Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2393511 C 2007/03/20

(11)(21) 2 393 511

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(86) Date de dépôt PCT/PCT Filing Date: 2000/11/08
(87) Date publication PCT/PCT Publication Date: 2001/06/14
(45) Date de délivrance/Issue Date: 2007/03/20
(85) Entrée phase nationale/National Entry: 2002/06/05
(86) N° demande PCT/PCT Application No.: NO 2000/000374
(87) N° publication PCT/PCT Publication No.: 2001/042136
(30) Priorité/Priority: 1999/12/08 (NO19996022)

(51) Cl.Int./Int.Cl. *C01B 33/037* (2006.01),
H01L 31/18 (2006.01)

(72) Inventeurs/Inventors:
CECCAROLI, BRUNO, NO;
FRIESTAD, KENNETH, NO

(73) Propriétaire/Owner:
ELKEM ASA, NO

(74) Agent: MACRAE & CO.

(54) Titre : PROCEDE DE RAFFINAGE DU SILICIUM DE QUALITE METALLURGIQUE
(54) Title: REFINING OF METALLURGICAL GRADE SILICON

(57) Abrégé/Abstract:
The invention relates to a method for purification of metallurgical grade silicon where a calcium containing compound is added to molten silicon prior to or after the silicon is tapped from the furnace. The silicon is cast and solidified at a relatively high cooling rate and the solidified silicon is crushed and subjected to a purification process consisting of two leaching steps. In the first leaching step the silicon is treated with an aqueous solution of $FeCl_3$ or $FeCl_3$ and HCl which causes disintegration of the silicon, and in the second leaching step the silicon is treated with an aqueous solution of HF or HF/HNO_3. Calcium-containing compound is added to the molten silicon in an amount necessary to provide between 0.3 and 0.95 % by weight of calcium in the molten silicon and the weight ratio between Al and Fe in the molten silicon is regulated to between 0.5 and 2.0 by addition of aluminum to the molten silicon.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 June 2001 (14.06.2001)

PCT

(10) International Publication Number
WO 01/42136 A1

(51) International Patent Classification[7]: C01B 33/037

(21) International Application Number: PCT/NO00/00374

(22) International Filing Date:
8 November 2000 (08.11.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
19996022 8 December 1999 (08.12.1999) NO

(71) Applicant *(for all designated States except US)*: **ELKEM ASA** [NO/NO]; Hoffsveien 65B, N-0377 Oslo (NO).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **CECCAROLI, Bruno** [NO/NO]; Rognelia 30, N-4622 Kristiansand (NO). **FRIESTAD, Kenneth** [NO/NO]; Barliveien 10, N-4621 Kristiansand (NO).

(74) Agent: **VINDENES, Magne**; Elkem ASA Patent Department, P.O. Box 8040, Vågsbygd, N-4675 Kristiansand (NO).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search 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.

WO 01/42136 A1

(54) Title: REFINING OF METALLURGICAL GRADE SILICON

(57) Abstract: The invention relates to a method for purification of metallurgical grade silicon where a calcium containing compound is added to molten silicon prior to or after the silicon is tapped from the furnace. The silicon is cast and solidified at a relatively high cooling rate and the solidified silicon is crushed and subjected to a purification process consisting of two leaching steps. In the first leaching step the silicon is treated with an aqueous solution of $FeCl_3$ or $FeCl_3$ and HCl which causes disintegration of the silicon, and in the second leaching step the silicon is treated with an aqueous solution of HF or HF/HNO_3. Calcium-containing compound is added to the molten silicon in an amount necessary to provide between 0.3 and 0.95 % by weight of calcium in the molten silicon and the weight ratio between Al and Fe in the molten silicon is regulated to between 0.5 and 2.0 by addition of aluminum to the molten silicon.

Title of Invention

Refining of metallurgical grade silicon.

Field of Invention

The present invention relates to a method for production of high purity silicon from metallurgical grade silicon.

