

UNITED STATES PATENT OFFICE

1,925,182

PROCESS FOR THE MANUFACTURE OF
RUSTLESS IRONAlexander L. Feild, Baltimore, Md., assignor to
Alloy Research Corporation, Baltimore, Md.No Drawing. Application September 4, 1931
Serial No. 561,303

17 Claims. (Cl. 75-45)

This invention relates to rustless irons and steels and more particularly to an art of producing the same.

One of the objects of my invention is the rapid, efficient and economical production of rustless irons and steels of desired physical characteristics such as hardenability, workability, incorrodibility, heat resistivity and the like made to a desired analysis of iron and chromium with or without supplementary additions of nickel, copper, manganese, tungsten, molybdenum, vanadium, aluminum, zirconium, titanium as well as permitted amounts of the elements carbon, sulphur, phosphorus and the like.

Another object is the production of rustless iron of the character indicated in a simple, practical and thoroughly reliable manner from inexpensive and readily available raw materials and utilizing known and tried furnacing and operating equipment.

Another object of my invention is the consistent production of a high grade of sound clean metal of the class indicated at a minimum cost of raw materials, power, labor, and the like and with minimum shut-down of furnacing equipment for replacement or repair.

Other objects in part will be obvious and in part pointed out hereinafter.

The invention accordingly consists in the combination of elements, composition of ingredients and mixture of materials, and 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 the preponderant tonnage of rustless iron manufactured today is still being made by the original process of incorporating expensive low-carbon ferro-chrome, containing in the neighborhood of 0.10 per cent carbon and 70 per cent chromium, in a molten bath of low-carbon iron, care being taken to keep absorption of carbon from the electrodes at a minimum.

Numerous processes other than the original process have been proposed for the manufacture of rustless iron from primary sources of chromium other than low-carbon ferro-chrome, the general idea in the case of these proposed processes being a lower ingot cost. For example, it has been proposed to employ a direct-reduction procedure whereby chromium is reduced directly from chromium ore into an underlying molten bath of low-carbon iron. Likewise, it has been proposed to

employ the relatively cheap high-carbon ferro-chrome, which contains as a rule from 4 to 6 per cent carbon and about 70 per cent chromium, as a primary source of chromium for the steel-making process instead of low-carbon ferro-chrome, the necessary carbon elimination being effected by suitable means.

It may be further noted that in the production of rustless irons and steels of the character indicated large quantities of rustless iron scrap become available about the steel plant, such as imperfect ingots, ingot butts, crop ends, and the like. Likewise, considerable quantities of rustless scrap become available in the various customer plants where rustless iron sheet, strip, bars, and the like are fabricated.

Heretofore known and/or used processes for producing rustless iron, however, in addition to being expensive and inefficient provide no commercial outlet for the large quantities of rustless iron scrap resulting as above indicated.

In addition to the various methods proposed and employed for the manufacture of rustless iron from primary sources of chromium, several procedures have been described for the remelting of rustless iron scrap. These proposed remelting processes are commercially inoperative or else severely restricted in their application by certain inherent characteristics. Such processes of remelting either yield an ingot containing a higher carbon content than the original rustless iron scrap, or a substantially lower chromium content, or both in combination. The inadequacy of such remelting processes is apparent.

One of the outstanding objects of my invention is the rapid, efficient and economical production of rustless iron and steel to a desired specification from readily available and inexpensive raw materials in which an outlet is provided for the large quantities of rustless iron scrap made available as indicated above.

Referring now more particularly to the practice of my invention, I prefer to employ an electric furnace of the well-known Heroult type, lined to a height of somewhat above the slag line with chromite brick carrying a superimposed rammed-in and formed layer composed of approximately three parts, by weight, of crushed chrome ore and one part of ground magnesite; water-glass serves as a good binder for this rammed-in part of the bottom lining. Side-walls and roof may be of silica brick in accordance with ordinary practice. Either carbon or graphite electrodes may be employed, the applied voltage being prefer-

ably available in several steps over the range from 100 to 180 volts.

I do not wish, however, to limit my invention to the use of any particular type of furnace or composition of bottom lining or applied voltage, since it will be readily understood by those skilled in the art that considerable latitude of choice exists in respect to means employed for holding and heating the charge.

