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PROCESS FOR THE REFINING OF ALLOYS

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This invention relates to the production of alloys, and more particularly to a method of refining alloys having an undesirable content of carbon.

The present invention has for its object a simple and efficient means of refining such alloys, and consists chiefly in causing the alloy to solidify under formation of crystalline particles with a low carbon content by means of an alloying component, e. g. silicon, which in the solidification of the alloy will cause the deposition of crystals with a low percentage of carbon and containing such alloying component; while the carbon originally contained in the alloy, e. g. in the form of carbide, completely or to a considerable degree will deposit as a component in particles having a more finely divided structure, e. g. as deposits or precipitates in the boundary interstice between the aforementioned coarser crystals or as components in a eutectic. The alloy is then brought into such a state of disintegration that the grain boundaries are laid bare, completely or to a considerable degree, after which it is subjected to a separation for the removal of ingredients richer in carbon.

In such cases where the alloy does not by itself tend to break up during or after its solidification to such a degree that the particle boundaries are laid bare, it is necessary to subject the alloy to a fine crushing by mechanical means. The degree of fine crushing required to free the crystals to the extent desired for the purification, will depend partly on the particle size of the chief crystal mass of the alloy, and partly also on the desired degree of purity of the material treated. The size of the crystal grains may be regulated by adjusting the time of solidification of the alloy. The fine crushing of the alloy should generally be carried to such an extent that the grain size of the crushed product will be less than 1 mm. As an example may be mentioned that very good results have been obtained when working according to the invention with a silicon-chromium-iron alloy, which was reduced to such a size that it could pass a sieve with 40 mesh per linear cm. The crushing may be either dry or wet e. g. by means of crushing rolls, gyratory breakers, tube- or ball mills or other known crushing or grinding implements. Crushers and such mode of crushing which will liberate the crystals without splitting up the liberated crystals too much, are preferred.

During the crushing, the crystals of the chief crystal mass will to a great extent become liberated from their mechanical combination with the impurities, which latter generally will be more finely dispersed than the chief crystal mass of the alloy. The final separation of the smallest particles liberated in the crushing from the other particles may be made according to any known method, e. g. by means of dry or wet screening. When air separation is used, this may in cases be directly combined with the crushing operation.

Among suitable methods of air separation may especially be mentioned the so called Pape-Henneberg process, according to which finely divided material is ejected from a disc rotating at high velocity and is met counter-currently by a stream of air, which takes up the finer particles and removes them centrally, while the comparatively heavier particles are allowed to settle in annular boxes or chutes arranged around the disc. By varying the number and size of the annular receptacles as well as the velocity of the revolving disc, it is possible to divide the comminuted product into a greater or smaller number of fractions (grain classes) as desired. The impurities will tend to accumulate in the finer fractions received by the separation. If the disintegration has not been carried far enough to lay the greater part of the grain boundaries free, the coarsest fraction will contain more of the impurities than the middle fractions. An after-refining is possible by subjecting the coarser fraction or fractions to a continued disintegration followed by a treatment of the thus received metallic powder for the removal of a further amount of finely divided impurities. Instead of by dry methods it is, however, also possible to remove the finely divided impurities from the metallic powder by some kind of wet separation e. g. a simple washing. A more complete separation is, however, obtained by treating the metallic powder in water flow apparatus e. g. spitz kasten, with or without means for introducing water counter-currently in the lower part of the box, classifiers, Dorr-apparatus, shaking tables etc. It is thus advantageous to let the metallic powder supended in water, e. g. in the form it is received from a wet grinding ball mill, flow through a series of classifying cones or the like, while withdrawing the coarsest grains from the first cone and finer grains in succession from the following ones. In the first classifying cone or cones it is advisable to let the particles sink through a counter-current of clear water (hydraulic water) introduced in the lower part of the cone or cones. The products received from the first cone or cones are as a rule of sufficient purity but may be subjected to a further refin-

ing, for instance by means of a shaking table. The overflow from the last cone contains a product which is enriched in regard to impurities and which in its entity is in such a fine state of subdivision that an after-separation on shaking tables for the salvaging of purified material is hardly warrantable.

