

## UNITED STATES PATENT OFFICE

2,082,783

## METHOD OF MAKING ALLOY STEELS

Thomas N. Armstrong, Jr., and Fred B. Anderson, Portsmouth, Va.

No Drawing. Application September 30, 1935,  
Serial No. 42,861

4 Claims. (Cl. 75-127)

(Granted under the act of March 3, 1883, as  
amended April 30, 1928; 370 O. G. 757)

This invention relates to the manufacture of corrosion resisting ferro-alloys, particularly of the austenitic stainless steel type, and has for its object to prevent the formation of undesirable carbides and in general to improve the quality of the product.

It is important that alloys of the type mentioned, usually containing approximately 18 per cent chromium and 8 per cent nickel, be free from oxides and from dissolved gases. The oxides are ordinarily removed by drawing off the oxidizing slag under which the charge has been melted down and refined and replacing it with a basic slag which is, in the final operation, brought to a reducing condition with carbon, silicon, ferro-silicon, or aluminum. When lime slags are employed these agents form calcium carbide, calcium silicate, and calcium aluminate respectively.

Austenitic steels of the 18-8 type usually contain more than 0.02 per cent carbon. It is generally accepted that this quantity is the maximum that is retained in solution, and all carbon in excess thereof unites with chromium to form chromium carbide. The formation of the chromium carbide impoverishes the iron of chromium and makes the metal susceptible to intergranular corrosion. It has been shown that the formation of chromium carbides can be prevented by adding to the alloy a sufficient quantity of some metal having greater affinity for carbon than has chromium. Titanium, vanadium, molybdenum and tungsten all have greater affinity for carbon than has chromium, but titanium is considered the most powerful carbide former. For this reason titanium is usually the metal added to the alloys of the 18-8 type to prevent formation of chromium carbide, and for this purpose the titanium is added in sufficient quantity to insure the presence of 6 times as much titanium as the carbon in excess of 0.02 per cent in the alloy. The titanium is usually added in the form of ferro-titanium or a low carbon, iron-chromium-titanium alloy. These alloys are costly and as a rule contain some carbon which necessitates adding additional titanium to compensate therefor.

Under the present method a reducing slag is formed without carbon or silicon and this slag reduces titanium from the inexpensive titanium oxide, or rutile, which is a titanium oxide ore. Any desired quantity of titanium, up to 4.0 per cent (probably higher) can be added by this method.

We subject the melt to any of the usual oxidizing slags, or if the charge is low in, or practically free from carbon, the charge is melted down with

lime and fluorspar. When the melt is practically free of carbon the oxidizing slag is removed and the bath is covered with a mixture of burnt lime and either titanium oxide or rutile. As soon as this mixture becomes fluid there is charged into the furnace, preferably in small portions, a mixture of lime, aluminum in the form of shot or turnings, and rutile. The quantity of titanium desired, which depends upon the carbon content, will determine the quantity of titanium oxide and lime added to the slag. Lime is added in small quantities as needed to prevent the slag from thinning down too greatly.

Theoretically, one pound of aluminum will reduce 2.22 pounds of titanium oxide to yield 1.34 pounds of titanium. In practice, because of the oxidized condition of the bath after being subjected to the oxidizing slag and because of the complexity of the slag formed, it requires more than the theoretical quantity of aluminum, and also more than the theoretical quantity of titanium oxide to obtain the desired recovery of titanium and to keep the slag in a reducing condition. Part of the titanium remains in the slag. It requires approximately four times the titanium oxide theoretically necessary. The following ratio, by weight, should be maintained:

|                     | Parts |
|---------------------|-------|
| Titanium oxide..... | 2 1/2 |
| Aluminum.....       | 1     |
| Lime.....           | 1     |

The slag is calculated on the quantity of titanium oxide required by the carbon in the melt. A higher percentage of recovery of titanium can be had by increasing the aluminum content but as the latter is more costly than titanium oxide the aluminum ratio is kept low.

Alloying metals, such as chromium and nickel, are added in small quantities at a time after the slag is in a reducing condition. A small addition of a mixture of lime and aluminum is usually made after each addition of the alloying metals. After the alloying metals have been added small quantities of the mixture of aluminum and titanium oxide are charged at intervals until the melt has the desired composition. Approximately five minutes after the last addition of aluminum and titanium oxide some lime is charged and the metal is tapped.

The invention described herein may be manufactured for use by or for the Government of the United States, without the payment of any royalties thereon.

What is claimed is:

1. A process of making ferrous alloys contain-

ing substantially 18 per cent chromium and 8 per cent nickel, the remainder being predominantly iron, which comprises refining molten steel under an oxidizing slag, removing the slag and covering the bath with a mixture consisting substantially of lime and titanium oxide which is substantially devoid of carbon-silicon-containing material, then after said covering has become fluid adding titanic oxide, burnt lime, and aluminum in proportions having the ratio  $2\frac{1}{3}:1:1$ , respectively, then adding chromium and nickel at intervals to supply the desired percentages of these two metals, with further additions of small quantities of lime and aluminum after each addition of chromium and nickel, and titanic oxide if necessary to maintain the said ratio, the quantity of titanic oxide supplied being such that the percentage of titanium ranges from the quantity thereof necessary to form carbide with the carbon in the metal in excess of the carbon held in solution up to 4 per cent of the total metal.

2. A process of making ferrous alloys containing substantially 18 per cent chromium, 8 per cent nickel and up to 4 per cent titanium, the remainder being predominantly iron, which comprises covering a bath of molten steel, that has been treated under an oxidizing slag, with a mixture consisting substantially of lime and titanium oxide which is substantially devoid of carbon-silicon-containing material, then after said covering has become fluid adding titanic oxide, lime and aluminum in proportions having the ratio  $2\frac{1}{3}:1:1$ , respectively, then adding chromium and nickel in the form of ferro alloys at intervals to supply the desired percentages of these two metals, with further additions of small quantities of lime and aluminum, and also titanic oxide if necessary to maintain the said ratio after each addition of chromium and nickel, the quantity of titanic oxide supplied being more than that necessary to form a carbide with the

carbon present in excess of 0.02 per cent and less than will leave in the alloy titanium substantially in excess of 4 per cent.

3. A process of making ferrous alloys containing nickel and chromium, which comprises covering a bath of molten steel, that has been treated under an oxidizing slag, with a mixture consisting substantially of lime and titanium oxide which is substantially devoid of carbon-silicon-containing material, then after said covering has become fluid adding titanium oxide, lime and aluminum in proportions having the ratio  $2\frac{1}{3}:1:1$ , respectively, then adding chromium and nickel in the form of ferro alloys at intervals to supply the desired percentages of these two metals, with further small quantities of lime and aluminum, and also titanium oxide if necessary to maintain the said ratio, after each addition of chromium and nickel.

4. A process of making ferrous alloys containing nickel and chromium, which comprises covering a bath of molten steel, that has been treated under an oxidizing slag, with a mixture consisting substantially of lime and titanium oxide which is substantially devoid of carbon-silicon-containing material, then after said covering has become fluid adding titanium oxide, lime and aluminum in proportions having the ratio  $2\frac{1}{3}:1:1$ , respectively, then adding chromium and nickel in the form of ferro alloys at intervals to supply the desired percentages of these two metals, with further small quantities of lime and aluminum, also titanium oxide if necessary to maintain the said ratio, after each addition of chromium and nickel, adding small quantities of aluminum and titanium oxide until the melt is in satisfactory condition, adding more lime approximately five minutes after the last addition of aluminum and titanium oxide, and then tapping the melt.

THOMAS N. ARMSTRONG, Jr.  
FRED B. ANDERSON.