

UNITED STATES PATENT OFFICE.

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PROCESS OF PRODUCING CHROMIUM-CONTAINING ALLOYS.

1,346,187.

Specification of Letters Patent.

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No Drawing.

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To all whom it may concern:

Be it known that I, FRANK A. FAHRENWALD, a citizen of the United States, residing at Cleveland Heights, in the county of Cuyahoga and State of Ohio, have invented a certain new and useful Improvement in Processes of Producing Chromium-Containing Alloys, of which the following is a full, clear, and exact description.

This invention relates to a process of producing certain metals, such as those of the chromium and iron groups, and their alloys either with each other or with other metals from outside those groups, free from non-metallic impurities of which carbon and silicon are the chief. The invention contemplates chiefly the production of alloys of iron and chromium, either pure or mixed with other metals, but is not restricted to this use; and while in the following description of one process by which my invention may be performed I have instanced chromite ore, it will be understood that I do not restrict myself except as specifically defined in my claims.

In the production of many alloys, such as those employed for high temperature work (as in heat treating boxes, retorts for the distillation of wood, coal and oil-shale, cutting tools, devices for working hot metal, etc.) it is desirable to employ alloys containing only a small amount of carbon and silicon, such for example as alloys of iron and chromium. The common source of all such alloys is the mineral chromite which consists essentially of the mixed oxids of iron and chromium together with silica, alumina, magnesia and calcium carbonate as impurities. According to the customary process heretofore employed this is reduced by carbon to form what is known as "ferro-chrome," the operation being carried out either in the electric furnace or blast furnace and at a fusing heat with a slag. This process entails the following disadvantages: first, about ten to fifteen per cent. of the chromium oxid is lost in the slag, which thereby becomes so infusible that it is sold for refractory bricks; considering that chromite ore generally costs about 25¢ per pound of chromium oxid contained this loss is a very serious one. Second, at the fusion temperature the silicon is reduced as well as the chromium and iron so that the resulting product contains from 2% to 4% of silicon. Third, the molten bath is very avid

of carbon and dissolves it readily; in order to minimize the loss of chromite in the slag it is customary to use an excess of carbon thus tending to produce a prompt reduction of the ore, but even if molecular proportions are employed the solution of chromite in the slag leaves an excess of carbon to dissolve in the metal, and if the carbon used be sufficiently restricted to avoid solution the chromite loss not only becomes financially fatal, but the slag becomes so refractory as to be unworkable. As a consequence the ferro-chrome produced from this reaction contains from 6% to 8% of carbon and costs on the market at the present time about 35¢ per pound of metallic chromium contained. By refusing and refining with additional chromite ore the carbon content can be reduced to about 2%, but the cost of the treatment is such that the market price of the product becomes at the present time about 70¢ per pound of chromium contained. Besides the tendency of the refining treatment is to increase the silicon content. In addition to the high cost of this process, and the waste of materials the alloys I have mentioned preferably contain a rather small amount of carbon and silicon such as cannot be secured at all by this process.

It is true that by the aluminothermic or Goldschmidt process the chromite can be reduced without admixture of either carbon or silicon and this process has frequently been employed in the production of such alloys, but the high cost of the chromium so produced (about \$2.50 per pound of contained chromium) has greatly diminished the use of the alloys.

By my improved method I can produce reduced iron and chromium from chromite ore, substantially free from dissolved carbon or silicon and absolutely without loss of chromite ore, while the expense of the operation is so small as to be less than the cost of the chromite which was formerly lost in the slag. According to my improved process the ore is first reduced without fusion after which it is purified by melting and slagging in the absence of reduction. While I do not restrict myself thereto the simplest and cheapest mode of reduction is generally by the use of carbon, and to this end I mix the crushed or pulverized ore with the molecular proportion of carbon or a little less, and inclose the mixture in crucibles, boxes, tubes,

or other containers which may be of clay, graphite, or fairly heat resistant metal. I then heat these containers for from eight to ten hours in any convenient manner to a temperature of about 1,000° C. Any temperature above about 800° C. will serve and the higher the temperature the shorter the time required although above about 1,000° C. the deterioration of the containers is too rapid. The result of this reduction is a spongy or soft mass of pure iron and pure chromium mixed with unreduced silica, alumina, magnesia and lime if any be present in the ore. Owing to the low temperature of reduction no slag is formed up to this stage even though all the materials for a slag be present. Owing to the fact that the reduction is effected at a temperature below that necessary to fuse the metal product, no tendency exists for any part of the reducing agent to become alloyed or dissolved in such metal.

In case lime be present as a preponderating impurity I add enough silica to combine therewith in slag form; in case silica be the prevailing impurity I add lime for the same purpose. Also if sulfur be present I add lime. If alumina be the main impurity it may be necessary to add both lime and silica. If magnesium silicate be present as the preponderating impurity which is the usual case, I add fluor spar to increase its fusibility.

