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PROCESS FOR THE MANUFACTURE OF
COMPLEX SILICON ALLOYS

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The present invention relates to the manufac-
ture of complex alloys of silicon with certain
metals and/or metalloids; it is applied in particu-
lar to the manufacture of alloys which may con-
tain with silicon not less than one element of
the group consisting of calcium, barium,
strontium, aluminum, magnesium, beryllium, zir-
conium, cerium, and rare earth-metals, titanium,
manganese, chromium, tungsten, molybdenum,
vanadium and boron.

The processes generally employed for obtain-
ing these alloys have a certain number of dis-
advantages.

The reduction by carbon of silica or of oxides
of metals which it is proposed to alloy with the
silicon is not always possible and leads some-
times to the formation of carbides.

The reduction of the metallic oxides by silicon
is sometimes too slow, difficult, and expensive.

Reduction by electrolytic aluminum is costly
and often accompanied by the formation of slags
which are not readily fusible which render diffi-
cult the collection of the metallic globules and
pouring.

The direct fusion of the metals to be alloyed
is also too costly, above all when the preparation
of alloys containing alkaline earth metals is con-
cerned.

The mixture by fusion of the binary alloys
obtained by electrothermic methods such as silico-
calcium and silico-aluminum, or the addition of
a third metal to one of these alloys is not always
economical and does not permit alloys of desired
composition to be obtained, for example with
large contents of alkaline earth metal.

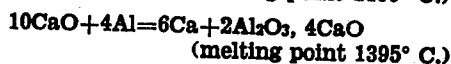
The present invention relates to a process which
permits these disadvantages to be avoided.

The invention consists for this purpose essen-
tially in reducing, with the application of ex-
ternal heat, by means of molten silico-aluminum
alloy, one or more oxygenated compounds reduc-
ible by the said alloy, of the metal or metal-
loid to be alloyed with the silico-aluminum, the
proportion of reducing alloy with respect to the
quantity of oxygenated compound to be reduced
being so calculated that a part only of this alloy
takes part in the reaction, the temperature of
the reducing alloy and the proportion of the
oxygenated compound being maintained on the
other hand at values so low that the reduction
takes place progressively. The metal or the
metalloid arising from the reduction alloys direct-
ly and immediately during and in proportion to
its formation with what remains of the silico-
aluminum alloy employed.

The excess of reducing alloy which takes part
in the reaction may be calculated either so that
it is only a part of the aluminum which it con-
tains, or the whole of this aluminum, or the whole
of this aluminum and a part of the silicon of the
alloy.

The setting into reaction of the silico-alumin-
ium in the molten state will take place so as
to maintain the conditions mentioned above for
moderation of the reaction. Thus a bath may be
prepared by means of silico-aluminum arising
from an ordinary furnace for the preparation of
this alloy and then having brought it to the tem-
perature known by experiment to be necessary
for the reduction of the oxygenated compound
of the metal to be alloyed with the silico-alumin-
ium, there may be introduced into this bath by
successive fractions the oxygenated compound in
question while heating the bath to prevent its
cooling below the temperature necessary for the
reduction. Alternatively, the silico-aluminum
and the oxygenated compound will be placed in
the solid state in a crucible and will be heated
until reduction is effected, taking care to main-
tain a temperature high enough for the reaction
to start and to proceed progressively. In both
cases the intensity of the heating will depend
upon the losses of heat from the crucible and the
degree of exothermicity of the reaction and will
be determined once and for all by experiment for
each determined oxygenated compound, or for
each mixture of said compounds.

The slag formed is a silico-aluminate with a
low silica content when the aluminum of the
silico-aluminum employed is not completely
utilised in the reaction; but in the converse case
its content of silica increases the more as the
silicon of the alloy takes more part in the re-
duction. The composition of this slag depends
moreover on the quantity of oxygenated com-
pound reduced and it is even possible to calculate
the proportions of reacting materials so that the
slag obtained has a predetermined composition,
this composition being able to correspond either
to readily fusible eutectics or to silico-aluminates
which disaggregate spontaneously. Eutectics
may for example be obtained in the case of re-
duction of lime by operating according to the
equations:



The fact that slags can be obtained with a

melting point as low as possible is particularly important, it permits operation to be performed at relatively low temperatures, the duration of the reaction to be reduced and the separation and pouring of the slag to be facilitated.

