Title: MONOLITHIC CASTABLE REFRACTORY

Abstract: A monolithic refractory material is provided. The refractory material comprises refractory aggregate and a binder, the binder comprising petroleum pitch and carbon black. Advantageously, the binder may further comprise graphite.
Monolithic Castable Refractory.

Specification.

Cross-reference to related applications.

[0001] This application claims the benefit under 35 U.S.C. §120 of the filing date of U.S. Provisional Application No. 60/530,831 filed December 18, 2003.

Field of the invention.

[0002] The present invention relates to monolithic refractory materials, and in particular a low-toxicity castable refractory having excellent corrosion resistance and spalling resistance.

Description of the related art.

[0003] In the processing and handling of molten metals, monolithic refractory materials are often used as linings for vessels such as ladles that transport the molten metal throughout the process. In order to help prevent corrosion and spalling of the refractory, carbon-bonded materials are typically used. The monolithic refractories generally comprise a refractory aggregate and a binder. Various binders have been used throughout the years, including binders utilizing coal tar pitch.

[0004] For example, U.S. Patent No. 4,184,883 discloses a pitch-bonded refractory that utilizes a cure accelerator such as calcium nitrate to accelerate the rate of increase of the softening point of the pitch in order to decrease the amount of spalling that occurs during burn-in and the early heats of the refractory. U.S. Patent No. 5,866,490 utilizes a pitch as a binder, the pitch having a high percentage of fixed carbon, as well as a high softening point. This is done in an effort to increase carbon bonding in order to prevent corrosion and spalling of the refractory. To this end, this reference also teaches the use of a phenol resin or a carbon fiber in addition to the pitch binder.

[0005] A common problem with the use of coal tar pitch is that it is a very toxic material, and when the material is heated, the toxic vapors can be released into the atmosphere. This requires the use of expensive safety equipment for those people working near the refractory material, as well as environmental safeguards to prevent the release of the toxic material into the air. Further, coal tar pitch is a known carcinogen, and therefore elimination of the material is generally desirable.

[0006] It is therefore desirable to produce a monolithic refractory material having good corrosion resistance and spalling resistance, but without the use of a coal tar pitch-based binder.

Summary of the invention.

[0007] In order to achieve the listed objectives, monolithic refractory material is provided in accordance with the present invention. The refractory material comprises refractory aggregate and a binder, the binder comprising petroleum pitch and carbon black. Advantageously, the binder may further comprise graphite.

[0008] Also provided in accordance with the present invention is a monolithic refractory material comprising a refractory aggregate and a binder, characterized in that the binder comprises
carbon black and petroleum pitch. The refractory aggregate comprises brown fused alumina and silicon carbide, the petroleum pitch has a mass particle size wherein 50 to 70% is smaller than 75 micrometers and has a carbon yield of about 45% to about 55%. The carbon black has an average particle size of about 200 nanometers to about 400 nanometers and an ash content of less than about 0.25% of the mass of the carbon black.

Further provided in accordance with the present invention is a monolithic refractory material comprising a refractory aggregate and a binder, characterized in that the binder comprises carbon black and petroleum pitch, the petroleum pitch has a mass particle size wherein 50 to 70% is smaller than 75 micrometers and has a carbon yield of about 45% to about 55%, and the carbon black has an average particle size of about 200 nanometers to about 400 nanometers and an ash content of less than about 0.25% of the mass of the carbon black.

Brief description of the several drawings.

FIG. 1 is a graphical comparison of carbon retention with refractories utilizing coal tar pitch and petroleum pitch, with and without added carbon black.

Detailed description of the preferred embodiments.

Except where otherwise noted, all percentages listed below, including in the claims, are on a weight basis and are a percentage of the monolithic refractory. The present invention is a monolithic refractory comprising a refractory aggregate and a binder, the binder comprising petroleum pitch and carbon black. The refractory may further comprise a dispersant. The refractory comprises about 1.0 to about 3.0% petroleum pitch, about 0.5% to about 1.5% carbon black, with the balance being a refractory aggregate. The refractory may also contain graphite to further increase the carbon content. Preferably, the refractory further comprises about 0.01% to about 0.15% of a dispersant.

The refractory aggregate used in accordance with the present invention may be any one of the refractory aggregates known by those in the art to be suitable for the present applications. Suitable refractory aggregates include, for example, brown fused alumina, bauxite, tabular alumina, silicon carbide, calcined bauxitic kaolins (such as Mulcoa 70, Mulcoa 60, and Mulcoa 47), andalusite, calcined fireclay, and combinations thereof. The refractory aggregate is present in amounts that depend on the amount of binder desired. However, the refractory aggregate will make up most of the material present in the monolithic refractory. The particle size for the aggregate is based on the principles of optimum particle packing commonly used to formulate ultra low cement castables. The maximum aggregate particle size is about 9.5 millimeters, with a minimum size of about 45 microns.

