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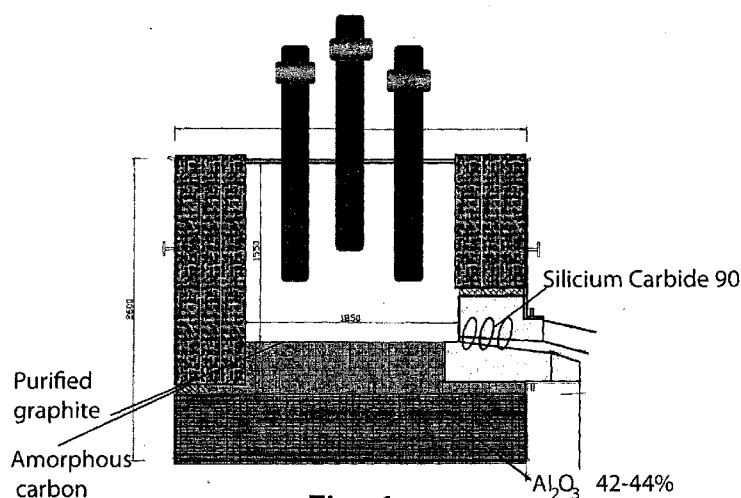


Fig. 1

(57) Abstract: The present invention relates to a method for producing high purity metallurgic grade silicon, particularly for use in photovoltaic field, said method being characterized in that it provides the steps of: a. selecting high purity raw materials in powder and lump form; b. mixing raw material powder; c. briquetting mixed material; d. realizing batches of briquettes and lump material; e. carrying out carbon reduction within an alternate current (AC) submerged arc furnace (SAF); f. stocking product within SAF furnace basin; g. taking out the product; h. carrying out purification into an inducted ladle; i. settling, skimming and filtering carbide and oxide particles.

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IMPROVED METHOD FOR THE PREPARATION OF METALLURGICAL GRADE HIGH PURITY SILICON
IN PARTICULAR FOR USE IN PHOTOVOLTAIC FIELD.

5 The present invention relates to an improved method for producing high purity metallurgic grade silicon, particularly for use in photovoltaic field.

More specifically, the invention concerns a method of the above kind obtained by reduction of high purity
10 silica, in presence of a reducing agent, preferably carbon black having a low content of boron (B) and phosphorous (P).

In other words, method suggested according to the present invention permits producing silicon via "direct
15 carbothermic route", reducing the use of quartz, utilizing high-purity raw material.

Still more specifically, the invention refers to a method permitting producing high purity silicon starting from quartz in powder and lump form (i.e.
20 pieces of quartz crushed, selected and screened with precise dimensions, both for lower dimensions and large dimensions) and carbon black in an electric furnace.

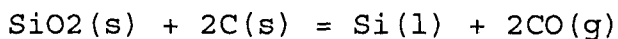
It is known that silicon to be particularly used in the photovoltaic field, produced by a metallurgic method,
25 is sensible to the chemical and electrical properties of raw material, so that reactivity and use of a reducing agent with low impurities is cumbersome.

The object of the present invention is that of permitting preparation of a high quality metallurgical
30 grade silicon starting from high purity raw material that can be used in the photovoltaic field, preventing

problems characterizing traditional purification methods, reducing their costs, the use of energy and production of potentially carcinogenic products.

As it is well known, metallurgical grade silicon, also
5 known as metallic silicon, typically with a Si 98,5% purity, is produced within electric arc furnace.

Silicon standard is produced by the carbothermic reduction of silica according to the overall reaction:



10 from which it can be noted that two moles of carbon are required to react with a mole of silicon dioxide to yield one mole of silicon and two moles of carbon monoxide.

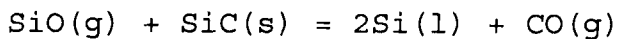
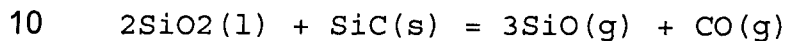
Contrary to what is often claimed in literature, silica
15 sand is not used for this method, being it preferred lumpy quartz (e.g. 10-100 mm) with appropriate purity and thermal resistance. Carbon raw material is generally comprised of metallurgical grade coal as well as woodchips and/or charcoal and coke. Quartz and
20 carbon are selected in order to achieve high product quality, to maximize furnace performances and to minimize the environmental damages, particularly emission of SO₂ and NO_x. Among factors relevant to obtain the above result (good furnace performance in
25 terms of high material yield, lower power consumption and good product quality), raw material reactivity and the consistency (for instance its porosity) of the mix of raw materials in the charge are included.

