Title: HIGH TEMPERATURE NON-WETTING REFRACTORY ADDITIVE SYSTEM

Abstract: A formulation produces non-wetting surfaces that are resistant to mechanical damage and to corrosion and penetration by alloys at high temperatures. The non-wetting additive is a combination of (a) calcium hexaaluminate and (b) barium sulfate, strontium carbonate, strontium sulfate, barium carbonate, or combinations of these materials. The non-wetting additive may be used with aggregate, a matrix, and silica fume.
Declarations under Rule 4.17:

— as to the identity of the inventor (Rule 4.17(i))
— as to applicant’s entitlement to apply for and be granted a patent (Rule 4.17(H))

Published:

— as to the applicant’s entitlement to claim the priority of the earlier application (Rule 4.17(Hi))
— of inventorship (Rule 4.17(iv))

— with international search report (Art. 21(3))
High-Temperature Non-Wetting Refractory Additive System

BACKGROUND OF THE INVENTION

(1) Field of the Invention

[0001] The invention relates to a formulation used to produce non-wetting surfaces that are resistant to mechanical damage and to corrosion and penetration by alloys at high temperatures.

(2) Description of the Related Art

[0002] Refractory materials are susceptible to corrosion by molten aluminum and aluminum alloys because of the ability of the molten aluminum to chemically convert oxide refractories to the elemental form. As the refractory is corroded, aluminum oxide (corundum) growth is promoted on the surface of the refractory, which limits service of the refractory and reduces furnace capacity.

[0003] Non-wetting additives are typically added to refractories in this application to improve the corrosion resistance of the refractory to the aluminum. Several non-wetting additives have been found to be effective in preventing corrosion under traditional operating temperatures (<1800°F, <1000°C).

[0004] Recent market demands have led aluminum furnace operators to increase production by increasing the operating temperatures of these furnaces in order to melt the aluminum charge more rapidly. Operating temperatures in the belly band zone have increased in excess of 2000°F (1100°C), increasing the rate of corrosion of the belly band refractory and causing premature wear on the furnace, because non-traditional wetting additives fail at the higher temperatures. A new range of non-wetting additives is
required to maintain corrosion resistance of the refractory at these high operating temperatures, up to and including 2200°F (1200°C).

[0005] Refractory castables require addition of a deflocculant and silica fume in order to develop high strength in the temperature range that is typical of aluminum furnace operations. The high strength is necessary to withstand mechanical wear during operation. The deflocculant aids in dispersion of the silica fume, allowing it to react with other fine matrix components and provide a strong bond system. In the absence of silica fume and a deflocculant, refractory strength does not develop until exposed to temperatures well above 2000°F (1100°C), where conventional ceramic bonding can take place.

[0006] The best current technology for resisting aluminum penetration and corrosion employs the use of barium sulfate as a non-wetting additive. It provides good protection against metal penetration under normal furnace operating temperatures, but it fails after exposure to temperatures exceeding 1800°F (1000°C).

[0007] Another technology that is reported to maintain non-wetting properties after high temperature prefiring is the addition of strontium compounds, such as strontium sulfate or carbonate, in place of barium sulfate. Addition of strontium carbonate in place of barium sulfate has been found to provide better protection against penetration after prefiring to 2192°F (1200°C), but there was still significant penetration.

[0008] Still another technology that is reported to maintain non-wetting properties after high-temperature prefiring employs calcium hexaaluminate aggregate (bonite), which is naturally non-wetting to molten aluminum. However, calcium hexaaluminate is unstable in the presence of silica fume because of liquid formation at elevated temperature which causes sintering and shrinkage of the refractory. Hence refractories employing calcium hexaaluminate aggregate
are very resistant to corrosion by molten alumina, but also have relatively low strength and are susceptible to mechanical wear during furnace cleaning operations.

BRIEF SUMMARY OF THE INVENTION

[0009] The present invention is directed to a high-temperature resistant, non-wetting, strong, mechanical-wear-resistant formulation that may be used as a refractory material to contain molten metals and alloys, such as molten aluminum and molten aluminum alloys.