The petroleum pitch used in accordance with the present invention accounts for about 1.0% to about 3.0% of the monolithic refractory. The petroleum pitch is preferably characterized by a mass particle size wherein 50-75%, typically 70% is smaller than about 75 micrometers. The petroleum pitch is also characterized by a carbon yield. Carbon yield is defined as the percent by weight of the pitch that is left as a carbonized residue after the pitch is heated under non-oxidizing conditions to about 800-1000°C to drive off volatiles. The petroleum pitches used
may have a carbon yield of about 45% to about 55%. Preferably, the petroleum pitch is characterized by a carbon yield of about 49%.

[0014] The carbon black used in accordance with the present invention accounts for about 0.5% to about 1.5% of the monolithic refractory. The carbon black has an average particle size of about 200 nanometers to about 400 nanometers. Preferably, the carbon black has an average particle size of about 300 nanometers. The carbon black is also characterized by an ash content of less than about 0.25% of the mass of the carbon black. It should be noted that as the amount of carbon black used increases, the amount of water that must be included also increases. This may limit the amount of carbon black that can be incorporated into the monolithic refractory. Graphite may be added to increase the carbon level beyond the limit for carbon black alone.

[0015] The monolithic refractory may further comprise a dispersant. If used, the dispersant accounts for about 0.01% to about 0.15% of the monolithic refractory. Suitable dispersants include sodium lignosulfonate, other lignosulfonate salts (Ca, K, etc.), or Sodium, potassium and Calcium salts of condensed naphthalene sulfonic acids.

Example

[0016] A wet spraysable refractory was produced comprising brown fused alumina, silicon carbide, calcium aluminate cement, petroleum pitch, carbon black and a sodium lignosulfonate dispersant powder. The petroleum pitch was a pitch commercially available under the name "Trolumen" from Smith-Facing of Cleveland, OH, having 70% finer than 75 micrometers and 49% carbon yield. The pitch made up 2.33% of the refractory. The carbon black made up 1% of the refractory and is available from Asbury Carbon of Asbury, NJ, and sold as #5991. The sodium lignosulfonate dispersant powder made up 0.05% of the refractory and is available from Lignotech of Rothschild, WI under the name "Ultrazine NA." The balance of the refractory was the aggregate (brown fused alumina, silicon carbide and calcium aluminate cement). The refractory was subjected to 1500°F for 5 hours, along with a similar refractory containing coal tar pitch instead of petroleum pitch, a similar refractory without carbon black, and a refractory without carbon black and with coal tar pitch instead of petroleum pitch, in the same amount. The carbon retention was measured for all 4 refractories. As illustrated in Fig. 1, the % carbon retention for the two refractories with petroleum pitch, while lower, was acceptably similar to the two refractories using coal tar pitch. Further, the refractories utilizing the carbon black had higher carbon retention than the two without the carbon black.

[0017] Obviously, 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.

We claim:

1. A monolithic refractory material comprising a refractory aggregate and a binder, characterized in that the binder comprises carbon black and petroleum pitch.

2. The monolithic refractory material of claim 1, wherein the refractory aggregate is selected from the group consisting of brown fused alumina, bauxite, tabular alumina, silicon carbide, calcined bauxitic kaolins, andalusite, and calcined fireclay and combinations thereof.

3. The monolithic refractory material of claims 1 to 2, characterized in that the refractory aggregate has a maximum particle size of about 45 microns to about 9.5 millimeters.

4. The monolithic refractory material of claims 1 to 3, characterized in that the refractory material comprises about 1.0% to about 3.0% petroleum pitch.

5. The monolithic refractory material of claims 1 to 3, characterized in that the refractory material comprises about 2.3% petroleum pitch.

6. The monolithic refractory material of claims 1 to 3, characterized in that the refractory material comprises about 0.5% to about 1.5% carbon black.

7. The monolithic refractory material of claims 1 to 3, characterized in that the refractory material comprises about 1.0% carbon black.

8. The monolithic refractory material of claims 1 to 7, further comprising a dispersant.

9. The monolithic refractory material of claim 8, characterized in that the dispersant is selected from the group consisting of sodium lignosulfonate, calcium lignosulfonate salt, potassium lignosulfonate salt, and sodium, potassium and calcium salts of condensed naphthalene sulfonic acids.

10. The monolithic refractory material of claims 8 to 9, characterized in that the dispersant comprises sodium lignosulfonate.

11. The monolithic refractory material of claims 8 to 10, characterized in that the refractory material comprises about 0.01% to about 0.15% of a dispersant.

12. The monolithic refractory material of claims 8 to 10, characterized in that the refractory material comprises about 0.05% of a dispersant.

13. The monolithic refractory material of claims 1 to 12, characterized in that the carbon black has an average particle size of about 200 nanometers to about 400 nanometers.

14. The monolithic refractory material of claims 1 to 12 characterized in that the carbon black has an average particle size of about 300 nanometers.

15. The monolithic refractory material of claims 1 to 14, characterized in that the carbon black has an ash content of less than about 0.25% of the mass of the carbon black.
16. The monolithic refractory material of claims 1 to 15, characterized in that the petroleum pitch has a mass particle size wherein about 50 to about 75% is smaller than about 75 micrometers.

