

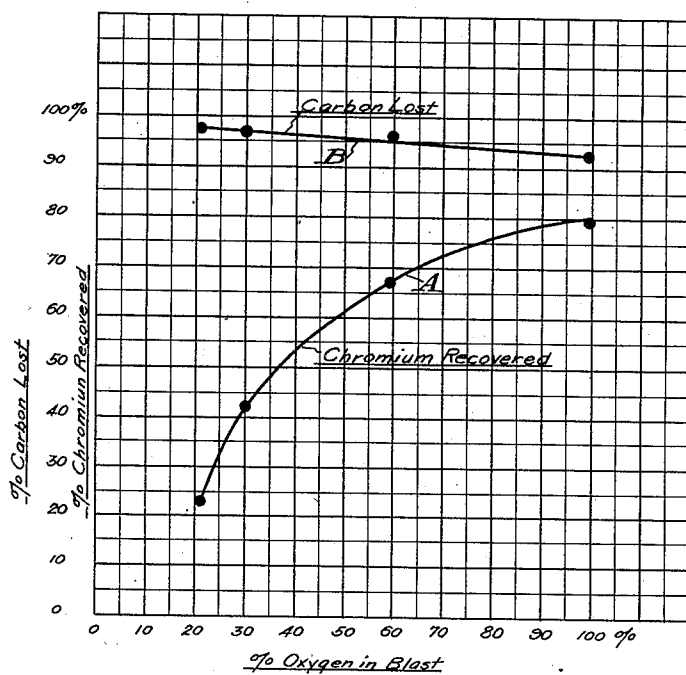
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PROCESS OF MAKING RUSTLESS IRON ALLOYS

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PROCESS OF MAKING RUSTLESS IRON ALLOYS

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This invention relates to the manufacture of low-carbon iron-chromium alloys, and particularly to those alloys of the so-called "rustless iron" type. Rustless iron, for the purposes of this invention, may be defined as an alloy consisting essentially of iron and chromium, with upward of about 9% of chromium and less than 0.2% of carbon. Nickel may also be present in varying proportions replacing the iron. A preferred composition contains about 12-14% of chromium and 0.12% or less of carbons. Another excellent composition contains around 16-18% of chromium, 7-8% of nickel, and around 0.12% or less of carbon.

Rustless irons have generally been produced by direct addition of low-carbon ferrochromium to a low-carbon iron bath or, alternatively, to a very limited extent by reducing chromium into such iron bath by means of a non-carbonaceous reducing agent, such as aluminum or silicon. Low-carbon ferrochromium is somewhat costly and to produce the chromium content desired in the rustless irons according to the alternative methods is even more expensive. High-carbon ferrochromiums, i. e. those containing from 4 to 7% of carbon on the other hand offer a relatively cheap source of chromium.

Edmands in U. S. Patent No. 1,063,341 and Morehead in U. S. Patent 1,063,285 have suggested Bessemerization as a method for reducing the carbon content of high-carbon ferrochromium. Our experiments have shown that when Bessemerizing with air it is impossible to obtain an alloy of a carbon content below about 2.0% or a chromium to carbon ratio of above 35 without causing serious losses in chromium recovery. When using enriched air or oxygen in such processes, the carbon content has been reduced to a greater extent, but when an attempt has been made to Bessemerize to such an extent that the chromium to carbon ratio in the product is greater than about 70 the loss of chromium has become practically prohibitive.

Our investigations have proven that by suitably controlling the conditions when Bessemerizing iron chromium alloys having a

chromium content corresponding to rustless irons it is possible to obtain a much higher chromium to carbon ratio than is possible when Bessemerizing ferrochromium. Thus, by direct action of oxygen-enriched air, or preferably commercially pure oxygen, applied to the molten alloy in a side blown converter, such lower chromium rustless irons may be commercially reduced in carbon content below about 0.2% and even as low as about 0.02%, or to such an extent as to reach a chromium to carbon ratio of from 75 to 500. In the manufacture of rustless iron particularly, we have thus realized decided economies, among which are a much greater speed of decarburization and a materially higher ratio of chromium to carbon in the product than have been heretofore attainable.

The preferred conditions, as disclosed by our investigations, are as follows:

1. The oxidizing blast should be decidedly richer in oxygen than atmospheric air, is desirably above 50% oxygen, and preferably is approximately pure oxygen. Under these conditions the oxidation of carbon, chromium, silicon, and any other readily oxidizable components of the melt, is extremely energetic, and the time required for the blow is correspondingly short. Nevertheless, we have demonstrated that under these conditions there is a certain definite selective tendency toward the oxidation of carbon, with the result that, for a given low carbon content, decidedly better recoveries of chromium are obtained as the oxygen concentration of the blast increases.