After-refining of a product which has been divided into fractions by dry methods may also be made on shaking tables. Similarly, coarser fractions received from a wet separation may to great advantage be subjected to a renewed disintegration followed by a separation.

The invention is especially useful for the removal of finely grained particles in the form of carbide from alloys of silicon with heavy metals, e. g. alloys of silicon with iron, chromium, manganese or vanadium, which alloys, after the performed refining, are particularly used for the production of alloys of said metals with a low content of silicon and carbon, in which cases the silicon content is utilized as a means of thermal reduction. Other impurities present in the boundaries between the crystals or as components in a eutectic in alloys, such as sulfides nitrides or phosphides, will also during the crushing of the alloy become liberated to a considerable degree from their mechanical combination with the chief crystal mass of the alloy and will be contained in the most finely divided material, so that these impurities too are removed when the finest material is withdrawn.

In the production of low-carbon chromium alloys according to the invention, an alloy suitable for the procedure of purification is first produced. This should preferably not contain more than 1% carbon, since there is otherwise a danger for part of the carbon to be contained in comparatively large crystals formed during the solidification of the alloy, which renders a separation difficult, because the separation in such cases will to a considerable degree depend on the degree of fineness to which it will be possible to reduce the crystal grains rich in chromium carbide, owing to their higher brittleness in regard to the rest of the crystal mass. It is thus preferred that the chromium alloy intended for purification should have a carbon content below 0.5%. In cases where chromium alloys with exceptionally low carbon content, down to traces of carbon are desired, it should preferably be started with an alloy having a still lower carbon content, e. g. 0.10–0.05%. The alloy should furthermore be given a certain content of such alloying compounds which in the solidifying of the alloy will, together with chromium and iron, cause the formation of such chromium containing crystals, which either directly after their formation are unable or only able to a very small degree to dissolve carbon, or otherwise during some interval of temperature below the temperature of solidification have no or slight faculty of dissolving carbon. Such alloying compounds are for instance silicon, aluminium, nickel, and titanium. It is thus preferred to produce an alloy containing both chromium and silicon, with the silicon preferably at least in such quantity that an alloy of a brittle nature is received. The silicon content should thus preferably not be below 10% and is generally kept considerably higher e. g. between 20% and 50%, because it is easier to obtain a low carbon content in the silicon-chromium alloy at such a high silicon content. The silicon-chromium alloy is, for instance, produced by smelting in an electric furnace according to some known method. The chromium may in such cases be added either by reduction of chromium oxide, chromium ore or slag high in chromium oxide, or else in the form of a ferro-chromium alloy containing carbon, e. g. with 60–70% Cr and 6–10% C. The silicon is added either by reduction of siliceous material, e. g. quartz, in connection with the smelting in the presence of carbon, in which case, if ferro-chromium containing carbon is present in the charge, this latter carbon will also serve as a reducing agent for part of the quartz, or else it may be added in the form of a silicon alloy. The whole of the desired silicon content may be added in one period of smelting, but it is also possible first to produce an alloy having a lower silicon content than desired and afterwards re-smelt this alloy together with siliceous material and carbon. This latter method is preferred when the chromium is added by reduction of chromium ore or slag rich in chromium oxide.

By working with such a large excess of silica in the smelting that a slag rich in silica is obtained, and by superheating this slag before tapping, a low carbon content in the silicon-chromium-iron alloy is attained. A certain quantity of a material containing aluminium oxide, e. g. firebrick, may suitably be added in the smelting, whereby a slag, chiefly consisting of aluminium oxide and silica, will cover the silicon-chromium-iron alloy obtained by the reduction and serve as a fining slag for this.

By regulating the process of solidification it is possible to create coarser or finer crystals. Even after solidification has set in there is, as a rule, a certain deposition of particles richer in carbon in the grain boundaries, owing to the fact that the alloying components richer in silicon will have a reduced dissolving power in regard to carbide at lower temperature. The rate of cooling should thus be regulated in such a manner that the deposition of carbide will become as complete as possible. For the same purpose, the alloy may also be subjected to a reheating to a temperature which favours the deposition of carbide. Such a reheating may also serve the purpose of increasing the size of the crystals.

