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METHOD FOR THE PRODUCTION OF ALLOYS

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This invention relates to an improvement in the production of alloys containing rare earths and more particularly, to a method of preparing rare earth silicides.

Rare earth metals and their alloys have become increasingly important in recent years. For example, it has been found that the quality of irons and steels can be improved by the addition of rare earths, either as a mixture of the free rare earth metals ("misch metal") or in the form of alloys thereof. Alloys of rare earths with metals such as calcium, magnesium and silicon have been produced by direct union of the metals on heating. A more recent development as described in U.S. Patent No. 2,926,080 involves reaction between rare earth salts or oxides with silicon and other metals at fusion temperatures to yield the desired alloys.

These prior art procedures are successful in producing alloys containing relatively small amounts of the rare earths. However, the manufacture of alloys containing high levels of rare earth metals has not been successful on a commercial scale primarily because the rare earths are extremely reactive. For example, the preparation of a silicon-base alloy containing about 40% "misch metal" by prior art methods has not been very successful due in large part to the catastrophic attack by yttrium and other rare earth metals on the graphite crucible in which the fusion was carried out.

It is an object of this invention to prepare alloys containing relatively large amounts of rare earth metals without the aforementioned disadvantages.

Another object is to provide an efficient and economic method for producing rare earth silicides on a commercial scale.

A further object of this invention is to provide an efficient means for the production of yttrium silicides.

These and other objects and advantages of the invention are attained by fusing rare earth compounds with silicon or metals containing silicon in an electric arc furnace and in the presence of silica using a graphite crucible and a graphite electrode. After reduction is complete, the alloy is separated from the slag and processed into a useful form.

The rare earth compounds which can be reduced by the process of the present invention include rare earth oxides, carbonates, phosphates, silicates and fluorocarbonates. Compounds in the form of ores or ore concentrates of the rare earths can be utilized as well as relatively pure materials such as cerium oxide or mixed cerium-lanthanum oxides. The following materials are examples of rare earth compounds which can be reduced to alloys by the method of the present invention:

(1) Pure yttrium oxide (99.5% quality).
(2) Yttrium concentrate, 70% yttrium oxide, the balance other rare earths.
(3) Rare earth oxides from monazite, with thorium removed.
(4) Rare earth oxides from monazite, with thorium and cerium removed.

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(5) Rare earth concentrates from bastnasite.
(6) Monazite sand.
(7) Ore source materials including fluorocarbonates such as bastnasite, silicates such as cerite and gadolinite, phosphates such as monazite and xenotime, euxenite, and fergusonite.

When using concentrates of the rare earths, it is preferred to calcine the material to remove volatile components prior to reduction. The calcining may be accomplished in a known manner such as by heating at about 800° C.

The following are examples of rare earth distribution in concentrates which were reduced to alloys by this invention.

(1) Monazite concentrate, thorium removed:

	Percent
Y_2O_3	1.8
La_2O_3	21.0
Ce_2O_3	46.0
Pr_6O_{11}	5.6
Nd_2O_3	19.0
Sm_2O_3	3.1
Eu_2O_3	0.11
Gd_2O_3	2.1
Tb_4O_7	0.19
Dy_2O_3	0.8
Ho_2O_3	<0.1
Er_2O_3	0.12
Tm_2O_3	<0.05
Yb_2O_3	0.05
Lu_2O_3	<0.05

(2) Yttrium concentrate after calcining:

	Percent
Y_2O_3	68
La_2O_3	1.5
CeO_2	1.0
Pr_6O_{11}	<0.5
Nd_2O_3	1.5
Sm_2O_3	1.7
Gd_2O_3	3.2
Tb_4O_7	1.0
Dy_2O_3	7.1
Ho_2O_3	1.8
Er_2O_3	6
Tm_2O_3	4.9
Yb_2O_3	0.9
Lu_2O_3	0.8

(3) Bastnasite concentrate with a rare earth content of about 70% as oxide, the balance being impurities:

	Percent
Y_2O_3	0.3
La_2O_3	31
CeO_2	49
Pr_6O_{11}	3.8
Nd_2O_3	11.5
Sm_2O_3	0.7
Eu_2O_3	0.11
Gd_2O_3	0.23

The method of the invention is extremely useful in providing "misch metal" alloys. Silicon must be present as a reducing metal which form alloys with the rare earths. Other metals which can be mixed with the silicon include calcium, iron, manganese, aluminum, nickel, magnesium and alkali metals such as sodium, potassium and lithium. Thus, ferromanganese alloys readily combine with the rare earths and silicon to form rare earth alloys containing silicon, iron and manganese.

