

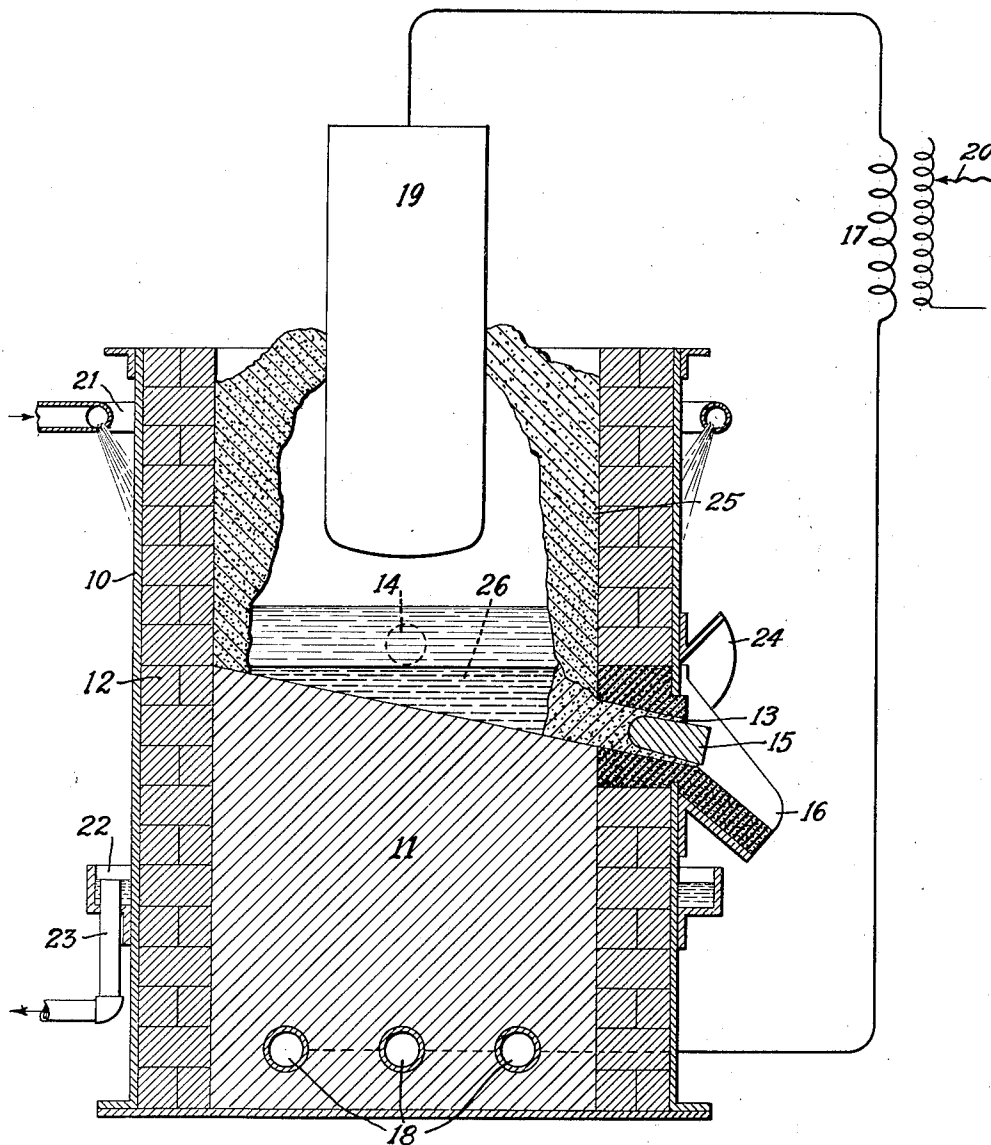
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PRODUCTION OF SILICON IRON AND ALUMINUM COPPER ALLOYS

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PRODUCTION OF SILICON-IRON AND ALUMINUM-COPPER ALLOYS.

Application filed March 7, 1923. Serial No. 623,370.