The separation of the slag from the complex alloy obtained may take place either by ordinary settling or by leaving the slag and alloy to cool until the beginning of solidification of the slag, and then at this moment pouring the alloy which has remained liquid. The slag in this latter case is removed by pouring after it has been sufficiently reheated.

The temperatures at which operation is performed depend on the nature of the oxygenated compounds to be treated, they may be theoretically between 650° C., melting point of silico-aluminum with a low silicon content, and 1800° C. approximate temperature of volatilisation of the silicon and of the aluminium, they are practically of the order of 1000-1500° C.

The following is a practical case of carrying the invention into effect for obtaining a silicon-aluminium-calcium alloy.

(1) 1000 grams of electrothermic silico-aluminum with 35% of Si and 50% of Al are melted in a graphite crucible placed in a high frequency electric furnace and the temperature is brought to about 1400° C.

(2) To the molten bath are added 200 grams of powdered lime and the temperature is raised until the reaction is produced. Then fresh additions of lime are made in portions of about 200 grams every five minutes up to a total of 650 grams.

The reaction ends about twenty minutes after the first addition, the slag is allowed to separate.

When the reaction is finished and the slag has separated from the alloy, pouring is performed, or:

(3) The whole is allowed to cool to about 1300° C. and the alloy which remains liquid is poured;

(4) the temperature is then raised for remelting and pouring the slag.

The melting and pouring of the slag may, moreover, be facilitated by the addition for example at the beginning of the operation of a small quantity of flux (such as CaF_2) which, moreover, will allow the alloy entrained by the slag to be more readily separated.

In this particular case the alloy contained 21% of calcium and 33% of aluminium and the slag 2.5% SiO_2 , 57% Al_2O_3 and 43% CaO .

Alloys with higher contents of calcium may be obtained in the same manner by increasing the proportions of lime introduced into the silico-aluminium. Thus by adding 1000 grams of lime to 1000 grams of the same silico-aluminium the alloy obtained then contains 29% of Ca, 22% of Al and the slag 49% of Al_2O_3 , 47% of CaO and 3% of SiO_2 . If 2000 grams of CaO are introduced into 1000 grams of silico-aluminium the alloy contains 32% of Ca and 16% of Al and the slag 65% of CaO , 29% of Al_2O_3 and 4% of SiO_2 .

There may thus be obtained by this process alloys whose calcium contents are nearly the same as those of industrial forms of silico-calcium and clearly higher than those of the aluminium-calcium alloys which hardly exceed 25%.

Complex silicon alloys containing other metals or metalloids: barium, strontium, magnesium, beryllium, zirconium, cerium, rare metals, titanium, manganese, chromium, tungsten, molybdenum, vanadium, boron, etc. may be obtained in

the same way by causing to react upon molten silico-aluminium oxygenated compounds of these metals or of these metalloids.

When the process is applied to silicates, borates, chromates, tungstates, molybdates, vanadates or other oxygenated salts, the silicon, boron, chromium or other elements likewise pass into the final alloy.

Different oxygenated compounds of the same metals may be employed or oxygenated compounds of different metals. The oxygenated compounds may be used either in the state of isolated compounds or in the state of ores.

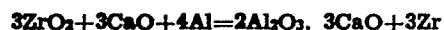
In the case where the oxygenated compound treated consists of an acid metallic oxide it is generally advantageous in order to obtain a reduction as complete as possible of this oxide at the same time as a readily fusible slag, to operate in the presence of a suitable quantity of a basic oxide like lime, magnesia, dolomite etc., employed in the free state or combined with the metallic oxide to be treated. The quantity of basic oxide employed may be calculated in particular so that it forms during the treatment with the aluminium resulting from the partial oxidation of the silico-aluminium taking part in the reaction, a slag whose composition corresponds to that of a readily fusible eutectic.