This is illustrated by the accompanying graph, in which the curve A represents chromium recoveries, from iron-chromium alloys containing chromium suitable for rustless iron and initially about 1.5% (average of four heats) of carbon, at a period of the treatment when about 96-98% of the contained carbon had been oxidized, as indicated by curve B. As appears from this graph the recovery of chromium using atmospheric air (21% oxygen) was only about 23%, under the specific test conditions; with 30% oxygen the recovery was 42%; with 60% oxygen

68%; and with 100% oxygen nearly 79%. It will of course be understood that these figures apply only to the test conditions, temperatures, scale of operation, etc., as actually employed, and are not intended to represent the maximum recoveries attainable in commercial practice. The graph very clearly indicates however the advantage of employing a blast having an oxygen content of at least 50%, and as near 100% as is available for use.

2. The blowing is carried out in a converter of the so-called "side-blown" type, in which the blast is introduced above and applied to the surface of the molten metal, or in an essentially equivalent apparatus.

Where atmospheric air is used for the blowing, broadly speaking, it is immaterial whether a side-blown or bottom-blown converter is employed, although neither of these is effective to oxidize the carbon without excessive losses of chromium. On the other hand, when high concentrations of oxygen are used as contemplated herein, we have found it undesirable, commercially, to employ a converter of the bottom-blown type on account of the rapid destruction of the bottom lining at the temperatures created by the exothermic reactions; but with a converter of the side-blown type linings of sufficiently refractory character have a satisfactory life. The best results have been obtained with a lining of chromium ore or a lining of magnesia, previously fused in the electric furnace.

Accordingly, our invention contemplates broadly the Bessemerization of iron-chromium alloys containing not more than about 2% carbon, to reduce the carbon content thereof below about 0.2% and in some instances as low as about 0.02%; and, more specifically, contemplates economically treating such alloys, so as to avoid prohibitive chromium losses, by using an oxidizing blast containing a substantially higher percentage of oxygen than is present in atmospheric air, and applying such blast in a side-blown converter or equivalent apparatus in which the blast is applied to the surface of the molten charge. So far as we are aware such conditions have not heretofore been so applied in the treatment of these alloys as to obtain the results stated.

Following are illustrative examples of procedure in accordance with our invention, but it is to be understood that the invention is not limited to the precise details described in such examples.

Steel scrap and high-carbon ferrochromium, with nickel or other appropriate metal if desired, in the proportions required to give the desired chromium content (taking the losses into consideration) are melted in an electric or other suitable furnace to a highly fluid condition. The molten charge is quickly

transferred to a side-blown converter which is then turned up to its operating position, whereupon a blast of oxygen or oxygen-enriched air is applied to the surface of the bath and adjusted until the flame from the converter indicates vigorous action. At first a very short flame issues from the converter; after a short blow this flame lengthens and becomes consistently brighter. The elimination of carbon is accompanied by an apparent boiling of the molten alloy, is very rapid, and the flame soon drops. The heat is blown for only a brief period, the duration depending upon the oxygen content of the blast and the carbon content desired in the product. Then the metal is poured into a ladle, the usual deoxidizers are added, and the metal discharged into ingot moulds. This final deoxidation may be accomplished in other ways, e. g., in an electric furnace where the operation is finished.

Alternatively, high-carbon chromium steel may be provided by smelting an appropriate mixture of chromium ore and iron ore or metallic iron, such as steel scrap, so as to produce an alloy of chromium content substantially suitable for rustless iron but containing an excessive per cent of carbon. This molten high-carbon low-chromium alloy is then transferred to a converter and side-blown with pure oxygen or enriched air to reduce its carbon content below 0.2 percent, as described in the preceding example.

A preferred procedure which we have successfully employed in the production of rustless iron involves the dilution of molten high-carbon ferrochromium with molten steel to initially reduce the carbon content of the resulting bath, the latter being tapped directly from the furnace in which it is produced and run into the side-blown converter containing the molten steel, where Bessemerization with oxygen or enriched air as already described further reduces the carbon content to a value below 0.2%. This conserves heat, reduces manipulation, and saves losses incidental to remelting.

Following is a specific example of our procedure in producing an iron-chromium alloy of the rustless iron type. Steel scrap and high-carbon ferrochromium were melted in an electric furnace in proportions to give an alloy of chromium content appropriate for the production of rustless iron by this process. A sample of the alloy taken at the end of this electric furnace heat analyzed 20.66% chromium, 1.24% carbon, and 0.14% silicon. This molten alloy from the electric furnace was rapidly transferred to a basic-lined, side-blown converter. In this case commercially pure oxygen served as the blast and the total blowing time was $5\frac{3}{4}$ minutes. Before the addition of deoxidizers, the alloy contained 17.71% chromium and 0.08% carbon. The ingots cast therefrom contained 17.74%

chromium, 0.10% carbon, and 0.24% silicon.