This invention relates chiefly to the production of aluminum-copper alloys of low iron and titanium content but containing large amounts of aluminum, from bauxite, 5 clay, alunite, leucite, and other aluminous materials, and relates more particularly to processes of the kind described and claimed in the copending application of William Hoopes, Francis C. Frary and Junius D. Edwards, Serial No. 608,283, now Patent 10 No. 1,534,316, issued April 21, 1925. Most of the naturally occurring minerals referred to above contain a considerable proportion of iron and titanium, together with varying 15 amounts of silica. In order to produce from these materials an aluminum-copper alloy low in iron and titanium, it is necessary to first remove the iron and titanium; preferably in the form of a ferro-silicon-titanium alloy (which may, and often does, 20 contain some aluminum), by electrothermally smelting the aluminous material with a reducing agent, preferably carbon, and with the addition of iron, iron ore, or other materials containing iron, if necessary. In 25 practice, on account of the fact that the heat of formation of titanium oxid is greater, per atom of oxygen, than that of silica, it is in most if not all cases desirable to reduce substantially all of the silica. Hence, in the 30 step in which the iron and titanium are to be removed, the electrothermal reduction should usually be carried to the point where practically all of those oxids which are more easily reduced than alumina have been 35 reduced. At this point a small amount of alumina will, in general, also be reduced. It has been found that in order to make a clean separation of the ferro-silicon-titanium alloy from the aluminous residue or slag, it is advantageous to have iron present in such amount that the silicon content of the alloy will not be more than about 30 per cent. 40 If there is not enough iron present in the clay or other raw materials for this purpose, it may be added in any convenient form, as for example metallic iron or an iron oxid.

50 The melting point of alumina is very high and the fused alumina is viscous. I have found that these two conditions militate against the economical production of the

ferro-silicon-titanium alloy, but that by the use of certain additional materials in this step the melting point of the alumina may 55 be lowered and its fluidity increased, with a decidedly greater output of smelted material, as well as a better separation of the alloy from the slag. In order that such additional material may remain with the molten alumina, it should be composed of compounds which are more difficultly reducible by carbon than is alumina itself. As examples of compounds usable for the purpose there may be mentioned alkalis, especially 60 compounds of sodium and potassium, alkaline earths, especially compounds of calcium and magnesium, and some of the rare earths, such as beryllium. It should be noted that although the oxids of some of these elements, notably oxids of the alkali 70 metals, are more easily reduced than alumina, they form compounds with alumina (aluminates) of such a character that the alkali metal oxids are thereby largely protected from reduction, although part of the losses of these metals found in practice may 75 be due to reduction.

In the course of extended investigation and practical tests it has been found that 80 the addition of sodium or potassium carbonates or chlorids, or the addition of minerals containing sodium or potassium, such as feldspar, or the use of oxids, carbonates or silicates of calcium or magnesium, has 85 decided advantages. Calcium chlorid is also applicable.

The presence of these agents (which appear to act somewhat in the manner of a flux and hence may be conveniently referred to as fluxes, fluxing agents, etc.) is 90 not only of advantage in the step in which the ferro-silicon-titanium alloy is produced, but it is of particular advantage in the step in which the copper-aluminum alloy is produced. It has been found that the presence 95 of a suitable flux not only tends to increase the quantity of copper-aluminum alloy produced in a given time by a given furnace, but also in some cases makes it possible to obtain as a final product an alloy containing a higher aluminum content. 100

While, as above stated, most of the naturally occurring aluminous materials contain

such amounts of iron and titanium as to make removal of these elements necessary or desirable before smelting for the production of aluminum-copper alloys, there are some materials, as for example certain grades of bauxite and certain deposits of alunite and residues from the treatment thereof, which are sufficiently low in iron and titanium so that they can be utilized to produce an acceptable aluminum-copper alloy without preliminary removal of iron and titanium. In the smelting of such materials, however, to produce alloys of aluminum and copper, it has been found desirable to add one or more of the above mentioned fluxing agents (especially magnesia) for the reasons explained. Accordingly the invention is applicable and advantageous in the production of aluminum-copper alloys from aluminous materials whether or not they occur naturally with sufficiently low content of iron and titanium to make a satisfactory alloy by direct reduction.

