Patented Nov. 4, 1947 2,430,131

# UNITED STATES PATENT OFFICE

2,430,131

## PRODUCTION OF STAINLESS STEEL

Donald L. Loveless, Baltimore, Md., assignor, by mesne assignments, to The American Rolling Mill Company, Middletown, Ohio, a corporation of Ohio

No Drawing. Continuation of application Serial No. 437,695, April 4, 1942. This application November 4, 1944, Serial No. 562,041

5 Claims. (Cl. 75—12)

1

This application for patent is a continuation of my copending application, Serial No. 437,695 filed April 4, 1942, and entitled Production of stainless steel, and the invention relates to the manufacture of stainless steel and more particularly to a process of producing stainless steel of the low carbon grades from readily available raw materials.

One of the objects of my invention is the production of low carbon stainless steel in a simple, highly efficient and economical manner, from readily available and comparatively inexpensive raw materials, using known and available melting and furnacing equipment.

Another object of my invention is the provision of a process of producing the low carbon grades of stainless steel which process is adapted for consumption of a wide variety of chromium-bearing ingredients, as well as numerous types of ferrous raw materials, and which, nevertheless, is practiced with exceptional expediency, giving a clean, sound, low carbon, high grade product of desired analysis.

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

The invention, accordingly, consists in the combination of materials and composition of ingredients, and in the several steps and the relation of each of the same to one or more of the others as described herein, 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 should be noted at this point that stainless steel is defined as an alloy steel, comprising from about 10% to about 35% chromium, either with or without supplementary additions of nickel, manganese or copper; or molybdenum or tungsten; or vanadium, titanium, columbium; or aluminum or silicon; or sulphur, and the like, for special purposes, and the balance substantially all iron. The carbon content desirably is under .10% and preferably is as low as .07% or even .05%.

Certain processes of producing stainless steel include preparing in a suitable furnace, a melt of low-carbon steel of high purity and introducing chromium in the melt through the addition of refined ferro-alloys such as low-carbon ferrochrome. In these processes a minor quantity of chromium also may be introduced as stainless steel scrap. Such processes, however, requiring the use of expensive consistently high-grade materials, are impractical where low ingot cost must be maintained. Moreover, a low-carbon product, say 0.07% carbon or less, may not be obtained

2

in this manner because such processes make no provision for carbon elimination and carbon introduced in the scrap and ferrochrome appears in the resulting product.

More recently developed processes such as those disclosed in the Feild Patent 1,925,182 and the Arness Patents 1,954,400 and 2,056,162, include the use of relatively cheap raw materials as a source of chromium and are directed toward the achievement of low ingot cost. These more recent processes essentially include melting in a suitable furnace, one or more cheap chromium-bearing ingredients, such as high-carbon ferrochrome, chrome ore, and stainless steel scrap, to produce an iron-chromium bath with an overlying slag; and then recover the metallic values of the slag by a suitable reducing agent to give the finished steel.

Especially in the more recent stainless steel processes, employing either or both of chrome ore and high-carbon ferrochrome, many difficulties are encountered in melting down the charge of ingredients, and subsequently in refining the melt. In the initial melt down of ingredients, which customarily is accomplished in an electric arc furnace, a bath of ferrous metal is formed containing large quantities of chromium and appreciable quantities of carbon. During the melt down, a carbon reactive slag is formed containing large amounts of iron oxide. This slag eliminates carbon but also oxidizes chromium from the bath. These oxides migrate into the slag, thus the slag contains considerable quantities of the oxides of iron and chromium.

Now the slag had in these processes, unfortunately is of thick consistency and becomes hard and crusty, in spite of the intense heat of the furnace electrodes. This ordinarily is attributed to the presence of large quantities of chromic oxide. The slag, because of its lack of fluidity, is not receptive to the introduction of stainless steel scrap or alloy ingredients during the initial melting operations. Added materials are withheld by the slag and thus do not pass into the melt to any satisfactory degree. Moreover, the hard crusty character of the slag limits its effectiveness in the removal of carbon, particularly is this felt in attempting to obtain a product having a carbon content of .07% or less.

Although the slag may be broken up, any disturbance of the thick slag, as for example, by furnace arc operation, by the addition of materials, or through stirring, leaves the metal bath unduly exposed to carbon contamination from external sources, notably the furnace electrodes.

Carbon picked up by the melt, particularly near the end of the oxidation heat of the metal and during the reduction heat, becomes a permanent alloy element and affects final carbon analysis of the finished steel.