Thus for example to make silico-titanium, it is not to be recommended simply to introduce into the molten silico-aluminium a suitable quantity of rutile; the slag, constituted predominantly by alumina will be only fusible to a small extent and will retain a considerable quantity of titanium oxide. Consequently, one may be obliged to operate at too high a temperature. It is thus preferable to use for example calcium titanate (perowskite) or a mixture of rutile and lime the proportions of which may be calculated based upon the following equation in which the aluminium of the silico-aluminium which takes part in the reaction likewise figures.



There may thus be obtained silico-titanium containing 40-50% of titanium.

In the same way silico-zirconium may be made by introducing into molten silico-aluminium a mixture of zirconia and lime in proportions calculated according to the following equation in which there appears as in the preceding case the aluminium of the silico-aluminium taking part in the reaction.



Thus there may readily be obtained silico-zirconium with 40-50% or zirconium.

The following are practical examples of the application of the method lastly described.

(1) In the electric furnace in a carbon crucible are fused 1000 grams of silico-aluminium with 35% of Si and 50% of Al, the temperature is then brought to about 1500° C. and there is then added in portions while maintaining the heating, a mixture of 1000 grams of rutile and 700 grams of granulated lime. The entire mass is finally brought to a temperature sufficient so that the alloy and the slag separate well and that pouring may be effected easily.

In this particular case about 1000 grams of silico-titanium are obtained with 50% of titanium and 32% of silicon and 1600 grams of slag containing 51% of Al_2O_3 and 42% of CaO .

(2) In the electric furnace 800 grams of silico-aluminium with 35% of Si and 50% of Al are

molten, then the temperature is brought to about 1500° C. and there is then added in portions while maintaining the heating a mixture of 1000 grams of baddeleyite with 75% of ZrO_2 and 18% of SiO_2 and 500 grams of granulated lime. Finally, the temperature of the whole mass is raised until the moment when the slag separates from the alloy and collects at the surface, then pouring is proceeded with.

10 In this particular case about 950 grams of silico-zirconium with 43% of zirconium and 32% of silicon are obtained and 1200 grams of slag containing 53% of Al_2O_3 and 40% of CaO .

The silico-alloys obtained in the above examples contain besides the principal elements, iron and titanium which are present in the silico-aluminium employed as reducing agent. But it is evident that if silico-aluminium resulting from the fusion in determined proportion of practically pure aluminium and silicon is employed as starting material, silico-alloys of determined composition (notably silicides) are obtained practically free from other elements.

25 In general the carbon contents of the silico-alloys made by the process according to the invention are relatively low; they lie most often between 0.2 and 0.5%.

What I claim is:

1. In a process for the manufacture of complex alloys of silicon with not less than one element selected from the group consisting of calcium, barium, strontium, aluminium, magnesium, beryllium, zirconium, cerium, and rare earth-metals, titanium, manganese, chromium, tungsten, molybdenum, vanadium and boron, by reduction by means of silico-aluminium alloy substantially free from calcium of an oxygenated compound of the said element reducible thereby, the step of causing to react in the molten state and with regulated application of external heat, upon the said oxygenated compound, an excess of said silico-aluminium alloy with respect to the quantity of oxygenated compound to be reduced.

2. In a process for the manufacture of complex alloys of silicon with not less than one element selected from the group consisting of calcium, barium, strontium, aluminium, magnesium, beryllium, zirconium, cerium, and rare earth-metals, titanium, manganese, chromium, tungsten, molybdenum, vanadium and boron, by reduction by means of silico-aluminium alloy substantially free from calcium of an oxygenated compound of the said element reducible thereby, the step of causing to react in the molten state and with regulated application of external heat, upon the said oxygenated compound an excess of said silico-aluminium alloy with respect to the quantity of oxygenated compound to be reduced, the quantity of aluminium contained in the silico-aluminium being proportioned with respect to that of the oxygenated compound so that the reduction of the oxygenated compound is effected exclusively by a part of the aluminium.

