

UNITED STATES PATENT OFFICE

2,031,152

MANUFACTURE OF ALLOYS OF IRON,
CHROMIUM, NICKEL, AND COPPER

Alexander L. Feild, Baltimore, Md., assignor, by
mesne assignments, to Rustless Iron and Steel
Corporation of America, Baltimore, Md., a cor-
poration of Delaware

No Drawing. Application August 10, 1932,
Serial No. 628,185

13 Claims. (Cl. 75-45)

The present invention relates to the manu-
facture of alloys of iron, chromium, nickel and
copper, and more particularly to an economical
method for the manufacture of low-carbon cor-
rosion-resistant nickel-chromium steels contain-
ing a substantial percentage of copper. The
process is particularly applicable to the manufac-
ture of the low-carbon steels commonly called
rustless irons, in which the carbon content is
usually in the neighborhood of .05 to .15%.

In producing the alloy, the nickel and copper
content is derived primarily from a cheap source
consisting of the calcined Sudbury ore contain-
ing nickel and copper which is employed as the
source of the alloy known commercially as
"Monel" metal and containing approximately 2
parts by weight of nickel to 1 part of copper.

In the manufacture of "Monel" metal from the
sulphide ores of the Sudbury district in the
Province of Ontario, Canada, a matte is first
produced containing about 25% copper, 55%
nickel and 20% sulphur. This matte is calcined
in an oxidizing atmosphere to eliminate the sul-
phur and convert the nickel and copper into their
oxides. This product, which contains the oxides
of the nickel and copper in the natural propor-
tions occurring in the ore is known as "Monel"
oxide. This is the material which I prefer to
employ in carrying out my process. It is now
an intermediate product in the making of "Mon-
el" metal and can be obtained relatively cheaply.
By using this product instead of "Monel" metal
I materially decrease the cost of making my alloys
of iron, chromium, nickel and copper. The nickel
and copper oxides, moreover, serve a function in
the process in reducing carbon to produce a low-
carbon steel.

The corrosion-resistant steel or alloy which
I produce preferably contains a relatively high
percentage of chromium, usually not less than
about 10%, so as to impart a rustless or stain-
less character to the metal. The carbon content
is preferably low, usually not more than about
.10%. I prefer that the finished rustless iron or
steel shall have a combined nickel and copper
content of not less than about 8% or over 25%.
I set the lower percentage of my preferred range
at about 8% because a combined percentage of
nickel and copper in this neighborhood is nec-
essary to yield an austenitic steel when the
chromium content is in the usual ranges of 16 to
19% for such austenitic steels. I set an upper
limit of my preferred range at 25% for the com-
bined percentage of nickel and copper because at
a chromium range of 16 to 19% it is not readily

possible to introduce more than this combined
percentage of nickel and copper from "Monel"
oxide without an appreciable sacrifice in economy
of operation. I do not, however, limit myself to
these preferred ranges. For example, the com-
bined percentage of nickel and copper may be low
enough to yield a martensitic or ferritic steel in-
stead of an austenitic steel.

According to my process, a suitable electric
furnace, such, for example, as the usual Heroult
steel-melting furnace, is given a charge consist-
ing principally of low-carbon steel scrap which
preferably consists, in part, of chromium-nickel-
copper steel scrap of the same general analysis as
that which is to be made; ordinary high-carbon
ferrochrome containing, as a rule, from 4 to 6%
carbon; and a relatively large quantity of "Mon-
el" oxide with or without the addition of a ma-
terial high in iron oxide, such as roll scale or
magnetic iron ore concentrate. The power is
applied and the charge is melted down forming a
bath of ferrous metal and a supernatant oxidizing
slag. The molten bath is brought to a relatively
high temperature which is continued until the
carbon content of the metal bath is at or below
the predetermined maximum percentage. Dur-
ing this oxidizing period, a considerable quantity
of chromium is oxidized along with the carbon
by the oxides of copper, nickel and iron con-
tained in the slag. The oxides of chromium
enter the slag. At the same time all or a sub-
stantial proportion of the nickel oxide and cop-
per oxide originally in the slag is reduced to me-
tallic nickel and copper and enters the metal
bath. When the carbon content of the metal
bath has fallen to the desired low figure, the
percentage of chromium in the bath is very sub-
stantially lower than that which is desired in the
finished product, and, in general, is less than
10%.

