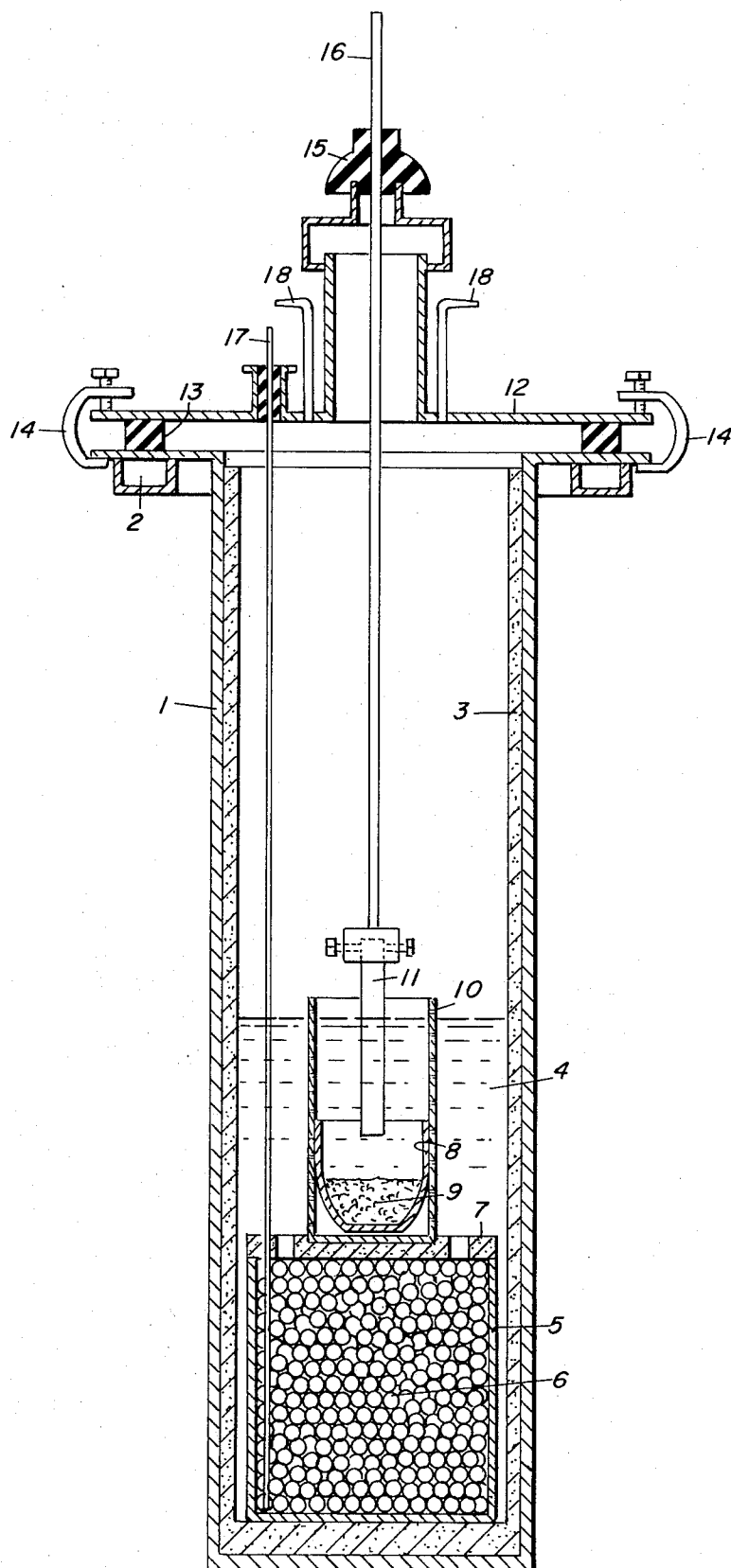


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FROM ALUMINUM SILICON ALLOYS
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1

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PROCESS FOR PRODUCING ALUMINUM AND SILICON FROM ALUMINUM SILICON ALLOYS

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10 Claims

ABSTRACT OF THE DISCLOSURE

Aluminum-silicon alloy produced, for example, by smelting aluminum-silicate ore, is employed as the anode in electrolysis in a molten salt electrolyte of



or NaCl-KCl-AlF_3 . Molten aluminum is produced at the cathode. Anode residue is acid leached to produce metallurgical grade silicon.

This invention relates to treating aluminum-silicon alloys.