Traditionally, raw material mix or charge is heated by
30 means of an intense electric arc sustained between the

tips of submerged electrodes and the electrical ground of the furnace.

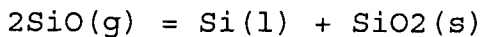
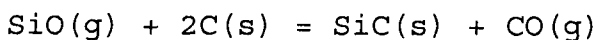
Liquid silicon metal is tapped from the bottom of the furnace, and the thoroughly mixed raw materials are charged on the top.

Conceptually splitting the furnace reaction inner space into an inner hot zone and an outer cooler zone, liquid silicon is produced in the inner zone, where the dominant chemistry is described by the reactions



Temperature in the inner zone is within the range of 1900°C to 2100°C, allowing a high proportion of SiO(g) in this zone, which is indispensable for further reduction according to reaction

In the outer zone, where the temperature is below 1900°C, SiO(g) and CO(g) coming from the inner zone meet and react with free carbon. Thus, silicon carbide SiC(s) and condensation products of Si(l) in a matrix of SiO₂(s,l) are formed as the partial pressure of SiO(g) drops:



However, silicon produced by traditional process has a relatively high degree of impurities. These impurities comprise metals, such as Al, Cr, Fe, Ti, V, Zr, besides Boron and Phosphorous.

In this technical picture, the same Applicant has suggested (Italian Patent Application MI2008A000185 - filed on June 16, 2008 - a new "Method for preparing

metallurgic grade silicon having a high purity".

Tests carried out on the method according to the Italian patent application '185 have evidenced some problems.

5 First of all, IT'185 method provides one single type of briquettes, said choice having shown serious problems for handling the charge in view of the excess of production of silicium carbide in the high part of the furnace, of the lack of porosity and of resistivity of
10 the same.

Further, charge descent was described in IT'185 as occurring autonomously.

Furthermore, refractory coating of IT'185 carbo-reduction furnace is made up of aluminous silicon.
15 Preventing risk of contamination with aluminium of the same refractory material.

Finally, in the above method it was not taken into consideration the problem of discharge outlet from furnace basin along a channel with an induced flow,
20 that in the operative phase creates a big problem, only solved by using polluting materials.

A simple nucleation of the silicon carbide was provided in IT'185 by decanting the same within a cold ladle (by ladle it is meant a melt metal containment and/or
25 transportation bin). Said choose cannot be technically supported in view of the reduction of temperature, with the consequent risk of solidification of the metal within the bin.

In view of the above, the Applicant has studied and
30 realised a new method producing high purity metallurgic

grade silicon, particularly for use in photovoltaic field, permitting solving all the above problems.

These and other results are obtained, according to the present invention, by a method suggesting using two
5 kind of briquettes, pieces of quartz and purified wood, so that a carbo-reduction method is realized that can be more easily managed, with higher efficiency and lower costs.

Method according to the invention further provides the
10 use of manual or mechanical arrangements using tools comprised of an/or coated with materials not polluting mixture and the use of procedures for handling mixture within the furnace.

Further, new solution suggested provides that
15 refractory material has a content of silica higher than 95%, thus remarkably limiting risk of pollution due to chemical elements that are present in small amounts within the same refractory materials.

Method, and system, according to the invention can be
20 indicated as an electromagnetic induction method, to heat and possibly melt material present within the hole of the induced ladle channel.

Finally, method according to the present invention provides using a induction heated ladle by using
25 oxidizing gases in order to purify silicon not only with respect to silicium carbide, but also with respect to metallic impurities.

Therefore, it is main object of the present invention that of providing a method for preparing high purity
30 grade silicon to be particularly used in solar cells,

by using a new mixture for carbothermic process.

Another object of the present invention is that of providing a new arrangement for producing briquettes, wherein contamination of raw material is at the minimum level.

Another object of the present invention is that of providing a new system for storing and withdrawing materials from furnace, in order to prevent contamination of raw materials and of liquid silicon.