17. The monolithic refractory material of claims 1 to 16, characterized in that the binder further comprises graphite.

18. A monolithic refractory material comprising a refractory aggregate and a binder, characterized in that the binder comprises carbon black and petroleum pitch, the refractory aggregate comprises brown fused alumina and silicon carbide, the petroleum pitch has a mass particle size wherein 50 to 70% is smaller than 75 micrometers and has a carbon yield of about 45% to about 55%, and the carbon black has an average particle size of about 200 nanometers to about 400 nanometers and an ash content of less than about 0.25% of the mass of the carbon black.

19. The monolithic refractory material of claim 18, characterized in that the refractory aggregate has a maximum particle size of about 45 microns to about 9.5 millimeters.

20. The monolithic refractory material of claim 18, wherein the petroleum pitch has a carbon yield of about 49%.

21. The monolithic refractory material of claims 18 to 20, further comprising a dispersant.

22. The monolithic refractory material of claim 21, characterized in that the dispersant is selected from the group consisting of sodium lignosulfonate, calcium lignosulfonate salt, potassium lignosulfonate salt, and sodium, potassium and calcium salts of condensed naphthalene sulfo acids.

23. The monolithic refractory material of claims 21 to 22, characterized in that the dispersant comprises sodium lignosulfonate.

24. The monolithic refractory material of claims 21 to 23, characterized in that the refractory material comprises about 0.01% to about 0.15% of a dispersant.

25. The monolithic refractory material of claims 21 to 23, characterized in that the refractory material comprises about 0.05% of a dispersant.

26. The monolithic refractory material of claims 18 to 25, characterized in that the binder further comprises graphite.

27. A monolithic refractory material comprising a refractory aggregate and a binder, characterized in that the binder comprises carbon black and petroleum pitch, the petroleum pitch has a mass particle size wherein 50 to 70% is smaller than 75 micrometers and has a carbon yield of about 45% to about 55%, and the carbon black has an average particle size of about 200 nanometers to about 400 nanometers and an ash content of less than about 0.25% of the mass of the carbon black.
28. The monolithic refractory material of claim 27, wherein the refractory aggregate is selected from the group consisting of brown fused alumina, bauxite, tabular alumina, silicon carbide, calcined bauxitic kaolins, andalusite, calcium aluminate cement and calcined fireclay and combinations thereof.

29. The monolithic refractory material of claims 27 to 28, characterized in that the refractory aggregate has a maximum particle size of about 45 microns to about 9.5 millimeters.

30. The monolithic refractory material of claims 27 to 28, wherein the petroleum pitch has a carbon yield of about 49%.

31. The monolithic refractory material of claims 27 to 30, further comprising a dispersant.

32. The monolithic refractory material of claim 31, characterized in that the dispersant is selected from the group consisting of sodium lignosulfonate, calcium lignosulfonate salt, potassium lignosulfonate salt, and sodium, potassium and calcium salts of condensed naphthalene sulfonic acids.

33. The monolithic refractory material of claims 31 to 32, characterized in that the dispersant comprises sodium lignosulfonate.

34. The monolithic refractory material of claims 31 to 33, characterized in that the refractory material comprises about 0.01% to about 0.15% of a dispersant.

35. The monolithic refractory material of claims 31 to 34, characterized in that the refractory material comprises about 0.05% of a dispersant.

36. The monolithic refractory material of claims 27 to 35, characterized in that the binder further comprises graphite.
Figure 1

% Carbon Retained after 1500°F/5 Hours in Air

- CTP: Coal Tar Pitch
- PP: Petroleum Pitch

% Carbon Retained

With added carbon black

Without Carbon Black
### INTERNATIONAL SEARCH REPORT

**International application No.**
PCT/US04/42861

#### A. CLASSIFICATION OF SUBJECT MATTER
- **IPC(7)**: C04B 35/10

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)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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

#### 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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</thead>
<tbody>
<tr>
<td>X</td>
<td>US 4,605,635 A (ZENBUTSU et al.) 12 August 1986 (12.08.1986), column 2 lines 7-20.</td>
<td>1-36</td>
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<td></td>
<td>US 4,521,357 A (KERNION et al.) 04 June 1985 (04.06.1985), column 2, line 33 and column 4, lines 10-11.</td>
<td>1-36</td>
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<tr>
<td>X</td>
<td>US 4,184,883 A (HUGHES et al.) 22 January 1980 (22.01.1980), see abstract and Example 1, line 54 in column 2.</td>
<td>1-36</td>
</tr>
<tr>
<td>X</td>
<td>US 4,071,593 A (FARRINGTON et al.) 31 January 1978 (31.01.1978), column 5, lines 35-40; column 5, line 65; and column 7, line 19.</td>
<td>1-36</td>
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</tbody>
</table>

Further documents are listed in the continuation of Box C.

See patent family annex.

- **"A"** document defining the general state of the art which is not considered to be of particular relevance.
- **"E"** earlier application or patent published on or after the international filing date.
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