Title: METHOD USING SINGLE FURNACE CARBOSTEMIC REDUCTION WITH TEMPERATURE CONTROL WITHIN THE FURNACE

Abstract: A start-up process of making aluminum using a single carbothermic reactor/furnace (11) having a single hollow reactor compartment with bottom resistance heating electrodes (16) (13) in the side of the reactor, involves adding Al₂O₃ and C (carbon) for start-up and melting the mixture to provide a (Al₂O₃-Al₅C₃) slag having a temperature between about 1875°C and 2000°C; and then adding Al₂C₃ to the slag and raising the temperature of the furnace (11) to form a top Al phase with 6 to 8 wt% C (21) and a bottom slag phase (22); and then adding Al₂O₃ is added to the Al-C/slag (21, 22) to produce an Al₂O₃ rich slag lower the reactant temperature and produce a decarbonization reaction (step 30) providing a top Al phase with less than 5 wt% C (23) which is then tapped after step (40). The remaining slag is the starting material.
as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG) as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations Published: without international search report and to be republished upon receipt of that report For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
METHOD USING SINGLE FURNACE CARBOThERMIC REDUCTION WITH TEMPERATURE CONTROL WITHIN THE FURNACE

Field of the Invention

[0001] The present invention relates to a method of producing low carbon aluminum in a single reactor compartment carbothermic furnace with control to lower or raise the temperature of reactants within the interior of the reactor compartment.

Background of the Invention

[0002] The direct carbothermic reduction of alumina has been described in U.S. Patent Specification Nos. 2,974,032 (Grunert et al.) and 6,440,193 B1 (Johansen et al.) as well as in Proceedings 6th Conference on Molten Slags, Fluxes and Salts, Edited by S. Seetharaman and D. Sichen “Carbothermic Aluminum”, K. Johansen, J. Aune, M. Bruno and A. Schei, Stockholm, Sweden-Helsinki Finland, June 12-17, 2002. It has long been recognized that the overall reaction:

\[ \text{Al}_2\text{O}_3 + 3\text{C} = 2\text{Al} + 3\text{CO} \]  

(1)

takes place, or can be made to take place, generally in steps such as:

\[ 2\text{Al}_2\text{O}_3 + 9\text{C} = \text{Al}_4\text{C}_3 + 6\text{CO} \text{ (vapor)} \]  

(2)

\[ \text{Al}_4\text{C}_3 + \text{Al}_2\text{O}_3 = 6\text{Al} + 3\text{CO} \text{ (vapor)} \]  

(3)

\[ \text{Al}_2\text{O}_3 + 2\text{C} = \text{Al}_2\text{O} \text{ (vapor)} + 2\text{CO} \text{ (vapor)} \]  

(4)

\[ \text{Al}_2\text{O}_3 + 4\text{Al} = 3\text{Al}_2\text{O} \text{ (vapor)} \]  

(5), and

\[ \text{Al} = \text{Al} \text{ (vapor)} \]  

(6).

[0003] Reaction (2) takes place at temperatures below 2000°C and generally between 1900°C and 2000°C. Importantly, reaction (3), which is the aluminum producing reaction, takes place at higher temperatures of about 2050°C, and requires substantial heat input. Very importantly, in addition to the species stated in reactions (2) and (3), volatile species including gaseous Al, reaction (6), and gaseous aluminum suboxide that is Al₂O, are formed in reaction (4) or (5). In the overall carbothermic reduction process, the Al₂O and Al gases are recovered by reacting them with carbon in a separate reactor usually called the vapor recovery unit or vapor recovery reactor.

[0004] Other patents relating to carbothermic reduction to produce aluminum include U.S. Patent Specification No. 4,099,959 (Dewing et al.), where dual reaction zones are described and where off gases are passed through granular carbon material and countercurrent to fresh coal or "green" coke in a gas scrubber. U.S. Patent Specification Nos. 4,033,757 and 4,388,107 (both Kibby) teach reduction of carbon content by heating the surface of the melt to about 2100°C while maintaining a lower temperature of about 1850°C.
in the slag thereby lowering C (carbon) in the metal. This however would seem to be
difficult in operation and would appear to cause excessive vaporization. The former Kibby
'757 patent uses arc heating and a plasma jet in a process that starts at 1850°C-1950°C, then
arc heats to 2100°C, producing Al with < 10 wt.% C. The latter Kibby '107 utilizes a
secondary furnace or separate decarbonization zone requiring transfer of very hot metal and
slag to and from the furnace.

