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MANUFACTURE OF UNSTAINABLE IRONS AND STEELS.

No Drawing. Original application filed February 5, 1923, Serial No. 617,172, and in Great Britain March 1, 1922. Divided and this application filed May 4, 1923. Serial No. 636,758.

The present invention is for improvements in or relating to the manufacture of chrome-irons and chrome-steels of the class known commercially as stainless or unstainable iron and steel, described and claimed in my co-pending application Serial No. 617,172, filed Feb. 5, 1923, of which this application is a division.

In the manufacture of these steels and irons the alloy ferro-chrome is employed. For the production of unstainable steels this alloy may contain a substantial proportion of carbon, say, 2 per cent or more, but for making unstainable chrome-irons it is the practice to use the grade of ferro-chrome known as carbon-free, i.e. ferro-chrome of a carbon content not exceeding 0.10 per cent. As the carbon-free alloy as ordinarily obtainable is comparatively costly, the manufacture therefrom of stainless iron is correspondingly expensive and the use of the latter is practically restricted to articles of high or relatively high price.

Ferro-chrome is usually prepared by reduction of chromite. This reduction may be effected with a silicon-reducer and silicon and certain silicides have been proposed for this purpose. It has also been proposed to obtain appropriately low-carbon ferro-chrome for the manufacture of unstainable metal by submitting a crude ferro-chrome in the molten state to an oxidizing blow, but our experience is that this process of decarbonization of an iron-chromium alloy of high-chromium content is commercially uneconomical by reason of the high loss of chromium through oxidation. The loss is specially high when the attempt is made to eliminate carbon by these means, while in the case of a silicon-containing ferro-chrome prepared as aforesaid, where it is practically only a question of removing silicon, the loss of chromium may also be such as to constitute a serious item in the production costs. The expense involved in the manufacture of high grade ferro-chrome is the main cause for the comparatively high price, and consequently of the relatively restricted field of application, of stainless metal.

The present invention has for its purpose to provide an improved and simplified process for the manufacture of stainless

metal whereby the aforesaid difficulties and manufacturing expenses may be reduced.

According to this invention, a molten crude ferro-chrome is admixed with molten iron or steel of appropriate purity in requisite proportion to provide an initial product of substantially the metallic composition of unstainable metal, and this product is then purified with an oxidizing blow, said crude ferro-chrome containing silicon as the only oxidizable impurity which is present in sufficient quantity as to give, on admixture with the iron or steel, an excess over that permissible in a finished unstainable metal which is to possess deformable properties. This excess is then removed by the blow, which may be continued to any desired further reduction of the silicon content.

The iron or steel bath is preferably substantially free from, or of low content in oxidizable impurities, such as carbon and silicon, and may advantageously contain oxygen or oxides (for example, the bath may be provided by recently blown Bessemer metal) for the purpose of reducing, by a preliminary oxidation as well as by dilution, the quantity of the impurities introduced by the crude ferro-chrome.

The crude ferro-chrome may be produced by reduction of a reducible compound of chromium in presence of iron (for instance, by reduction of an oxidized iron-chromium compound such as chromite) with approximately the equivalent of a substantially carbon-free or low-carbon silicon-reducer, for the purpose of obtaining a low-carbon ferro-chrome and consequently a crude unstainable metal therefrom which is free or substantially free from excess carbon, and is practically associated only with excess of a foreign element, namely, silicon, which is more readily and economically removed than carbon by an oxidizing blow.

In the preferred mode of operation of the invention the low-carbon silicon-containing ferro-chrome is produced in situ, by effecting said reduction with the silicon-reducer within the bath of iron or steel, and I generally prefer to follow this procedure than the alternative of first preparing the low-carbon ferro-chrome and then admixing it with the molten iron or steel.

By the expression "low-carbon" is meant

any quantity of carbon which if introduced into or present in metal of the composition of unstainable metal would be therein insufficient adversely to affect the unstainable character, and a "carbon-free" product is therefore comprised by the expression.

