United States Patent Office 2,755,178 Patented July 17, 1956

2,755,178

ELECTRIC SMELTING PROCESS FOR PRODUCTION OF SILICON-ALUMINUM ALLOYS

Robert T. C. Rasmussen, Albany, Oreg.

No Drawing. Application July 30, 1952, Serial No. 301,810

3 Claims. (Cl. 75—10)

(Granted under Title 35, U. S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government of the United States for governmental purposes without the payment to me of any royalty thereon in accordance with the provisions of the act of April 30, 1928 (Ch. 460, 45 Stat. L. 467).

This invention relates to a method for the manufacture of silicon-aluminum alloys by reducing silica and alumina-containing raw materials, such as pyrophyllite, clay, and the like, with carbon in an electric furnace.

The expression "silicon-aluminum alloys" as used herein refers to alloys containing in excess of 50 per cent aluminum content as well as to alloys in which the silicon content exceeds the aluminum content.

Since the carbothermic reduction of aluminum and silicon oxides requires a very high temperature, in the order of 2000° C., it has been proposed to carry out such operations by electric furnace methods, similar to those employed for production of ferrosilicon. However, satisfactory operation of the electric furnace method for production of silicon-aluminum alloys has been extremely difficult. Use of a charge containing coke in proportions theoretically required to reduce the oxides of the raw materials with formation of an equivalent amount of carbon monoxide proved to be unsatisfactory because of high power requirements, excessive electrode consumption, and unfavorable conditions within the furnace requiring frequent shut-downs.

It has also been proposed to achieve operable conditions in a single-phase, bottom-electrode furnace by use of a charge containing coke in an amount providing less than the stoichiometric carbon requirement. However, in a three-phase, top-electrode furnace, a deficiency of carbon tends to result in selective reduction of the silica with an accumulation of an aluminum oxide slag on the furnace hearth. Continuous operation of the furnace with a charge containing coke in either the stoichiometric quantity or in a lesser quantity is difficult, due to crusting of the charge accompanied by violent gas blows, requiring rodding down at frequent intervals to break the tough crust and permit descent of the charge. Losses of metal occur by vaporization during the glas blows, and the metal yield from the ore smelted is correspondingly low.

The use of charcoal in the charge to supply the necessary carbon for reduction eliminates crusting and gas blows, but continuous operation with this material is unsuccessful since fused and unreduced material collects on the hearth of the furnace to such an extent as to require shut-down.

Accordingly, it is an object of this invention to provide an improved reduction process for the production of silicon-aluminum alloys in an electric furnace.

Another object of the invention is to provide a process for the electric smelting of silicon-aluminum alloys in which the temperature of the smelting zone is maintained several hundred degrees Centigrade above the melting temperature of the ore.

Another object of this invention is to provide a reduction process for the continuous production of silicon-aluminum alloys in an electric furnace in which power requirements and electrode consumption are low and in which the amount of carbon in the charge is sufficient theoretically to reduce all of the oxides in the charge.

A further object of this invention is to provide a process for the continuous production of silicon-aluminum alloys in an electric furnace in which proper operating conditions are maintained in the furnace by properly adjusting the charge constituents.

A still further object of the invention is to provide a process for the continuous production of silicon-aluminum alloys from clays and like materials in an electric furnace with low power and electrode consumption in which the rate at which the ore descends through the furnace is controlled by properly adjusting the charge constituents.

Other objects and advantages of the invention will be apparent as the description proceeds.

This invention resides in an improvement in the continuous electric-furnace carbothermic reduction process for the production of silicon-aluminum alloys from clay, pyrophyllite, or similar ores and raw materials, which comprises supplying the furnace with ore and with carbon in at least that amount theoretically required to reduce all of the oxides of the ore, and maintaining a deep and porous cover of unfused charge over the molten bath of the furnace and retarding the rate of descent of the ore through the furnace by supplying at lease a portion of the total carbon requirement to the furnace as a bulky form of carbon, whereby the necessary high temperature for reduction is attained and maintained in the melting zone.