Of the various fluxing agents mentioned above, the alkalis have a very satisfactory action, but their advantages are somewhat offset by their cost and volatility. Salts of calcium are quite advantageous in the first stage, but are somewhat less so in the second, because they tend to produce after some time an infusible lump which may perhaps contain either calcium carbide or a calcium aluminate rich in calcium oxide. Magnesia or other magnesium compounds, however, have the great advantage of being relatively non-volatile, and of producing a liquid slag within a considerable range of composition, so that if magnesia (MgO) to the extent of 3 to 10 per cent of the weight of the alumina (Al_2O_3) be present in the charge, the greater part of the alumina may be reduced to metal in the production of the aluminum-copper alloy and a fused slag containing magnesia may be removed and returned for re-use at a suitable point in the process, as for example as a part of the charge used in the production of the aluminum-copper alloy.

By the use of the process herein described, it is possible to produce from clay containing considerable proportions of the oxides of iron and titanium, an aluminum-copper alloy, containing between 30 and 40 per cent of aluminum, and not more than about 2 or 3 per cent of iron-plus-titanium. If it is desired to have a substantial amount of silicon also in this alloy, as is usually the case when the alloy is to be used in an electrolytic refining process for the production of aluminum, as for example the process described in the copending application of William Hoopes, Francis C. Frary, and Junius D. Edwards, Serial No. 608,284, now Patent No. 1,534,317, issued April 21, 1925, it may be necessary to add silicon in suitable form with the copper in the second step. The

fluxes used may be added in any convenient form, since such impurities as silica, oxides of iron, etc., are not detrimental in the first part of the present process. Also, if the residue or slag from the first step does not contain a sufficient amount of flux for the second step of the process, more flux may be added at this point, in the form, for example, of common salt, sodium carbonate, high-grade feldspar, magnesia, or a high grade of calcined magnesite or magnesium carbonate. Similar fluxes would be used in the melting of materials (as for example the high grade bauxites and other materials mentioned hereinbefore) low enough in iron and titanium for direct production of aluminum-copper alloy.

Ordinarily only a small quantity of fluxing material is needed. For example magnesia to the amount of from 3 to 10 per cent of the alumina present in the charge will in most cases give advantageous results. In general no more need be used than enough to have the desired effect on the melting point and fluidity of the slag. The amount of iron and reducing agent in the first step and the amount of copper and reducing agent in the second depend, generally, upon the oxide content of the material to be treated and the extent of the reduction desired. As a specific example it may be assumed that clay is to be used having an alumina content between 45 and 50 per cent, silica between 30 and 35 per cent, titanium oxide (TiO_2) about 2 per cent, and iron oxide (say Fe_2O_3) about 3 per cent. The clay may contain some magnesia, say up to 1 per cent of the alumina present, and sufficient magnesia is added to bring the amount up to about 6 per cent of the alumina. The iron content of the charge, including the iron in the clay, should be in amount sufficient to take up and hold the desired amount of silicon, after allowing for loss of silica by volatilization, and the reducing agent used should be sufficient to reduce all the iron and titanium oxides and silica. The carbon of the electrodes in the electric furnace employed supplies part of the reducing agent, and account should therefore be taken of this fact. Assuming that from a clay of the above composition a ferro-silicon-titanium alloy is to be produced containing substantially all the iron, titanium and silicon (except that lost by volatilization), the charge for the first step may consist of clay about 60 per cent, iron (metallic) about 25 per cent, coke about 10 per cent, and magnesia about 2 per cent. The resulting alloy will then have approximately 65 per cent of iron, 30 per cent of silicon, 2 per cent of titanium, and possibly a little aluminum; though ordinarily aluminum is not desired here but rather in the final aluminum-copper alloy intended for use in the production of

aluminum by electrolytic refining. At the same time the slag or residue of the first step will contain all or nearly all of the magnesia and substantially all of the unreduced alumina.

