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PRODUCTION OF ALLOYS

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This application is a continuation-in-part of our application Ser. No. 215,785, filed August 9, 1962, now abandoned.

The invention relates to the production of calcium-silicon alloys containing rare earth metals as additional ingredients.

Calcium-silicon alloys have been used in the steel industry for a long time as deoxidizing agents. Rare earth metals, i.e., metals of the atomic numbers 21, 39, 57 through 71 (except 61 which does not occur naturally) are being used increasingly in the preparation of steels and other high strength construction materials having exceptional properties. However, the preparation of rare earth metals from their oxides is difficult, due to their very high oxygen affinity. One of the best known rare earth metal combinations, cerium-mischmetal, has been prepared for this reason under a salt blanket to prevent contact with air.

In order to reduce the high cost of rare earth metal production, attempts have been made to combine the production of other alloys such as ferro-silicon and calcium-silicon in the electric arc furnace with the production of rare earth metals. However, this procedure was not successful because it is uneconomic to change the charge in large electric furnaces. Before a final desired end alloy is produced, there is a considerable output of intermediate alloys which would not be marketable. A still greater disadvantage is the difficulty to employ relatively cheap rare earth concentrates. If such concentrates are heavy, they pass between the lumps of the other charge; if they are specifically light, they are blown out by the developing gases. In both cases, the produced alloys have not the required homogeneous composition.

We have now found that the difficulties of the former production methods can be avoided and that rare earth metals can be incorporated from cheap oxidic starting materials into prealloys when such starting materials are added to a calcium-silicon melt in a low frequency induction furnace lined with a carbon material, e.g., graphite. In order to ensure good slag separation, slag-forming compounds have to be added to the melt, either subsequently to the rare earth metal oxides, or together therewith, whereby such solid mixture is preferably added in portions and suitable intervals. Suitable slag-forming compounds are, e.g., fluorspar, quartz sand, lime, and others.

Suitable calcium-silicon compounds have the composition 28–45% Ca, 48–62% Si, the balance being iron and small amounts of carbon and aluminum.

The use of low frequency makes it possible to make use of the pinch effect to obtain a homogeneous charge already within very short times though the components of the charge may have very different specific weights; the specific weight of CaSi is about 2.5 g./cm.^{3} whereas that of columbite, e.g., is 5.3–6.0 g./cm.^{3}.

A measure of the agitation of the melt is given by the meniscus of the bath which is given by the equation

$$h=h_{th}-h_o$$

wherein h_o is the height of the bath level above the current portion of the induction coil and h_{th} is the theoretically calculated height. The latter is calculated according to the formula

$$h_{th}=\frac{3.22}{\sqrt{\rho \cdot f}}\frac{W_2}{A}\frac{1}{\gamma}$$

wherein ρ is the specific electric resistance of the melt, f the frequency, W_2 the electrical input, A the area of energy transfer where current-carrying portion of coil and melt face each other and γ is the specific weight of the melt. It will be seen that the higher f, the lower is the height of the meniscus.

The magnitude of the pinch effect depends also to a certain extent on other factors such as the dimensions of the crucible and the level of the charge therein. The essential feature of the invention is that the pinch effect, which develops only at low frequencies, is used in addition to the heating effect of the induced currents simply by operating with the low frequency of the A.C. mains frequency, which in this country is 60 and in other countries 50 hertz. Thereby, best results are obtained when the level of the charge is on the same plane as the upper end of the current carrying induction coil. A result of the pinch effect is that the molten contents of the crucible, due to the applied electromagnetic force, flow in the direction of the vertex of the bath meniscus and then flow down therefrom in all directions. The maximum speed of such flow will depend on the height h, and as the rare earth oxides are admixed at the surface of the melt, the stirring effect will be the greater the higher the meniscus h.

Generally, the reduction of the rare earth oxides will be the faster, the finer the starting material. Therefore, the grain size should be in the range of 0.05 to 2.5 mm. Larger grains must be ground before admixture to the melt.

After completion of the reduction, the entire contents of the crucible are poured out. The large excess of the calcium-silicon forms with the reduced rare earth metal the desired alloy. Separation of the slag takes place readily in the ladle after solidification of the block, due to the difference in the specific weights of alloy and slag. The slag can also be separated by means of a slag trap before the charge is collected in the ladle.

The great advantages of our process consist in the possibility of using low cost rare earth oxide starting materials and in the small scale production of homogeneous alloys in high yields in a single reducing and alloying operation.

A further economic advantage is that mis-charges are avoided as no useless intermediate alloys are produced when the composition is changed, and as the furnace is always available for processing such new formulations within a very short time.

Though the process is of particular value for the production of rare earth metal alloys, it can be used in the same way to produce prealloys of calcium-silicon with refractory metals such as zirconium, titanium, niobium, tungsten, vanadium, or mixtures thereof.

The following examples illustrate the invention. All parts are given by weight unless indicated otherwise. In all cases, a commercial low frequency induction furnace was used which was operated at 50 hertz and 250 or 420 kva., respectively.

Example 1

10 parts of quartz and (grain size <1 mm.). The Production of a rare earth-Ca-Si-Fe alloy.