Other conditions being comparable, silicon is both more easily and satisfactorily removed than carbon by an oxidizing blow, and hence by choosing a low-carbon silicon-reducer a metal specially favourable to economic purification by blowing may be obtained; the loss of chromium through oxidation is reduced, both by reason of the comparatively short time required for removing silicon and by the relatively low proportion of chromium present consequent upon the dilution which precedes the blowing operation. Moreover, the presence in the crude unstainable metal of a comparatively high proportion of silicon raises the temperature of the molten mass during the blow, and this condition also tends to reduce the degree of oxidation of the chromium.

The preferred silicon-reducer is ferro-silicon, which may advantageously be a ferro-silicon of high-silicon content, for instance, 80 per cent silicon or more.

The carbon content of the ferro-silicon or the like should be known so that allowance may be made therefor in preparing the bath, according to the nature of the final metal desired.

By operating according to the present invention, it is readily possible to obtain an unstainable chrome-iron or chrome-steel of low average content in oxidizable impurities, such as carbon and silicon, and properly deformable, that is to say, possessing the physical attributes necessary to enable the metal to be deformed or shaped by forging, rolling, drop-stamping, cold-drawing or pressing, and like processes commonly employed in the manufacture of objects for which metal of this unstainable type is suitable.

By a low average content in oxidizable impurities is meant a content in carbon such, as is known in the art, is insufficient deleteriously to effect the unstainable properties of the metal, and a content in silicon not exceeding about 1 per cent. By the aforesaid reduction with a low-carbon silicon-reducer followed by blowing of the crude unstainable metal, however, a product of a considerably lower content in silicon than 1 per cent may be readily obtained.

In the case of the preparation of unstainable steel, the necessary proportion of carbon may be supplied at any convenient stage of the process by the addition of suitable carbon-containing materials as are known in the art, for example, either by way of the metal employed for the dilution bath or

by addition to the latter or the dilution product of the requisite quantity of pig-iron, or by coal or charcoal added to the metal in the ladle.

The invention may be carried out in any available furnace provided that the latter is capable of maintaining complete fusion of the materials throughout the operations and of permitting the finished product to be poured or tapped. External heating may be applied in order to maintain the requisite high temperature throughout the reduction, or at any stage during or subsequent to the passage of the blow. An electric furnace, for instance, of the Heroult or Snyder type, may conveniently be employed.

Advantageously a suitable deoxidizer is introduced into the dilution product prior to tapping or to blowing. For example, the metal to be blown may contain from about 1 up to 2.5 per cent of manganese. The manganese may be introduced by effecting reduction of the chromium compound in presence of the manganese, or of a reducible manganese compound.

The use of manganese in quantity in excess of a minimum of $2\frac{1}{2}$ per cent, for the protection of the chromium component of crude unstainable metal during blowing is described and claimed in my specification, Serial No. 617,171.

The following examples are illustrative of the invention:

Example I.

A ferro-chrome was first prepared by reducing a crushed and washed chromite with the calculated quantity of a high-silicon ferro-silicon, whereby there was obtained an alloy containing 0.20 per cent of carbon and 12 per cent of silicon. To this alloy was added ferro-manganese containing 80 per cent manganese and 7 per cent carbon in such proportion as to give a metal containing:—

	Per cent.
Chromium-----	58.50
Manganese-----	8.00
Silicon-----	10.90
Carbon-----	0.88

The molten mass was run into a hot converter, lined with chromite, and about four times the weight of molten blown Bessemer metal, free from slag, and containing approximately 0.12 per cent of oxygen was run in whereby an alloy was produced having:—

	Per cent.
Chromium-----	11.70
Manganese-----	1.60
Silicon-----	2.18
Carbon-----	0.18

The contents of the converter was then

submitted to an oxidizing blow, the purified metal assaying as follows:—

	Per cent.
Chromium-----	12.00
Manganese-----	0.60
Silicon-----	0.18
Carbon-----	0.08

Example II.