The second stage of the operation consists in
the addition of relatively large quantities of burnt
lime and ferrosilicon, preferably crushed, to the
bath. The silicon reacts with the reducible ox-
ides in the slag and enriches the bath in chro-
mium up to the desired percentage without any
increase in carbon content. In addition to chro-
mium and iron, a certain small percentage of
nickel and copper may be also transferred to the
metal bath from the slag. Recovery of the chro-
mium, nickel and copper is practically complete
and the final finishing slag is of the well-known
calcium silicate type.

As a specific example of my process, the fol-
lowing procedure employed for the manufacture

of ingots containing 16 to 18% chromium, about 6% nickel, about 3% copper, and not more than .10% carbon, is described: 6,360 pounds of steel scrap, analyzing approximately 16½% chromium, 6% nickel and 3% copper, and 5,000 pounds of ordinary low-carbon steel scrap, were first charged onto the bottom of a six-ton Heroult electric furnace. Along with the scrap was charged 2,500 pounds of lump high-carbon ferrochrome, analyzing approximately 5% carbon and 70% chromium; 1,600 pounds of "Monel" oxide, analyzing approximately 40% nickel and 18% copper; and 2,000 pounds of roll scale, analyzing about 69% iron. The electric power was applied the charge was melted down, and thereafter superheated to a degree sufficient to permit the charging of an additional 1,000 pounds of roll scale. The iron, nickel and copper oxides form an oxidizing slag. The temperature was maintained at superheat until a metal test showed .09% carbon. No reliable method is known to me for accurately determining the temperature of the metal bath under the slag blanket, but it is estimated that this temperature should be approximately 3050 to 3200° F., which is some 100 to 250° F. higher than that usually employed in ordinary electric steel melting practice. The superheating of the bath to a temperature above that ordinarily employed in electric steel melting practice is preferred, since the superheat renders the action of the iron, nickel and copper oxides more energetic in oxidizing the carbon from the metal.

Next, 1,450 pounds of crushed 75% ferrosilicon and 3,300 pounds of burnt lime were added to the slag as rapidly as conditions permitted. The silicon reducing agent reacted with the reducible oxides contained in the slag forming metals, which gravitated into the bath of molten metal, and silicates, which remained in the slag overlying the bath. When the light green appearance of the slag indicated that its reducible oxide content was low, final additions of lump ferrosilicon and low-carbon ferromanganese were made to the bath and the metal was poured. Ladle tests showed analysis of 16.2% chromium, .08% carbon, 6% nickel and 2.9% copper, together with manganese, silicon, phosphorous and sulphur in normal amounts. The product of the heat weighed approximately 17,000 pounds.

When the initial scrap charge used consists entirely of ordinary low-carbon steel scrap, instead of a mixture of ordinary scrap with chromium-nickel-copper scrap as shown in the above example, it is necessary to employ a considerably larger quantity of "Monel" oxide. For example, in such a case the roll scale was entirely omitted and replaced with an equal weight of "Monel" metal oxide, and the product of a heat of similar weight analyzed approximately 10.5% nickel and 6% copper.

To secure an alloy containing the maximum percentages of nickel and copper and made in accordance with my process, the ordinary steel scrap and roll scale are dispensed with and an initial charge is used consisting of chromium-nickel-copper steel scrap, high carbon ferrochrome, and an oxidizing agent consisting entirely of "Monel" metal oxide. Following such procedure an alloy containing approximately 17% nickel and 8% copper was produced.

In my process I employ a cheap source, not only of nickel and copper, but also a cheap source of chromium, namely, high-carbon ferrochrome.

Moreover, by virtue of the energetic oxidizing nature of the nickel and copper oxides, my process makes possible the efficient and cheap removal of carbon from the high-carbon ferrochrome employed. In other words, my process represents an unusual case where two cheap sources of alloying elements, one a natural mixture of oxides and the other a high-carbon ferro alloy, are employed in such a way as to take advantage of their particular characteristics in order to produce a low-carbon alloy.

While I prefer to use high-carbon ferrochrome on account of its cheapness, and because the carbon can be efficiently oxidized by the oxides employed, low-carbon ferrochrome can be employed if desired. Also, while I prefer to use "Monel" oxide containing nickel and copper in the proportions naturally occurring in the ore, on account of its cheapness and because the proportions of nickel and copper are suitable in most cases to supplement the chromium in securing stainlessness and rust-resistance, and obtaining, when desired, an austenitic steel, other sources of nickel and copper may be employed, with different proportions of the nickel and copper oxide if desired, as, for example, a mixture of nickel and copper oxides, or "Monel" oxide modified by the addition to it of other nickel or copper oxides. While I prefer to use as a reducing agent a ferrosilicon having a relatively high proportion of silicon, such as 75% ferrosilicon, other grades of ferrosilicon may be used or even silicon metal. Also, other exothermic reducing agents may be employed, such as aluminum, magnesium, etc.