Still another object of the present invention is a new method to make a SAF type furnace operating, with briquettes and quartz lumps.

It is therefore specific object of the present invention a method for producing high purity metallurgic grade silicon, particularly for use in photovoltaic field, said method being characterized in that it provides the steps of:

- a. selecting high purity raw materials in powder and lump form;
- b. mixing raw material powder;
- c. briquetting mixed material;
- d. realizing batches of briquettes and lump material;
- e. carrying out carbon reduction within an alternate current (AC) submerged arc furnace (SAF);
- f. stocking product within SAF furnace basin;
- g. taking out the product;
- h. carrying out a purification into an inducted ladle;
- i. settling, skimming and filtering carbide and oxide particles.

Preferably, method according to the invention is

carried out within a SAF furnace between 200 KVA and 3000 KVA..

Further features of the method according to the present invention will be evident from the dependent claims.

5 Particularly, steps of the method according to the invention provide

1. selecting quartz powder and lump having a content of boron (B) lower than 0,2 ppm by weight, of phosphorus lower than 0,1 ppm by weight, and of metallic
10 impurities not exceeding 30ppm by weight.

2. selecting carbon black having a boron content lower than 0,1 ppm by weight, of phosphorous lower than 0,1 ppm by weight and of metallic impurities not exceeding 30 ppm by weight.

15 3. selecting an organic binding agent with high purity from the group of saccharine.

4. selecting high purity woodchips, which is relevant for metallurgic conduction within furnace.

5. weighting and mixing quartz powder, carbon black
20 and organic binder in ratio with distillate water.

6. briquetting of mixed material thus producing briquettes approximately with a size of 2,54 cm (1 inch) of more.

7. drying the briquettes up to 180°C in tunnel furnace
25 by combusting methane gas.

8. composition of suitable stoichiometric ratio of all components of the batch, i.e. briquettes plus quartz plus purified woodchips, is carried out.

Tapping process and oxidation refining of silicon melt
30 in inducted ladle.

10. settling and skimming is carried out within inducted ladle.

11. carrying out filtering process.

In each one of said steps, impurity contribution that
5 must be taken into consideration, and of which presence must be prevented, are:

a. contamination of powder material from the metallic
tools in contact with raw material during the mixing,
briquetting, drying and movement of briquettes into
10 SAF.

b. within SAF furnace, contamination during the
stocking operation into the same furnace and during
tapping process from furnace.

c. contamination during the discharge step from
15 inducted ladle by refractory and slags.

d. contamination during the filtering process in
contact with filter and the refractory material of the
same mould.

The present invention will be now described for
20 illustrative, but not limitative, purposes, with particular reference to the figures of the enclosed drawings, wherein:

figure 1 is a schematic section view of refractory
material of a submerged arc furnace;

25 figure is cavity of electrode of furnace of figure;

figure 3 shows a different type of briquette;

figure 4 shows a CA furnace and a tapping apparatus;

figure 5 is a schematic section view of tapping of
inducted ladle;

30 figure 6 is a schematic section view of silicon

filtering support within mould.

Observing now figures of the enclosed drawings, and making reference to the steps of method listed in the above, selection of raw materials is carried out first
5 to prepare high purity silicon to be used in photovoltaic field.

Particularly, as already said, raw material is comprised of quartz, sand, carbon black in the briquettes form, quartz lump and woodchips.

10 Powder of quartz or sand, and carbon black are mixed each other by a high purity organic binder.

All raw materials are chosen and chemically analysed before their use, in order to use in the method according to the invention, materials that are
15 characterized by a suitable degree of purity. As already said, in particular, the phosphorus content must be lower than 0,1ppm by weight (excluding the purified wood chips), the boron content must be lower than 0.1 ppm by weight, and the content of metallic
20 impurities must not exceed 30 ppm by weight.

A selection of over 20 sources of silica has been carried out, from which the quartz that can meet purity goals was obtained.

Maximum values tolerated are indicated in the enclosed
25 table 1.

Silicon powder is characterised by a dimensional distribution of particles between 100 and 300 μm .