In producing rare earth silicides containing other metals such as iron, manganese and nickel, it is preferred that the latter materials be present in the alloy in proportions of about 10% to about 50% of the weight of the alloy. A preferred reducing material is a calcium-silicon alloy and particularly one containing about 30% calcium.

It is vitally important for the success of the operation that silica (SiO_2) preferably in the form of sand be present in the reaction mixture. Since the silica melts during the process, any form of this ingredient in any particle size can be used. This critical ingredient serves a twofold purpose: first, it prevents catastrophic attack upon the operating equipment (e.g., graphite crucible) by the highly reactive rare earth metals and yttrium in particular. Secondly, silica facilitates separation and removal of the alloy from other products. The minimum amount of silica added is highly critical and at least about 3% must be employed. A preferred amount of SiO_2 is about 10% based on the combined weight of rare earth compound and reducing metal. The proportion of SiO_2 is preferably not greater than about 15% because as the amount of silica increases above 15%, there may be serious slag interference which may diminish the effectiveness of the reduction.

The reducible rare earth compounds are generally high melting materials and the reduction must be carried out in an electric arc furnace. The means employed to produce an electric arc are known to those skilled in the art. The applied potential difference across the electrodes may be either direct current or alternating current.

For the purpose of this invention it is vital that a "cold-wall" graphite crucible and a graphite electrode by utilized. A graphite-lined crucible can be used if desired. In a "cold-wall" crucible, the temperatures are progressively cooler from the melt to the outside crucible wall. Conventional electric furnaces which provide heat through the walls of the crucible cannot be employed and heat must be applied directly to the melt. The graphite also aids in promoting the reduction of the rare earth compounds.

The power requirements to be employed are within the purview of a skilled operator in the art. The requirements should be selected to insure that the melt is maintained in a completely molten condition throughout the reaction. An important factor to be considered in determining power requirements is the specific rare earth compound being reduced. Thus, it has been observed that yttrium oxide requires more power for reduction than other rare earth oxides.

Another important advantage of the invention is that the entire melting and casting operation may be carried out under atmospheric conditions. There is no necessity to employ a protective atmosphere during reduction.

The following examples illustrate the products and method according to the present invention.

Example I

The following charge was added to an electric arc furnace in a "cold-wall" graphite crucible using a graphite electrode:

	Lbs.
Rare earth oxide (bastnasite concentrate identified above)	10
Calcium-silicon alloy (⅛ inch O.D.)[1]	15
Sand (SiO_2)	2.5

[1] 30% calcium.

The furnace was operated as a direct current arc at 1400 amperes and 35 volts for about 50 minutes. After reduction, the alloy was cast into molds. Ingot alloy recovery was 16 lbs. per run. The ingots could readily be broken

in a jaw crusher into useful sizes. Any slag-like material remaining in the melt generally was cast into the last molds. The entire melting and casting operation was conducted in the absence of a protective atmosphere.

The misch metal silicide produced had the following composition:

[Total rare earth content was 42.5% (49.8% expressed as oxide)]

	Percent
Y_2O_3	0.06
La_2O_3	17.0
CeO_2	24.0
Pr_6O_{11}	2.45
Nd_2O_3	5.7
Sm_2O_3	0.4
Eu_2O_3	0.04
Gd_2O_3	0.12
Si	51.0
Ca	4.6
Fe	1.9

(All other rare earths were less than 0.1%)

The iron content was obtained from impurities present in the initial charge.