[0005] Other art in this area, includes, for example, U.S. Patent Specification Nos.
4,334,917 and 4,533,386 (both Kibby) which appear to teach either multiple reactors or
additional decarbonization zones. U.S. Serial No. 10/646,507, filed August 23, 2003 (J.
Aune et al.-Docket 03-0668) teaches an electrode arrangement for a single reactor
compartment carbothermic furnace, where side wall electrodes, each connected to the other,
substitute for a bottom lining as an electrical contact and vertical electrodes are submerged in
the liquid slag both.

[0006] In the carbothermic process, the use of dual reaction zones or a plurality of
furnaces, adds expense to the process, and unnecessary complication. What is needed is an
efficient and simple method for recovering lower carbon containing aluminum. Therefore, it
is one of the main objects of this invention to provide a more cost and energy effective,
 Improved aluminum production process, by use of a single reactor compartment,
carbothermic furnace with temperature control of the reactor compartment.

Summary of the Invention

[0007] The above needs are met and the above problems solved by providing a
method of using a single carbothermic reactor to produce aluminum with low carbon content,
comprising: (a) providing a single furnace having a single hollow, interior reactor
compartment with a plurality of bottom resistance heating electrodes and one or more
optional vertical top electrodes; and then; (b) adding Al₂O₃ and C for start-up of the process
to the inside of the furnace and melting their mixture, to provide a (Al₂O₃-Al₄C₃) slag and
excess Al₄C₃ having a temperature between about 1875°C and 2000°C; and then (c) adding
Al₄C₃ to the slag, and raising the temperature of the furnace to form a top Al phase with
about 6 wt% to 7 wt% C and a bottom slag phase having a temperature between about
2050°C and 2100°C; and then (d) adding Al₂O₃ to the Al-C slag, which Al₂O₃ addition results
in producing Al₂O₃ rich slag and in lowering the temperature to between about 1800°C and
1900°C, to produce a decarbonization reaction within the single reactor compartment,
providing a top Al phase with less than (<) 5 wt% C and a bottom (Al₂O₃ rich-Al₄C₃) slag
having a temperature between about 1800°C and 1900°C; and then (e) tapping the top Al <5
wt% C phase; and (f) repeating steps (b) to (e). This slag is then used to begin the next cycle. The next cycle is begun by adding some C and Al₂O₃ to the bottom slag and repeating steps (c) to (e). Preferably the tapped aluminum phase is Al < 3 wt% C and the Al₄C₃ added in step (c) is from a vapor recovery unit associated with the reactor.

[0008] In step (b), arc heating using retractable, at least one vertical top electrodes are preferably used to provide slag. In step (d), addition of Al₂O₃ at this stage, very importantly, lowers the temperature within the furnace and changes the slag composition transferring a substantial amount of C from aluminum to the slag. This provides a very simple method to produce lower carbon containing aluminum, where only one furnace or reactor is used in the process.

Brief Description of the Drawings

[0009] The invention is further described with reference to the accompanying non-limiting drawings in which:

[0010] Fig. 1 is a flow sheet showing one example of a previously conceptualized system of a carbothermic reduction process for the production of aluminum, including an off-gas vapor recovery reactor to recover the Al₂O₃ and Al vapors as Al₄C₃ and/or Al₂O₃ solids (and Al₄C₃-Al₂O₃ slag); and

[0011] Fig. 2 is flow sheet showing the steps involved in this invention to produce low carbon aluminum utilizing a single reactor.

Detailed Description of Preferred Embodiments

[0012] Fig. 1 is a simplified illustration of one embodiment of a carbothermic reaction process to produce Al and, recover Al, Al₂O₃ and CO in the off-gases as Al₄C₃, Al₂O₃ and slag and passes this material to the smelting furnace. In Fig. 1, gas flows are shown as dashed lines and flows of solids and molten substances are shown as solid lines.