To 110 parts of a liquid and overheated calcium-silicon melt (about 42% Ca., 52% Si, 5% Fe; temp. 1300–1400° C.), there was added in increments a mixture of 60 parts of rare earths concentrate (flotation products of bastnasite of low P content, containing about 90% rare earths oxides, grain size below 0.15 mm.) and

10 parts of quartz sand (grain size <1 mm.). The reduction was completed after 25 minutes, after which time the contents of the crucible were completely liquid. Tipping and separation from the slag was carried out over a slag trap.

There were obtained 115 parts of an alloy consisting of

	Percent
Rare earths (rare earths yield=86.8%)	33.8
Ca	15.6
Si	45.6
Fe	3.0

The slag contained

	Percent
Rare earth oxides	8.3
CaO	55.0
SiO_2	30.1

Example 2

Production of a rare earth=Ca=Si=Fe alloy.

Into 88 parts of a liquid overheated calcium-silicon melt (about 30% Ca, 61% Si, balance Fe; temp. 1300–1400° C.), there was added with stirring portionwise a mixture of 24.5 parts of rare earth oxides (obtained from monazite sand; 99% rare earth oxides, grain size <0.10 mm.) and 4 parts of fluorite (<0.1 mm.). The reduction was completed after 20 minutes; then, 20 parts of steel scrap was added. After the scrap had been dissolved and the melt homogenized, it was tipped over a slag trap.

The were obtained 110 parts of an alloy consisting of

	Percent
Rare earths (yield 95.1%)	17.5
Ca	15.1
Si	43.1
Fe	21.9

The slag contained

	Percent
Rare earth oxides	2.5
CaO	about 55.0
SiO_2	33.0

The following examples show the application of calcium silicon melts for the reduction of oxides of refractory metals and the incorporation of the metals to corresponding multiple alloys.

Example 3.—Production of a silicon-zirconium-calcium-iron alloy with medium zirconium content

64 parts of calcium-silicon (about 30% Ca, 60% Si, 7% Fe) were placed in a crucible which had been preheated to about 800° C., molten, and heated at about 1500° C. Then 22.2 parts of zirconium sand (65.3% ZrO_2; 32.6% SiO_2), 3.6 parts of quartz sand, and 2.4 parts of fluorspar were introduced in portions, and the mixture was heated for a further period of 15 minutes, whereby the temperature of 1500° C. was maintained.

After switching off the current, the content of the crucible was poured into a mold lined with carbon bricks. The obtained block consisted of 55.5 parts of alloy, and slag. The analysis of the alloy was a follows:

	Percent by weight
Zirconium	[1] 18.4
Calcium	9.4
Silicon	66.8
Iron	5.1

[1] 95.3% Zr yield.

The slag readily separated from the alloy; it was self-disintegrating, and contained

	Percent
ZrO_2	2.0
CaO	57.2
SiO_2	39.7

Example 4.—Production of a silicon-zirconium-calcium-iron of medium zirconium content

Charge:

50 parts of calcium-silicon (about 30% Ca, 60% Si, 7% Fe)
33 parts of zirconium sand (65% ZrO_2; 32.6% SiO_2)
10 parts of crude calcium (96% Ca)
5 parts of quartz sand
2.5 parts of fluorspar

The calcium-silicon was placed in a preheated crucible, and after melting, the crude calcium was added at a temperature of about 1200° C. Subsequently, the zirconium sand, the quartz sand, and the fluorspar were added portionwise. After a melting time of 15 minutes at about 1500° C., the crucible could be emptied. There were obtained 50 parts of an alloy containing

	Percent by weight
Zirconium	[1] 27.1
Calcium	8.6
Silicon	55.7
Iron	5.0

[1] 85% Zr yield.

while the slag contained 2.2% ZrO_2, 58.3% CaO, and 37.2% $SiSO_2$; it was self-disintegrating and could be readily separated from the alloy.

Example 5.—Production of a silicon-calcium-zirconium-iron alloy with medium calcium and low zirconium content

Charge:

95 parts of calcium-silicon (about 30% Ca, 60% Si, 7% Fe)
12 parts of badeleyite (98% ZrO_2)
8 parts of quartz sand
2 parts of fluorspar

Melting procedure as in Examples 3 and 4. After the alloy was formed, the slag was viscous and deposited on the bottom of the crucible. The alloy could be completely separated from the slag by careful tipping, whereupon the slag could be discharged from the mold.

91 parts of an alloy were produced, which contained

	Percent by weight
Zirconium	[1] 8.95
Calcium	15.3
Silicon	64.4
Iron	6.7

[1] 92% Zr yield.

The slag had the following composition:

	Percent
ZrO_2	0.4
CaO	54.6
SiO_2	38.2

Example 6.—Production of a silicon-titanium-iron-calcium alloy with medium titanium and low calcium content

Charge:
70 parts of calcium-silicon (30% Ca, 60% Si, 7% Fe)
4 parts of crude calcium
23.4 parts of rutile concentrate (96% TiO_2)
5 parts of quartz sand
2.5 parts of fluorspar

First the calcium-silicon was molten, then calcium was added at about 1200° C., and subsequently rutile, quartz sand and fluorspar were added portionwise while the tem-

perature was increased to about 1500° C. After a reduction period of 20 minutes at said temperature, the current was switched off and the melt was discharged.