These substances may if desired be added before the reduction in view of the low temperature of this reaction, or the reduced mass may be crushed and these substances added afterward. There are advantages and disadvantages both ways. If the slag materials are not added until after the reduction it is sometimes well to add a little ferric oxid with it to increase its fusibility. Whichever course is pursued the reduced mass mixed with the slag-forming materials is now subjected to a considerably increased temperature in an electric or other furnace whereupon the slag-forming materials melt together into a superincumbent glass and the metallic ingredients, which are wholly insoluble therein, fuse together into an alloy consisting of approximately iron 55% and chromium 45% which can be cast into pigs if desired. This fusion being effected after reduction is complete, it is possible to effect the same without the danger of dissolving a part of the reducing agent in the molten metal.

In case the reduced metals are to be alloyed with other substances, I have found it a very simple and easy matter to briquet them under moderate pressure, since they yield very readily to this treatment.

In case the reduced metals are to be used immediately in the manufacture of heat and corrosion resisting alloys containing both

iron and chromium, the second step can be omitted or rather merged with the adjustment of the alloy.

For example a furnace charge of turnings, borings, etc. can be melted and the briquets afterward introduced. Or the powder can be introduced directly into the molten bath in case a reducing atmosphere be maintained. Or the loose powder can be inclosed in cloth bags or metallic containers and introduced below the surface of the molten charge. The carbon content of the final alloy can be adjusted by a proper selection of borings or by adding coke; the silicon content can be increased by the addition of ferro-silicon; manganese if desired is added as ferro-manganese; nickel, cobalt, tungsten, molybdenum, titanium, zirconium and aluminum, if used, are added in the metallic form. It is true that only a few of the ingredients are added in a pure form but generally in pairs, but by having the ferro-chromium in a pure form without any uncertain admixture of carbon and silicon as heretofore it becomes possible to regulate the composition of the alloy with great exactness.

It should be noted that not all ores can be reduced by this method with equal facility; this method operates best upon ores wherein the silicon impurity does not occur in combination with the iron or chromium. If any of the iron or chromium is combined with the silicon in the form of silicate, that portion cannot be reduced short of fusion temperature, but in many chromite ores the silicon occurs in combination with aluminum, calcium, or magnesium and in these a complete reduction of the metallic constituents can be obtained at low temperature.

It will be understood that I do not restrict myself to the use of my improved process to the reduction of this particular ore or to the making of these particular alloys nor otherwise than as defined in the annexed claims or as limited by the prior art.

Having thus described my invention what I claim is:—

1. The method of reducing ferrous metal ores which contains the steps of mixing the ore with sufficient carbon to reduce substantially all the metallic constituents substantially without overplus heating such mixture for a protracted time to a temperature sufficiently high to reduce the metallic constituents and too low to reduce silicon, and afterward raising the temperature to a point sufficient to melt the reduced metal and to slag out the unreduced constituents.

2. The method of reducing chromite which contains the steps of mixing the ore with such an amount of carbon as will be substantially all consumed in the reduction of the metallic constituents, heating the mixture in closed containers for a protracted

time at a temperature sufficient to reduce the metallic constituents but insufficient to reduce silicon, and afterward melting the reduced metal out of the unreduced constituents.

3. The method of reducing chromite ore which contains the steps of mixing the ore with such an amount of carbon as will be substantially all consumed in the reduction of the metallic constituents, heating the mixture in closed containers for a protracted time at a temperature sufficient to reduce the metallic constituents but insufficient to reduce silicon, adding slag forming materials, and subjecting the mass to a fusion temperature after the substantially complete consumption of the carbon.

4. The method of securing a chromium containing alloy substantially free from carbon and silicon which consists essentially of first reducing the ore in closed vessels with a deficiency of carbon at a temperature below the reduction temperature of silicon, and afterward fusing the resulting mass with slag forming materials.

5. The process of producing chromium containing alloys which contains the steps of first reducing chromite with a deficiency of carbon at a temperature below that of the reduction of silicon, and subsequently fusing the reduced mass with an added quantity of one or more iron group metals in the presence of slag-forming ingredients.

6. The process of producing metals hav-

ing atomic weights between 52 and 60 which shall be wholly or substantially free from dissolved carbon and silicon which comprises the steps of first reducing the oxygenore of such metal by heating the same in contact with a deficiency of carbon at a temperature sufficient to reduce the metal but insufficient to reduce silicon, collecting into parcels the product of such reduction, and subsequently fusing such parcels in contact with slag-forming materials.

7. The process of making a high-temperature and corrosion-resisting alloy which comprises the steps of first heating the oxides of the preponderating constituents of such alloy in contact with a deficiency of reducing agent to a temperature sufficient to reduce the metallic oxides but not sufficient to reduce any non-metallic oxides which may be present, and subsequently melting the resulting product in contact with substances which shall form a slag with the unreduced constituents and with other metals which shall alloy with the reduced constituents.

8. The process of reducing chromite ore which contains the steps of first reducing the metallic constituents of the ore without concurrent fusion, and subsequently fusing the same without concurrent reduction in the absence of any excess reducing agent.

In testimony whereof I hereunto affix my signature.

FRANK A. FAHRENWALD.