TABLE 1

| | | | | | | | | | | | | | | | | |
|---------------|-----------|-----------|-----------|----------|------------|-------------|------------|---------|----------|------------|-------------|------------|----------|-------------|--------------|------------|
| Quartz powder | B <0,1 | P <0,1 | Al <16 | Ca <1 | Cr <0,1 | Cu <0,05 | Fe <0,8 | K <1 | Li <1 | Mg <0,2 | Mn <0,05 | Na <3,5 | Ti <6 | Zr <0,02 | Total <30 | µm <300 |
|---------------|-----------|-----------|-----------|----------|------------|-------------|------------|---------|----------|------------|-------------|------------|----------|-------------|--------------|------------|

5 Furthermore, several carbon sources were examined as potential reductants: carbon black, sugar, activated carbon and purified wood chips. Only carbon black and wood chips purified meet the requirements according to the invention. Particularly, carbon black is

10 characterized by low content of Boron and Phosphorous and by the absence of polycyclic aromatic hydrocarbons and.

Table 2

| | | | | | | | | | | | | | | | |
|--------------|-----------|-----------|----------|----------|-------------|-------------|------------|---------|----------|------------|-------------|------------|----------|------------|-------|
| Carbon Black | B <0,1 | P <0,1 | A <16 | Ca <1 | Cr <0,04 | Cu <0,05 | Fe <0,8 | K <1 | Li <1 | Mg <0,2 | Mn <0,05 | Na <3,5 | Ti <6 | Zr 0,02 | Total |
|--------------|-----------|-----------|----------|----------|-------------|-------------|------------|---------|----------|------------|-------------|------------|----------|------------|-------|

15 Third component is high purity binder agent that is used to form a mechanically strong interface inside the briquettes between the silica powder and particles of carbon black. The binder agent is selected from the group consisting of saccharine (which is the preferred

20 one), starch, cellulose, polyvinyl alcohol and NaSiO₃. As already said, another very important component for production of metallurgical grade silicon according to the invention is purified wood chips, that react as catalyst in chemical reactions thus ensuring a high

25 resistivity and porosity of charge in the furnace. Until now, in the so called "direct metallurgical

route" technique, it was excluded the use of wood chips as component of charge within the furnace, because they have too high concentration of boron and phosphorus. However, it has been surprisingly found that wood have
 5 low contamination and the yield of wood chips is very low, so that during the operation of furnace major quantity is lost.

| | | | | | | | |
|---------------------|------|-------|----|------|------|------------------|--|
| Elements | B | P | Al | Ca | Fe | Fixed carbon (%) | |
| Purified Wood Chips | <0,3 | <3,16 | <9 | <450 | <156 | < 28 | |
| Elements | B | P | Al | Ca | Fe | Fixed carbon (%) | |
| Purified Wood Chips | <0,3 | <3,16 | <9 | <450 | <156 | < 28 | |

(Table 3)

10 Obviously, it is impossible completely avoid the contamination of raw materials, especially quartz powder, during briquetting process, due to the contact with metallic tools of equipments. To avoid said contamination apparatuses (for weighing, mixing,
 15 movement and compacting) they are lined with suitable polymer to avoid abrasive phenomena.

All components of briquetting equipment employed in the method according to the invention are studied to reduce contamination. Preferably, lining will be comprised of
 20 fluorinated material such as ARC BX1, ARC 855, polyvinylidene fluoride (Kynar[®]), or polyethylene, for examples high density polyethylene (HDPE).

In the following steps of the method according to the

invention, quartz powder and carbon black are mixed, and thus subjected to briquetting preparing briquettes with a size of 32,5 x 25,7 x 14,3mm, or larger.

5 Components are mixed so as to comply with the stoichiometry of the process. Distillate water is added in a concentration between 7% and 25% by weight, in function of the type of briquettes. Water is added in order to improve the distribution of the binder agent, to improve solubility of the binder and to reduce the
10 carbon black volume.

Briquettes thus obtained are subjected to a drying treatment at a temperature up to 280°C, in order to give them the wished mechanical strength.

15 It is thus obtained polymerization of binder inside the briquettes, function of the movement speed of furnace, of temperature and of quantity of briquettes. Outside the furnace, it is necessary a cooling of briquettes with air to crystallize the binder agent.

20 By the method according to the invention they are produced two types of briquettes, each one having a different role in the overall chemical process within furnace.

25 At the end of drying process, briquettes (both types) with quartz lump and wood chips in stoichiometry ratio, are transferred in batch into a submerged arc furnace, wherein the carbon reduction process occurs.

