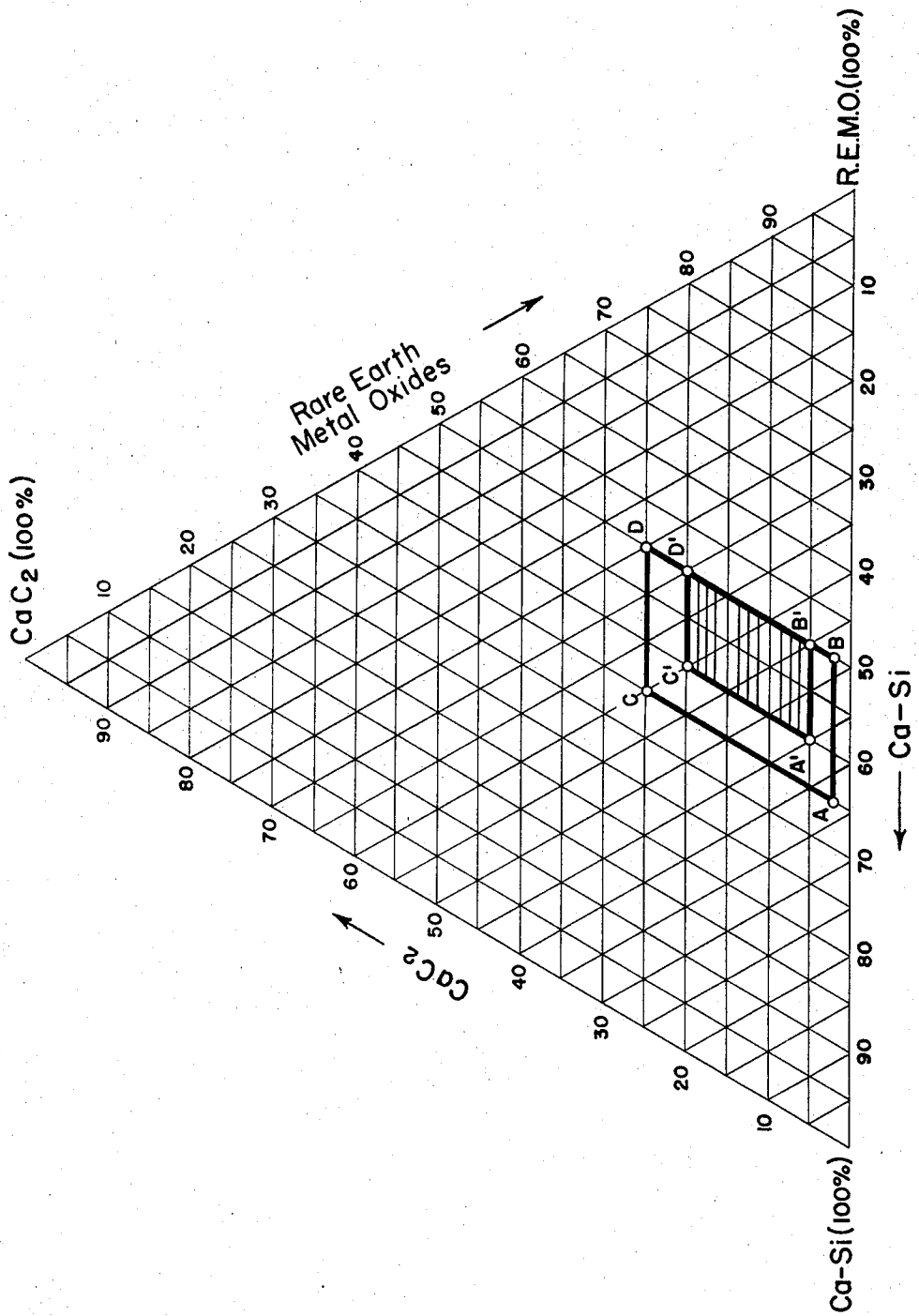
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PROCESS OF MAKING RARE EARTH METALS AND SILICON ALLOYS

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PROCESS OF MAKING RARE EARTH METALS AND SILICON ALLOYS

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ABSTRACT OF THE DISCLOSURE

Master alloys of the rare earth metals and silicon containing at least about 40 percent by weight of rare earth metals are prepared by forming a reaction mixture containing about 35–50 percent by weight of rare earth metal oxides or rare earth metal salts, between about 25 and 62.5 percent by weight of a calcium and silicon alloy containing between 5 and 40 percent by weight of calcium, and between about 2.5 and 25 percent by weight of calcium carbide, the reaction mixture then being heated at a temperature of between about 1200 and 1800° C. to reduce the rare earth metal oxides or salts and to obtain a rare earth metal-silicon master alloy product containing at least about 40 percent by weight rare earth metals.

This invention relates to the alloys of the rare earth metals and silicon, and more particularly to the production of misch metal silicides containing at least 40% by weight rare earths by the pyrometallurgical reduction of rare earth metal oxides and salts with alloys of silicon and calcium.