While the product obtained is preferably a low-carbon stainless or rustless steel of the type ordinarily called stainless or rustless iron, the process can be employed in the manufacture of stainless or rustless steels containing higher percentages of carbon.

The preferred product is an austenitic steel containing chromium from 10 to 20%, preferably 16 to 19% of chromium, and from 8 to 25% combined nickel and copper, preferably 8 to 12% combined nickel and copper, in the proportions of approximately 2 parts of nickel and 1 part of copper. The carbon content of the iron or steel is preferably low, about .05% to .15%, giving a metal that is especially resistant to corrosion, that readily lends itself to forming operations such as hot or cold rolling, deep-drawing, and the like, and which is comparatively free from carbide precipitation after severe heating and is thus free from intergranular attack upon being subsequently exposed to corrosive media. The steel may be made, however, containing other proportions of chromium, nickel and copper, such as 15 to 20% chromium, or even 10 to 30% chromium; 6 to 14% nickel, or even 5 to 18% nickel; and 3 to 7% copper, or even 2 to 8% copper, the balance being principally iron. In general irons and steels of the higher chromium contents require the higher percentages of nickel and copper in order to produce an austenitic alloy, and, similarly, lower chromium contents permit lower amounts of nickel and copper; the proportion of nickel to copper, however, as indicated above, is preferably maintained in the ratio of about 2 to 1.

Since, for reasons of efficiency and economy, a silicon-containing reducing agent is preferably employed in the practice of my process in the matter of reducing the oxides contained in the slag there is a tendency toward silicon contamination of the metal. In order that a readily

formable metal which lends itself to an ease of heat treatment may be consistently produced the silicon content of the metal is kept to a low value, in spite of the tendency toward silicon contamination where a high recovery of the oxides from the slag is desired, by the exercise of care in making the ferro-silicon additions during the reducing stage of the process. By this means the silicon content may be maintained under 1.00%.

Minor proportions of other alloying elements may be employed, such as manganese, vanadium, titanium, cobalt, tungsten, molybdenum, etc., either singly or in combination. These additional alloying elements may be incorporated in the metal bath during the steel-making operation in accordance with well-known methods.

The copper apparently supplements the nickel in imparting certain desirable characteristics to a high chromium steel, such as remarkable resistance to corrosion.

While I have described the preferred embodiment of my invention, it is to be understood that the invention may be otherwise practiced within the scope of the following claims.

I claim:

1. The process of making low-carbon iron-chromium-nickel alloys, which comprises charging a furnace with low-carbon steel scrap, high-carbon ferrochromium and "Monel" oxide, and heating the charge to a temperature sufficient to fuse the scrap and form a supernatant layer of molten slag and to cause a reduction of nickel and copper from their oxides to the metallic state accompanied by the oxidation of the carbon in the bath, thereafter adding to the slag a silicon reducing agent and lime to reduce chromium together with residual nickel and chromium from their oxides in the slag.

2. The process of making low-carbon iron-chromium-nickel alloys, which comprises charging a furnace with low-carbon steel scrap, high-carbon ferrochromium and "Monel" oxide, and heating the charge to a temperature sufficient to fuse the scrap and form a supernatant layer of molten slag and to cause a reduction of nickel and copper from their oxides to the metallic state accompanied by the oxidation of the carbon in the bath, thereafter adding to the slag a silicon reducing agent to reduce chromium together with residual nickel and chromium from their oxides in the slag.

3. The process of making iron-chromium-nickel-copper alloys, which comprises heating in a furnace a charge containing iron scrap, high-carbon ferrochromium and nickel and copper oxides to a temperature sufficient to fuse the scrap and form a supernatant layer of molten slag and cause a reduction of nickel and copper to the metallic state, and thereafter adding an exothermic reducing agent to the slag to reduce the oxides in the slag to a metallic state.

