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(54) Title: HIGH DURABILITY REFRACTORY COMPOSITION

(57) Abstract: A high temperature hot strength magnesia-based refractory composition having high durability at elevated temperatures wherein a sulfamic acid in combination with an independent calcia source is added to magnesia-based refractory material. The invention also provides for a refractory gunning composition for use in the production or repair of metallurgical furnace linings.

High Durability Refractory Composition

FIELD OF THE INVENTION

5 This invention relates to refractory compositions. More particularly, this invention relates to magnesia-based refractory compositions useful in maintenance gunning of metallurgical vessels, in ramming mixtures, in castable refractories, and in basic refractory brick. Most particularly this invention relates to refractory compositions, especially gunning mixtures, which are chemically adhered by means of a binder system having high temperature hot strength.

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BACKGROUND OF THE INVENTION

 In the production of steel, the refractory brick linings of conventional process vessels generally wear unevenly due to hot spots, slag attack, or other operating parameters. In the ongoing attempt to minimize production costs, a major concern of steel makers is the wearing of the refractory brick lining of the vessel and the resultant consumption of refractory composition to replace the lining. In order to extend the useful life of such linings, it has become acceptable practice to repair excessively worn areas between heats by means of gunning granular refractory compositions onto the brick surfaces. For example, a dry mixture including granular refractory grain is pneumatically delivered to a nozzle of a spray gun where it is mixed with water, resulting in a bonded composition that is projected against the irregularly worn surface, thereby filling in or patching the unevenly worn refractory lining with the refractory composition. Under the usual

circumstances, gunning is initiated within minutes after the molten steel is tapped from the hot vessel. When properly constituted and emplaced the gunning mixture is a relatively stiff pliable mass that adheres to the hot vessel lining and which quickly converts to a relatively hard non-pliable mass. As the temperature of the furnace rises during the next heat, components of the mixture more permanently bond the refractory grains to themselves and to the unevenly worn lining.

The granular refractory material used in gunning mixtures is typically composed of magnesia having a periclase crystalline phase. Such materials include dead burned natural magnesite and a synthetic periclase product derived from seawater or brine. Because of their comparatively lower cost in the market, dead burned dolomite and/or chrome ore grog, along with dead burned magnesite in different combinations, have also been conventionally employed as refractory material in gunning mixtures. However, due to the lack of any bonding when wetted with water, refractories must additionally include a binder to provide at least temporary strength to the composition throughout its entire use temperature range (110 degrees Celsius to 1760 degrees Celsius). Optionally, a clay mineral may also be included in the mixture as a gelling or plasticizing agent.

Both organic and inorganic binders have been employed for use in gunning mixtures. Representative organic binders have included starch, dextrin, various organic sulfonic acids and salts, and tars, pitches and resins, but all of these binders suffer a variety of drawbacks, which render them detrimental for use in gunning mixtures. For example, refractory mixtures

containing organic sulfonic acids as a low temperature binder have been found to ignite and burn when applied between heats to the refractory brick lining of a hot (1200 degrees Celsius) metallurgical vessel, thereby compromising their ultimate utility. For the most part, organic additives contribute excessive porosity to the refractory composition thereby diminishing the repaired linings durability and strength.

Inorganic binders also pose problems when employed in gunning mixtures. Solid inorganic binders capable of being dissolved or dispersed in water have been in common use in gunning mixtures, and typical of these are chromic acid, sodium silicate, phosphate glasses, Epsom salts, and magnesium chloride. As with the organic additives, most of these binding agents suffer one or more disadvantages such as slowness of reaction or air setting, lack of strength at intermediate temperatures, poor slag resistance to name a few.

Silicates, phosphates and sulfates are generally the binders of choice for bonding magnesia-based refractory compositions, due primarily to their generally acceptable mechanical strength, slag resistance, and durability of the resultant products. Steel producers are constantly looking for compositions that will increase durability relative to current technology. This would decrease downtime and reduce the frequency of maintenance the metallurgical vessel requires for repair.