Subsequent to the solidifying and cooling of the obtained silicon-chromium alloy, it is pulverized and subjected to a separation in above described manner. The fraction or fractions higher in carbon may either be used as additions in producing a fresh quantity of silicon-chromium-iron alloy, or else be used for making ferro-chromium with a carbon content e. g. between 0.2–1% C., by smelting together with chromium ore or slag rich in chromium oxide, and lime, while utilizing the silicon content of the alloy as a means of thermal reduction of the oxides of iron and chromium contained in the chromium ore.

The low-carbon fractions of the silicon-chromium alloy may be utilized for the production of low carbon ferrochromium, e. g. by smelting together with chromium ore and lime in an electric furnace, in which case care is taken, by choosing a suitable distribution of current and tension, to prevent as much as possible a taking up of carbon from the electrode or electrodes. The carbon remaining in the silicon-chromium-iron alloy after its purification will as a rule be entirely transferred to the final ferrochromium, low in carbon and silicon.

In such cases where a specially low carbon content, e. g. one or a few hundredths of a per-

cent, is desired in the silicon-chromium alloy, my process can be started with a low-carbon alloy, e. g. containing about 0.1% C, or else with a silicon-chromium-iron alloy with a higher carbon content, e. g. 0.20–0.50% C, which is purified, after which the so obtained low-carbon fractions of the alloy are re-smelted for the production of a low-carbon silicon-chromium-iron alloy, e. g. with about 0.1% or less, which re-smelted alloy is then pulverized and refined by removal of an additional amount of carbon in above described manner. The above mentioned primary refined product may either be smelted alone, or else in the re-smelting receive a further addition of silicon, e. g. by smelting a mixture of the refined alloy with siliceous material and carbon.

Another form of the invention provides the carrying out of said re-smelting while utilizing part of the silicon content of the alloy as a means of thermal reduction, e. g. for the reduction of slag rich in chromium oxide, chromium ore or iron ore. The silicon content of the alloy should, however, in such case not be utilized to a higher degree than to still allow of an easy crushing of the alloy received from the re-smelting. The silicon content should for this reason not be brought below 10% and is preferably kept considerably higher. This mode of utilizing part of the silicon content in connection with the re-smelting of the alloys brings about the advantage that the quantity of slag high in chromium oxide, which is formed in the final removing of the silicon content of the alloy by oxidation, will become considerably less than would otherwise be the case. The chromium oxide contained in the charge at the said re-smelting is practically completely reduced to metal thanks to the high silicon content of the resulting alloy.

To facilitate the separation of the carbon content in the alloy it may in certain cases be advisable to adjust the content in the alloy of silicon or aluminium or both so, that carbides of silicon or aluminium will form upon solidification of the alloy. These have a lower specific weight than chromium carbide and are thus easier to remove. Aluminium may be added to the alloy by reduction of materials containing aluminium oxide, in connection with the production of the chromium alloy, but aluminium may in certain cases also be directly added during or after tapping the alloy from the furnace, which method for instance is used to advantage for adding a smaller amount of aluminium to a high-silicon chromium alloy.

What has been said above in regard to the production and refining of silicon-chromium alloys does in relevant parts also apply to the production and refining of other silicon alloys, e. g. ferrosilicon and silicon-manganese. My invention is particularly applicable with alloys of metals having atomic numbers of from 23 to 28. The refining of alloys of chromium, manganese and other metals with aluminium and titanium, is also made in an analogous way.