As an example of the practice of my invention in the manufacture of rustless iron ingots containing 16 to 18 per cent chromium, and not more than 0.10 per cent carbon, ten thousand, five hundred pounds, (10,500) of rustless iron scrap, analyzing approximately 16.5 per cent chromium, 0.10 per cent carbon, 0.35 per cent manganese, 0.40 per cent silicon, 0.03 per cent phosphorus, and 0.02 per cent sulphur is first charged onto the bottom of a 6-ton Heroult furnace; this bottom having been installed in accordance with the procedure above described and pre-heated for reception of the charge by the usual method of arcing on electrode butts.

To prevent excessive carbon contamination of the rustless iron scrap, as more particularly described hereinafter, suitable oxidizing slag forming ingredients such as roll scale, analyzing about 69 per cent iron, and magnetic iron ore concentrate, analyzing about 65 per cent iron, are preferably added along with the rustless iron scrap. There is also preferably added a material high in chromium content in sufficient quantity to bring the chromium content of the tapped heat of metal (considerably diluted by the large quantities of iron coming from the iron oxide slag) up to the desired value. For this purpose the relatively inexpensive high-carbon ferrochrome analyzing approximately 5 per cent carbon and 69 per cent chromium is found satisfactory.

In determining the required amounts of oxidizing slag forming ingredients and the material high in chromium content (for example high-carbon ferrochrome) it is necessary to determine the relative proportions of these ingredients so as to allow sufficient oxide in the slag to remove the carbon coming from the high-carbon ferrochrome as well as to prevent or preclude contamination of the metal by carbon coming from the carbon electrodes and, at the same time, add sufficient chromium to make up for the diluting effects of the reduced iron oxide on the metal so as to achieve a tapped metal of the desired analysis. These figures are ordinarily determined empirically. For the amount of rustless iron scrap indicated above the quantities of roll scale and magnetic iron ore added at the first instance are about 1000 pounds and 1200 pounds respectively and the quantity of high-carbon ferrochrome of the approximate analysis indicated is about 1650 pounds.

Under the action of the intense heat of the electric arcs playing upon the charge the various ingredients begin to melt down to form pools of metal beneath the several carbon containing electrodes. There are also formed blankets of strongly oxidizing slag covering the respective pools of metal. Both the various oxidizing slags and the pools of metal, especially the upper surfaces of these pools, are at high temperature due to the proximity of the several respective electric arcs. The importance of this feature will appear more fully hereinafter.

The pools of metal contain chromium together

with appreciable quantities of carbon, the chromium coming from the rustless iron scrap and the ingredient high in chromium content, preferably high-carbon ferrochrome, and the carbon coming from the scrap and from the ingredient of high chromium content, (the carbon coming from this latter source is considerable where high-carbon ferrochrome is employed).

During the melting of the various ingredients as indicated above large quantities of carbon in a highly active state become available within the furnace and especially in and about the electric arcs established from the several electrodes to the ingredients first and later to the pools of metal covered by slag formed beneath the several electrodes as above indicated.

Due to the immediate presence of large quantities of carbon in highly active state in the furnace atmosphere and in and about the electric arcs, and due to the avidity with which chromium containing ferrous metal absorbs carbon, there is a great tendency towards carbon contamination of the melted metal directly traceable to the carbon containing furnace electrodes as indicated above. This tendency toward carbon pick-up by the metal is prevented by the oxidizing slag covering the metal and intervening between the metal and the electric arc. As a result of the strongly oxidizing character of this slag and the high temperature at which the slag and upper surface of the melted metal are maintained the large quantities of carbon which would ordinarily become absorbed by the metal are oxidized and such absorption effectively precluded; carbon from the furnace electrodes is thus directly excluded from the metal.

As the heating action of the furnace continues more and more of the initial charge of ingredients around and beneath the pools of metal melts; the melting being largely due to convection currents in the several pools caused by the temperature difference between the top and bottom of the pools and between the center and edges as well as by the electric forces within the pools and the metallurgical reactions of the various melting ingredients.