The furnace requires large amounts of electrical energy to convert quartz into silicon metal. Said energy is supplied through consumable carbon electrodes. For
30 example, power of a furnace that can produce 2.4 tons

of silicon/day is 2,25MVA, with three electrodes and 2 tapping spouts. The height of the furnace is lower than 2m; the upper section is lower than 2m, with the bottom section of 2m. Diameter of electrode is proportional to electrical power of furnace.

Refractory lining may potentially contribute to presence of impurities. Central part of furnace is comprised of purified graphite to avoid the contamination of silicon metal. Bottom and upper section of the furnace is silica bricks (see figure 1). Material, construction and hole of tapping spout are very important to ease tapping process and minimize contamination of silicon liquid.

Also dimensioning of SAF furnace is very important for properly carrying out operation of the method according to the invention. Electrode diameter must be small enough so as not to create a too large cavity within the furnace. The insulation effect is obtained by a sufficiently large furnace diameter (see figure 2).

Cavity surrounding the electrode has walls comprised of hard sintered material, consisting of partially reacted raw material and silicon carbide. Obviously, unreacted materials are in the external part of the cavity protecting the refractory, thus blocking, or reducing, the contamination from lining.

Graphite electrodes are used to supply the arc at high temperature for the carbothermic reduction process within the SAF. Experience during tests has shown that consumable graphite electrode contributes for about 90 - 120kg/1000kg of silicon metal. Thus, also graphite

electrodes must be purified to reduce contamination.

In method according to the invention, quartz powder has two roles: 1) as component in the briquettes to produce SiC; 2) as additive in carbon black briquettes. In the
5 first case, quartz powder is provided in a suitable ratio with carbon black to produce SiC inside the briquettes. In the second case, quartz powder is added with low content to enhance integrity of briquettes, with the role of nucleation for making SiC inside the
10 second briquettes.

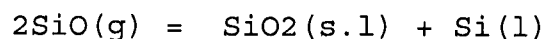
Figure 4 schematically shows features of two types of briquettes.

When carrying out the method according to the invention, it is important that SiC reaction is much faster than
15 that of the known method.

Gas rich of hot SiO rich makes charge mix passing from inner zone to outer zone.

Gas is then cooled and the condensation reaction, with high production of heat is obtained:

20



SiC- forming reaction is potentially more efficient than the reaction with C in capturing SiO from outer zone. The effect of the briquettes charge has a good
25 behaviour in obtaining SiC.

However, efficiency of the process is based on rapidity of the reaction. SiC formation occurs in upper part of the furnace, but at different levels of furnace with respect to standard process with lump materials.

30 For the above reasons, stocking step (distribution and

movement of the material) is very important in method with briquettes charge. Unfortunately, it demonstrates that the crust formation in the upper part of furnace is a rapid process and if stocking process is badly managed, it will be difficult operating the furnace. Stocking equipment must be enough pure to avoid contamination of materials.

Also tapping is a critical operation in the method according to the invention. It has a direct impact on the total performances of the furnace and particularly in contamination of tapped silicon. If tapping of silicon from the furnace fails or is delayed, production must be stopped. Good draining of the molten metal in the furnace is essential to obtain an optimum yield and a minimum contamination (figure 4).

silicon metal is periodically poured within mould and/or in inducted ladle for the purification process. When melt silicon is tapped from furnace at a temperature of 1580°C - 1620°C, melt silicon melt will be saturated with oxygen and carbon, respectively as oxide and SiC. The slag oxidation refining is the basic process used in the inventive method for purification of metal within inducted ladle. Choose of refractory materials having the same features of materials used for SAF furnace for lining inducted ladle lining allows avoiding introduction of impurities into silicon at the molten state.

The first purification step of melt silicon comprises partial removal of carbon and metals.

It is important that settling and skimming are carried

out before pouring silicon within the specific mould.

First step provides removing SiC particles and any other type of heavy slags by settling.

Floating slags are taken away by a slag or dross phase,
5 while precipitate goes in the lower portion of the inducted ladle.

By temperature profile and settling time into inducted ladle, it is possible managing decantation and settling inclusions (see figure 5).

10 Silicon liquid is filtered during pouring (figure 6) from the inducted ladle into special mould. Casting speed and casting temperature, type and dimensions of ceramic filter, pore size distribution and filter porosity are extremely relevant.