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Therefore, what has been found to be new and novel is a refractory composition that improves upon the performance characteristics, such as hot strength, slag resistance, and overall

durability, compared to current compositions being used to produce or repair refractory linings.

It is an objective of the present invention to provide a magnesia-sulfamic acid-calcia product having improved hot strength. Another objective of the present invention is to provide a magnesia-sulfamic acid-calcia refractory product exhibiting outstanding refractoriness i.e. this composition will not form deleterious low melting compounds that are formed when traditionally bonded compositions are used. A further objective of the present invention is to provide a magnesia-sulfamic acid-calcia refractory product outstanding in overall durability.

Additional objectives and features will become apparent from the following detailed description of the embodiments of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph comparing the 1370 degrees Celsius hot breaking strength of two high purity magnesia refractory compositions that are currently used for repairing refractory linings, with the hot breaking strength of the present invention.

Figure 2 is a graph comparing the 1510 degrees Celsius hot breaking strength of two high purity magnesia refractory compositions that are currently used for repairing refractory linings, with the hot breaking strength of the present invention.

SUMMARY OF THE INVENTION

The present invention provides a magnesia-sulfamic acid-calcia refractory composition that includes from about 87.0 percent to about 98.0 percent by weight of the total composition
5 magnesia-based refractory material, from about 1.0 percent to about 5.0 percent by weight of the total composition sulfamic acid and from about 1.0 percent to about 8.0 percent by weight of the total composition calcium hydroxide.

Another aspect of the present invention provides a magnesia-sulfamic acid-calcia
10 refractory composition that includes from about 91.0 percent to about 95.0 percent by weight of the total composition magnesia-based refractory material, from about 2.0 percent to about 4.0 percent by weight of the total composition sulfamic acid and from about 3.0 percent to about 5.0 percent by weight of the total composition calcium hydroxide.

15 A further aspect of the present invention provides a magnesia-sulfamic acid-calcia refractory composition that includes from about 92.0 percent to about 94.0 percent by weight of the total composition magnesia-based refractory material, from about 2.5 percent to about 3.5 percent by weight of the total composition sulfamic acid and from about 3.5 percent to about 4.5 percent by weight of the total composition calcium hydroxide.

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In still a further aspect of the present invention provides a magnesia-sulfamic acid-calcia refractory composition that includes from about 92.0 percent to about 94.0 percent by weight of

the total composition magnesia-based refractory material, from about 2.5 percent to about 3.5 percent by weight of the total composition sulfamic acid and from about 3.5 percent to about 4.5 percent by weight of the total composition calcium hydroxide, and, optionally a wetting agent from about 0.05 percent to about 0.5 percent by weight of the total composition may also be
5 added.

In order to improve existing refractory repair compositions extensive research was done in an effort to find a refractory composition that would improve hot strength and overall durability. It was found when a combination of sulfamic acid and calcium hydroxide is added to
10 a magnesia-based refractory material, a refractory lining is produced having greater durability and hot strength than currently used compositions. When the refractory composition of the present invention is used in gunning applications, a wetting agent may additionally be added to the composition.

15 DETAILED DESCRIPTION OF THE INVENTION

A magnesia based refractory material is admixed with sulfamic acid and an independent calcia source such as calcium hydroxide and/or calcium oxide. It was discovered that the use of sulfamic acid in combination with calcium hydroxide and/or calcium oxide results in a magnesia
20 based refractory composition, having improved physical properties, at temperatures from about 110 degrees Celsius to about 1760 degrees Celsius over compositions currently used for production or repair of refractory furnace linings.

In one embodiment, the refractory composition of the present invention is a magnesia based refractory material in combination with sulfamic acid and calcia.

5 In another embodiment, the refractory composition of the present invention is a gunning composition of a magnesia based refractory material in combination with sulfamic acid, calcia and a wetting agent. The wetting agent may be any suitable dispersant, superplasticizer, anionic, cationic or nonionic surfactant, the selection of which for any particular composition would be understood by one of ordinary skill in the art of refractories.

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In another embodiment the calcia is calcium oxide.