[0010] One general form of the formulation is a low-cement castable based upon calcined bauxite aggregate, with a high purity alumina matrix and an addition of silica fume to improve strength. In some embodiments of the invention, silica fume may be omitted from the formula. The non-wetting system in the matrix may be a combination of (a) calcium hexaaluminate and (b) barium sulfate, strontium carbonate, strontium sulfate, barium carbonate, or combinations of these materials. Aggregates other than calcined bauxite (e.g., lower purity alumina-silica aggregates), can be combined with or substituted for calcined bauxite aggregates in the coarse particle size fractions without reducing the function of the non-wetting additive mixture. For example, the non-wetting additive system in the matrix may be a combination of 6 wt% calcium hexaaluminate and 3 wt% barium sulfate. The non-wetting system works with the addition of silica fume in quantities of, for example, 0.1 % wt% to 6 wt%, 0.5 wt%, 1 wt%, 2 wt% 3 wt%, 4 wt% or 5 wt% silica fume.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING(S)

[0011] Figure 1 is a photograph of a cross-section of a sample of bauxite-based low cement castable with 6% barium sulfate after an immersion test;
Figure 2 is a photograph of a cross-section of a sample of bauxite-based low cement castable with 6% strontium sulfate after an immersion test;

Figure 3 is a photograph of a cross-section of a sample of bauxite-based low cement castable with 6% barium sulfate with a 1500°F (815°C) prefire after an immersion test;

Figure 4 is a photograph of a cross-section of a sample of bauxite-based low cement castable with 6% barium sulfate with a 2192°F (1200°C) prefire after an immersion test;

Figure 5 is a photograph of a cross-section of a sample of bauxite-based low cement castable with 6% calcium hexaaluminate with a 1500°F (815°C) prefire after an immersion test;

Figure 6 is a photograph of a cross-section of a sample of bauxite-based low cement castable with 6% calcium hexaaluminate with a 2192°F (1200°C) prefire after an immersion test;

Figure 7 is a photograph of a cross-section of a sample of bauxite-based low cement castable with 11% calcium hexaaluminate with a 2192°F (1200°C) prefire after an immersion test;

Figure 8 is a photograph of a cross-section of a sample of bauxite-based low cement castable with 6% calcium hexaaluminate and 2% barium sulfate with a 1500°F (815°C) prefire after an immersion test;

Figure 9 is a photograph of a cross-section of a sample of bauxite-based low cement castable with 6% calcium hexaaluminate and 2% barium sulfate with a 2192°F (1200°C) prefire after an immersion test;
Figure 10 is a photograph of a cross-section of a sample of bauxite-based low cement castable with 6% calcium hexaaluminate and 6% barium sulfate with a 2192°F (1200°C) prefire after an immersion test;

Figure 11 is a photograph of a cross-section of a sample of bauxite-based low cement castable with 6% calcium hexaaluminate and 3% strontium carbonate with a 2192°F (1200°C) prefire after an immersion test;

Figure 12 is a photograph of a cross-section of a sample of bauxite-based low cement castable with 6% calcium hexaaluminate and 3% barium sulfate with a 1562°F (850°C) prefire after an immersion test;

Figure 13 is a photograph of a cross-section of a sample of bauxite-based low cement castable with 6% calcium hexaaluminate plus 3% barium sulfate with a 2192°F (1200°C) prefire after an immersion test;

Figure 14 is a photograph of a cross-section of a sample of bauxite-based low cement castable with 6% calcium hexaaluminate plus 3% barium sulfate with 4% silica fume with a 2192°F (1200°C) prefire after an immersion test; and

Figure 15 is a photograph of a cross-section of a sample of a low cement castable based on Mulcoa 70 aggregate with 6% calcium hexaaluminate and 4% barium sulfate with a 2192°F (1200°C) prefire after an immersion test.

DETAILED DESCRIPTION OF THE INVENTION

The following components may be found in a composition of the invention:

(A) An aggregate
(B) Non-cement matrix

(C) Silica fume

(D) Cement

(E) A non-wetting additive system

Except where otherwise stated, composition percentages are given on a dry weight basis.

Calcined bauxite is a customarily used aggregate. However, other aggregates, such as mullite or mullitic grain (50-70% alumina content), tabular or white fused alumina, or silicon carbide, may be substituted. The total aggregate content may be in the range of 55-80% by weight of the total composition. Lower purity alumina-silica aggregates may be incorporated into the coarse particle size fractions.

MULCOA 70 may be used in the aggregate fraction. MULCOA is a refractory calcine containing at least 68.0 wt% aluminum oxide and at most 1.5 wt% iron (III) oxide. MULCOA 70 contains 68.8 wt% Al₂O₃, 26.8 wt% SiO₂, 2.82% TiO₂, 1.22% Fe₂O₃, 0.06% CaO, 0.07% MgO, 0.07% Na₂O, 0.05% K₂O, and 0.11% P₂O₅.