15 Ceramic filter 2 is placed inside a filling cone 3. It is very important the selection of mould refractory lining.

Liquid silicon from inducted ladle, after the purification, step is allowed to solidify in air, under
20 an uncontrolled atmosphere, and a very low refining is noticed by directional solidification.

The present invention has been described, for illustrative, but not limitative, purposes with particular reference to its preferred embodiments, but
25 it is to be understood that modifications and changes can be introduced by those skilled in the art, without departing from the relevant scope.

CLAIMS

1. Method for producing high purity metallurgic grade silicon, particularly for use in photovoltaic field,
5 said method being characterized in that it provides the steps of:
- a. selecting high purity raw materials in powder and lump form;
 - b. mixing raw material powder;
 - 10 c. briquetting mixed material;
 - d. realizing batches of briquettes and lump material;
 - e. carrying out carbon reduction within an alternate current (AC) submerged arc furnace (SAF);
 - f. stocking product within SAF furnace basin;
 - 15 g. taking out the product;
 - h. carrying out purification into an inducted ladle;
 - i. settling, skimming and filtering carbide and oxide particles.
2. Method according to claim 1, characterized in that
20 steps e. and f. are carried out within a SAF furnace between 200 KVA and 3000 KVA.
3. Method according to one of the preceding claims, characterized in that said step a. provides selecting quartz powder and lump having a content of boron lower
25 than 0,2 ppm by weight, of phosphorus lower than 0,1 ppm by weight, and of metallic impurities not exceeding 30ppm by weight.
4. Method according to one of the preceding claims, characterized in that said step a. provides selecting
30 carbon black having a boron content lower than 0,1 ppm

by weight, of phosphorous lower than 0,1 ppm by weight and of metallic impurities not exceeding 30 ppm by weight.

5 5. Method according to one of the preceding claims, characterized in that said step a. provides selecting an organic binding agent with high purity from the group of saccharose.

10 6. Method according to one of the preceding claims, characterized in that said step a. provides selecting high purity woodchips.

7. Method according to one of the preceding claims, characterized in that said step b. comprises weighting and mixing quartz powder, carbon black and organic binder in ratio with distillate water.

15 8. Method according to one of the preceding claims, characterized in that said step c. comprises briquetting of mixed material thus producing briquettes approximately with a size of 2,54 cm (1 inch) of more.

20 9. Method according to claim 8, characterised in that said step c. comprises drying the briquettes up to 180°C in tunnel furnace by combusting methane gas.

25 10. Method according to one of the preceding claims, characterized in that a composition of suitable stoichiometric ratio of all components of the batch, i.e. briquettes plus quartz plus purified woodchips, is carried out.

30 11. Method according to one of the preceding claims, characterized in that said step g. is carried out by

tapping process and oxidation refining of silicon melt in inducted ladle.

12. Method according to one of the preceding claims, characterized in that said step i. of settling and
5 skimming is carried out within inducted ladle.