Due to the continuous circulation of the metal within these pools the upper surface of this metal is in a continual state of flux and the metal of appreciable chromium and carbon contents is brought into contact with the over-lying blanket of oxidizing slag. Under the oxidizing action of the slag and the high temperature employed carbon supplied the melted metal from the rustless scrap and high-carbon ferrochrome is oxidized and eliminated from the process. The rate at which carbon elimination proceeds however does not greatly exceed the rate at which carbon is gained from the melting ingredients rustless scrap and high-carbon ferrochrome so that the pools of metal have appreciable carbon contents which ordinarily decrease but slightly during the continuous melting down of the raw materials.

There is however a continual oxidation of carbon from the pools of metal as above indicated this action being accompanied by oxidation of chromium from the metal and a transfer of the chromium oxide formed into the slag blanket over-lying the metal.

Continued heating of the charge causes the pools of metal beneath the furnace electrodes to increase in size and finally flow together or merge into a single pool or bath of metal covered by a single oxidizing slag. The elimination of carbon from this bath of metal, accompanied by the ox-

idation of chromium, continues as described above with an ever increasing chromium oxide content of the slag which soon renders the slag stiff, refractory and generally unworkable.

In order to assure the formation of the bath of ferrous metal from the various constituents as indicated above, and, furthermore, to permit maximum ease in furnacing these materials, the ingredient high in chromium content (high-carbon ferrochrome) is added before the slag covering the bath of metal becomes hard and stiff; conveniently this addition is made along with the scrap as illustratively described above.

The heating of the charge is continued until all of the materials are melted and the entire bath of metal and slag is brought up to a temperature of super-heat.

No reliable method is known to me for accurately determining the temperature of the bath or pools of metal immediately under the slag blanket but it is estimated that this temperature, which is referred to herein as a temperature of superheat, should be approximately 3250° F. which is some 200 to 250° F. higher than that usually obtained in ordinary electric steel practice.

At this time an additional 1000 pounds of roll scale and 1200 pounds of magnetic iron ore concentrate are conveniently charged onto the bath of slag and metal to increase the oxidizing character of the slag which is considerably diminished thru reaction with the ingredients of the bath and appreciably diluted by the products of this reaction (largely chromium oxide) which, as indicated above, find their way into the slag.

In order to bring the carbon content of the bath of metal down to a desired low value metal and slag are maintained at the temperature of super-heat until a sample taken from the bath indicates that the low value is reached. During this period, ordinarily referred to as the oxidizing period, the carbon is oxidized by the iron oxide supplied to the bath of metal and slag; this action being accompanied by further oxidation of chromium from the metal.

The following table exhibits in a general way the relation between carbon and chromium during the oxidizing period:

Per cent carbon	Per cent chromium
.30	15.0-17.0
.20	14.0-15.0
.14	11.0-13.0
.12	9.0-11.5
.10	8.5-10.5
.08	7.5-10
.06	7 - 9.5

It may be noted that when the carbon content of the bath of metal is not over 0.12 per cent the weight of chromium contained in the slag as chromium oxide is roughly equal to the weight of chromium in the metal.

The oxidizing period is preferably continued so as to bring the carbon content to an even lower value.

After the second addition of roll scale and magnetic iron ore concentrate becomes incorporated in the slag and about four hours and twenty-five minutes after the first application of power, a sample taken from the metal bath shows a carbon content of 0.06 per cent and the oxidizing period is at an end.

Eighteen hundred and fifty (1850) pounds of crushed 50 per cent ferrosilicon and 3000 pounds of freshly burned lime are then added to the slag

as rapidly as furnacing conditions permit. When the appearance of the slag indicates that the iron oxide and chromium oxide content have fallen to a relatively low value, final additions of lump low-carbon ferromanganese and lump ferrosilicon are made to the metal bath.

The heat is tapped and poured into 10 x 10 inch ingot molds. Ladle tests show the product of the heat to analyze 17.23 per cent chromium, 0.08 per cent carbon, 0.34 per cent manganese, 0.48 per cent silicon, 0.030 per cent phosphorus, and 0.025 per cent sulphur. The product of the heat weighs approximately 16,000 pounds indicating a recovery of chromium of more than 90 per cent.

Supplementary additions of copper, tungsten, molybdenum, vanadium, aluminum, zirconium, titanium and the like may be made as desired any time before tapping. Of the chromium content of the tapped metal about three-fifths comes from the chromium contained in the rustless scrap utilized and two-fifths comes from the high-carbon ferrochrome employed; the chromium coming from these respective sources being in the ratio of about three to two.