Many aluminum-containing domestic ores are unsuitable for use in present processes for the production of aluminum. However, research into methods for the utilization of such ores has shown that many of them can be utilized for the preparation of aluminum-silicon alloys. Numerous studies have been made into methods of preparing aluminum-silicon alloys from domestic clays, bauxites, and other aluminum ores.

The possibility of extracting aluminum from aluminum-silicon alloys has been investigated using several processes. One approach has been to extract aluminum by dissolution with another metal such as zinc, magnesium, or mercury. The aluminum is then recovered from the solute metal by distillation or other means. Technical difficulties in both the solution of the aluminum and in the distillation step have hindered the utilization of these processes.

A process for treating aluminum-silicon alloy with aluminum monochloride to extract the aluminum has also been explored. While the technical feasibility of the method was demonstrated, other difficulties have prevented the commercial utilization of this process.

Several processes for the use of low-temperature electrolytes (90°-600° C.) for the extraction of aluminum from crude aluminum have been patented. All of these processes rely on the deposition of solid aluminum at the cathode. The necessity for frequent removal of the dendritic deposits on the cathodes and consolidation of the aluminum without oxidation have been the chief obstacles to utilization of these low-temperature processes.

We have now developed a process for electrowinning aluminum from aluminum-silicon alloys by molten salt electrolysis in NaCl-KCl-AlCl_3 or NaCl-KCl-AlF_3 electrolytes. Additionally, a metallurgical grade silicon product can be prepared by acid-leaching the residue of the electrolysis step from the anodes of aluminum-silicon alloys that contained only aluminum and silicon as the major elements.

By combining such molten salt electrolysis with a smelting step, a process is provided for extracting aluminum from aluminum silicate ore materials and clays.

The phrase "metallurgical grade silicon" as used throughout the specifications and claims means a purity of at least 98.5 percent silicon.

It is therefore an object of the present invention to separate aluminum from aluminum-silicon alloys.

Another objective is to recover metallurgical grade silicon.

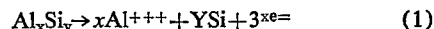
2

A still further object is to recover said aluminum in a molten state.

In the practice of the present invention the aluminum silicate source material such as clay or offgrade bauxite is smelted in the prior art manner so as to produce Al-Si alloys. U.S. Bureau of Mines Report of Investigation No. 5575 (1960) describes such a smelting procedure. Carbothermic smelting of such materials is described in (1) "The Chemical Background of Aluminum Industry," Royal Institute of Chemistry, London, 1955, pp 72-82, and (2) "Carbothermic Smelting of Aluminum," Aluminum Company of America, Alcoa Research Laboratories, New Kensington, Pa., 1964, pp. 42,45.

Thereafter, the aluminum-silicon alloy is employed as the anode in molten salt electrolysis. The theory of operation of the electrolytic process is the selective electrolytic oxidation of aluminum from an aluminum-silicon alloy anode in a molten salt electrolyte and the simultaneous reduction and recovery of aluminum at the cathode. Silicon, undissolved aluminum, and other impurities remain at the anode from which the silicon can be recovered as metallurgical-grade silicon. Molten electrolyte used in the process is used at an electrolyte temperature range of 670° C. to 1,000° C. so that the aluminum recovered as metal is in a liquid form to facilitate its removal from the system and reduce electrolyte dragout losses. The reactions taking place during electrolysis in the molten electrolyte may be expressed:

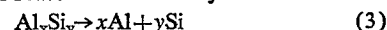
At the anode:



At the cathode:



With the overall reaction on electrolysis:



where x and y represent the proportions of Al and Si in various alloy compositions. Thus, aluminum-silicon alloys are broken down into their elements by the electrolytic oxidation of the aluminum, leaving elemental silicon and the reduction of the extracted aluminum ion to aluminum metal.

Exemplary apparatus used in the extraction of aluminum from aluminum-silicon alloys is shown in the figure. Reference numeral 1 designates a nickel crucible with a flanged top and cooling gland 2. A graphite crucible 3 inserted in the nickel crucible 1 is used to contain the molten electrolyte 4. A perforated graphite anode crucible 5 is used to contain Al-Si alloy anode 6. A graphite support ring 7 resting on top of the anode crucible 5 supports an alumina crucible 8 in which the extracted aluminum 9 is collected and also supports a perforated graphite shield 10 which surrounds the alumina crucible 8 and the cathode 11. The cell lid 12 rests on a rubber gasket 13 and is sealed to the nickel crucible by means of C-clamps 14. A sliding seal of rubber tubing 15 provides an air-tight seal on the cathode lead 16 and permits raising and lowering of the cathode. The anode lead 17 is electrically insulated from the cell lid. The space over the electrolyte is filled with an inert gas through the gas ports 18. The cell is heated to the operating temperature in a resistance heating furnace.