13. System for carrying out a method according to previous claims.

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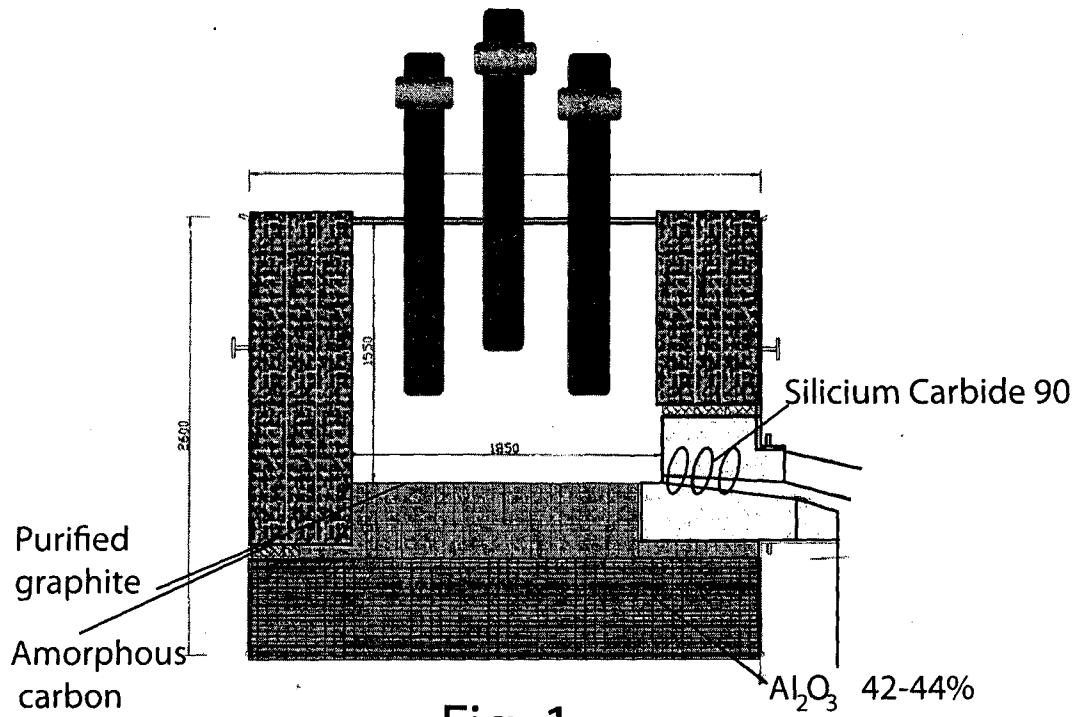