The rare earth metals are the 15 elements of the lanthanide series having atomic numbers 57 to 71 inclusive, although the element yttrium (atomic number 39) is commonly found with and included in this group of metals. The most common alloy of the rare earth metals which contains the metals in the approximate ratio in which they occur in their most common naturally occurring ores is known as misch metal, and intermetallic compounds of rare earth metals and silicon are known as misch metal silicides.

The rare earth metals, and particularly cerium which is the most plentiful of these metals, are valuable alloying additives for improving the metallurgical properties of alloyed and unalloyed steel, cast iron and other metals. However, as the rare earth metals exhibit a great tendency to be oxidized, particularly at high temperatures, the direct addition of these metals (for example, as misch metal) to molten iron and steel ordinarily results in excessively high loss of the rare earth metals. As a result, the rare earth metals are ordinarily added to the molten metal in the form of silicon alloys or silicides containing a relatively small proportion of rare earth metals. Typical master alloys might contain from 35 to 60% silicon, up to 15% rare earth metals, and the remainder such metals as calcium, iron, aluminum and the like.

German Patent 1,116,414 describes a method for the production of master alloys of the rare earth metals and silicon in which the oxides or salts of the rare earth metals are added to a molten starting or base alloy of silicon and calcium or magnesium. All of the calcium or magnesium content of the base alloy must be compounded intermetallically with silicon when the alloy is in the solid state, and the base alloy must contain sufficient silicon to meet this requirement. As a result, the amount of rare earth metal that can be introduced into the base alloy is limited by the amount of calcium or magnesium in the base alloy available to reduce the rare earth metal oxides or salts, and the amount of calcium or magnesium present in the

base alloy is, in turn, limited by the relatively large quantity of silicon necessarily present in the alloy in order to form the aforementioned intermetallic composition. Master alloys containing up to 2%, or slightly higher, rare earth metals can be produced by this method, the valance of the alloy being mainly silicon. However, master alloys which have such a large proportion of silicon in relation to the rare earth metal content thereof are of limited value as additives in the production of iron and steel alloys.

German Patent 1,131,417 describes an improvement in the aforementioned procedure that is predicated on the teaching that the presence of a basic metal such as calcium or magnesium in the silicon-containing starting alloy is undesirable. Accordingly, the starting or base alloy contains no significant amount of calcium, the reducing agent for the rare earth metal oxides or salts being incorporated therein being relatively pure silicon or calcium-free silicon alloys. The reaction is carried out in a carbon crucible in an electric arc furnace, and furthermore is carried out in the presence of a lime-containing calcium fluoride flux. Silicon alloys containing as much as 28% by weight of rare earth metals have been obtained by this process. However, the process is unsatisfactory due to the highly corrosive character of the flux employed, to the technical difficulties inherent in electric arc furnace operations employing such highly reactive materials as the highly basic lime-fluorite flux, to the unpredictable behavior of the reaction mixture and in particular to the evolution of toxic fumes resulting from the decomposition of the basic lime-fluorite flux in the electric arc, to the health hazard created by the evolution of such fumes, and to the difficulty in obtaining a uniform and reproducible alloy product by means of the process.

The present invention relates to an improved process for producing silicon-rare earth metal master alloys which is devoid of technical difficulties, the results of which are predictable and reproducible, and which yields a product containing 40% or more of rare earth metals. The process is based on the discovery that if the silicon starting or base alloy contains between about 5 and 40% by weight calcium, if a portion of the calcium-silicon base alloy is replaced or augmented by a predetermined quantity of calcium carbide, and if the mixture of calcium-silicon alloy and calcium carbide is reacted with a predetermined quantity of rare earth metal oxides or salts at an elevated temperature, a silicon alloy containing 40% or more rare earth metals can be produced without difficulty and with a high degree of reproducibility.

Accordingly, pursuant to the present invention the improved process comprises forming a reaction mixture containing between about 35 and 50% by weight, and preferably between about 40 and 50% by weight, rare earth metal oxides or the equivalent thereof contained in rare earth metal salts, between 25 and 62.5% by weight, and preferably between about 30 and 55% by weight, of a calcium-silicon alloy containing between about 5 and 40% by weight calcium, and between 2.5 and 25% by weight, and preferably between about 5 and 20% by weight, calcium carbide. The reaction mixture is heated to a temperature within the range of about 1200 to 1800° C., and preferably to within the range of 1400 to 1600° C., to effect reduction of the rare earth metal compounds and to form the desired rare earth metal-silicon master alloy product. The resulting silicon-rare earth metal master alloy containing at least 40% by weight of said rare earth metals is then separated from the slaggy secondary products of the reaction and is recovered. Advantageously, the reaction is carried out in the presence of a flux which absorbs the slaggy secondary products of the reaction, the flux preferably comprising one or more chlorides or fluorides of the alkaline earth metals, and preferably being added to the

reaction mixture in an amount such that the overall mixture contains from about 5 to 20% by weight of said flux.