During the reduction stage, where chromium and iron are recovered from the oxide slag through the addition of noncarbonaceous reducing material, such as ferrosilicon, the sluggish character of the slag is responsible for considerable losses of chromium and iron. Oxides are reduced only partially by virtue of improper admixture of thick slag and reducing material, and yielded base metal is impeded by the thick slag and thus cannot gravitate into the bath. Considerable base metal, as well as valuable oxides, therefore, remain in the slag and are lost in slagging off.

One of the objects of my invention is the provision of a process of producing stainless steel of the low carbon grades, under .10% carbon and preferably under .07% carbon, employing a maximum of inexpensive raw materials and yielding clean, sound metal of desired analysis all in a minimum of time, and with optimum ease of furnace operation.

Referring now more particularly to the practice of my invention, I preferably employ an electric arc furnace of the well known Heroult type of 13-ton capacity. This is lined to a height somewhat above the slag line with chromite brick, with side-walls and roof lined with silica brick. The electrodes are of carbon or graphite, operable under an applied voltage available in several stages, within the approximate range of 100 to 275 volts.

In order to protect the chromite brick lining from erosion by molten metal and slag, I apply a coating of burnt lime to the lining. Usually a proportion of lime approximating 10 to 20 pounds per ton of steel is sufficient for this purpose. The furnace then is preheated, in any suitable manner, as a final step preparatory to charging.

In the production of a heat of stainless steel, I charge into the prepared furnace an inexpensive source of chromium including one or both of the raw materials high-carbon ferrochrome and chrome ore. In addition to these ingredients there preferably is included in the charge a substantial quantity of stainless steel scrap. The scrap comprises one or more of such materials as pit and scull scrap, high-carbon, high-chromium scrap and castings, ingot butts, crop ends, roll scale, punchings, clippings, grinding dust, and the like, commonly available, as for example, about the melt shop, rolling mill, and the various customer plants. The chromium-bearing materials chrome ore and high-carbon ferrochrome conveniently are used separately, or in such proportions with respect to the stainless steel scrap as to be consistent with satisfactory furnace operation, giving recognition to variations in availability of the materials and to fluctuations in their market prices.

I also charge into the furnace a substantial quantity of a material rich in oxide of titanium, illustratively, ilmenite, titanite, or rutile. Where needed, ordinary iron or steel scrap also is added. In addition, I charge a substantial quantity of oxide of iron, such as low-carbon steel roll scale.

Power is applied to the furnace and the charge is melted down and forms a bath of alloy metal, having a supernatant slag. This slag is of a fluid consistency. Moreover, it is high in iron oxide content. The melt-down is, therefore, under strongly oxidizing conditions so that there is a rapid elimination of any carbon in the melt. The carbon content of the stainless steel scrap present as well as that of any base steel scrap is rapidly eliminated. So also is the substantial carbon content of any high carbon ferrochrome employed. Unfortunately, however, along with the oxidation of carbon there is an oxidation of chromium contained in the bath of metal, this migrating into the slag as oxides of chromium. At the conclusion of the melting period, therefore, the melt consists of a bath of low-carbon steel of appreciable chromium content, with an overlying blanket of slag.

As illustrative of the practice of my invention, the production of a 16-ton heat of metal to a specification, for example, of 18% to 20% chromium, 8% to 10% nickel, less than 0.07% carbon, less than 0.65% each of manganese and silicon, and the remainder substantially all iron, 4700 pounds of chrome ore analyzing 48% chromium oxide ($Cr_2O_3$) are shoveled onto the banks of the furnace. I then charge the furnace with 19,200 pounds of stainless steel scrap having an average analysis of about 18.3% chromium, 8.5% nickel, less than 0.20% carbon, and the balance substantially iron; 190 pounds of low-carbon, 7% nickel steel scrap; 500 pounds of low-carbon, 8% chromium, 3% nickel steel scrap; 480 pounds of high-carbon ferrochrome analyzing approximately 65% chromium, 5% carbon and the balance substantially iron; 5300 pounds of plain low-carbon steel roll scale; and 725 pounds of ilmenite ($FeTiO_3$) comprising approximately 42% titanium oxide ($TiO_2$), 34.2% iron oxide (FeO), 2.75% silica, 1.35% alumina, and 1.90% magnesia. Alternating current electrical energy is supplied the furnace and the charge of ingredients melts down, leaving a bath of metal with an overlying slag.

In accordance with my invention, the function of the bath of metal and its overlying slag is greatly facilitated by the ilmenite or other fluidifying agent contained in the charge. The fusing slag is fluid and smooth as compared to heretofore known melt-down slag conditions. It is more reactive. Moreover, it is well distributed over the surface of the metal bath, and its efficiency is greatly enhanced.