The non-cement portion of the matrix or binder may include alumina (for example, tabular, white fused, calcined alumina, various reactive aluminas and combinations of these materials) in quantities of, for example, 5-25% by weight.
[0036]  (C) Silica fume may be present in amounts ranging from, and including 1% by weight to, and including, 6% by weight. For example, formulations of the invention may contain 2% by weight silica fume, or 4% by weight silica fume.

[0037]  (D) The cement component can be a calcium aluminate cement. Particular embodiments of the invention may contain 70% alumina cement (such as Secar 71) or an 80% alumina cement (such as Secar 80), or a combination of the two. The total cement content can vary from 1% by weight to 15% by weight; or from 2 wt% to 6 wt%.

[0038]  (E) One component of the non-wetting additive system, designated Component A, may be dense calcium hexaaluminate (Bonite, as supplied by Almatis). The calcium hexaaluminate content of the formulation may be in the range 3-15% by weight, with a particle size less than 0.5 mm. Unless otherwise stated, particle size is defined by the largest particle diameter within the distribution, or by the maximum and minimum particle diameter within the distribution. A formulation may contain 5-8% calcium hexaaluminate by weight, and have a particle size less than 45 microns (0.045 mm). The formulation may contain 4-10 wt% calcium hexaaluminate, or 6% by weight calcium hexaaluminate.

[0039]  Other compounds that can serve as components of the non-wetting additive system, designated component(s) B, are barium sulfate, barium carbonate, strontium sulfate, and strontium carbonate. The non-calcium-hexaaluminate component(s) of the non-wetting additive system may constitute 0.5-6% of the formulation by weight, or may constitute 1-4% of the formulation by weight.

[0040]  In certain embodiments of the formulation of the invention, the percentage by weight of additive component A (calcium hexaaluminate) is greater than the percentage by weight of additive component B (barium sulfate,
strontium sulfate, strontium carbonate and combinations of these compounds). Also within the scope of the invention are formulations in which additive component B has a weight within the range of 10%-99% or 10-80% by weight of additive component A. Also within the scope of the invention are formulations in which additive component B has a weight within the range of 40-70% by weight of additive component A.

[0041] The formulation can also contain additives such as deflocculants or a dispersant. Sodium hexametaphosphate or sodium polycarboxylate may be added as dispersants; citric acid or boric acid may be added as set retarders; burnout fibers may also be present to aid in dryout.

[0042] Certain embodiments of the invention may be described as a low cement castable, which is defined here as a castable refractory which contains hydraulic-setting calcium aluminate cement, with a total lime (CaO) content between 1.0 and 2.5% on a calcined basis. Relative to a conventional castable containing >2.5% lime, the cement is partially replaced with reactive alumina, silica fume, and a deflocculant or dispersant (to reduce water demand).

[0043] Calcium aluminate cement is defined here as a high purity hydraulic cement containing CaO · Al2O3, with lesser amounts of other calcium aluminate phases. The nominal composition of a 70% alumina product (such as Secar 71) is 30% CaO and 70% Al2O3. The nominal composition of an 80% alumina product (such as Secar 80; also contains free alumina) is 19% CaO and 81% Al2O3. Either will react with water to harden by forming hydrates as a binder phase.

[0044] Calcium hexaaluminate is defined here as a calcium aluminate phase formed by sintering, consisting primarily of CaO · 6Al2O3 (CA6) with minor
amounts of free Al2O3. CA6 is essentially non-hydraulic (does not react with water). The composition is approximately 7-9% CaO and 90-92% Al2O3.

[0045] Ultralow cement castable is defined here as a castable similar to a low cement castable, with a total lime (CaO) content between 0.2 and 1.0% on a calcined basis.

[0046] Silica fume is defined here as a fine-grained, amorphous, thin-walled, and very high surface area silica. It is typically produced as a by-product of production of elemental silicon or ferrosilicon alloys by an electric arc furnace. High purity grades of silica fume are also produced during production of zirconia (ZrO2) from zircon (ZrSiO-t), and during manufacture of fiber optic cable.

[0047] Figures 1-14 show cross-sections of castable formulation samples subjected to laboratory immersion tests at 1562°F (850°C) in molten Al-5% Mg alloy. The test duration is 4 days, and the samples are prefired either to 1500°F (815°C) or to 2192°F (1200°C).

