes in the slag thereby limiting an objectionable carbon pick-up from the furnace electrodes.

After all of the ferrosilicon, lime and chrome ore have been added and have fused and completed their reactions with the ingredients contained in the slag and metal and a substantially complete recovery of the oxides of chromium in the slag is achieved, as evidenced by a change in color of successive samples of slag taken from the furnace from a black to a light green or gray color, the reducing period is at an end. The slag from which the metals, iron and chromium, are recovered is then substantially completely drawn off the bath of molten metal.

In accordance with ordinary melting practice the heat of metal is refined under a suitable basic finishing slag. For the illustrative embodiment described above, about 500 pounds of burnt lime and 40 pounds of fine ferrosilicon of a 75% grade are conveniently charged onto the bath of metal as a mixture and the heating of the bath continued at the reduced power input necessary to maintain the metal at a desired temperature.

During this period lump ferrosilicon and lump ferro-manganese, or conveniently silico-manganese, are added to finally adjust the silicon and manganese contents of the heat of metal. A desired percentage of silicon and manganese is achieved in the example given by the addition of 90 pounds of silico-manganese toward the end of the refining period.

After a suitable refining of the metal is achieved, the application of power to the furnace is terminated, the electrodes are raised and the heat of metal is tapped into a ladle for teeming. For the example given the heat of metal produces 18,400 pounds of rustless iron ingots analyzing approximately, 17.5% chromium, .10% carbon, .47% silicon, .54% manganese with the usual low percentages of sulphur and phosphorus and the balance substantially iron. The metal is clean and sound and comparatively free of objectionable oxide inclusions.

Where desired, supplementary additions of nickel, copper, tungsten, vanadium, aluminum, titanium, zirconium and the like, may be made either in the furnace or in the ladle in accordance with standard practice.

Thus, it will be seen that there has been provided in this invention an art of producing rustless iron and steel in which the various objects hereinbefore noted, together with many thoroughly practical advantages are successfully achieved. It will be seen that the process lends itself to the rapid, efficient, economical and reliable manufacture of rustless iron and steel employing a maximum of available and inexpensive raw materials consistent with the production of clean metal. The process is particularly favorable to achieving a desired economic balance between the raw materials utilized, especially the chromium-containing ingredients, rustless iron scrap, chrome ore and high carbon ferrochrome, by relatively adjusting the proportions of these several ingredients (to such an extent as is consistent with satisfactory furnace operating conditions) in accordance with variations in the availability of these materials and the fluctuations in their market prices.

While as illustrative of the practice of my invention substantial quantities of chrome ore are added, both along with the initial charge of ingredients subsequently melted down and with the reducing agent added after melt-down is complete, in order to take advantage of the comparatively long melt-down and reduction periods to effect a thorough heating of this highly refractory ingredient, it will be understood that a portion of the chrome ore may be added during the melt-down period, especially toward the end of this period when samples of metal have been taken and the heat of metal is being held in the furnace awaiting a report of the carbon analysis, in order to realize the benefits of a long uninterrupted heating and the use of available furnace heat at little additional expense where such procedure is found desirable. Likewise, it will be understood that, where furnacing conditions permit, substantially all of the charge of chrome ore may be added during the melt-down period, thereby achieving a full realization of the thorough heating permitted by this procedure. In this manner the addition of a minimum of chrome ore during the later stages of the heat is assured with a consequent decrease in the possibility of picking up carbon from the electrodes, and contamination of freshly reduced metallic iron and chromium from the particles of chrome ore. There is also achieved a consequent shortening of the necessary reducing period.

While in the practice of my invention excellent results are achieved by employing rustless iron or steel scrap in substantially the same proportions that this scrap is available about the steel plant, ordinarily amounting to about 25% to 50% of the tapped metal, it will be understood that where the shortage of rustless iron or steel becomes acute good results are achieved where lesser quantities of rustless iron or steel scrap (or rustless iron or steel scrap of an average chromium content lower than that of the tapped metal) are employed, and that under certain circumstances highly beneficial results are obtained with a substantial absence of rustless iron or steel scrap in the charge. Likewise, while in the practice of my invention best results are achieved by employing chrome ore and a ferrochrome of high carbon content in proportions giving substantially the same amounts of available chromium to achieve metal comparatively free of oxide inclusions at a minimum expense, certain advantages are realized, such as an improved economy of production, where a preponderance of chrome ore is employed up to an amount tending to give operating troubles because of the large volumes of slag encountered, while other advantages are achieved by employing a desired preponderance of ferrochrome.

As many possible embodiments may be made of my invention and as many changes may be made in the embodiment hereinbefore set forth, it will be understood that all matter described herein is to be interpreted as illustrative, and not in a limiting sense.

I claim:

1. In the production of rustless irons and steels in an electric arc furnace, the art which includes, melting down a charge comprising ordinary iron or steel scrap, rustless iron or steel scrap, a ferrochrome of substantial carbon content, chrome ore and an iron oxide, thereby forming a bath of ferrous metal containing carbon and chromium covered by a slag rich in iron oxide for oxidizing the carbon from said bath and containing substantial quantities of chromium oxide inhibiting

the corresponding oxidation of chromium from the bath, a portion of carbon of said bath serving to minimize oxide inclusions dispersed throughout the bath; and after said charge is completely melted down and the carbon content of said bath has reached a desired low value, adding a reducing agent to said bath and slag thereby reducing the oxides of iron and chromium in the slag and enriching the bath in the resulting metals.