3. In a process for the manufacture of complex alloys of silicon with not less than one element selected from the group consisting of calcium, barium, strontium, aluminium, magnesium, beryllium, zirconium, cerium, and rare earth-metals, titanium, manganese, chromium, tungsten, molybdenum, vanadium and boron, by reduction by means of silico-aluminium alloy substantially free from calcium of an oxygenated compound of the said element reducible thereby, the step of causing to react in the molten state

and with regulated application of external heat, upon the said oxygenated compound an excess of said silico-aluminium alloy with respect to the quantity of oxygenated compound to be reduced, the quantity of aluminium contained in the silico-aluminium being proportioned with respect to that of the oxygenated compound, so that the reduction of the oxygenated compound is effected exclusively by the aluminium.

4. In a process for the manufacture of complex alloys of silicon with not less than one element selected from the group consisting of calcium, barium, strontium, aluminium, magnesium, beryllium, zirconium, cerium, and rare earth-metals, titanium, manganese, chromium, tungsten, molybdenum, vanadium and boron, by reduction by means of silico-aluminium alloy substantially free from calcium of an oxygenated compound of the said element reducible thereby, the step of causing to react in the molten state and with regulated application of external heat, upon the said oxygenated compound an excess of said silico-aluminium alloy with respect to the quantity of oxygenated compound to be reduced, the quantity of aluminium contained in the silico-aluminium alloy being proportioned with respect to that of the oxygenated compound, so that the reduction of the oxygenated compound is effected by the whole of the aluminium acting first and then by a portion of the silicon.

5. In a process for the manufacture of complex alloys of silicon with not less than one element selected from the group consisting of calcium, barium, strontium, aluminium, magnesium, beryllium, zirconium, cerium, and rare earth-metals, titanium, manganese, chromium, tungsten, molybdenum, vanadium and boron, by reduction by means of silico-aluminium alloy substantially free from calcium of an oxygenated compound of the said element reducible thereby, the step of causing to react in the molten state and with regulated application of external heat, upon the said oxygenated compound an excess of said silico-aluminium alloy with respect to the quantity of oxygenated compound to be reduced, the quantity of said silico-aluminium alloy and the quantity of oxygenated compound being proportioned with respect to one another so that the slag formed during the operation has a composition near that of an eutectic.

6. In a process for the manufacture of complex alloys of silicon with not less than one element selected from the group consisting of calcium, barium, strontium, aluminium, magnesium, beryllium, zirconium, cerium, and rare earth-metals, titanium, manganese, chromium, tungsten, molybdenum, vanadium and boron, by reduction by means of silico-aluminium alloy substantially free from calcium of an oxygenated compound of the said element reducible thereby, the step of causing to react in the molten state and with regulated application of external heat, upon the said oxygenated compound an excess of said silico-aluminium alloy with respect to the quantity of oxygenated compound to be reduced, the quantity of said silico-aluminium alloy and the quantity of oxygenated compound being proportioned with respect to one another so that the slag formed during the operation has a composition near that of the eutectic having the lowest melting point.

7. In a process for the manufacture of complex alloys of silicon with not less than one element selected from the group consisting of calcium, barium, strontium, aluminium, magnesium,

beryllium, zirconium, cerium, and rare earth-metals, titanium, manganese, chromium, tungsten, molybdenum, vanadium and boron, by reduction by means of silico-aluminium alloy substantially free from calcium of an oxygenated compound of the said element reducible thereby, the step of causing to react in the molten state and with regulated application of external heat upon the said oxygenated compound, an excess of said silico-aluminium alloy with respect to the quantity of oxygenated compound to be reduced, the oxygenated compound being introduced into the bath of molten silico-aluminium alloy by fractions so that taking into account heat losses and the external application of heat, the reaction starts and continues regularly.