For the treatment of the above slag or residue (or other aluminous material suitably low in iron and titanium) the copper needed to absorb the aluminum may be supplied in any suitable form, say as metal or as oxid. Assuming that the slag is to be treated for the production of an aluminum-copper alloy containing about 35 per cent of aluminum and about 60 per cent of copper, the charge used in the second step may be of about the following composition: slag 50 per cent, metallic copper 35 per cent, and coke (or charcoal or a mixture of the two) 15 per cent. In this case, too, account should be taken of the fact that the carbon of the furnace electrodes helps in the reduction of the alumina, and accordingly less coke and charcoal need be added than otherwise would be needed. The slag or residue from this step contains any alumina remaining unreduced and some of the magnesia. The slag, withdrawn separately, or otherwise separated from the aluminum-copper alloy, goes back into the process, as already stated, and hence part of the magnesia simply circulates through the process, with sufficient additions to make up for unavoidable losses due apparently to reduction and vaporization. The dust and vapors escaping from the furnace may be collected and the magnesium recovered (usually as oxid) by electrostatic precipitation.

Some of the fluxing agents mentioned, notably magnesia, lime, and barium carbonate, suffer but little loss in the ferro-silicon step, but in the case of other agents there may be a substantial loss in the step mentioned, and where this occurs it may be necessary or advisable to supply additional flux in the aluminum-copper step.

The process may be performed in electric furnaces of the type described in the above-mentioned patent of William Hoopes, Francis C. Frary and Junius D. Edwards, No. 1,534,316. A suitable furnace of that class is shown in vertical section in the accompanying drawing. Therein, 10 designates an open-topped steel shell of upright cylindrical form, containing a carbon bottom 11 and a refractory side lining 12 composed of fire-brick, bauxite-brick or other suitable material. The carbon bottom slopes toward a tap hole 13 for withdrawing ferro-silicon or aluminum-copper-silicon alloy, as the case may be. A tap hole 14 at a higher level permits withdrawal of slag independently of the underlying alloy. All these openings may be closed in any convenient manner. For example, a plug of pine wood may be driven into the hole, as indicated at 15. The

heat encountered causes the plug to burst into flame immediately and it is converted into charcoal in a few minutes, but it lasts long enough to stop the flow of metal or slag and permit solidification back of the plug. The spout 16, preferably rather steep so as to prevent clogging by freezing due to rapid cooling of the slag or metal, may be lined with a mixture of magnesite and fire clay moistened with a solution of water-glass.

Conducting members are embedded in the carbon bottom or lower electrode 11 for connection with one terminal of a source of alternating current represented by the transformer 17. Preferably the conducting members are in the form of steel pipes, as indicated at 18, through which water may be passed for cooling purposes. The upper electrode is a carbon cylinder 19, connected to the other terminal of the secondary of the transformer 17. Any suitable means, not shown, may be provided to raise and lower the electrode and hold it in position. The energy input can be regulated in any convenient way, for example by varying the number of ampere turns in the transformer, preferably in the primary thereof, as indicated by the adjustable primary terminal 20.

The furnace may be cooled, if necessary or desirable, by water discharged upon the outer shell from an encircling pipe 21, arranged at the upper part of the shell and connected to a source of supply, not shown. The water running down the shell can be caught by a trough 22 and carried away by a drain pipe 23. To keep water out of the tap holes the latter may be provided with suitable shields, as 24.

When it is used for producing ferro-silicon and the aluminous slag, the furnace builds up a lining, as indicated at 25, for example, composed, especially in the lower part of the furnace, of charge and solidified slag.

The process may be started by striking arcs between the upper electrodes and a layer of coke on the bottom of the furnace, and thus heating the interior. The charge is then delivered to the furnace. When the temperature has increased sufficiently the reaction begins, reducing the iron, silicon, and titanium oxides, and producing a mixture of the corresponding elements, which mixture as ferro-silicon-titanium alloy sinks to the bottom, whence it is withdrawn from time to time through the tap hole 13. In the drawing the molten alloy is indicated by the layer 26. The aluminum-copper alloy furnace may be of the same construction and may be started and operated in the same manner, withdrawing the alloy through the lower tap hole and the flux-bearing slag through the upper.