2. In the production of rustless irons and steels in an electric arc furnace, the art which includes, melting down a charge comprising ordinary iron or steel scrap, rustless iron or steel scrap, high carbon ferrochrome, chrome ore and an iron oxide, thereby forming a bath of ferrous metal containing carbon and chromium covered by a slag rich in iron oxide for oxidizing the carbon from said bath and containing substantial quantities of chromium oxide inhibiting the corresponding oxidation of chromium from the bath, a portion of the carbon of said bath serving to minimize oxide inclusions dispersed throughout the bath; and after said charge is completely melted down and the carbon content of said bath has reached a desired low value, adding a further quantity of chrome ore and a silicon reducing agent to said slag whereby the oxides of iron and chromium present are reduced thereby enriching the bath in these metals.

3. In the production of rustless irons and steels in an electric arc furnace, the art which includes, melting down a charge comprising ordinary iron or steel scrap, high carbon ferrochrome, chrome ore and an iron oxide, thereby forming a bath of ferrous metal containing carbon and chromium covered by a slag rich in iron oxide for oxidizing the carbon from said bath and containing substantial quantities of chromium oxide inhibiting the corresponding oxidation of chromium from the bath, a portion of the carbon of said bath serving to minimize oxide inclusions dispersed throughout the bath; and after said charge is completely melted down and the carbon content of said bath has reached a desired low value adding a further quantity of chrome ore, a silicon containing reducing agent and burnt lime whereby the oxides of iron and chromium supplied said slag are reduced under basic slag conditions thereby effecting a high recovery of iron and chromium.

4. In the production of rustless irons and steels in an electric arc furnace, the art which includes, melting down a charge including rustless iron or steel scrap, high carbon ferrochrome and chrome ore in such relative proportions that approximately 25% to 50% of the chromium of said iron or steel is supplied by said rustless iron or steel scrap and the remainder is supplied by said ferrochrome and chrome ore in substantially equal proportions, said charge forming a bath of ferrous metal containing carbon and chromium covered by an oxidizing slag for oxidizing the carbon from said bath and containing substantial quantities of chromium oxide inhibiting the corresponding oxidation of chromium from the bath, a portion of the carbon of said bath serving to minimize oxide inclusions dispersed throughout the bath; and after said charge is completely melted down and the carbon content of said bath has reached a desired low value reducing the oxides of iron and chromium contained in said slag thereby effecting an enrichment of the bath.

5. In the production of rustless irons and steels in an electric arc furnace, the art which includes, melting down a charge including rustless iron or steel scrap, high carbon ferrochrome, chrome ore and an oxide of iron in such proportions that approximately 35% of the chromium of said iron or steel is supplied by said rustless iron or steel scrap, said charge forming a bath of ferrous metal containing carbon and chromium covered by an oxidizing slag for oxidizing the carbon from said bath and containing substantial quantities of chromium oxide inhibiting the corresponding oxidation of chromium from the bath, a portion of the carbon of said bath serving to minimize oxide inclusions dispersed throughout the bath; and after said charge is completely melted down and the carbon content of said bath has reached a desired low value adding to said bath and slag a further quantity of chrome ore and a reducing agent to said slag whereby the oxides of iron and chromium present are reduced thereby enriching the bath.

6. In the production of rustless irons and steels in an electric arc furnace, the art which includes, melting down in said furnace, at a high temperature or a temperature of super-heat, a charge comprising rustless iron or steel scrap, ordinary iron or steel scrap, high-carbon ferrochrome, chrome ore and an oxide of iron, thereby forming a bath of ferrous metal containing carbon and chromium covered by a slag, the carbon of said bath reacting with the iron oxide present giving a desired circulation of metal and minimizing the oxide particles coming into the metal throughout the practice of the process; and after said charge is completely melted down and the carbon content of the bath has reached a desired low value reducing the iron and chromium oxides present in the slag to effect a recovery of their metallic values and a consequent enrichment in the bath of metals iron and chromium.

7. In the production of rustless irons and steels in an electric arc furnace, the art which includes, melting down in said furnace, at a high temperature or a temperature of super-heat, a charge comprising ordinary iron or steel scrap, high-carbon ferrochrome, chrome ore and an oxide of iron, thereby forming a bath of ferrous metal containing carbon and chromium covered by a slag, the carbon of said bath reacting with the iron oxide present giving a desired circulation of metal and minimizing the oxide particles coming into the metal throughout the practice of the process; and after said charge is completely melted down and the carbon content of the bath has reached a desired low value charging a silicon-containing reducing agent and burnt lime onto said slag and metal, whereby the oxides of iron and chromium present are reduced under basic conditions thereby effecting a high recovery of iron and chromium.

WILLIAM B. ARNESS.