In another embodiment the calcia is calcium hydroxide.

15 In another embodiment the wetting agent is selected from the group consisting of a sulfonated naphthalene condensate, polycarboxylic ether and maleic acid copolymer superplasticizer.

In another embodiment the wetting agent is a sulfonated naphthalene condensate
20 superplasticizer.

In another embodiment, the calcium hydroxide and/or calcium oxide concentration is from about 1.0 percent to about 8.0 percent by weight of the total refractory composition.

In another embodiment, the calcium hydroxide and/or calcium oxide concentration is from about 2.0 percent to about 4.0 percent by weight of the total refractory composition.

5 In another embodiment, the calcium hydroxide and/or calcium oxide concentration is from about 3.5 percent to about 4.5 percent by weight of the total refractory composition.

In another embodiment the sulfamic acid is from about 1.0 percent by weight to about 8.0 percent by weight of the total refractory composition.

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In another embodiment the sulfamic acid is from about 3.0 percent by weight to about 5.0 percent by weight of the total refractory composition.

15 In another embodiment the sulfamic acid is from about 2.5 percent by weight to about 3.5 percent by weight of the total refractory composition.

In another embodiment the composition is a magnesia-based refractory composition for use in the production or repair of metallurgical furnace linings from about 1.0 percent by weight to about 5.0 percent by weight of the refractory composition is sulfamic acid; and from about 1.0 percent by weight to about 8.0 percent by weight of the refractory composition is calcium hydroxide.

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In another embodiment the composition is a magnesia-based refractory composition for use in the production or repair of metallurgical furnace linings is from about 2 percent to about 4 percent by weight of the refractory composition is sulfamic acid; and from about 3 percent to about 5 percent by weight of the refractory composition is calcium hydroxide.

5

In another embodiment the composition is a magnesia-based refractory composition for use in the production or repair of metallurgical furnace linings from about 2.5 percent by weight to about 3.5 percent by weight of the refractory composition is sulfamic acid; and from about 3.5 percent by weight to about 4.5 percent by weight of the refractory composition is calcium hydroxide.

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In another embodiment the composition is a magnesia-based refractory composition for use in the production or repair of metallurgical furnace linings from about 1.0 percent by weight to about 5.0 percent by weight of the refractory composition is sulfamic acid; and from about 1.0 percent by weight to about 8.0 percent by weight of the refractory composition is calcium oxide.

15

In another embodiment the composition is a magnesia-based refractory composition for use in the production or repair of metallurgical furnace linings is from about 2 percent to about 4 percent by weight of the refractory composition is sulfamic acid; and from about 3 percent to about 5 percent by weight of the refractory composition is calcium oxide.

20

In another embodiment the composition is a magnesia-based refractory composition for use in the production or repair of metallurgical furnace linings from about 2.5 percent by weight to about

3.5 percent by weight of the refractory composition is sulfamic acid; and from about 3.5 percent by weight to about 4.5 percent by weight of the refractory composition is calcium oxide.

In another embodiment the composition is a magnesia-based refractory gunning composition
5 for use in the production or repair of metallurgical furnace linings wherein from about 1.0 percent by weight to about 5.0 percent by weight of the gunning composition is sulfamic acid; and 1.0 percent to about 8.0 percent by weight of the gunning composition is calcium hydroxide; and from about 0.05 percent to about 0.5 percent by weight of the gunning composition is a wetting agent.

10 In another embodiment the composition is a magnesia-based refractory gunning composition for use in the production or repair of metallurgical furnace linings wherein from about 2.0 percent by weight to about 4.0 percent by weight of the gunning composition is sulfamic acid; and 3.0 percent to about 5.0 percent by weight of the gunning composition is calcium hydroxide; and from about 0.05 percent to about 0.5 percent by weight of the gunning composition is a wetting agent.