In accordance with the invention, it has been discovered that successful continuous operation of the electric furnace process for the production of silicon-aluminum alloys is dependent upon the maintenance of a charge within the furnace covering the entire surface of the molten bath and containing at least the stoichiometric quantity of carbon and of such consistency that it will remain open for free passage of gasses and that its ore component will descend slowly enough to permit attainment of a reduction temperature in the smelting zone several hundred degrees above the melting temperature of the ore. The use of the bulky carbon in the charge in proper proportions in relation to the total carbon permits the maintenance of a deep but porous cover charge and limits the rate at which the ore component of the charge mixture descends through the furnace and smelting zone thereby permitting attainment of the necessary high reduction temperature. Since at least the stoichiometric proportion of total carbon is present, all of the oxides are reduced and there is no undesirable formation of a slag of unreduced material to accumulate on the hearth.

Where an open and freely descending charge is maintained in the electric furnace, as by the use of charcoal to supply the carbon, as aforementioned, lack of crusting or other means for retarding the rate of flow permits the ore to descend through the furnace as fast as it is melted in the vicinity of the electrode tips and the necessary reduction temperature cannot be attained. Thus fused and unreduced material collects on the furnace hearth.

On the other hand, where coke is employed to supply the carbon to the charge, crusting and bridging in the furnace occurs to such an extent that frequent rodding down is neceessary, the temperature may periodically be too low or unnecessarily high, and furnace operation is irregular.

These difficulties are now overcome by supplying a substantial proportion of the necessary carbon to the charge in the form of wood waste or other bulky form of carbon. Sawdust, wood chips, wood waste known to the timber industry as hog fuel, or a combination of these materials are the preferred bulky forms of carbon, but the invention is not restricted to these materials. Other bulky

carbonaceous material such as corn cobs, nut shells, fruit pits, peat, and lignite also may be used as the bulky form of carbon in the smelter charge. Bulky cellulosic materials are generally satisfactory. The remainder of the necessary carbon is supplied as a dense form of carbon, preferably as petroleum coke. From the following tabulation, it is apparent that 5.7 cubic feet of wood waste is required to supply the same quantity of carbon as one cubic foot of wood charcoal, and that 18.5 cubic feet of wood waste is required to supply the same quantity of carbon as one cubic foot of petroleum coke.

Fuel	Fixed carbon, percent	Weight per cu. ft., lb.	Fixed carbon, per cu. ft., lb.	Volume per 100 lb., cu. ft.
Wood waste (hog fuel)	11.0	18.0	2.0	5.6
Wood charcoal	74.0	15.25	11.3	6.6
Sub-bituminous coal	43.3	52.0	22.5	1.9
Coal char	74.7	32.0	23.9	3.1
Metallurgical coke	89.7	29.5	26.5	3.4
Petroleum coke	96.0	38.5	37.0	2.6

Use of the correct proportions of wood waste and coke in the smelter charge performs the vital function of controlling the feed rate of the ore while permitting the correct proportion of total carbon for reduction to be contained in the charge. The wood waste, by virtue of its great bulk, limits the rate of descent of the ore in the furnace while at the same time permitting the charge mixture to be fed to the furnace at the necessary rate to maintain dry top conditions, thereby permitting attainment and maintenance in the smelting zone of a reduction temperature several hundred degrees centrigrade higher than the melting point of the ore.

The wood waste also serves the function of keeping the charge open and free from crusting and bridging, so that the charge descends freely in the furnace and the reaction gases escape uniformly over the entire surface of the charge. With these conditions, virtually no rodding down of the charge is required, as the charge descends gradually and in periodic slumps, principally in the delta between the electrodes. The thick dry top cover of charge is maintained at all times, thereby providing excellent insulation to confine the heat to the smelting zone and preventing loss of silicon and aluminum by vaporization. The absence of metal fumes emanating from the furnance top, together with the absence of slag formation, makes for extremely high metal yield and low consumption of power and of electrodes per pound of metal tapped from the furnace.