Example II

The procedure of Example I was followed employing the rare earth oxide concentrates identified above and a calcium-silicon alloy containing 30% calcium. One rare earth silicide produced had the following analysis:

[Total rare earth content=28.2% (33.1% expressed as oxide)]

Rare earth distribution:	Percent
Y_2O_3	0.5
La_2O_3	13.5
CeO_2	2.4
Pr_6O_{11}	3.3
Nd_2O_3	10.9
Sm_2O_3	1.7
Gd_2O_3	0.8
Si	65.0
Ca	6.2
Fe	0.6

(All other rare earths were less than 0.1%)

Example III

A ferromanganese alloy was fused with a silicon-calcium alloy and rare earth oxides by the method described in Example I. The feed material added to the graphite crucible in an electric arc furnace was as follows:

	Lbs.
Rare earth oxide	240
Calcium-silicon alloy (30% Ca)	360
Ferromanganese alloy	200
SiO_2 (sand)	50
Graphite consumed	35

The rare earth oxide (98–99% purity) employed was the thorium-free monazite concentrate identified above.

About 500 lbs. of crushed metal product was recovered exhibiting the following analysis:

	Percent
Rare earth metal	34
Manganese	16
Calcium	6
Iron	5
Carbon	0.16
Silicon	Bal.

The rare earth content of the finished alloy contained 15.3% cerium, 4.8% neodymium, 6.6% lanthanum, 1.5% praseodymium and 5.8% other rare earth metals including yttrium.

This alloy exhibited very surprising properties. The addition of manganese was found to increase the density of the alloy, produce a marked drop in the freezing point of the alloy, and greatly improve the "melting-in" properties when the alloy was added to iron and steel melts.

Microscopic examination of the products showed rare earth silicon phases in a silicon matrix. The shape of the rare earth-rich phase grains depends upon the particular rare earth material used in the process. The phases rich in rare earths appear as dark areas upon etching with dilute hydrofluoric acid. The silicon-rich matrix appears as a light area after etching with the same reagent.

It will be observed from the above disclosure that the applicant has discovered a means of producing rare earth alloys containing relatively large amounts of rare earth metals without the disadvantageous results of prior art procedures. The method of the invention involves a unique combination of several critical factors which must be observed while melting a rare earth compound and at least one metal:

(1) Silica must be present in critical amounts.

(2) An electric arc must be employed.

(3) A "cold-wall" graphite crucible and graphite electrode must be used.

It will occur to those skilled in the art that there are many modifications to the invention as specifically described herein. It is intended to include all such modifications within the scope of the appended claims.

I claim:

1. A method of manufacturing an alloy which comprises fusing a reducible rare earth compound with a member selected from the group consisting of silicon and silicon-containing materials in the presence of at least about 3% by weight of silica sufficient to protect the operating equipment from attack by the rare earth metals, the fusion being carried out in an electric arc furnace using a graphite crucible and graphite electrode.

2. A method of manufacturing an alloy which comprises fusing a rare earth oxide with a member selected from the group consisting of silicon and materials containing silicon in an electric arc furnace in the presence of more than about 3% and less than about 15% SiO_2 based on the weight of the material and the oxide, the fusion being carried out in a graphite crucible using a graphite electrode.

3. A method of manufacturing an alloy which comprises: (a) melting a rare earth oxide and a calcium-silicon alloy in a graphite crucible using an electric arc and a graphite electrode and in the presence of about 10% silica based on the weight of the alloy and oxide and (b) separating a rare earth silicide.

4. A method according to claim 3 wherein the calcium-silicon alloy contains about 30% calcium.

5. In the method of fusing a reducible rare earth oxide with at least one reducing agent selected from the group consisting of silicon and metals containing silicon, the improvement which comprises carrying out the reduction in a graphite crucible using an electric arc and graphite electrode and in the presence of an amount of silica which is greater than about 3% and less than about 15% by weight of the oxide and reducing agent.

6. A method according to claim 5 wherein the reducing agent contains at least one metal selected from the group consisting of lithium, aluminum, magnesium, calcium, beryllium, strontium, barium, titanium, and zirconium.

7. A method which comprises fusing a reducible compound of yttrium in an electric arc furnace with a reducing agent selected from the group consisting of silicon and metals containing silicon using a graphite crucible and graphite electrode, the fusion taking place in the presence of about 10% silica based on the weight of the yttrium compound and the reducing agent, and thereafter recovering yttrium silicide.

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