8. A process for the manufacture of silicon alloys by reduction by means of silico-aluminium alloy substantially free from calcium, of an oxide of a non-ferrous metal to be alloyed with the silicon said oxide having an acid character, consisting in causing to react in the molten state and with regulated application of external heat, upon the said metallic oxide, an excess of said silico-aluminium alloy with respect to the quantity of oxide to be reduced, in the presence of a sufficient quantity of a basic oxide to produce a readily fusible slag.

9. A process for the manufacture of silicon alloys by reduction by means of silico-aluminium alloy substantially free from calcium, of an oxide of a non-ferrous metal to be alloyed with the silicon said oxide having an acid character, consisting in causing to react in the molten state and with regulated application of external heat upon the said metallic oxide, an excess of said silico-aluminium alloy with respect to the quantity of oxide to be reduced, in the presence of a sufficient quantity of a basic oxide of the group consisting of lime, magnesia and dolomite to produce a readily fusible slag.

10. A process for the manufacture of silicon alloys by reduction by means of silico-aluminium alloy substantially free from calcium, of an oxide of a non-ferrous metal to be alloyed with the silicon said oxide having an acid character, consisting in causing to react in the molten state and with regulated application of external heat, upon the said metallic oxide, an excess of said silico-aluminium alloy with respect to the quantity of oxide to be reduced, in the presence of a sufficient quantity of a basic oxide in the free state to produce a readily fusible slag.

11. A process for the manufacture of silicon alloys by reduction by means of silico-aluminium, of an oxide of the metal to be alloyed with the silicon said oxide having an acid character, consisting in causing to react in the molten state and with regulated application of external heat, upon the said metallic oxide, an excess of silico-aluminium with respect to the quantity of oxide to be reduced, in the presence of a sufficient quantity of a basic oxide combined with the oxide of the metal to be alloyed with the silicon to produce a readily fusible slag.

12. A process for the manufacture of silicon alloys by reduction by means of silico-aluminium alloy substantially free from calcium, of an oxide of a non-ferrous metal to be alloyed with the silicon said oxide having an acid character, consisting in causing to react in the molten state and with regulated application of external heat, upon the said metallic oxide, an excess of said silico-aluminium alloy with respect to the quantity of oxide to be reduced, in the presence of a quantity of a basic oxide such that this latter forms during the treatment with the alumina arising from the partial oxidation of the silico-aluminium alloy taking part in the reduction, a slag whose composition corresponds to that of a readily fusible eutectic.

13. The process of making alloys rich in silicon, which comprises reducing an oxygen compound of a non-ferrous metal by means of an excess of silico-aluminum alloy over that required to reduce said oxygen compound, the silico-aluminum alloy being substantially free from calcium, and while carrying out the reduction maintaining the temperature low enough so that the aluminum reduces the oxygen compound without substantial reduction of the oxygen compound by the silicon while the silico-aluminum alloy contains any substantial amount of aluminum, and alloying the metal from said oxygen compound with the silicon of the silico-aluminum.

14. The process of making alloys rich in silicon, which comprises reducing an oxygen compound of a non-ferrous metal by means of an excess of silico-aluminum alloy over that required to reduce said oxygen compound, the silico-aluminum alloy being substantially free from calcium, and while carrying out the reduction maintaining the temperature between about 1000° C. and 1500° C., so that the aluminum reduces the oxygen compound without substantial reduction of the oxygen compound by the silicon while the silico-aluminum alloy contains any substantial amount of aluminum, and alloying the metal from said oxygen compound with the silicon of the silico-aluminum.

15. The process of making alloys rich in silicon, which comprises reducing at least one oxygen compound of a metal of the group consisting of calcium, barium, strontium, molybdenum, vanadium and boron by means of an excess of silico-aluminum alloy over that required to reduce said oxygen compound, the silicon-aluminum alloy being substantially free from calcium, and while carrying out the reduction maintaining the temperature between about 1000° C. and 1500° C., so that the aluminum reduces the oxygen compound without substantial reduction of the oxygen compound by the silicon while the silico-aluminum alloy contains any substantial amount of aluminum, and alloying the metal from said oxygen compound with the silicon of the silico-aluminum.

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