As will be readily understood, the voltage and current needed depend largely upon the

composition of the charges, the size of the electrodes, the capacity or size of the furnace, and the effectiveness of its heat-insulation, and the rate at which the reactions are desired to proceed. In the ferro-silicon step the lowest desired temperature is in the neighborhood of 1600° C. Reduction of the alumina, in the aluminum-copper alloy step, begins at about 1800° C. and proceeds freely at about 1950° C. At temperatures mentioned the iron and copper can absorb and hold large amounts of silicon and aluminum.

As described in connection with the furnace illustrated the invention produces the two alloys simultaneously yet separately, but the process is by no means confined to that method. Nor is the invention limited to other specific details herein described, but can be practiced in various ways without departure from its spirit.

I claim as the invention of FRANK D. SHUMAKER, deceased:

1. In a process of making silicon-iron and aluminum-copper alloys from materials containing oxids of aluminum, silicon, iron, and titanium, the steps comprising electrothermally smelting the aluminous material in the presence of iron and with a suitable fluxing agent, and producing thereby ferro-silicon alloy containing more or less of the iron and titanium of the aluminous material treated, and a highly aluminous material or slag of low iron and titanium content but containing fluxing agent; and electrothermally smelting the flux-bearing slag in the presence of copper and producing thereby an aluminum-copper alloy low in iron and titanium.

2. In a process of making silicon-iron and aluminum-copper alloys from materials containing oxids of aluminum, silicon, iron, and titanium, the steps comprising electrothermally smelting the aluminous material in the presence of iron and with a suitable fluxing agent, and producing thereby ferro-silicon alloy containing more or less of the iron and titanium of the aluminous material treated, and a highly aluminous material or slag of low iron and titanium content but containing fluxing agent; electrothermally smelting the flux-bearing slag in the presence of copper, producing thereby an aluminum-copper alloy low in iron and titanium, and a slag containing more or less of the fluxing agent; and returning the last-mentioned slag to the process.

3. In a process of making silicon-iron and aluminum-copper alloys from materials containing oxids of aluminum, silicon, iron and titanium, the steps comprising electrothermally smelting the aluminous material with carbon and a fluxing agent less easily reducible by carbon than is alumina, and producing thereby ferro-silicon alloy, and a highly aluminous material or slag low in

iron and titanium but containing the major portion of the fluxing agent; and electrothermally smelting such flux-bearing slag in the presence of copper to produce an aluminum-copper alloy low in iron and titanium.

4. In a process of making silicon-iron and aluminum-copper alloys from materials containing oxids of aluminum, silicon, iron, and titanium, the steps comprising electrothermally smelting the aluminous material with carbonaceous reducing agent and magnesia as a fluxing agent, to produce a ferro-silicon alloy and an aluminous material or slag of low iron and titanium content but containing the major portion of the magnesia present; and electrothermally smelting said magnesia-bearing slag in the presence of copper to produce an aluminum-copper alloy low in iron and titanium.

5. In a process of making silicon-iron and aluminum-copper alloys from materials containing oxids of aluminum, silicon, iron, and titanium, the steps comprising electrothermally smelting the aluminous material with carbonaceous reducing agent and magnesia as a fluxing agent, to produce a ferro-silicon alloy and an aluminous material or slag of low iron and titanium content but containing the major portion of the magnesia present; electrothermally smelting said magnesia-bearing slag in the presence of copper to produce an aluminum-copper alloy low in iron and titanium, and a slag containing at least a portion of the fluxing agent; and returning more or less of the last mentioned slag to the process.

6. In a process of making aluminum-copper alloys of low iron and titanium content from naturally occurring materials containing alumina, silica, and oxids of iron and titanium, the steps comprising reducing the iron and titanium oxids of the material, and more or less of the silica, in the presence of magnesia to produce a non-metallic mixture containing alumina and silica and sufficient magnesia to make the mixture freely fluid when fused; and smelting said mixture with a suitable reducing agent in the presence of copper to produce aluminum-copper alloy low in iron and titanium but containing a substantial amount of silicon.