The silicon and aluminum-containing raw materials treated by this process may be obtained from any suitable source. Ores higher in silica content than used in the Bayer process may be satisfactorily employed. Silica alone may be used with corresponding production of silicon. If alloys high in aluminum are desired, high-alumina raw material such as Bayer-grade bauxite may be added to the lower grade alumina materials or, possibly, may be used alone. Fluxing oxides may be used with the charge as desired. It is preferred to use cheap materials, such as clay or pyrophyllite, from deposits which are low in iron and titanium. Clays which have been pretreated to remove iron and titanium may also be used.

The proportion of carbon in bulky form to carbon in dense form in the charge mixture and the proportion of total carbon in the charge will vary somewhat with the nature of the silicon and alumina-containing raw material. The remainder of the stoichiometric amount of carbon and any excess carbon is supplied in a bulky form, such as wood waste. Best results are obtained when the total carbon is somewhat in excess of the amount theoretically necessary to reduce all of the oxide of the ore. Too much carbon is indicated by abnormal rising of the electrode tips and results in build-up of carbon or carbides beneath the electrodes, but adjustment of this condition is easier than adjustment when too little carbon is used. Increase in the proportion of bulky form of carbon above the optimum results in a higher temperature in the smelting zone than necessary thereby resulting in higher than optimum power consumption.

The process is further illustrated by the following examples of practice. In carrying out these examples an open-top, three-phase, top-electrode furnace was employed. It is understood, however, that the invention is not limited to this type of furnace but may be adapted to any arc-resistance type electric furnace known to the art. Although the highest degree of process development was attained in the smelting of pyrophyllite to produce alloy of about 23 per cent aluminum content, alloy containing as much as 60 per cent aluminum has been produced from clay.

EXAMPLE 1

A charge mixture was prepared by mixing 100 pounds of pyrophyllite with 48 pounds of charcoal. This charge contained about the stoichiometric quantity of carbon for complete reduction of silica and of all metals in the pyrophyllite. This mixture was charged into the furnace and smelting operations were started. After about 25 hours operation with charges of this composition, it became certain that accretion formation on the hearth would stop further operations employing this charge.

EXAMPLE 2

For a period of several days a charge containing calcined clay and petroleum coke in proportions of 100 pounds of clay to 37 pounds of coke, representing about the stoichiometric carbon requirement, was fed to the furnace while carbon in excess of the stoichiometric amount was fed to the furnance in the form of hog-fuel. The quantity of hog-fuel in the charge was varied from time to time with a view to obtaining a charge that was open enough to permit escape of the gases and that would descend freely in the furnace without undue crusting, as well as to permit enough bulk of charge to maintain a good dry-top cover in the furnace. During a substantial portion of this period the charge contained 100 pounds of hog-fuel in addition to the 37 pounds of petroleum coke and 100 pounds of calcined clay. Eventually the electrodes failed to properly descend through the charge, indicating accumulation of carbon or carbide on the hearth and resulting in an inoperable condition requiring correction.

EXAMPLE 3

Pyrophyllite, petroleum coke, and hog-fuel were charged to the furnace in proportions of 50 pounds of pyrophyllite, 8 pounds of petroleum coke and 100 pounds of hog fuel. The coke provided about 42 per cent of the stoichiometric quantity of carbon and the total carbon in the charge represented about 101 per cent of the stoichiometric amount. The furnace was successfully operated for a sustained period of 96.5 hours by feeding additional charges of this composition more or less continuously as required to maintain charge level and periodically tapping the accumulated metal from the hearth.