[0048] ALUGARD® 80T is a low cement vibration castable based on calcined bauxite and alumina aggregates reinforced with silicon carbide. It contains 65.4% calcined bauxite, 5.0% silicon carbide, 12.5% tabular alumina, 5.0% reactive alumina, 4.0% Secar 71 cement, 2.0% Microsilica 971 , 6.0% barium sulfate, and 0.1% dispersant. Test results for a bauxite-based low cement based upon ALUGARD® 80T are depicted in Figures 1-15.

[0049] Figures 1 and 2 show corrosion in bauxite-based low cement castable after an Al-5%Mg immersion test at 1562°F (850°C), comparing differences in corrosion between 6% barium sulfate addition (Figure 1) and 6% strontium sulfate addition (Figure 2). Both samples contained 2% silica fume. Both samples were prefired to 2192°F (1200°C). Corrosion by the alloy is indicated by the dark discoloration at the surface of each sample in Figures 1 and 2 (arrows).
Metal penetration of 2-5 mm is seen in the sample shown in Figure 1. Metal penetration of 0-2 mm is seen in the sample shown in Figure 2.

[0050] Figures 3 and 4 show test results obtained for bauxite-based low cement castable with 6% barium sulfate after an Al-5%Mg immersion test at 1562°F (850°C). Both samples contained 2% silica fume. No corrosion was found after a 1500°F (815°C) prefire (Figure 3) but some penetration occurred in an immersion test conducted at 2192°F (1200°C) (Figure 4). No metal penetration is visible in Figure 3. Metal penetration of 1-3 mm is seen in the sample shown in Figure 4.

[0051] Figures 5 and 6 show test results obtained for bauxite-based low cement castable containing 6% calcium hexaaluminate after an Al-5%Mg immersion test at 1562°F (850°C). Both samples contained 2% silica fume. Corrosion occurred after both the 1500°F (815°C) prefire (Figure 5) and after the 2192°F (1200°C) prefire (Figure 6). Metal penetration of 2-3 mm is visible in the sample shown in Figure 5. Metal penetration of 1 mm is seen in the sample shown in Figure 6.

[0052] Figure 7 shows test results obtained for bauxite-based low cement castable containing a total of 11% calcium hexaaluminate after an Al-5%Mg immersion test at 1562°F (850°C). This sample contained 2% silica fume. This sample exhibited metal penetration of 0-2 mm after prefire to 2192°F (1200°C).

[0053] Figures 8 and 9 show test results obtained for bauxite-based low cement castable containing 6% calcium hexaaluminate plus 2% barium sulfate after an Al-5%Mg immersion test at 1562°F (850°C). Both samples contained 2% silica fume. No corrosion occurred after prefire to 1500°F (815°C) (Figure 8). No corrosion occurred after prefire to 2192°F (1200°C) (Figure 9). No metal penetration in visible in the samples shown in Figures 8 and 9.
Figure 10 shows test results obtained for bauxite-based low cement castable with 6% calcium hexaaluminate plus 6% bahum sulfate. This sample contained 2% silica fume. Corrosion occurred after prefiring to 2192°F (1200°C). Metal penetration of 2-5 mm is visible in the sample shown in Figure 10.

Figure 11 shows test results obtained for bauxite-based low cement castable with 6% calcium hexaaluminate plus 3% strontium carbonate after an Al-5%Mg immersion test at 1562°F (850°C). This sample contained 2% silica fume. No metal penetration occurred after prefiring to 2192°F (1200°C).

Figure 12 shows test results obtained for bauxite-based low cement castable with 6% calcium hexaaluminate plus 3% barium sulfate after an Al-5%Mg immersion test at 1562°F (850°C). This sample contained 2% silica fume. No metal penetration occurred after prefiring to 2192°F (1200°C).

Figure 13 shows test results obtained for bauxite-based low cement castable with 6% calcium hexaaluminate plus 3% barium sulfate with 2% silica fume after an Al-5%Mg immersion test at 1562°F (850°C). No metal penetration occurred after prefiring to 2192°F (1200°C).

Figure 14 shows test results obtained for bauxite-based low cement castable with 6% calcium hexaaluminate plus 3% barium sulfate with 4% silica fume after an Al-5%Mg immersion test at 1562°F (850°C). No metal penetration occurred after prefiring to 2192°F (1200°C).