To a bath of $5\frac{3}{4}$ cwts. of iron and steel scrap, containing 0.07 per cent of carbon, were added 71 lbs. of ferro-silicon, assaying 83 per cent of silicon, equivalent to 212 lbs. of chromium sesquioxide. To this ferro-silicon-containing bath were then added in successive charges 400 lbs. of chrome-iron ore, containing 211 lbs. of chromium sesquioxide, together with 35 lbs. of limestone and 24 lbs. of fluorspar. At this stage the molten metal corresponded to approximately $5\frac{3}{4}$ cwts. of an alloy steel of the following composition:—

	Per cent.
Chromium-----	14.50
Silicon-----	1.33
Carbon-----	0.11

This metal was then submitted to an oxidizing blow, and then after the addition of $7\frac{1}{2}$ lbs. of ferro-manganese (80 per cent manganese) and the usual small percentage of aluminium, and tapping, assayed as follows:—

	Per cent.
Chromium-----	11.60
Silicon-----	0.21
Manganese-----	0.35
Carbon-----	0.17

The yield of unstainable metal so obtained was 5 cwt. 1 qr. 20 lbs. the loss of chromium due to oxidation by the blow being approximately 20 per cent, of the metal present at the conclusion of the reduction stage.

The above examples are given for illustrative purposes and not by way of limitation. For instance, the invention is not restricted to the production of unstainable metal containing the percentage of chromium given, but may be applied to any metal of this class in which the proportion of chromium is sufficient to confer the property known as stainless or unstainable.

Iron and steel free from undesirable impurities and of low and known carbon content are readily and cheaply obtainable; while silicon-reducers, such, for instance, as ferro-silicon, of low-carbon content may also be obtained without difficulty. In contradistinction to the manufacture of high-grade ferro-chrome as ordinarily employed, the preparation of ferro-chrome containing silicon is both cheaper and more readily carried out. As previously stated, silicon is more readily removed than carbon by an oxidizing blow, and, as is known, its presence in mol-

ten metal facilitates the blowing operation, and when the latter is carried out upon a metal of comparatively low chromium content, such as unstainable metal, the loss of chromium through oxidation may be maintained within practicable limits. The present invention therefore provides through this combination of conditions a simplified process for the manufacture of unstainable chrome-irons and chrome-steels with improved economy and expedition.

The expression "unstable metal" as used in the claims of this specification means an iron-chromium alloy wherein the chromium is the minor metallic component and in such proportion as to confer unstable properties, and of such a content in carbon as, consistently with the retention of unstable properties, corresponds to an unstable alloy of the class either of chrome-iron or chrome-steel. Similarly, a "ferrous bath" means a bath composed of molten iron or steel, or one compounded of the two together.

I claim:—

1. The manufacture of unstable metal which comprises diluting with molten iron of low-carbon content, the iron-chromium product of reducing a substantially non-carboniferous compound of iron and chromium with a low-carbon silicon reducer, so as to obtain a dilution product in the form of a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstable metal and uncontaminated with carbon, phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstable metal, and then submitting the dilution product to purification by an oxidizing blow.

2. The manufacture of unstable metal which comprises diluting with molten iron of low-carbon content, the iron-chromium product of reducing a substantially non-carboniferous compound of iron and chromium with a low-carbon silicon reducer, so as to obtain a dilution product in the form of a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstable metal and uncontaminated with carbon phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstable metal, and then submitting the dilution product to purification by an oxidizing blow under application of external heat.

3. The manufacture of unstable metal which comprises diluting with molten iron of low-carbon content, the iron-chromium product of reducing a substantially non-carboniferous compound of iron and chromium with a low-carbon silicon reducer, so as to obtain a dilution product in the form

of a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and uncontaminated with carbon phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting the dilution product to purification by an oxidizing blow in presence of manganese up to approximately 2.5% of said initial alloy.

4. The manufacture of unstainable metal which comprises diluting with molten iron of low-carbon content, the iron-chromium product of reducing a substantially non-carboniferous compound of iron and chromium with a low-carbon silicon reducer, so as to obtain a dilution product in the form of a low-carbon silicon-contaminated initial alloy of iron and chromium having a chromium content of substantially between 9 and 16% and uncontaminated with carbon phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting the dilution product to purification by an oxidizing blow.

5. The manufacture of unstainable metal which comprises diluting with molten iron of low-carbon content, the iron-chromium product of reducing a substantially non-carboniferous compound of iron and chromium with a low-carbon silicon reducer, so as to obtain a dilution product in the form of a low-carbon silicon-contaminated initial alloy of iron and chromium having a chromium content of substantially between 9 and 16% and uncontaminated with carbon phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting the dilution product to purification by an oxidizing blow in presence of manganese up to approximately 2.5% of said initial alloy.