Example 1

A silicon-chromium-iron alloy, containing 37% Cr, 45.7% Si and 0.32% C, was crushed to such a size that it passed a screen with 40 mesh per linear cm. upon which it was treated in a classifying device consisting of two conical boxes, whereby from the first cone was drawn about 75% of the alloy with a carbon content of 0.09% and from the second cone about 10% with a content of 0.29% C. The overflow from the second cone was conveyed to a shaking table. Samples taken from 3 places of discharge on the table showed 0.10% C, 0.18% C, and 2.10% C, respectively. The last sample was taken from that part of the finest slime which settled in a small settling tank near the table. The finest particles, richest in carbon, of the slime did not have enough time to settle in the tank. The product from box 2 may also be refined by hydraulic classification on shaking tables.

Example 2

A silicon-chromium-iron alloy containing 42.1% Cr, 38.6% Si, and 0.57% C, was crushed to same particle size as in previous example and thereupon directly treated on shaking table. A main product with 0.13% C and a smaller quantity of a middle grade with 0.18% C was thereby obtained, while the settling slime showed a carbon content of 2.50%.

Example 3

A silicon-chromium-iron alloy containing 47% Cr, 32% Si, and 0.11% C, was crushed to same particle size as in previous examples and the finest dust removed by washing. The refined product showed a carbon content of 0.02%.

I claim:

1. A process for the refining of alloys containing carbon as a component and with the carbon at least partly concentrated in particles of smaller size than the average size of the crystals of the alloy, comprising the step of removing at least part of the finest particles after disintegration of the alloy.

2. A process for the refining of alloys containing carbon, in which the carbon is at least partly concentrated in particles of smaller size than the average size of the crystals of the alloy, comprising subdividing such an alloy into its crystal particles to at least a considerable extent, and removing at least part of the finest particles by a mechanical process of separation.

3. A process for producing low carbon alloys comprising forming an alloy by means of chemical reduction, said alloy containing silicon in amount sufficient to form a readily disintegrated alloy, after solidification containing crystals having a lower carbon content than the average carbon content of the alloy, and as one of its main constituents at least one heavy metal of the group consisting of vanadium, chromium, manganese, iron, cobalt and nickel, and mechanically reducing the carbon content of the alloy by disintegration and removal of at least part of the finest particles liberated by the disintegration.

4. A process for the refining of alloys containing carbon, in which the carbon content is at least partly concentrated in particles of a smaller size than the average size of the crystals of the alloy, comprising subdividing such an alloy into its crystal particles and removing at least part of the finest particles by a process of air separation.

5. A process for producing low carbon metals and alloys, comprising forming an alloy containing as its main constituent a heavy metal of the group consisting of vanadium, chromium, manganese, iron, cobalt and nickel, and containing also silicon in excess of 10 per cent and having its carbon content chiefly in the form of carbides deposited in the interstices of the chief crystal mass of the alloy, reducing the carbide content of said alloy by disintegration of the alloy and removal of at least part of the finest particles, and finally oxidizing at least part of the silicon

in the alloy by smelting the thus refined alloy with a material containing an oxide of a heavy metal of the group consisting of vanadium, chromium, manganese, iron, cobalt and nickel.

6. A process for producing a refined chromium alloy, comprising forming a chromium alloy by means of a reduction process, said alloy containing at least 10 per cent of silicon, and impurities of carbon, subdividing said alloy into its crystal particles at least to a considerable extent, and removing at least part of the finest particles.

7. A process for producing a refined alloy, comprising forming a chromium alloy, containing silicon, in amount sufficient to form a readily disintegrated alloy, after solidification containing crystals having a lower carbon content than the average carbon content of the alloy and less than 1 per cent of carbon by fusing a charge containing material rich in silica, chromium containing materials and carbonaceous reducing agents, disintegrating the alloy and removing at least part of the finest particles by a mechanical process of separation.

8. A process for producing a refined alloy, comprising forming an alloy by smelting, said alloy containing as main constitutents chromium, iron and silicon, the latter in excess of 20 per cent and between 0.5 to 0.05 per cent of carbon, subdividing said alloy into its crystal particles at least partly and removing at least part of the finest particles.