7. In a process of making aluminum-copper alloys of low iron and titanium content from naturally occurring materials containing alumina, silica, and oxids of iron and titanium, the steps comprising reducing the iron and titanium oxids of the material, and more or less of the silica, in the presence of magnesia to produce a non-metallic mixture containing alumina and silica and sufficient magnesia to make the mixture freely fluid when fused; smelting said mixture with a suitable reducing agent in the presence of copper to produce aluminum-copper alloy

low in iron and titanium but containing a substantial amount of silicon, with a residue containing a substantial amount of the original magnesia; and collecting the aluminum alloy, and returning more or less of said residue to the process.

8. In a process of making aluminum-copper alloys of low iron and titanium content from naturally occurring materials containing alumina, silica, and oxides of iron and titanium, the steps comprising producing from the material by electrothermal reduction in the presence of magnesia a highly aluminous material or slag low in iron and titanium but containing sufficient magnesia to give the slag a suitable melting point and render it freely fluid when fused; treating said slag with a suitable reducing agent, in the presence of copper, and at a temperature high enough to reduce a substantial amount of the alumina, whereby aluminum-copper alloy and a magnesia-bearing slag are produced; and collecting the alloy and returning more or less of the last mentioned slag to the process.

9. In a process of making aluminum-copper alloys of low iron and titanium content from naturally occurring materials containing alumina, silica, and oxides of iron and titanium, the steps comprising reducing the iron and titanium oxides of the material, and more or less of the silica, in the presence of magnesia to produce a non-metallic mixture containing alumina and silica and sufficient magnesia to make the mixture freely fluid when fused; smelting said mixture with siliceous material and a suitable reducing agent in the presence of copper to produce aluminum-copper alloy low in iron and titanium but containing a substantial amount of silicon, with a residue containing a substantial amount of the original magnesia; and collecting the aluminum alloy, and returning more or less of said residue to the process.

10. In a process of making aluminum-copper alloys from aluminous materials, the step comprising subjecting the material to electrothermal reduction in the presence of a fluxing agent to lower the melting point and increase the fluidity of the alumina.

11. In a process of making aluminum-copper alloys from aluminous materials, the step comprising subjecting the material to electrothermal reduction in the pressure of

55 magnesia as a fluxing agent to lower the melting point and increase the fluidity of the alumina.

12. In a process of making aluminum-copper alloys from aluminous materials, smelting alumina-containing material low in iron and titanium in the presence of magnesia as a fluxing agent to lower the melting point and increase the fluidity of the alumina, and as the alumina is reduced absorbing the resulting aluminum in molten copper.

13. In a process of making aluminum-copper alloys from aluminous materials, smelting aluminous material low in iron and titanium in the presence of a fluxing agent to produce aluminum, absorbing the aluminum in molten copper, separating the resulting alloy from the unreduced material containing more or less of the fluxing agent, and returning said unreduced material to the process.

14. In a process of making aluminum-copper alloys from aluminous materials, smelting aluminous material in the presence of magnesia and copper to produce an aluminum-copper alloy and an unreduced residue containing magnesia, separating the alloy and residue, and utilizing the latter in the smelting step to furnish magnesia for smelting additional aluminous material.

15. In a process of making aluminum copper alloys from aluminous materials, treating aluminous material under reducing conditions in the presence of a fluxing agent to produce aluminum, absorbing the aluminum in molten copper to produce aluminum-copper alloy and leave a non-metallic residue containing fluxing agent, collecting the said alloy, and utilizing the said residue to supply fluxing agent for smelting additional aluminous material.

16. In a process of making aluminum-copper alloys, from aluminous materials, smelting alumina-bearing material in the presence of copper and an added agent having a higher reduction temperature than alumina and capable of lowering the melting point and increasing the fluidity of alumina.

In testimony whereof I hereto affix my signature.

JOSEPHINE J. SHUMAKER,
Executrix of the last will and testament of
Frank D. Shumaker, Deceased.