The production of sound clean metal containing a minimum of oxide particles, as compared with heretofore known processes, is assured by the use of the chromite furnace bottom which is especially resistant to the attack of the strongly oxidizing slag at the high temperatures employed assuring minimum contamination of slag and metal, maximum life of bottom and a reliability of furnace operation unknown in heretofore known and/or used processes of the class indicated. The freedom of contamination from bottom material permits full effect of the oxidizing slag forming ingredients and the realization of an undiluted condition of the slag. Likewise, in the production of rustless irons and steels of the class indicated, many practical advantages, such as an improved efficiency, economy and reliability of furnace operation, are achieved by employing an electric arc furnace having a chromite bottom which furthermore permits the production of metal comparatively free of pits, pockets and other effects of gas inclusions found in metal produced in accordance with heretofore known processes.

As a second example of the practice of my invention, ten thousand five hundred pounds (10,500) of rustless iron scrap analyzing approximately 19 per cent chromium, 8.5 per cent nickel, and 0.10 per cent carbon is first charged onto the bottom of a 6-ton Heroult furnace, lined with chromite. Along with the rustless iron scrap there is preferably charged 700 pounds of high-chromium, high-nickel scrap analyzing approximately 65 per cent nickel, 14 per cent chromium, and 0.20 per cent carbon, 2,000 pounds of roll scale, and 1,200 pounds of high-carbon ferrochrome. Thus the chromium contributed by the rustless iron scrap and chromium-nickel scrap is then about three times that contributed by the high-carbon ferrochrome, or the ratio is about three to one.

This charge is then melted down and brought to a degree of super-heat sufficient to permit the charging of an additional 2,000 pounds of roll scale. The bath is preferably maintained in a condition of super-heat throughout the oxidizing period.

After this addition of roll scale becomes thoroughly incorporated in the slag a sample of metal

taken from the metal bath shows a carbon content of 0.04 per cent. Fifteen hundred (1500) pounds of crushed 50 per cent ferrosilicon and 3500 pounds of burned lime are then added to the slag as rapidly as furnacing conditions permit.

The heat is tapped when the slag shows a relatively low content of iron and chromium oxide and after a final addition of low carbon ferromanganese has been made. Ladle test shows the heat to analyze 19.34 per cent chromium, 8.59 per cent nickel, 0.07 per cent carbon, 0.39 per cent manganese, and 0.40 per cent silicon. The product of the heat weighs 15,400 pounds.

Thus it will be seen that there has been provided in this invention an art in which the various objects hereinbefore set forth together with many thoroughly practical advantages are successfully achieved. It will be seen that the process is simple, economical and thoroughly practical and that a wide range of rustless irons and steels of high quality may be produced from inexpensive and available raw materials and an outlet provided for large quantities of rustless iron scrap which, heretofore, was of little practical value.

While in the two illustrative examples given above, a portion of roll scale and magnetic iron ore concentrate, (for the iron-chromium alloy) or merely roll scale (for the iron-chromium-nickel alloy) is added with the initial charge and the remainder after melting-down, my invention is not limited to this particular feature of practice. All of the oxidizing material may at times be included with the initial charge when such procedure is found desirable.

In the practice of my invention certain advantages in production are achieved by so adjusting the proportions of roll scale (or other iron oxide material) to charge that when the metal bath has reached the desired degree of super-heat the carbon content of the bath has been concurrently lowered to the desired low percentage.

Likewise, while I prefer to employ roll scale (or iron ore) without admixture of other materials, it will be readily understood that other ingredients may be admixed therewith in judicious proportions without materially decreasing the oxidizing power thereof.

While in the illustrative embodiments of my invention, as set forth above, high carbon ferrochrome is used as a source of iron and chromium in addition to the rustless iron scrap employed, it will be understood that in the production of rustless iron many practical advantages are achieved where rustless iron scrap is used as a source of iron and chromium, either with or without an additional source of chromium, depending upon the analysis desired in the final product and the analysis of the rustless iron scrap available.