There were produced 63 parts of an alloy containing

	Percent
Ti	[1] 16.0
Ca	8.1
Si	63.0
Fe	10.9

[1] 73% titanium yield.

The slag consisted of	Percent
TiO_2	5.2
CaO	55.6
SiO_2	39.2

Example 7.—Production of a silicon-columbium-tantalum-iron calcium alloy with a medium columbium-tantalum content

Charge:
60 parts of Ca-Si (30% Ca; 60% Si; 7% Fe)
18 parts of columbite (73.3% Nb_2O_5/Ta_2O_5; 10.9% MnO; 1.2% TiO_2; 7.8% FeO)
8 parts of quartz sand
2.4 parts of fluorspar

The columbite, quartz sand and fluorspar were added portionwise to the molten calcium-silicon which had been overheated to about 1500° C. After a melting time of 30 minutes at said temperature, the current was switched off and the melt was poured into a mold. There were obtained 60 parts of an alloy containing

	Percent
Nb	[1] 11.0
Ta	[1] 3.6
Mn	3.6
Ti	0.2
Fe	10.1
Ca	8.5
Si	61.8

[1] 86% Nb-Ta yield.

The slag could be readily separated from the alloy and contained

	Percent
Nb_2O_5/Ta_2O_5	2.4
CaO	55.6
SiO_2	41.6

Example 8.—Production of a silicon-calcium-tungsten-iron alloy with medium tungsten and calcium content

Charge:
50 parts of calcium-silicon (30% Ca; 60% Si; 7% Fe)
13.6 parts of tungsten ore concentrate (70% WO_3)
3.5 parts of quartz sand
2.0 parts of fluorspar

Calcium-silicon was molten in a crucible and overheated to about 1500° C.; tungsten ore, quartz sand and fluorspar were introduced in portions, and reduced for 30 minutes at said temperature. There were obtained 50 parts of an alloy containing

	Percent
W	[1] 13.7
Ca	17.3
Si	56.7
Fe	10.7
Mn	0.6

[1] 90.8% W yield.

The slag contained only 4.8% WO_3 and was easily separated from the alloy.

Example 9.—Production of a silicon-iron-calcium-vanadium alloy with low vanadium content

For the production of this alloy, we used a low percent vanadium flue dust which could not be processed directly to an alloy by any other procedure.

Charge:
30 parts of calcium-silicon (30% Ca; 60% Si, 7% Fe)
27.8 parts of vanadium flue dust (10.6% V_2O_5; 10.8% SiO_2; 43.1% CaO; 5% Fe_2O_3; Balance=ignition loss)
10.0 parts of quartz sand
2.0 parts of fluorspar

The calcium-silicon was molten and overheated to about 1500° C., and the fine dust and admixtures were introduced in portions; subsequently, the melt was heated for 15 minutes at about 1500° C. The discharged alloy (30 parts) had the following composition:

	Percent
V	[1] 4.0
Ca	10.2
Si	70.7
Fe	Balance

[1] 72.3% vanadium yield.

The slag contained	Percent
CaO	48.4
SiO	43.4
V_2O_5	1.8

In spite of the extremely light and dusty vanadium starting material, the dust development could be maintained within reasonable limits.

Example 10.—Production of a silicon-iron-manganese-zirconium alloy

40 parts of calcium-silicon (about 30% Ca, 60% Si, 7% Fe) were molten and overheated to about 1500° C., and then 18 parts of zirconium sand (65.3% ZrO_2; 32.6% SiO_2), 4 parts of quartz, and 1 part of fluorspar were introduced portionwise. The reduction of the ZrO_2 at 1500° C. was terminated after 15 minutes, and the contents of the crucible were completely liquid. Then 75.4 parts of 75% ferrosilicon and 12.7 parts of siliconmanganese (70% Mn, 19% Si) were added and molten, the melt was briefly homogenized at about 1450° C., and then discharged. There were obtained 122 parts of an alloy containing

	Percent
Si	67.8
Zr	[1] 7.0
Mn	[2] 7.1
Fe	15.6
Ca	1.8

[1] 98% zirconium yield.
[2] 97.3% manganese yield.

The obtained slag was easily separated from the alloy and contained

	Percent
SiO_2	49.9
CaO	48.2
ZrO_2	1.3

We claim:

1. The method of producing a rare earth-calcium-silicon alloy comprising melting a calcium-silicon alloy in a carbon-lined crucible by means of low frequency induction heating, adding to said molten alloy a solid rare earth metal oxide having a grain size of about 0.5 to 2.5 mm. and a slag-forming compound, further heating and agitating said mixture by said low frequency induction until said oxide has been substantially reduced to the metal,

and separating the thus obtained alloy and slag from each other.

2. The method as claimed in claim 1 wherein a carbon crucible is used.

3. The method as claim in claim 1 wherein the ratio of the oxygen-equivalent of the rare earth oxides to calcium-silicon melt does not exceed 90% of the total calcium-silicon.

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