The relative proportions of the rare earth metal oxides, the calcium-silicon alloy and calcium carbide in the reaction mixture should fall within the area defined by the points A, B, C and D plotted on the three coordinate diagram comprising the single figure of the accompanying drawing, and in a particularly advantageous embodiment of the process the relative proportions of the three constituents of the reaction mixture fall within the area defined by the points A', B', C' and D' plotted on the aforesaid diagram. The actual values of the points A, B, C and D and A', B', C' and D' are set forth in the following table:

	Rare earth metal oxides	Ca-Si alloy	CaC_2
A	35	62.5	2.5
B	50	47.5	2.5
C	35	40	25
D	50	25	25
A'	40	55	5
B'	50	45	5
C'	40	40	20
D'	50	30	20

The calcium-silicon alloys employed in the practice of the process contain between about 5 and 40% by weight calcium and may be of commercial grade, a typical alloy containing about 64% silicon, 27% calcium, 4% iron, 2% aluminum and the remainder carbon and other impurities. Similarly, the calcium carbide employed in the process is advantageously of commercial or techincal grade, a typical calcium carbide starting material containing about 80% CaC_2 with the balance comprising mainly carbon and metallic impurities. The impurities present in the calcium-silicon alloy and in the calcium carbide starting material appear for the most part in the slag or the alkaline earth metal halide flux, although the desired rare earth metal-silicon master alloy product of the process may contain insignificant amounts of non-injurious impurities.

A comparison of the results obtained by the practice of the present invention and the results obtained by the practice of the process of German Patent 1,116,414 clearly demonstrates the greater efficiency and improvement in product obtained by the present process. In the case of a more or less similar total yield of misch metal, the quantity of misch metal obtained per kilogram of calcium-silicon alloy employed amounted to 0.68 kg. misch metal when the reduction of the rare earth metal oxides was carried out pursuant to the present invention as compared with a yield of 0.5 kg. misch metal when the reduction of the rare earth metal oxide was carried out in the absence of added calcium carbide. This amounted to an increase of better than 35% in the yield of misch metal per kilogram of calcium-silicon alloy employed.

The following examples are illustrative but not limitative of the practice of the invention.

EXAMPLE I

A reaction mixture was formed having the following composition: 24 gm. of commercial mixed rare earth metal oxides, 27 gm. of a commercial calcium-silicon alloy, 9 gm. of commercial calcium carbide and 15 gm. of commercial calcium fluoride as a flux. The calcium-silicon alloy contained 64.3% Si, 27.3% Ca, 3.8% Fe, 1.9% Al, 0.65% C and the remainder other impurities, and the calcium carbide contained about 80% CaC_2. After reacting the mixture in a carbon crucible at a temperature of about 1550° C. the reaction mixture separated smoothly into a molten metal product and a slag. The metal product weighed 30 grams and had a specific gravity of 4.48. The composition of the metal product

was 54.6% misch metal, 30.9% silicon, 5.7% calcium and the remainder iron, aluminum, carbon and other impurities. Approximately 83% of the rare earth metal content of the rare earth metal oxide starting material was recovered in the misch metal-silicon master alloy product.

EXAMPLE II

A reaction mixture was prepared having the following composition: 10 kg. of commercial roasted bastnasite having a rare earth metal oxide content of 90.5%, 9.8 kg. of a commercial calcium-silicon alloy of the same composition as that employed in Example I, 3.2 kg. of commercial calcium carbide, and 4 kg. of commercial calcium chloride as a flux. The reaction mixture was reacted at a temperature of about 1500° C. in a graphite crucible to obtain 13.4 kg. of misch metal-silicon master alloy product. The master alloy product contained 50.2% misch metal, 32.1% silicon, 7.5% calcium, and the remainder iron, aluminum, carbon and other impurities. The yeild of misch metal based on the rare earth metal content of the bastnasite starting material was 89%.

From the foregoing description it will be seen that the present process is an important contrbution to the art to which the invention relates.

We claim:

1. Process for the production of master alloys of the rare earth metals and silicon containing at least about 40% by weight of rare earth metals which comprises:

forming a reaction mixture containing between about 35 and 50% by weight of mixed rare earth metal oxides selected from the group consisting of rare earth metal oxides and rare earth metal salts (calculated as equivalent oxides), between about 25 and 62.5% by weight of a calcium-silicon alloy containing between 5 and 40% by weight of calcium, and between about 2.5 and 25% by weight of calcium carbide,

heating said reaction mixture to a temperature of between about 1200 and 1800° C. to reduce said rare earth metal oxides constituent of the reaction mixture and to obtain a rare earth metal-silicon master alloy product containing at least about 40% by weight rare earth metals and a slaggy secondary product containing those impurities not present in the master alloy product, and

recovering the desired master alloy product.

2. The process according to claim 1 in which the reaction is carried out at a temperature within the range of about 1400 to 1600° C.

3. The process according to claim 1 in which the reaction mixture comprises between about 40 and 50% by weight of said rare earth metal oxides, between about 30 and 55% by weight of said calcium-silicon alloy, and between about 5 and 20% by weight of calcium carbide.

4. The process according to claim 1 in which the reaction is carried out in the presence of a flux comprising at least one alkaline earth metal halide selected from the group consisting of alkaline earth metal fluorides and alkaline earth metal chlorides.

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