To operate, the cell is first charged with the salts that compose the electrolyte. The cell temperature is raised to 700° C. to melt the salts. Any moisture in the salts is removed by sweeping the atmosphere over the molten salts with a flow of inert gas (helium, argon, or nitrogen may be used). When the salt is molten, the aluminum-silicon alloy to be used is charged into the anode crucible 5 and lowered into the molten salt 4 along with the alumina crucible 8 and shield 10. The lid 12 of the cell

3

is clamped on the cell, and any air admitted is replaced by flushing with inert gas by means of ports 18. Direct current is then applied to the anode and cathode leads 17 and 16, respectively, and electrolysis is started. On electrolysis, the aluminum is solubilized by electrolytic oxidation at the anode and reduced on the surface of the cathode 11. Because the temperature of operation is higher than the melting point of aluminum, the aluminum deposited on the cathode drips off and is collected in the alumina crucible 8. Electrolysis is continued until the majority of the aluminum content of the aluminum-silicon alloy has been removed. The aluminum is recovered by opening the cell and removing the alumina crucible 8. The anode crucible 5 containing the anode residue is also removed and the residue dumped from it. A new charge of aluminum-silicon alloy is added to the anode crucible 5 and replaced in the cell. The aluminum in the alumina crucible is poured into a mold and the alumina crucible 8 returned to the cell. The cell lid is then replaced and the cathode 11 inserted and electrolysis started again. The aluminum prepared is primary grade (at least 99% purity) or better aluminum. The anode residue from the anode basket may be acid leached to remove any residual aluminum, leaving the silicon as a metallurgical-grade silicon (at least 98.5% purity). The perforated graphite screen 10 is used to prevent any fine silicon liberated at the anode from floating into the cathode compartment and contaminating the aluminum metal.

In the following examples, the specific apparatus and procedures described above were employed to test the process of the present invention of various aluminum-silicon alloys.

EXAMPLE 1

A commercial 50-50 aluminum-silicon alloy (50.0 percent Al, 45.8 percent Si, and 0.3 percent iron) was processed using a NaCl-KCl-AlCl₃ electrolyte at 750° C. The electrolyte was an equimolar mixture of NaCl and KCl, to which 10% AlCl₃ was added to provide the aluminum carrier ion. Aluminum of 99.98 percent purity was prepared. A recovery of 82 percent of the aluminum and a cathode current efficiency of 98 percent were achieved.

EXAMPLE 2

A commercial 65-35 aluminum-alloy (65.0 percent Al, 34.2 percent Si, and 0.13 percent Fe) was processed using a NaCl-KCl-AlCl₃ electrolyte of the same composition as Example 1 at 750° C. Aluminum of 99.99 percent purity was prepared. A recovery of 88 percent of the aluminum and a cathode current efficiency of 91 percent were achieved.

EXAMPLE 3

An aluminum-silicon-iron alloy (19.6 percent Al, 55.3 percent Si, 19.7 percent Fe, and 0.2 percent Ti) prepared by smelting of aluminum silicate was processed using a NaCl-KCl-AlCl₃ electrolyte (same as previous examples) at 750° C. Aluminum of 99.70 percent purity was prepared. A recovery of 94 percent of the aluminum and a cathode current efficiency of 89 percent were achieved.

EXAMPLE 4

A crude aluminum-silicon alloy (60.0 percent Al, 26.7 percent Si, 6.1 percent Fe, 4.2 percent Ti, and 0.5 percent C) was processed using a NaCl-KCl-AlCl₃ electrolyte (same as previous examples) at 750° C. Aluminum of 99.99 percent purity was prepared. A recovery of 82 percent of the aluminum and a cathode current efficiency of 90 percent were achieved.

EXAMPLE 5

A refined aluminum-silicon alloy (65.1 percent Al, 23.5 percent Si, 9.5 percent Fe, 1.3 percent Ti and 0.1 percent

4

C was processed using a NaCl-KCl-AlCl₃ electrolyte (same as previous examples) at 750° C. Aluminum of 99.99 percent purity was prepared. A recovery of 81 percent of the aluminum and a cathode current efficiency of 90 percent were achieved.