[0013] In Fig. 1, the off-gas from a carbothermic smelting furnace here, for simplicity, comprising a first stage 1 and possibly a second stage 2 is forwarded via conduits 3 and 4 to an enclosed off-gas reactor 5 operating at a temperature of about 1600°C to 2050°C depending on the type reactor. There could be more than one such reactor, for example, one for stage one smelter 1 and one for stage two smelter 2. The reactor 5 could be a counter-current moving bed reactor or a fluid bed or a series of fluid beds. The Al-components of the off-gas entering the reactor 5 react with the carbon to form Al₄C₃, Al₂O₃ and Al₄C₃-Al₂O₃ slag material. Conduit 6 can be used to pass this material to stage 2.

[0014] The gas from reactor 5 contains primarily CO, and possibly some H₂ from the volatile part of the charcoal reactor charge and little or no Al or Al₂O. The off gas from
reactor 5 has a high energy value as hot CO and could be used to produce electrical energy in a gas turbine or conventional boiler. The aluminum vapor species will have reacted to carbide, condensed to Al₂O₃ and C or formed an Al₂O₃-Al₄C₃ slag. The Al₄C₃-Al₂O₃ slag and unreacted carbon is fed into the second stage of the carbothermic smelter via conduit 6. An Al-C liquid alloy exits smelter stage 2 as shown in Fig. 1, where (s) means solid, (v) means vapor and (liq) means liquid in Fig. 1.

Fig. 2 illustrates the basic steps, reactions and reactants in the method of this invention. This new process uses a single furnace, so no slag recycle is required, and slag resistance heating to avoid excess vaporization. In the first step of the process, Al₂O₃ and carbon are added and Al₂O₃-Al₄C₃ slag is produced which can contain excess Al₄C₃ above saturation. The furnace operates at about 1875°C to 2000°C to produce slag. The second step produces an Al-6-8 wt% C alloy at about 2050°C to 2100°C and requires additional energy and additional Al₄C₃, part of which is the excess from the first step and the remainder is from the vapor recovery unit. Next, room temperature Al₂O₃ is added to the furnace, an Al₂O₃ rich slag is produced and the temperature decreases to about 1850°C. This removes the carbon into the alumina rich Al₂O₃-Al₄C₃ slag. This will remove about 65 wt% of the carbon, that is, the carbon in the aluminum will decrease from 6 wt% to 2 wt%. The overall process is much simpler since it is not a multi-stage reactor and does not require transfer of hot liquid slag.

In the first step 10 of Fig. 2, slag is produced. In the second step 20 metal 21 is produced with about 5 to 7 wt% C on top of a slag phase 22 and gases are released (not shown for the sake of simplicity). In the third step 30, an extraction or decarbonization reaction is provided, at lowered temperatures to reduce vapor loss, where added Al₂O₃, is at ambient temperature (about 20°C to about 35°C), and importantly, helps lower both temperature substantially and provides an alumina rich slag in step 40. Here, C is transferred from the Al phase to provide an aluminum phase containing less than (<) 5 wt% C phase, preferably a < 3 wt% C phase 23, which is then tapped. Steps 30 and 40 merge somewhat.

In summary, in the process, we have:

Slag Making: To start up the process, Al₂O₃ and carbon are added to make a liquid slag, 77% Al₂O₃-23% Al₄C₃ (mole percent) at about 1900°C–2000°C and some excess Al₄C₃. Some Al₂O and Al vapors are formed and go to the vapor recovery reactor 5. Once the process is at a steady state, the starting point for slag making is the slag remaining after decarbonization in the previous cycle.
[0019] Metal Making: Metal is produced by the following reaction at about 2050°C-2100°C:

$$\text{Al}_2\text{O}_3 + 3\text{Al}_4\text{C}_3 = 6\text{Al} + 3\text{CO}.$$ 

Aluminum carbide is added from the vapor recovery reactor 5. About 17% of the Al will vaporize as Al$_2$O and Al. It is not possible to react all of the slag since the energy is supplied by slag resistance heating through the slag and some slag must remain in the furnace. About 20% of the slag does not react and remains for resistance heating. Some decarburation can occur by raising the temperature after all the carbide is added and reducing the carbide content of the slag and carbon in the metal but this will result in large amounts of Al$_4$O and Al vaporization.