9. A process for producing a refined alloy comprising smelting for the formation of an alloy containing impurities of carbon, said alloy containing as main constituents at least one heavy metal of the group consisting of vanadium, chromium, manganese, iron, cobalt and nickel, and at least one light metal of the group consisting of aluminum and silicon producing brittleness in said alloy and forming a light carbide having a lower specific weight than chromium carbide, in amount sufficient to cause precipitation of said light carbide on solidification of the alloy, subjecting said alloy to a treatment by which at least a considerable part of the precipitated carbide particles of the alloy are rendered mechanically separable and removing at least part of such particles containing carbides.

10. A process for producing low carbon chromium alloys, comprising a smelting process for the formation of an alloy, containing particles to a considerable extent consisting of carbide, and comprising as the main constitutent particles substantially consisting of silicon, chromium, and iron, disintegrating said alloy to such extent that at least a considerable liberation of its particles is obtained and removing at least part of the particles containing carbide, and finally smelting the alloy with a material containing chromium oxide for the purpose of oxidizing the silicon in the refined alloy.

11. A process for producing low carbon chromium alloys, comprising forming a chromium alloy, containing from 20 to 50 per cent of silicon, by fusing a charge containing materials rich in silica, chromium containing materials and carbonaceous reducing matter, subdividing said alloy into its crystal particles at least partly and removing at least part of the finest particles and finally fusing the alloy with a material containing an oxide of a heavy metal of the group consisting of vanadium, chromium, manganese, iron, cobalt and nickel for the purpose of oxidizing the silicon.

12. A process for producing low carbon alloys containing iron and chromium, comprising fusing ferro-chromium of high carbon content with materials rich in silica and carbonaceous reducing agents for the production of an alloy containing, in addition to chromium and iron, such a high content of silicon, that the main part of the chromium and iron is upon solidification of the alloy precipitated as crystals of low carbon content containing silicon, while the carbon impurities of the formed alloy are concentrated in crystal particles having a lower silicon content, subdividing said alloy into its crystal particles at least to a considerable extent, and at least partly separating the thus liberated carbon impurities.

13. A process for producing a refined alloy, comprising smelting to form a chromium alloy containing at least about 10 per cent silicon, and impurities of carbon, distintegrating said alloy and removing at least part of the finest particles liberated, thereupon re-smelting the refined alloy, distintegrating the thus formed alloy at least partly and removing at least part of the finest particles liberated.

14. A process for producing a refined alloy, comprising reducing the carbon content of an alloy containing chromium in substantial amounts by fusing it with materials rich in silica and carbonaceous reducing agents, separating a further amount of carbon from the thus formed alloy containing chromium and silicon by subdividing said alloy into its crystal particles at least partly and removing at least part of the finest particles, thereafter resmelting said refined alloy with siliceous material and carbonaceous reducing agents, subdividing said refined alloy into its crystal particles at least partly, and removing the finest particles.

15. A process for producing low carbon chromium alloys, comprising forming an alloy containing chromium as a main constituent, silicon in excess of 20 per cent and impurities containing carbon, disintegrating said alloy and removing at least part of the finest particles liberated by disintegration, thereafter removing part of the silicon content by fusing the refined alloy with a material containing an oxide of a heavy metal of the group consisting of vanadium, chromium, manganese, iron, cobalt and nickel, disintegrating the formed alloy and removing at least part of the finest particles liberated by disintegration, and finally fusing the refined alloy with an oxidizing agent for silicon.

16. A process for producing refined alloys, comprising forming an alloy containing as its main constituents silicon, at least one heavy metal of the group consisting of vanadium, chromium, manganese, iron, cobalt and nickel and impurities of carbon, maintaining said alloy for a certain period of time at a temperature suitable for crystal growth, at least partly subdividing said alloy into its crystal particles at a lower temperature, and removing at least part of the carbon containing impurities.

17. A process for producing a refined alloy, comprising heating a carbon bearing alloy, containing crystals with a silicon component which at a temperature below that of their formation at least to a considerable extent lose their faculty of dissolving carbide, to such a temperature that carbide impurities are precipitated out of the silicon containing crystals, subdividing said alloy into its crystal particles to at least a considerable extent, and removing at least part of the carbide impurities.

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