Background Art

Metallurgical grade silicon contains several metallic and non-metallic impurities which make it unsuited for use in solar cells. The non-metallic impurities such as boron and phosphorus can be reduced mainly by choice of suitable raw materials for production of silicon metal, but this is only possible to a certain degree as regards the most important metallic impurities Fe, Al, Mn, Cu, Ni and others. Raw materials of high purity are however very expensive and it is therefore desirable to procure a simple and cheap purification process by which the metallic impurities can be removed and/or reduced to such a low degree that the purified silicon is suitable for production of solar cells.

It is known that a number of the metallic impurities are rejected by the silicon metal during the crystallization, and that they will crystallize along the grain borders of the silicon, either as intermetallic compounds or as silicides. This is particularly the case for iron and aluminum. The purification of silicon can therefore be done by effecting the crystallization so that the impurities can be collected and removed, for instance by means of crystal drawing, zone melting or similar methods, or by dissolving the impurities by means of an acid which does not attack the silicon m etal.

Crystal drawing as well as zone melting are very effective purification methods, but are extremely expensive and require at least double purification of the metallurgical grade silicon before satisfactory solar cell quality is obtained.

From US patent No. 4,539,194 it is known a method where molten silicon is alloyed with 1 - 10 % by weight of calcium whereafter the solidified alloy is leached in two steps. In the first leaching step it is used an aqueous solution of $FeCl_3$ and HCl which causes disintegration of the silicon into small silicon particles. In the second leaching step it is used an aqueous solution of HF and HNO_3. By this method it is obtained a good purification for both iron and aluminum and also to some extent also for phosphorus. The method according to US patent No. 4,539,194 does, however, have some drawbacks. Thus the addition of relatively large amounts of calcium to silicon is costly as the calcium losses during alloying are high and increases with increasing amount of calcium in the silicon. Further, it is difficult to control the leaching reactions in both leaching steps due to high heat evolution and due to formation of silane and H_2-gas which can cause self-ignition and explosion. Finally, the high amount of calcium in the silicon causes a relatively high loss of silicon in the form of very fine particulate silicon which are lost in the washing steps carried out after the leaching steps.

SUMMARY OF INVENTION

The invention comprises a method for purification of metallurgical grade silicon using a furnace where a calcium containing compound is added to molten silicon prior to or after the silicon is tapped from the furnace, whereafter the silicon is cast and solidified at a relatively high cooling rate and the solidified silicon is crushed and subjected to a purification process consisting of two leaching steps where the silicon in the first leaching step is treated with an aqueous solution of $FeCl_3$ or $FeCl_3$ and HCl which causes disintegration of the silicon, and where the silicon in the second leaching step is treated with an aqueous solution of HF or HF/HNO_3, characterized in that the calcium-containing compound is added to the molten silicon in an amount necessary to provide between 0.3 and 0.95% by weight of calcium in the molten silicon and that the weight ratio between Al and Fe in the molten silicon is regulated to between 0.5 and 2.0 by addition of aluminum to the molten silicon.

Disclosure of Invention

It has now surprisingly been found that a good purification effect, particularly of Fe, can be obtained by addition of a smaller amount of calcium provided that the weight ratio between Al and Fe in the metallurgical grade silicon to be refined is kept within certain limits. At the same time it has been found that a low amount of calcium in the silicon to be refined, results in lower losses of fine particulate silicon.

Accordingly, the present invention relates to a method for purification of metallurgical grade silicon where a calcium containing compound is added to molten silicon prior to or after the silicon is tapped from the furnace, whereafter the silicon is cast and solidified at a relatively high cooling rate and the solidified silicon is crushed and subjected to a purification process consisting of two leaching steps where the silicon in the first leaching step is treated with an aqueous solution of $FeCl_3$ or $FeCl_3$ and HCl which causes disintegration of the silicon, and where the silicon in the second leaching step

is treated with an aqueous solution of HF or HF/HNO_3, said method being characterized in that the calcium-containing compound is added to the molten silicon in an amount necessary to provide between 0.3 and 0.95 % by weight of calcium in the molten silicon and that the weight ratio between Al and Fe in the molten silicon is regulated to between 0.5 and 2.0 by addition of aluminum to the molten silicon.