In the process, the fluid slag, containing large amounts of iron oxide, is highly effective in oxidizing carbon, as for example, that entering the process from the furnace charge and from the furnace electrodes. Iron oxide added with the charge is in excess of that theoretically required to combine with the carbon in the charge, plus the carbon pick-up during melting. The greater the chromium in the charge and the greater the amount of carbon to be oxidized, the greater must be the excess of iron oxide. The initial presence of a relatively large quantity of chromium oxide in the slag inhibits the oxidation of chromium from the molten metal, since the vigor of chromium oxidation is inversely proportional to the amount of chromium oxide already contained in the slag. Slag fluidity ensures intimate contact between iron oxide in the slag and carbon in the melt, or carbon coming from an external source, and, moreover, prevents the electric furnace arc from kicking away the slag and exposing underlying bath metal to the furnace atmosphere. With the fluid slag, a vigorous reaction is rapidly achieved causing a type of oxidation, or distribution of oxidation reaction, which quickly gives a low-carbon product and

which renders the metal more susceptible to cleansing and refining in subsequent stages of the process.

Melting of the charge and elimination of carbon further are expedited and are rendered more effective by employing a high melt-down temperature. The oxidizing effect of the slag is intensified at elevated temperatures and the extremely fluid conditions of the slag then obtaining. Oxidation of carbon from the melt is greatly accelerated. By employing a high melt-down temperature, and a fluid slag, melt-down of ingredients and removal of carbon from the melt, is successfully achieved in about one and one-half house, thus effecting a substantial saving in melting time.

While I know of no reliable method for determining the temperature of molten metal immediately beneath the slag blanket, it is estimated that this temperature falls within the range of 3100° F. to 3250° F., which incidentally is some 150° F. to 300° F. above the temperatures ordinarily employed in the usual electric steel-making processes. This high temperature is referred to hereinafter as a temperature of superheat.

After melting down the charge of ingredients at a temperature of superheat, samples of metal are taken from the bath for carbon analysis. The sampling and analyzing steps together require about 15 minutes of the total process period. For the example given, the samples indicate a carbon content of 0.03%, which is considerably below the maximum carbon value specified.

In order to achieve maximum economy commercially, the oxides of iron and chromium in the slag are recovered during a subsequent reducing period. In recovering iron and chromium from the slag, an amount of non-carbonaceous reducing agent such as crushed ferro-silicon, alsifer (aluminum-silicon-iron alloy), or crushed ferrochrome-silicon, chemically in excess of the reducible oxides of iron and chromium in the slag, is charged onto the slag overlying the metal bath. Power applied to the furnace electrodes is diminished somewhat below that required in producing a temperature of superheat, and the non-carbonaceous reducing agent fuses into the fluid oxide slag. The fluid condition of the slag permits thorough reaction between reducing agent and iron and chromium oxides of the slag. Iron and chromium recovered gravitate readily through the fluid slag and pass into the bath. Where an ingredient rich in titanium oxide, such as ilmenite, titanite, or rutile, is employed, the ingredient is not decomposed by the non-carbonaceous reducing agent. Moreover, it is not decomposed by the heat of the furnace and the electric arc. The titanium oxide containing ingredient thus maintains slag fluidity throughout the reducing period, without introducing titanium into the melt.

For the illustrative heat of metal indicated above, a substantially complete recovery of iron and chromium is achieved by charging onto the fluid slag, successive quantities of ferrosilicon amounting in total to 4370 pounds of 50% grade ferrosilicon and 500 pounds of 75% grade ferro-silicon.

Silicon contamination of the molten metal, during the reducing stage of the process is substantially prevented by supplementary addition to the fluid slag of burnt lime in amount sufficient to ensure the maintenance of basic slag conditions. The fluid condition of the slag established through the presence of the titanium oxide ingredient, such as ilmenite, enables more complete dispersion of the lime and non-carbonaceous reducing agent throughout the slag, thus giving more complete reduction of iron and chromium oxides in the slag, and ensuring more positive formation of stable basic calcium silicates as slag components. It will be understood that the lime conveniently is charged onto the slag in successive batches alternating with the addition of successive quantities of ferrosilicon, along with supplemental amounts of fluidifying ingredient where needed. As an alternative, I find it practical to mix the lime and ferrosilicon on the melt shop floor and to charge successive batches of the mixture onto the slag. In the illustrative heat, I find that 9200 pounds of burnt lime prevent silicon contamination of the melt despite the large quantities of ferrosilicon employed.