Materials charged and consumed

Pyrophyllite, lb	14,000
Silica, lb	25
Petroleum coke, lb	2,246
Hog fuel, lb	28,450
Electric power, kw.-hr	41,530
Graphite electrode (approximate), lb	741
Carbon in charge, per cent of stoichiometric	101.6
Power consumption, kw. hr. per lb. of ore smelted	2.96
Power consumption, kw. hr. per lb. of alloy produced	6.35
Electrode consumption, lb./ton of alloy produced	228

Silicon-aluminum alloy produced

Uncontaminated alloy as tapped, lb	4,639
Alloy contaminated with iron (90% of actual weight), lb.[1]	1,901
Total metal, adjusted weight, lb	6,540
Total alloy yield, per cent	100.4
Silicon recovered in alloy, per cent [2]	95.8
Aluminum recovered in alloy, per cent [2]	101.7
Average analysis of alloy:[2]	
Al, per cent	22.6
Si, per cent	71.4
Fe, per cent	1.8
Ti, per cent	0.76

[1] The iron in the contaminated metal melted from the iron bar used to open the tap hole or to clear hole during tapping. Ninety per cent of the weight of the iron-contaminated metal was arbitrarily used in summing up the total metal produced.

[2] Exact average aluminum and silicon analyses are difficult to establish because of analytical difficulties and because part of the alloy produced was contaminated with iron during tapping. However, the figures given are reasonably accurate, and recoveries of both aluminum and silicon are better than 95 per cent.

During the operation of the process with the charge proportions as in Example 3, the furnace operated very smoothly, the electrodes descended properly through the charge, there was no evidence of vaporization loss, and no accretion formation on the hearth.

It is evident from the foregoing description and examples that proper adjustment of the charge proportions, in accordance with this invention, with use of wood waste or similar bulky carbonaceous material to provide a part of the required quantity of carbon provides conditions for smooth, trouble-free smelting operations in the furnace in which the charge mixture needs only to be fed to the furnace at the proper rate to maintain the desired charge level and in which the product alloy is tapped from the furnace periodically.

The process of this invention is useful in providing silicon and aluminum for casting alloys. In this use the product will serve as a master alloy to provide the silicon and part of the aluminum contained in the commercial aluminum-silicon alloys. The product can also be used as a deoxidizer and reducing agent in the refining and extraction of other metals. Aluminum-silicon alloys are also becoming increasingly important as new methods for separating the aluminum and silicon from the alloys are developed.

It will be appreciated from a reading of the foregoing specification that the invention herein described is susceptible of various changes and modifications without departing from the spirit and scope thereof.

What is claimed is:

1. In the process of continuously producing silicon-aluminum alloy in an electric furnace by reduction of alumina and silica-containing raw material with carbon, in which a mixture of said raw material and carbon is fed onto and continuously maintained upon a smelting zone, heat is continuously applied to the mixture in the smelting zone, and molten product is tapped from the furnace, said raw material having a melting temperature below its reduction temperature, the improvement which comprises sufficiently diluting the raw material in said mixture with bulky carbonaceous matter to retard the rate at which the raw material enters the smelting zone so that the temperature of the smelting zone is increased to the required reduction temperature for the raw material, said dilution being a minimum of about 5.6 cubic feet of said carbonaceous matter per 100 pounds of said raw material and such volume of said carbonaceous matter containing not more carbon than the correct amount required for the reduction of said raw material.

2. The process according to claim 1, wherein the alumina and silica-containing raw material is calcined clay and the bulky carbonaceous matter is hog fuel, and in which the mixture contains about 100 parts by weight of said hog fuel to 100 parts by weight of said calcined clay plus enough petroleum coke to furnish the remainder of the required carbon reductant, said mixture containing about 5.6 cubic feet of said hog fuel per 100 pounds of said calcined clay.

3. The process according to claim 1, wherein the alumina and silica-containing raw material is pyrophyllite and the bulky carbonaceous matter is hog fuel, and in which the mixture contains about 200 parts by weight of said hog fuel to 100 parts by weight of said pyrophyllite plus enough petroleum coke to furnish the remainder of the required carbon reductant, said mixture containing about 11.2 cubic feet of said hog fuel per 100 pounds of said pyrophyllite.

References Cited in the file of this patent

UNITED STATES PATENTS

432,383	Eames	July 15, 1890
1,379,523	Burgess	May 24, 1921
1,565,689	Van Slyke	Dec. 15, 1925
2,014,873	Wildman	Sept. 17, 1935

FOREIGN PATENTS

500,722	Great Britain	Feb. 13, 1939