Figure 15 shows test results obtained for a low cement castable based on Mulcoa 70 aggregate, with 6% calcium hexaaluminate plus 4% barium sulfate after an Al-5% Mg immersion test at 1562°F (850°C). This sample contained 2% silica fume. No metal penetration occurred after prefiring to 2192°F (1200°C).
The tests depicted in Figures 11 and 12 show that the addition of calcium hexaaluminate in combination with strontium carbonate yielded the same improvements in high-temperature non-wetting properties as did addition of calcium hexaaluminate in combination with barium sulfate.

The tests depicted in Figures 13 and 14 show that an increase in the silica fume content of the base mix with the combined additive system from 2% to 4% had no negative effect on the non-wetting properties after high temperature prefiring.

The test depicted in Figure 15 shows that the use of a lower purity alumina-silica aggregate in place of calcined bauxite had no negative effect on the non-wetting properties after high temperature prefiring.

Figures 8 and 9 relate to a bauxite-based low cement castable containing 6% calcium hexaaluminate plus 2% barium sulfate. The formulation contains 4.0% calcined bauxite 3/8” x 3 mesh, 22.0% calcined bauxite 3 x 6 mesh, 19.4% calcined bauxite 6 x 16 mesh, 16.0% calcined bauxite -16 mesh, 5.0% silicon carbide -100 mesh, 6.5% Tabular alumina -28 mesh, 7.6% reactive alumina A20SG, 4.6% reactive alumina A152SG, 0.8% reactive alumina RG4000, 4.0% Secar 71 cement, 2.0% barium sulfate, 6.0% Bonite 45MY, 2.0% silica fume and 0.1 % dispersant. In general terms, the formulation contains 61.4% calcined bauxite aggregate, 5.0% silicon carbide -100 mesh, 6.5% tabular alumina -28 mesh, 13.0% reactive alumina, 4.0% Secar 71 cement, 2.0% barium sulfate, 6.0% Bonite 45MY, 2.0% silica fume, and 0.1 % dispersant.

Figure 15 relates to a low cement castable formulation, based on Mulcoa 70, containing 6% calcium hexaaluminate plus 4% barium sulfate. The formulation contains 32.4% Mulcoa 70 3 x 8 mesh, 15.0% Mulcoa 70 8 x 20 mesh, 12.0% Mulcoa 70 -20 mesh, 11.0% tabular alumina -28 mesh, 8.0% tabular alumina -325 mesh, 3.5% reactive alumina A152SG, 2.0% reactive
alumina RG4000, 4.0% Secar 71 cement, 4.0% barium sulfate, 6.0% Bonite 45MY, 2.0% silica fume and 0.1% dispersant. In general terms, the formulation contains 59.4% Mulcoa 70 aggregate, 19.0% tabular alumina, 5.5% reactive alumina, 4.0% Secar 71 cement, 4.0% barium sulfate, 6.0% Bonite 45MY, 2.0% silica fume and 0.1% dispersant.

[0065] A castable composition of the present invention may therefore comprise aggregate, non-cement matrix, cement, an additive component A comprising or consisting of calcium hexaaluminate, and an additive component B comprising or consisting of a substance selected from the group consisting of barium sulfate, strontium sulfate, strontium carbonate, barium carbonate and combinations of these compounds, wherein the weight percentage of additive component b in the composition is less than the weight percentage of additive component A in the composition. This composition may further comprise silica fume, present in an amount, for example, in the range from 1 wt% to 6 wt% of the total composition. The aggregate may comprise calcined bauxite, mullite, mullitic grain, tabular alumina, white fused alumina, alumina-silica aggregates, or silicon carbide. The aggregate may be present in an amount in the range from 55 wt% to 80 wt% of the total composition. The cement may comprise a material selected from the group consisting of 70 wt% alumina cement, 80 wt% alumina cement, and a combination of 70 wt% alumina cement and 80 wt% alumina cement. The cement may be present in an amount in the range from 1 wt% to 15 wt% of the total composition. Calcium hexaaluminate may be present in an amount in the range from 3 wt% to 15 wt% of the total composition, or in the range from 5 wt% to 8 wt% of the total composition. A substance selected from barium sulfate, strontium sulfate, strontium carbonate, barium carbonate and combinations of these compounds may be present in an amount in the range from 0.5 wt% to 6 wt% of the total composition, or in the range from 1 wt% to 4 wt% of the total composition, and may be present in an amount in the range from 10 wt% to 80 wt% of the weight of calcium hexaaluminate present, or an amount in the range
from 40 wt% to 70 wt% of the weight of calcium hexaaluminate present. The cement in the composition may be calcium aluminate cement.