Fig. 1

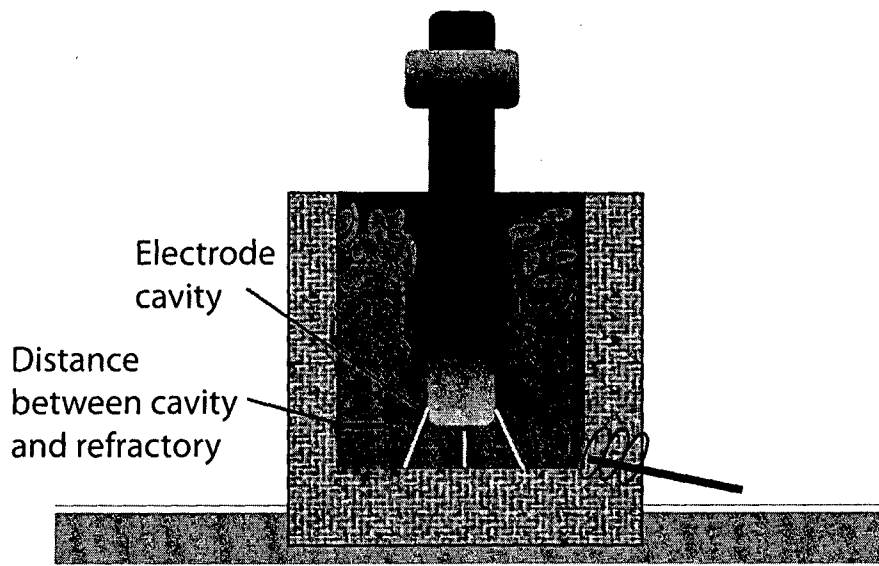


Fig. 2

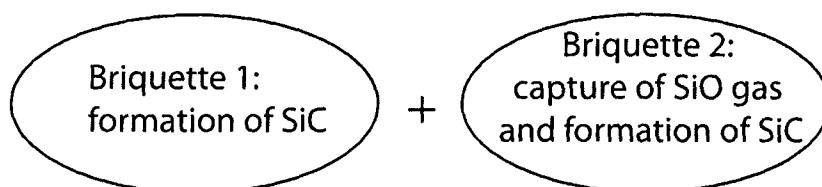


Fig. 3

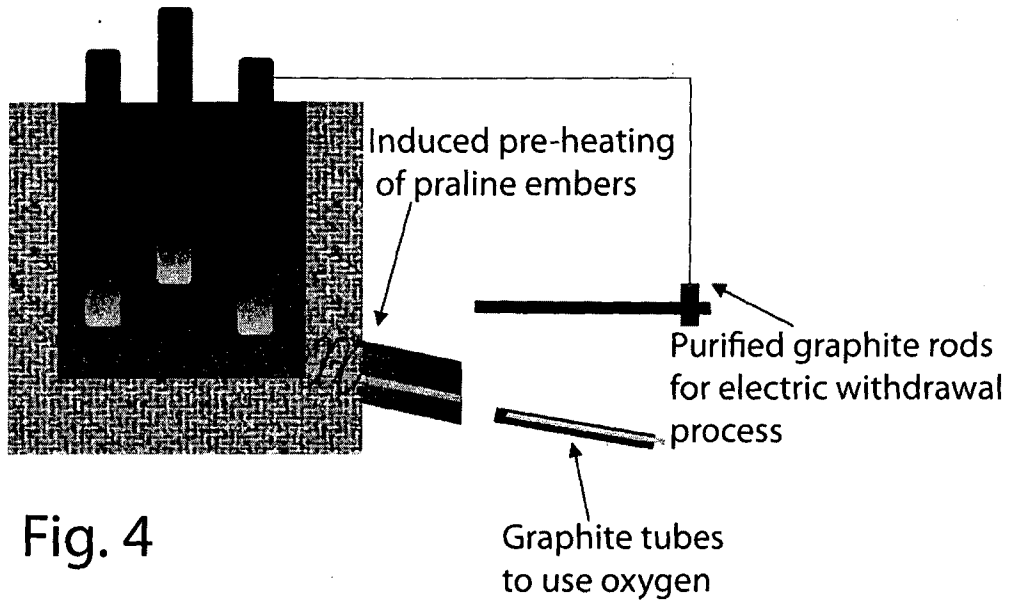


Fig. 4

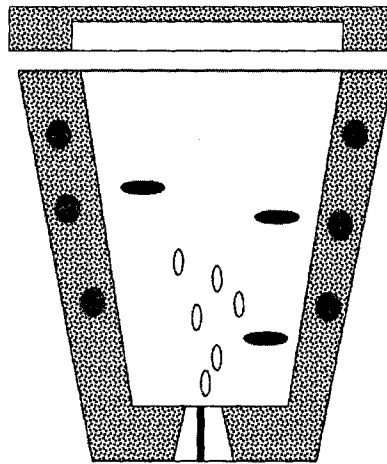


Fig. 5

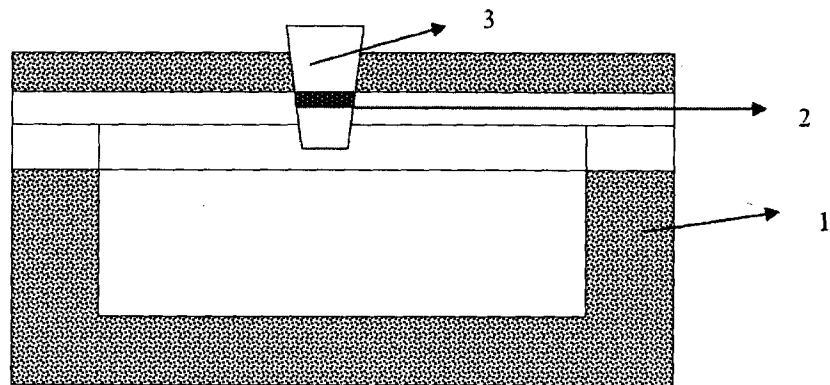


Fig. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/IT2012/000247

| A. CLASSIFICATION OF SUBJECT MATTER INV. C01B33/025 ADD. | | |
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| According to International Patent Classification (IPC) or to both national classification and IPC | | |
| B. FIELDS SEARCHED | | |
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| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | |
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| Y | US 5 782 955 A (SALES MAURICE [FR] ET AL) 21 July 1998 (1998-07-21) example 1 ----- | 1-13 |
| A | WO 2007/106860 A2 (REACTION SCIENCES INC [US]; AMENDOLA STEVEN [US]) 20 September 2007 (2007-09-20) page 7, line 20 - page 10, line 33; examples 7,9 ----- -/-- | 1-13 |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex. | | |
| * Special categories of cited documents : | | |
| "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed | | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family |
| Date of the actual completion of the international search 3 January 2013 | | Date of mailing of the international search report 10/01/2013 |
| Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016 | | Authorized officer Werner, Håkan |

INTERNATIONAL SEARCH REPORT

International application No
PCT/IT2012/000247

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| A | US 7 404 941 B2 (BALUAIS GERARD) 29 July 2008 (2008-07-29) column 3, line 37 - column 4, line 38; examples 1,2 ----- | 1-13 |

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