The average physical properties of specimens of the product obtained by the procedure described in the preceding paragraph were found to be: yield point, 58600 lbs.; ultimate strength, 86600 lbs.; elongation, 23%; and reduction in area, 51.7%. In an electric furnace finished product similarly produced and analyzing 15.75% chromium, 0.12% carbon, 0.32% silicon, the following physical properties were ascertained: yield point, 61300 lbs.; ultimate strength, 87250 lbs.; elongation, 27% and reduction in area, 67.5%.

As a result of our extensive investigations in which blasts with pure oxygen and air enriched with various proportions of oxygen have been employed, it has been shown that the temperature of the metal increases rapidly as the oxygen content of the blast increases, the time necessary for a given reduction of carbon content diminishes, and the slag that accumulates on the surface of the metal decreases in volume,—each of these features contributing materially to the feasibility and efficiency of the process. Experience has shown also that it is advantageous to have the blast applied adjacent to the surface of the bath in the converter, preferably so that it impinges directly onto the surface of the metal, in order that the oxygen of the blast may effectively burn out the carbon contained in the metal; and furthermore, that increased blast pressures are desirable for blasts of low oxygen content and at the start of all side-blown heats. The use of higher percentages of oxygen in the blast increases the velocity of the exothermic reactions which results in diminished chromium losses through shortening the time during which the metal is subjected to the action of the oxygen. A criterion of the extent of the carbon removal has been discovered in the flame "drop". This "drop" in the long, bright flame issuing from the converter indicates that the carbon in the alloy has been reduced to about one-quarter of one percent, in the case of alloys having the chromium content of rustless irons. The additional time of blowing required is a function of the carbon content desired in the alloy and of the oxygen content of the blast.

We find our improved process especially advantageous for making rustless iron alloys, since our investigations have proven that, at the electric furnace temperature employed (upwards of 1600° C.) a substantially higher chromium to carbon ratio (consistent with a given chromium recovery) can be obtained in the rustless iron so produced than heretofore. We are unable to state the maximum temperature attained in our process during the blow but believe it to be considerably above 1600° C. Those skilled in this art will, of course, recognize the practical im-

possibility of measuring these temperatures under the conditions existing in the converter. A comparison of the results attainable by prior processes with the superior results flowing from our procedure convinces us that the temperature and conditions under which our process is operated have not been employed heretofore.

In connection with some prior proposals for removing carbon by Bessemerization, the molten alloy is held at such temperatures during the blow as to bring about a greater affinity between oxygen and carbon than between oxygen and chromium, it being stated that under these conditions the carbon may be largely or substantially eliminated by oxidation before any considerable percentage of chromium is removed. At the blowing temperature we use, such conditions do not exist but, on the contrary, chromium is in fact strongly oxidized throughout the blow, that is to say, many pounds of chromium oxidize for each pound of carbon eliminated, especially toward the end of the blow; and the deterioration of the converter lining proceeds very rapidly and becomes prohibitive in bottom blowing. However, we have discovered that the temperature we employ is practicable and decidedly economical because, by proper control of this temperature and preferably by side blowing with oxygen enriched air or substantially pure oxygen, the removal of carbon is so greatly expedited that a carbon content as low as about 0.02 per cent may be attained economically; and the total chromium losses are materially reduced, although the rate of chromium oxidation or pounds of chromium oxidized per unit of time appears to be increased. In other words, while the higher concentration of oxygen may expedite the oxidation of chromium as well as carbon, the carbon content is reduced to the desired percentage so much quicker than heretofore that the total quantity of chromium lost during the blow is greatly diminished. Moreover, the blowing period is so much shortened that the oxygen of the blast is economically utilized, and any objectionable attack on the converter lining is materially reduced, bringing our procedure well within practical and economical operating requirements.

We claim:

1. The process of making a low-carbon iron-chromium alloy of the rustless iron type which comprises preparing a molten bath consisting essentially of iron, chromium and carbon, the carbon being present in a substantial proportion not exceeding 2.0% and the chromium content corresponding to that of rustless iron, side-blowing the bath with a blast containing from 50% to 100% of free oxygen whereby oxidation of constituents of the bath including carbon and a minor portion only of the chromium takes place and the temperature of the bath is raised to and

maintained at above 1600° C. solely by means of the exothermic reaction induced by the blowing operation, and continuing the blowing until the carbon content of the bath is reduced to not more than 0.2%.

2. The process of making a low carbon iron-chromium alloy of the rustless iron type which comprises preparing a molten bath consisting essentially of iron, chromium and carbon, the carbon being present in a substantial proportion not exceeding 2.0% and the chromium content corresponding to that of rustless iron, side-blowing the bath with a blast of commercially pure oxygen whereby oxidation of constituents of the bath including carbon and a minor portion only of the chromium takes place and the temperature of the bath is raised to and maintained at above 1600° C. solely by means of the exothermic reaction induced by the blowing operation, and continuing the blowing until the carbon content of the bath is reduced to not more than 0.2%.

In testimony whereof, we affix our signatures.

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