The weight ratio between Al and Fe is preferably regulated to between 0.6 and 1.2.

It has surprisingly been found that by the method of the present invention it is possible to obtain an iron content in the purified silicon which is as low as in silicon treated according to the method of US patent No. 4,539,194 even if the amount of calcium added to the molten silicon is substantially lower than according to the method of US patent No. 4,539,194. Further it is obtained an improved control of the reactions which take place in the two leaching steps due to the fact that the amount of silane which forms is substantially reduced and thus reduces the possibility of explosions is reduced. The method according to the invention gives an improved yield of silicon as losses in the form of fine particulate silicon has shown to be reduced with a lower calcium content.

Detailed description of the Invention

EXAMPLE 1

Varying amounts of calcium and aluminum were added to molten metallurgical grade silicon.

The alloys were cast in moulds at a relatively high cooling rate. The solidified alloys were crushed to a particle size of less than 120 mm and for some of the alloys to a particle size of less than 30 mm. The chemical compositions of these alloys and the weight ratio of Al to Fe are shown in table 1.

Alloy Nos. 2 and 3 in table 1 are in accordance with the invention, while alloy Nos. 1 and 4 in table 1 have a weight ratio of Al to Fe outside the invention.

TABLE 1

Element	Fe ppmw	Al ppmw	Al/Fe	Ca ppmw	Ti ppmw	P ppmw	B ppmw
Alloy 1	2980	660	0.22	9200	140	39	7
Alloy 2	2100	1300	0.62	8500	120	52	7
Alloy 3	2410	1850	1.18	9200	180	38	7
Alloy 4	2280	5860	2.57	10200	170	40	7

The alloys were thereafter leached in a first leaching step using an aqueous solution of $FeCl_3$ and HCl. The undissolved silicon from the first leaching step was washed with water and thereafter subjected to a second leaching step using a 5 % HF solution. The solid silicon from the second leaching step was washed with water.

The purified silicon alloys were analysed for impurities, the results are shown in table 2.

TABLE 2

Element	Fe ppmw	Al ppmw	Ca ppmw	Ti ppmw	P ppmw	B ppmw
Alloy 1	82	52	450	10	24	6
Alloy 2	50	70	310	< 10	16	8
Alloy 3	55	162	441	7	20	6
Alloy 4	75	210	255	11	20	6

As can be seen from table 2, the removal of impurities is substantially better for alloys Nos. 2 and 3 than for alloy Nos. 1 and 4, where the Al/Fe weight ratio is respectively lower and higher than for alloys Nos. 2 and 3.

CLAIMS:

1. A method for purification of metallurgical grade silicon using a furnace where a calcium containing compound is added to molten silicon prior to or after the silicon is tapped from the furnace, whereafter the silicon is cast and solidified at a relatively high cooling rate and the solidified silicon is crushed and subjected to a purification process consisting of two leaching steps where the silicon in the first leaching step is treated with an aqueous solution of $FeCl_3$ or $FeCl_3$ and HCl which causes disintegration of the silicon, and where the silicon in the second leaching step is treated with an aqueous solution of HF or HF/HNO_3, characterized in that the calcium-containing compound is added to the molten silicon in an amount necessary to provide between 0.3 and 0.95% by weight of calcium in the molten silicon and that the weight ratio between Al and Fe in the molten silicon is regulated to between 0.5 and 2.0 by addition of aluminum to the molten silicon.

2. The method of claim 1, characterized in that the weight ratio between Al and Fe is regulated to between 0.6 and 1.2.