As many possible embodiments may be made of my invention and as many changes may be made in the embodiments hereinbefore set forth, it is to 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 iron, the art which includes, charging rustless iron scrap and an oxidizing slag forming ingredient into a chromite lined electric arc furnace having carbon containing electrodes; melting down said scrap and said slag forming ingredient thereby giving a bath covered by an oxidizing slag, and main-

taining said bath and slag at a temperature of superheat during further melting of said scrap and slag forming ingredient to preclude carbon contamination of said bath by said electrodes, the attack of the furnace lining by said slag at the high temperature involved and consequent contamination of the slag being inherently prevented by said chromite.

2. In the production of rustless iron, the art which includes, charging rustless iron scrap and an oxidizing slag forming ingredient into a chromite lined electric arc furnace having carbon containing electrodes; melting down said scrap and said slag forming ingredient thereby giving a bath covered by an oxidizing slag, maintaining said bath and slag at a temperature of superheat during the further melting of the charge to preclude carbon contamination of said bath, this action being accompanied by a loss of chromium into the slag; and then adding a reducing agent to the slag whereby chromium contained in the slag is precipitated into the underlying bath to effect an enrichment of said bath.

3. In the production of rustless iron, the art which includes, melting down in an electric arc furnace having a chromite bottom chromium iron scrap and a material containing substantial quantities of alloyed chromium in the presence of an oxidizing slag thereby forming a bath of metal covered by an oxidizing slag; maintaining said slag at a high temperature thereby oxidizing carbon contained in said bath and incidentally oxidizing some of the chromium content, the oxidized chromium passing into the slag; and then deoxidizing the chromium oxide passed into the slag and permitting a return of chromium to the bath.

4. In the production of rustless iron in an electric furnace, the art which comprises, melting together rustless iron scrap and a high carbon ferrochrome, thereby forming a ferrous metal bath containing carbon and chromium; preparing an oxidizing slag overlying said bath; and maintaining said bath beneath said slag at a temperature of superheat until the carbon content of the bath is reduced to a desired low value.

5. In the production of rustless iron in an electric furnace, the art which comprises, melting together rustless iron scrap and a high carbon ferrochrome, thereby forming a ferrous metal bath containing carbon and chromium; preparing a strongly oxidizing slag overlying said bath; and maintaining said bath beneath said slag at a temperature of superheat until the chromium content of the bath has been lowered an appreciable amount.

6. In the production of rustless iron, the art which comprises, melting together rustless iron scrap and a high carbon ferrochrome, thereby forming a ferrous metal bath containing carbon and chromium; and maintaining said bath beneath an oxidizing slag at high temperature until the carbon content of said bath is reduced to a desired low value, said reduction in carbon content being accompanied by a loss of chromium into the slag; and then deoxidizing said slag, thereby achieving a recovery of the chromium so lost from said bath.

7. In the production of rustless iron, the art which comprises, melting together iron scrap containing a substantial amount of chromium and a ferrous alloy relatively high in carbon and chromium, thereby forming a ferrous metal bath containing carbon and chromium; maintaining said bath beneath an oxidizing slag at high temperature, thereby reducing the carbon content of said

bath to a desired low value and oxidizing a substantial part of the chromium thereof, the chromium so oxidizing entering the slag; and then deoxidizing the chromium oxide contained in said slag until there is achieved a desired chromium content of said bath.

8. In the production of low-carbon ferrous alloys relatively high in chromium, the art which comprises, forming a ferrous metal bath containing carbon and chromium and a slag from rustless iron scrap, a material high in iron oxide, and a chromium ferro-alloy relatively high in carbon; removing carbon and chromium from said bath until the bath contains a substantially lower percentage of chromium than that desired in the finished product by maintaining said bath and slag at a relatively high temperature, the chromium removed passing into the slag; and enriching the metal in chromium until the desired percentage is achieved by adding a reducing agent and a basic material to said slag.

9. In the conversion of rustless iron scrap into rustless iron ingots or other castings having substantially the same or a higher percentage of chromium, the art which comprises, melting rustless iron scrap in the presence of high-carbon ferro-chrome and an iron oxide, to form a molten bath of ferrous metal containing carbon and chromium covered by a slag, maintaining said bath at a relatively high temperature until the carbon content of the metal has fallen to a desired low percentage chromium incidentally passing into the slag as an oxide; and then adding to said slag a silicon reducing agent and lime thereby reducing the oxide of iron and chromium in the slag and substantially increasing amount of iron and chromium in the metal bath.