EXAMPLE 6

An aluminum-silicon casting alloy (87.0 percent Al, 11.9 percent Si, 1.5 percent Fe and 0.2 percent Ti) was processed using a NaCl-KCl-AlCl₃ electrolyte (same as previous examples) at 750° C. Aluminum of 99.99 percent purity was prepared. A recovery of 89 percent of the aluminum and a cathode current efficiency of 81 percent were achieved.

EXAMPLE 7

A commercial 50-50 aluminum-silicon alloy (same as Example 1) was processed using a NaCl-KCl-AlF₃ electrolyte at 750° C. The electrolyte was composed of equimolar mixture of NaCl and KCl, with 7% added AlF₃. Aluminum of 99.98 percent purity was prepared. A recovery of 97 percent of the aluminum and a cathode current efficiency of 96 percent were achieved.

EXAMPLE 8

A commercial 65-35 aluminum silicon (same as Example 2) was processed using a NaCl-KCl-AlF₃ electrolyte (same as Example 7) at 750° C. Aluminum of 99.95 percent purity was prepared. A recovery of 93 percent of the aluminum and a cathode efficiency of 93 percent were achieved.

EXAMPLE 9

An aluminum-silicon-iron alloy (same as Example 3) was processed using a NaCl-KCl-AlF₃ electrolyte (same as Example 7) at 750° C. Aluminum of 99.83 percent purity was prepared. A recovery of 94% of the aluminum and a cathode current efficiency of 92 percent were achieved.

EXAMPLE 10

The anode residue from a test using a commercial 50-50 aluminum silicon alloy (same as Example 1) was leached using hot dilute hydrochloric acid. After filtering, washing, and drying, the undissolved silicon product contained only 0.33 percent aluminum and 0.23 percent iron and met metallurgical grade silicon specifications (98.5% silicon).

EXAMPLE 11

The anode residue from a test using a commercial 65-35 percent aluminum silicon alloy (same as Example 2) was leached using hot dilute hydrochloric acid. After filtering, washing, and drying the undissolved silicon product contained only 0.25 percent aluminum and 0.11 percent iron and met metallurgical grade silicon specifications.

The preparation of aluminum from aluminum silicon alloys using a wide variety of alloy compositions has been accomplished. The aluminum content of the alloy has ranged from 19.6 to 87 percent aluminum. The silicon content of the alloys has ranged from 11.9 to 55.3 percent silicon. In addition, the alloys contained iron ranging from 0.1 to 19.7 percent iron. Successful extraction of aluminum from all these alloys was demonstrated.

The electrolyte composition of equimolar quantities of NaCl and KCl with 5 to 15 percent AlCl₃ is most suitable for the all-chloride electrolyte. The electrolyte composition of equimolar quantities of NaCl and KCl with 3 to 10 percent AlF₃ is most suitable for the chloride-fluoride electrolyte.

Electrolysis in the chloride electrolyte is most favorable at an effective voltage of 1.2 volts and 100 to 150 amps/ft.². Electrolysis in the chloride-fluoride is most favorable at an effective voltage of 2.0 volts and 150-200 amps/ft.².

5

The most favorable temperature range for the electrolytic process is from 700° to 800° C.

In the leaching of the anode residue, suitable acids such as HCl or H₂SO₄ can be employed. Acid concentrations are 5 to 30 percent.

What is claimed is:

1. A process for removing aluminum from an aluminum-silicon alloy comprising

electrowinning said aluminum by molten salt electrolysis at a temperature of about 670° C.-1000° C. with an electrolyte selected from the group consisting of NaCl—KCl—AlCl₃ and



2. The process of claim 1 wherein the anode residue of said electrolysis is leached with an inorganic acid to remove impurities and leave behind metallurgical grade silicon.

3. The process of claim 1 wherein said temperature is about 700–800° C.

4. The process of claim 1 wherein said electrolyte is NaCl—KCl—AlCl₃ containing equimolar quantities of NaCl and KCl with 5 to 15% AlCl₃.

5. The process of claim 1 wherein said electrolyte is NaCl—KCl—AlF₃ containing equimolar quantities of NaCl and KCl with 3 to 10% AlF₃.

6

6. The process of claim 1 wherein said aluminum-silicon alloy is produced by smelting an aluminum-silicate ore material.

7. The process of claim 2 wherein said temperature is about 700–800° C.

8. The process of claim 4 wherein during said electrolysis the voltage is about 1.2 volts and the current density is 100–150 amps/ft.².

9. The process of claim 5 wherein during said electrolysis the voltage is about 2.0 volts and the current density 150–200 amps/ft.².

10. The process of claim 7 wherein said aluminum-silicon alloy is produced by smelting an aluminum-silicate ore material.

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