6. The manufacture of unstainable metal which comprises reducing within a molten ferrous bath of low-carbon content, by means of a low-carbon silicon-reducer, a reducible substantially non-carboniferous compound of iron and chromium, so as to obtain a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and uncontaminated with carbon phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting said molten alloy to purification by an oxidizing blow.

7. The manufacture of unstainable metal which comprises reducing within a molten ferrous bath of low-carbon content, by means of a low-carbon ferro-silicon, a reducible substantially non-carboniferous compound of iron and chromium, so as to obtain a low-

carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and uncontaminated with carbon phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting said molten alloy to purification by an oxidizing blow.

8. The manufacture of unstainable metal which comprises reducing within a molten ferrous bath of low-carbon content by means of a low-carbon silicon-reducer and in presence of manganese in quantity sufficient to give up to 2.5% in the resulting alloy, a reducible substantially non-carboniferous compound of iron and chromium, so as to obtain a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and uncontaminated with carbon phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting said molten alloy to purification by an oxidizing blow.

9. The manufacture of unstainable metal which comprises reducing chromite within a molten ferrous bath of low-carbon content, by means of a low-carbon silicon-reducer, so as to obtain a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and uncontaminated with carbon phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting said molten alloy to purification by an oxidizing blow.

10. The manufacture of unstainable metal which comprises reducing chromite within a molten ferrous bath of low-carbon content, by means of a low-carbon ferro-silicon, so as to obtain a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and uncontaminated with carbon phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting said molten alloy to purification by an oxidizing blow.

11. The manufacture of unstainable metal which comprises reducing within a molten ferrous bath of low-carbon content, by means of a low-carbon silicon-reducer, a reducible substantially non-carboniferous compound of iron and chromium, so as to obtain a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and uncontaminated with carbon phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstainable

metal, and then submitting said molten alloy to purification by an oxidizing blow in the presence of substantially 1 to 2.5% of manganese.

5 12. The manufacture of unstainable metal which comprises reducing chromite within a molten ferrous bath of low-carbon content, by means of low-carbon ferro-silicon, so as
10 to obtain a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstainable metal and
15 uncontaminated with carbon phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting said molten alloy to purification by an oxidizing blow in
20 presence of substantially 1 to 2.5% of manganese.

20 13. The manufacture of unstainable metal which comprises diluting with molten iron of low-carbon content, the iron-chromium product of reducing a substantially non-carboniferous compound of iron and chromium with a low-carbon silicon reducer, so
25 as to obtain a dilution product in the form of a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals
30 are present in unstainable metal and uncontaminated with carbon phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then blowing the dilution product until the
35 content in silicon is reduced below 0.5%.

40 14. The manufacture of unstainable metal which comprises reducing within a molten ferrous bath of low-carbon content, by means of a low-carbon silicon-reducer, a reducible substantially non-carboniferous compound of iron and chromium, so as to
45 obtain a low carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these

metals are present in unstainable metal and 45 uncontaminated with carbon phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then blowing the molten alloy until the content in silicon is reduced below 50 0.5%.

15. The manufacture of unstainable metal which comprises diluting with molten recently blown Bessemer metal, the iron-chromium product of reducing substantially non- 55 carbonaceous compound of iron and chromium with a low-carbon silicon reducer, so as to obtain a dilution product in the form of a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals 60 are present in unstainable metal and uncontaminated with carbon phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstainable 65 metal, and then submitting the dilution product to purification by an oxidizing blow.

16. The manufacture of unstainable metal which comprises diluting with molten recently blown Bessemer metal from which 70 the Bessemerizing slag has been removed, the iron-chromium product of reducing a substantially non-carboniferous compound of iron and chromium with a low-carbon silicon reducer, so as to obtain a dilution prod- 75 uct in the form of a low-carbon silicon-contaminated initial alloy containing iron and chromium in the relative proportions in which these metals are present in unstain- 80 able metal and uncontaminated with carbon phosphorous and sulphur beyond the tolerance limits for these impurities in finished unstainable metal, and then submitting the dilution product to purification by an oxidizing blow. 85

In testimony whereof I affix my signature.

RONALD WILD.