10. In the conversion of rustless iron scrap into rustless iron ingots or other castings having substantially the same or a higher percentage of chromium, the art which comprises, incorporating a pre-determined quantity of high-carbon ferro-chrome in a molten bath of ferrous metal containing carbon and chromium formed from rustless iron scrap and a material high in iron oxide such as roll scale; maintaining said bath at a relatively high temperature until the carbon content has fallen to a desired low percentage, the drop of carbon being accompanied by the oxidation of chromium and then adding lime and ferrosilicon to said bath, thereby enriching the metal in chromium until the desired percentage is achieved.

11. In the production of rustless iron the art which comprises, incorporating rustless iron scrap, high-carbon ferro-chrome and iron oxide in a highly heated bath of metal and slag, charging an additional quantity of iron oxide, removing excess carbon from the metal by maintaining said bath and slag at a relatively high temperature, adding a silicon reducing agent and lime to said bath of metal and slag and maintaining said bath in a molten condition until the slag is substantially free from iron and chromium.

12. In the remelting of rustless iron scrap without degradation of the chromium content thereof, the art, which comprises, incorporating rustless iron scrap and high-carbon ferrochrome in molten ferrous metal to form a bath containing carbon and chromium, maintaining said bath under an oxidizing slag at a relatively high temperature until the carbon content has fallen to the desired low percentage, and then reducing chromium oxide and iron oxide contained in said

slag by means of a suitable reducing agent, thereby enriching the metal bath in chromium until the desired percentage is achieved.

13. In the remelting of low-carbon high chrome steel scrap without degradation of the chromium content, the art which comprises forming a molten ferrous metal bath containing carbon and chromium from said scrap and high-carbon ferrochrome, maintaining said bath under an oxidizing slag at a relatively high temperature until the carbon content has fallen to the desired low percentage, and then reducing chromium oxide and iron oxide contained in said slag by means of a suitable reducing agent, thereby enriching the metal bath in chromium until the desired percentage is achieved.

14. In the remelting of rustless iron scrap to produce a low-carbon alloy containing chromium and a supplementary alloy element such as nickel, the art which comprises, incorporating a predetermined quantity of said supplementary alloy element in a bath of ferrous metal containing carbon and chromium formed from said rustless iron scrap, high-carbon ferro-chrome and iron oxide, maintaining said bath and supplementary addition at a relatively high temperature until the carbon content of the metal has fallen to the desired low percentage, and then adding lime and a silicon reducing agent to the bath, thereby enriching the metal in chromium until the desired percentage is achieved.

15. In the production of a low-carbon ferrous alloy having a relatively high chromium content from rustless iron scrap having substantially the same chromium content as the alloy to be produced, the art which comprises, melting a charge containing pre-determined quantities of said scrap, high carbon ferro-chrome, and an iron oxide, to form a molten bath of metal and slag, maintaining said bath at a relatively high temperature until sufficient carbon has been removed from the bath by oxidation due to the iron oxide, during which operation a portion of the chromium forms a chromium oxide in said slag, and charging a suitable agent to reduce said chromium oxide thereby enriching the metal in chromium until the desired content is achieved.

16. In the production of rustless iron, the art which includes, melting down chromium containing scrap and a chromium containing ferro-alloy in such quantities that the chromium contributions thereof are respectively from about 3—2 to 3—1; providing an oxidizing slag on the melt thus formed; maintaining said slag at a high temperature thereby oxidizing objectionable carbon contained in the melt together with a substantial amount of chromium, the chromium thus oxidized entering the slag; and then deoxidizing the chromium so oxidized whereby a chromium recovery of the melt is achieved.

17. In the production of rustless iron, the art which includes, melting down rustless iron scrap and high-carbon ferro-chrome in proportions of from about 3—2 to 3—1 for the respective chromium contents of these ingredients; providing an iron oxide slag on the melt thus formed; bringing said melt and slag up to a temperature of superheat thereby oxidizing carbon from the melt together with a substantial amount of iron and chromium, the iron and chromium thus oxidized entering the slag; and then deoxidizing the oxides of iron and chromium contained in said slag whereby a recovery of these elements is achieved.