A quantity of chrome ore (3300 pounds for the illustrative example given) is conveniently charged, along with the non-carbonaceous reducing agent and burnt lime in corresponding successive batches, further quantities of the titanium oxide bearing ingredient being introduced where necessary. The chrome ore used in the process at this stage enables better control over slag volume during the earlier melt-down period and is reduced readily in the fluid slag to metallic chromium. It will be understood, however, that the use of chrome ore may be dispensed with in both the melt-down and reducing stages, or may be used solely in one or the other of the stages.

After all of the ferrosilicon and lime (and chrome ore where used) have been added and have fused and completed their reactions with ingredients contained in the fluid slag and molten metal, which incidentally requires about 1¾ hours, the reducing period is at an end. This is evidenced by a change in color of successive samples of slag, taken from the furnace, from a black to a light green or light gray color. The fluid slag from which the metals iron and chromium are recovered with a very minimum of waste to the slag, then is substantially completely drawn off the bath of molten metal.

Where nickel enters the process, as in the illustrative heat of metal, I find it advantageous to include a major source of nickel in the initial furnace charges, as for example, in the form of alloy nickel scrap. The original charge of nickel, however, is advisedly controlled so as to introduce into the melt, a quantity of nickel somewhat less than that specified so as to avoid overshooting specifications in the final analysis. Nickel in the original charge does not oxidize in the furnace and, therefore, has little effect upon the slag. Later, as toward the end of the reducing period, or during the metal finishing stage, an amount of electrolytic nickel, ferro-alloy nickel, or nickel in other form which is free of contaminating materials, is added to the melt to finally adjust nickel analysis of the alloy metal. During the reducing period, particularly after recovery of iron and chromium from the fluid slag, an accurate analysis of the bath is conveniently made, and the amount of nickel, as well as the amounts of other alloy elements needed can be closely determined. Although the nickel, or other supplemental alloy elements such as tungsten, vanadium, columbium, molybdenum, and the like mentioned hereinbefore, may be added in the furnace during the metal finishing stage or in the ladle, metal added at or near the end of the reducing period enables more thorough melt-down and

better dispersion of the added metal throughout the bath. In the embodiment described above, I add 1010 pounds of electrolytic nickel to the metal bath, preferably at the end of the reducing period.

Following slag-off after the reducing period, I build up a non-carbonaceous finishing slag on the bath of metal. With the finishing slag, oxidation is prevented and final refinement or deoxidation of the metal is achieved. (For the illustrative embodiment described above, a mixture comprising approximately 400 pounds of burnt lime; 35 pounds of fine 75% grade ferrosilicon; and 75 pounds of fluorspar, or an amount of other slag fluidifying material is charged onto the bath. The charged mixture melts down and a supplemental 400 pounds of burnt lime, and about 75 more pounds of fluorspar or amounts of other fluidifying ingredient are added to complete build-up of the finishing slag.) Where desired, lump ferrosilicon and lump ferromanganese, or conveniently silico-manganese, are added to finally adjust the manganese and silicon contents of the heat of metal.

After suitable refining of the metal is achieved, the application of power to the furnace is terminated, furnace electrodes are raised and the heat of metal is tapped into a ladle for teeming. The finishing period, measured from the time of slag-off following the reduction period, to the time of tapping the furnace, amounts to about 1½ hours. For the example given, the heat of metal produces a total of 29,700 pounds of stainless steel ingots analyzing approximately, 18.6% chromium, 8.9% nickel, 0.05% carbon, 0.62% manganese, 0.42% silicon, and the balance substantially iron. The butt scrap comes to 1250 pounds, giving a total for the melt of 30,950 pounds. The metal is sound and virtually free of objectionable oxide inclusions.

Following the tapping of the metal, the furnace lining is repaired with chromite and once more covered with a protective coating of lime. The furnace is charged with ingredients for melt-down, the furnace electrodes are lowered, electric power is applied, and the process is repeated in accordance with the provisions hereinbefore set forth. The time required after tapping to the beginning of melt-down of the charged ingredients amounts to about 45 minutes. A complete process cycle, accordingly, is achieved in substantially less than 6 hours time, this being considerably shorter than the time required in carrying out heretofore known processes, including the use of cheap melt-down ingredients.