[0020] Decarburation: Al$_2$O$_3$ is added to the furnace to remove carbon from the metal. Some electric power is necessary to heat and melt the Al$_2$O$_3$ while some of the energy comes from the sensible heat of the slag since its temperature is higher than required for decarburation. The slag-metal system is allowed to cool to about 1850°C. The slag becomes rich in Al$_2$O$_3$ and carbon is transferred from the metal to the slag (Al$_4$C$_3$). The metal is tapped and the resulting Al$_2$O$_3$ rich liquid slag is the starting point for return to slag making.

[0021] After the metal is tapped the temperature is increased to about 1900°C-2000°C and Al$_2$O$_3$ and carbon are added once more, to produce the desired liquid slag composition and excess Al$_4$C$_3$ for metal making. In the process, substantial amounts of CO are produced which carry Al as Al and Al$_2$O gaseous species. These are converted to Al$_4$C$_3$ in the vapor recovery reactor 5 and returned to the furnace during metal making, all as shown in Fig. 2.

[0022] Generally, in step 10, a single furnace 11, having side walls and a bottom, and a single, hollow reactor compartment 13, as shown in Fig. 2, is used solely in this invention; without interior underflow partition walls/baffles or the like. The furnace can have a substantially rectangular, square, circular or oval shape. Within the side walls of the furnace are bottom resistance heating electrodes 16, preferably located in the side(s) of the reactor as shown. In step 10, preferably, at least one top vertical retractable exterior electrode 12 is used. It can provide an arc to melt the solid Al$_2$O$_3$ and C at start-up or at steady state, added to producing molten slag phase Al$_2$O$_3$ – Al$_4$C$_3$ slag plus additional Al$_4$C$_3$.

[0023] The electrodes 12 and 16 can be made from carbon, graphite, or non-consumable inert ceramic materials, where each is individually supplied with electricity by electric current means 19. The bottom resistance heating electrodes are preferably horizontal and used in metal making to reduce super heating the metal and causing excessive
vaporization. The bottom electrodes 16 are also preferably disposed at/adjacent to the bottom phase molten slag phase/level 22, as shown in steps 20, 30 and 40. In step 10 and 20, \( \text{Al}_2\text{O}_3 \), vapor, CO and Al exit as streams 3 and 3'. The \( \text{Al}_2\text{O}_3 \), C, \( \text{Al}_4\text{C}_3 \) supply means in steps 10 to 30 are preferably gas tight. The purified aluminum stream 26 may then be passed to any number of apparatus, for example, degassing apparatus to remove, for example, \( \text{H}_2 \) fluxing apparatus to scavenge oxides from the melt and eventually to casting apparatus to provide unalloyed primary shapes such as ingots or the like of about 50 lb. (22.7Kg) to 750 lb. (341 Kg). These ingots may then be remelted for final alloying in a holding or blending furnace or the melt from fluxing apparatus may be directly passed to a furnace for final alloying and casting as alloyed aluminum shapes.

[0024] Whereas particular embodiments of this invention have been described above for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details of the present invention may be made without departing from the invention as defined in the appended claims.

[0025] An example of how this process would work beginning with the metal making stage, 100 moles of a 77% \( \text{Al}_2\text{O}_3 \)-23% \( \text{Al}_4\text{C}_3 \) slag. As the temperature increases, reaction (3) occurs. \( \text{Al}_4\text{C}_3 \) would be added to the slag to maintain the slag composition. The reaction proceeds until there are 15 moles of \( \text{Al}_2\text{O}_3 \) and 5 moles of carbide remaining in the furnace. The process will produce 372 moles of \( \text{Al} \) but 62 moles will vaporize leaving 310 moles of liquid \( \text{Al} \) containing about 7.5 wt% C.

[0026] The \( \text{Al} \) vaporized will produce about 15 moles of carbide. During slag making enough \( \text{Al} \) is vaporized to produce 10 moles of carbide. A total of 62 moles of carbide are required in the metal making step. With 28 moles of carbide reacting from the slag and about 25 moles from the vapor recovery reactor ("VRR") there is a deficit of about 9 moles of \( \text{Al}_4\text{C}_3 \). This additional carbide can be produced in slag making so the actual starting point is:

100 k moles of slag containing 77% \( \text{Al}_2\text{O}_3 \)-23% \( \text{Al}_4\text{C}_3 \) and 9 k moles of \( \text{Al}_4\text{C}_3 \)

About 25 k moles of \( \text{Al}_4\text{C}_3 \) are added from the VRR.