4. The process of making low-carbon chromium-nickel-copper rustless steel, which comprises melting in an electric furnace steel scrap, high-carbon ferrochromium, and nickel and copper oxides so as to fuse the scrap, reduce metallic nickel and copper from their oxides and oxidize carbon from the charge, and form a supernatant layer of molten slag containing chromium oxide, and thereafter adding to the bath a suitable reducing agent and lime to reduce the chromium from the slag back into the metal.

5. The process of making low-carbon chromium-nickel-copper rustless steel, which comprises melting in an electric furnace steel scrap,

high-carbon ferrochromium, and "Monel" oxide so as to fuse the scrap, reduce metallic nickel and copper from their oxides and oxidize carbon from the charge, and form a supernatant layer of molten slag containing chromium oxide, and thereafter adding to the bath a suitable reducing agent and lime to reduce the chromium from the slag back into the metal.

6. That step in the process of making low-carbon nickel-copper rustless steel in an electric arc furnace, which consists in heating in said furnace a charge containing steel scrap, high-carbon ferrochromium and nickel and copper oxides to a temperature sufficient to fuse the scrap and cause a reduction of nickel and copper to a metallic state, forming thereby a bath of ferrous metal of low-carbon content containing chromium, nickel and copper.

7. That step in the process of making low-carbon nickel-copper rustless steel in an electric arc furnace, which consists in melting in said furnace a charge containing steel scrap, high-carbon ferro-chromium and "Monel" oxide to a temperature sufficient to fuse the scrap, oxidize the greater part of the carbon and cause a reduction of nickel and copper, whereby a low-carbon chromium-iron alloy containing metallic nickel and copper is produced.

8. In the production of rustless iron containing nickel and copper, the art which includes, reducing oxides of nickel and copper with high-carbon ferrochromium in the presence of molten ferrous metal, forming thereby a bath of ferrous metal low in carbon and containing chromium, copper and nickel.

9. In the production of a low-carbon ferrous alloy containing chromium, nickel and copper, the art which includes, preparing a ferrous metal bath containing chromium covered by a blanket of slag rich in the oxides of chromium, nickel and copper, and reducing the metallic oxides contained in the slag with a silicon reducing agent, thereby enriching the bath in the metals, chromium, nickel and copper.

10. In the production of rustless iron containing nickel and copper, the art which includes, preparing a low-carbon ferrous metal bath containing chromium and an overlying blanket of slag rich in the oxides of chromium, nickel and copper, and reducing the metallic oxides contained in the slag with a non-carbonaceous reducing agent, thereby enriching the bath in the metals, chromium, nickel and copper.

11. In the production of low-carbon iron-chromium-nickel-copper alloys in an electric arc furnace, the art which includes, melting down in said furnace a charge including high carbon ferrochrome, and copper and nickel oxides, forming thereby a bath of ferrous metal containing chromium, copper and nickel with a supernatant slag containing oxides of copper and nickel; and thereafter reducing the oxides present in the slag to effect a recovery of their metallic values and an enrichment of the bath in the metals copper and nickel.

12. In the production in an electric arc furnace of low-carbon rustless steel containing copper and nickel, the art which includes, melting down in said furnace rustless iron or steel scrap, high-carbon ferrochrome, copper and nickel oxides, and an oxide of iron, forming thereby a low-carbon bath of ferrous metal containing chromium and a supernatant slag containing the oxides of chromium, copper and nickel; and thereafter reducing the oxides present in the slag

to achieve a recovery of their metallic values and an enrichment of the bath in the metals chromium, copper and nickel.

5 13. In the production of low-carbon iron-chromium-nickel-copper alloys in an electric arc furnace, the art which includes, forming in said furnace a low-carbon bath of ferrous metal containing chromium with a supernatant slag con-

taining the oxides of chromium, copper and nickel; and thereafter reducing the oxides present in the slag under basic conditions and employing a non-carbonaceous reducing agent to effect a recovery of the metallic values in the slag and an enrichment of the bath in the metals chromium, copper and nickel. 5

ALEXANDER L. FEILD.

CERTIFICATE OF CORRECTION.

Patent No. 2,031,152.

February 18, 1936.

ALEXANDER L. FEILD.

It is hereby certified that the name of the assignee in the above numbered patent was erroneously written and printed as "Rustless Iron and Steel Corporation of America" whereas said name should have been written and printed as Rustless Iron and Steel Corporation, as shown by the records of assignments in this office; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 31st day of March, A. D. 1936.

(Seal)

Leslie Frazer
Acting Commissioner of Patents.