Thus it will be seen that there has been provided in this invention an art of producing stainless steel wherein the various objects hereinbefore noted, together with many practical advantages, are successfully achieved. It will be seen further that with the invention, a wide variety of raw materials are utilized rapidly and efficiently, giving maximum economy in the production of clean, sound, stainless steel, and that various combinations of raw materials are permitted, consistent with availability of materials and expeditious furnace operation.

While as illustrative of the practice of my invention, one or more chromium-bearing ingredients such as stainless steel scrap, chrome ore, and high-carbon ferrochrome, and titanium oxide containing material, with oxide of iron such as roll scale and/or an ingredient source of base iron or steel, are initially charged into the furnace; it will be understood that, where practical, any one or more of the materials may be added in part during or at the conclusion of the melt-down or oxidation period. Likewise, it will be understood that although I find great advantage in employing the titanium oxide bearing material throughout both oxidation and reduction periods, considerable advantage is achieved even where the material is added only during the oxidation period or only the reduction period.



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 stainless steel of carbon content not exceeding 0.10% in an electric arc furnace, the art which comprises; melting down under oxidizing conditions a charge of ingredients comprising steel scrap and a source of chromium together with a titanium-oxide bearing material, said steel scrap and source of chromium essentially including at least one of the group consisting of stainless steel scrap, high-carbon ferrochrome and chrome ore, whereby there is had a bath of metal of low carbon content having a supernatant fluid melt-down slag principally consisting of the oxides of iron and chromium and additionally including said oxide of titanium; and at the conclusion of the melting operation and without withdrawing said slag adding to the slag a non-carbonaceous reducing agent and further quantities of the titanium-oxide containing ingredient to recover metallic iron and chromium from the oxides present in the slag.

2. In the production of stainless steel of carbon content not exceeding 0.10% in an electric arc furnace, the art which comprises; melting down a charge including stainless steel scrap, high-carbon ferrochrome, iron oxide and a substantial amount of material rich in the oxide of titanium, whereby there is had a bath of molten metal of substantial chromium content and of very low carbon content having a supernatant fluid melt-down slag principally consisting of the oxides of iron and chromium and additionally including said oxide of titanium; and at the conclusion of the melting operation and without withdrawing said slag adding to the slag a non-carbonaceous reducing agent and further quantities of the titanium-oxide containing ingredient to recover metallic iron and chromium from the oxides present in the slag.

3. In the production of stainless steel of carbon content not exceeding 0.10% in an electric arc furnace, the art which comprises; melting a charge including steel scrap, chrome ore, and a substantial quantity of a material rich in the oxide of titanium, whereby there is produced a bath of molten metal having a carbon content of about 0.03% and having a supernatant fluid melt-down slag principally consisting of the oxides of iron and chromium and additionally including the oxide of titanium; and while retaining the slag adding thereto further quantities of the titanium-oxide containing ingredient and a non-carbonaceous reducing agent, whereby slag fluidity is maintained and the oxides of iron and chromium present in the slag are reduced to metallic iron and chromium.

4. In the production of stainless steel of carbon content not exceeding 0.10% in an electric arc furnace, the art which comprises; melting down under oxidizing conditions a charge including

stainless steel scrap, chrome ore and a titanium-oxide containing ingredient, whereby there is had a bath of molten metal having a low carbon content with a supernatant slag principally consisting of the oxides of iron and chromium and additionally including the oxides of titanium; and while retaining the slag adding thereto further quantities of chrome ore and the titanium-oxide containing ingredient and a non-carbonaceous reducing agent, whereby the oxides of iron and chromium are reduced to metallic iron and chromium.

5. In the production of stainless steel of carbon content not exceeding 0.07% in an electric arc furnace, the art which comprises; melting down under oxidizing conditions a charge including stainless steel scrap, high-carbon ferrochrome, chrome ore, and a substantial quantity of ilmenite, whereby there is had a bath of molten metal of substantial chromium content and a carbon content not exceeding about 0.05% and having a fluid supernatant slag principally consisting of the oxides of iron and chromium and additionally including titanium oxide; and while retaining the slag adding thereto further quantities of ilmenite and a non-carbonaceous reducing agent to recover metallic iron and chromium from their oxides present in the slag.



DONALD L. LOVELESS.


## REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

| Number | Name | Date |
|---|---|---|
| 1,622,977 | Shackelford et al. | Mar. 29, 1937 |
| 2,076,885 | Feild | Apr. 13, 1937 |
| 2,021,979 | Arness | Nov. 26, 1935 |
| 2,027,868 | Kinzel | Jan. 14, 1936 |

OTHER REFERENCES

The Journal of the Iron and Steel Institute, 1938, No. 2, pp. 298P and 299P.