For metal making, the slag + \( \text{Al}_4\text{C}_3 \) is heated to a higher temperature (2050°C-2100°C) producing 310 k moles aluminum metal containing about 7.5 wt.% C. About 20 k moles of slag remain for resistance heating.

For decarburization 75 k moles of \( \text{Al}_2\text{O}_3 \) is added making the resulting slag 90 k moles \( \text{Al}_2\text{O}_3 \) and 12 moles \( \text{Al}_4\text{C}_3 \). The temperature is decreased to about 1850°C. At the lower temperature, the carbon distribution ratio between slag and metal increases. The carbon content of the metal is reduced from about 6.0% to 2.5%. This is based on a carbon
distribution ratio between slag and metal of 2 and 8904 kg of metal and 9900 kg of slag. The metal is tapped and the remaining slag, 90 k moles $\text{Al}_2\text{O}_3$-12 k moles $\text{Al}_4\text{C}_3$, is the starting point for slag making.

[0027] After the metal is tapped the temperature is increased to about 2000°C and $\text{Al}_2\text{O}_3$ and carbon are added to produce the desired liquid slag composition and excess $\text{Al}_4\text{C}_3$ for metal making. This will require about 225 k moles of C and 37 k moles of $\text{Al}_2\text{O}_3$. After the slag is made the metal making step is repeated.

[0028] Having described the presently preferred embodiments, it is to be understood that the invention may be otherwise embodied within the scope of the appended claims.
What is claimed is:

1. A method of using a single carbothermic reactor to produce aluminum with low carbon content, comprising:
   (a) providing a single furnace having a single hollow, interior reactor compartment with a plurality of bottom resistance heating electrodes in the furnace walls and one or more optional vertical electrodes;
   (b) adding Al₂O₃ and C for start-up of the process to the inside of the furnace and melting their mixture, to provide a (Al₂O₃-Al₄C₃) and excess Al₄C₃ slag having a temperature between about 1875°C and 2000°C;
   (c) adding Al₄C₃ to the slag, and raising the temperature of the furnace to form a top Al₂ phase with about 6 wt% to 8 wt% C and a bottom slag phase having a temperature between about 2050°C and 2100°C;
   (d) adding Al₂O₃ to the Al-C slag which Al₂O₃ addition results in producing an Al₂O₃ rich slag and in lowering the temperature to between about 1800°C and 1900°C, to produce a decarbonization reaction within the single reactor compartment, providing a top Al phase with less than < 5 wt% C and a bottom (Al₂O₃ rich-Al₄C₃) slag having a temperature between about 1800°C and 1900°C;
   (e) tapping the top Al<5 wt% C phase; and
   (f) repeating steps (b) to (e).

2. The method of claim 1, wherein at least one vertical top electrode is used to provide arc heating in step (b).

3. The method of claim 1, wherein, in step (d) addition of Al₂O₃ changes the slag composition, transferring C from Al to the slag, and where in step (d) the top Al phase has < 3 wt% C, which is tapped in step (e).

4. The method of claim 1, wherein off-gas comprising Al₂O, CO from step (b) and step (c) Al result are fed to a reactor to produce Al₄C₃ and Al₂O₃ or Al₄C₃ Al₂O₃ slag which is added to the slag in step (e).

5. The method of claim 1, wherein, in step (d) the top Al phase has < 3 wt% C, which is tapped in step (e).
6. The method of claim 1, wherein after step (e) the temperature is increased from about 1875°C to 2000°C and Al₂O₃ and C are added to begin step (a).

7. The method of claim 1, wherein, in step (d) during decarbonization C is transferred from the Al phase to the slag.

8. The method of claim 1, wherein, Al₂O, CO, and gaseous Al are passed to an off gas reactor, where C is added to produce solid Al₄C₃ and Al₂O₃ and Al₄C₃-Al₂O₃ slag which is returned to the furnace.

9. The method of claim 8, wherein the Al₄C₃ is returned during step (c).

10. The method of claim 1, wherein the bottom resistance heating electrodes are disposed in the side of the furnace adjacent the bottom slag phase and are of a material selected from the group consisting of carbon, graphite or non-consumable inert anode material comprising ceramic.

11. The method of claim 1, wherein the slag from step (d) is used as a starting material for the next cycle, along with additional Al₂O₃ and C.
FIG. 1
PRIOR ART