[0066] Numerous modifications and variations of the present invention are possible. It is, therefore, to be understood that within the scope of the following claims, the invention may be practiced otherwise than as specifically described.
CLAIMS

I claim:

1. (Original) A castable composition comprising:
   Aggregate;
   Non-cement matrix;
   Cement;
   An additive component A comprising calcium hexaaluminate; and
   An additive component B comprising a substance selected from the group
   consisting of barium sulfate, strontium sulfate, strontium carbonate, barium
   carbonate and combinations of these compounds;
   wherein the weight percentage of additive component B in the composition is
   less than the weight percentage of additive component A in the composition.

2. (Original) The composition of claim 1, further comprising silica fume.

3. (Original) The composition of claim 2, wherein silica fume is present in an
   amount in the range from 1 wt% to 6 wt% of the total composition.

4. (Original) The composition of claim 1, wherein the aggregate comprises
   calcined bauxite.

5. (Original) The composition of claim 1, wherein the aggregate comprises a
   material selected from the group consisting of mullite, mullitic grain, tabular
   alumina, white fused alumina, alumina-silica aggregates, and silicon carbide.

6. (Original) The composition of claim 1, wherein aggregate is present in an
   amount in the range from 55 wt% to 80 wt% of the total composition.
7. (Original) The composition of claim 1, wherein the cement comprises a material selected from the group consisting of 70 wt% alumina cement, 80 wt% alumina cement, and a combination of 70 wt% alumina cement and 80 wt% alumina cement.

8. (Original) The composition of claim 1, wherein the cement is present in an amount in the range from 1 wt% to 15 wt% of the total composition.

9. (Original) The composition of claim 1, comprising calcium hexaaluminate in an amount in the range from 3 wt% to 15 wt% of the total composition.

10. (Original) The composition of claim 1, comprising calcium hexaaluminate in an amount in the range from 5 wt% to 8 wt% of the total composition.

11. (Original) The composition of claim 1, comprising additive component B in an amount in the range from 0.5 wt% to 6 wt% of the total composition.

12. (Original) The composition of claim 1, comprising additive component B in an amount in the range from 1 wt% to 4 wt% of the total composition.

13. (Original) The composition of claim 1, wherein the additive component B is present in an amount in the range from 10 wt% to 80 wt% of the weight of component A.

13. (Original) The composition of claim 1, wherein the additive component B is present in an amount in the range from 40 wt% to 70 wt% of the weight of component A.

14. (Original) The composition of claim 1, wherein the cement comprises calcium aluminate cement.
15. (Original) The composition of claim 14, wherein the cement comprises calcium aluminate cement having a total lime content in the range from 1.0 wt% to 2.5 wt% on a calcined basis of the weight of the cement.
Prior Art

Fig. 1
Prior Art

Fig. 2
Prior Art

Fig. 3
Prior Art

Fig. 4
Prior Art

Fig. 5
Prior Art

Fig. 6
Prior Art

Fig. 7
Fig. 11
INTERNATIONAL SEARCH REPORT

International application No. PCT/US2013/034274

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C04B 35/10 (2013.01)
USPC - 501/127

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) - B05D 1/12;7/22;B29C 39/02;C04B 7/32;14/04.28;02/02.28/06.33/02.35/00.35/01.35/03.35/10.35/14.35/16.35/18.35/66 (2013.01)
USPC - 106/38; 692, 817; 264/30, 31, 71, 334; 427/180, 181; 501/1, 87, 88, 89, 94, 107, 120, 124, 126, 127, 128, 133

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
CPC - B05D 1/12;7/22;B29C 39/02;C04B 7/32.14/04.28/02.28/06.33/02.35/00.35/01.35/03.35/10.35/14.35/16.35/18.35/66 (2013.01)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase, Google Patents, Google, ProQuest

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tbody>
<tr>
<td>Y</td>
<td>US 7,368,010 B2 (MCGOWAN) 06 May 2008 (06.05.2008) entire document</td>
<td>1-15</td>
</tr>
<tr>
<td>A</td>
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[ ] Further documents are listed in the continuation of Box C.

Special categories of cited documents:
“A” document defining the general state of the art which is not considered to be of particular relevance
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“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
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Date of the actual completion of the international search
23 May 2013

Date of mailing of the international search report
10 JUN 2013

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Form PCT/ISA/210 (second sheet) (July 2009)