15 In another embodiment the composition is a magnesia-based refractory gunning composition for use in the production or repair of metallurgical furnace linings wherein from about 2.5 percent by weight to about 3.5 percent by weight of the gunning composition is sulfamic acid; and 3.5 percent to about 4.5 percent by weight of the gunning composition is calcium hydroxide; and from
20 about 0.05 percent to about 0.5 percent by weight of the gunning composition is a wetting agent.

In another embodiment the composition is a magnesia-based refractory gunning composition for use in the production or repair of metallurgical furnace linings wherein from about 1.0 percent by weight to about 5.0 percent by weight of the gunning composition is sulfamic acid; and 1.0 percent to about 8.0 percent by weight of the gunning composition is calcium oxide; and from about
5 0.05 percent to about 0.5 percent by weight of the gunning composition is a wetting agent.

In another embodiment the composition is a magnesia-based refractory gunning composition for use in the production or repair of metallurgical furnace linings wherein from about 2.0 percent by weight to about 4.0 percent by weight of the gunning composition is sulfamic acid; and 3.0
10 percent to about 5.0 percent by weight of the gunning composition is calcium oxide; and from about 0.05 percent to about 0.5 percent by weight of the gunning composition is a wetting agent.

In another embodiment the composition is a magnesia-based refractory gunning composition for use in the production or repair of metallurgical furnace linings wherein from about 2.5 percent
15 by weight to about 3.5 percent by weight of the gunning composition is sulfamic acid; and 3.5 percent to about 4.5 percent by weight of the gunning composition is calcium oxide; and from about 0.05 percent to about 0.5 percent by weight of the gunning composition is a wetting agent.

In another embodiment a monolithic refractory lining is formed on a metallurgical vessel by
20 gunning onto at least a portion of the inside surface of the vessel, a magnesia-based refractory composition containing sulfamic acid, calcia and a wetting agent.

The following non-limiting examples are merely illustrative of some embodiments of the present invention, and are not to be construed as limiting the invention, the scope of which is defined by the appended claims.

5

EXAMPLE 1

Four high purity magnesia refractory compositions were tested to determine high-temperature modulus of rupture in an oxidizing atmosphere and under action of a force or stress that is increased at a constant rate using the “Standard Test Method for Modulus Rupture of Refractory Materials at
10 Elevated Temperatures” as defined under ASTM Designation C 583–80 (Reapproved 1995), except a three hour soak time was employed and two inch by two inch by nine inch test samples were used.

Four refractory compositions were compared to determine hot strength or modulus of rupture at 1370 degrees Celsius and 1510 degrees Celsius. Two compositions produced in accordance with
15 the present invention, Sample 1 with wetting agent and Sample 2 without wetting agent, both of which are a high purity magnesia material that is bonded with a combination of sulfamic acid and calcium hydroxide, were compared to Sample 3, which is a premium quality, high purity magnesia, silicate bonded refractory gunning product and Sample 4, which is a high purity magnesia, sulfamic acid bonded refractory gunning product. The results are shown in Figure 1 and Figure 2.

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The 1370 degrees Celsius Hot Modulus of Rupture result show that the compositions made in accordance with the present invention have higher Hot Modulus of Rupture Strength compared
5 with traditional silicate and sulfamic acid bonded refractory compositions.

The 1510 degrees Celsius Hot Modulus of Rupture result show that the compositions made in accordance with the present invention have higher Hot Modulus of Rupture Strength compared
with traditional silicate and sulfamic acid bonded refractory compositions.
10

Other embodiments of the invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope of the invention being defined by the following claims.

THE CLAIMS

We claim:

1. A refractory composition consisting essentially of:
 - 5 (a) a magnesia based refractory material;
 - (b) sulfamic acid; and
 - (c) calcia.

2. The refractory composition of Claim 1 wherein the calcia is selected from calcium hydroxide or
10 calcium oxide.

3. The refractory composition of Claim 2 wherein the calcia is selected from calcium hydroxide.

4. The refractory composition of Claim 2 wherein the calcia source is calcium oxide.
15

5. The refractory composition of Claim 3 wherein the calcium hydroxide concentration is from
about 1.0 percent to about 8.0 percent by weight of the total refractory composition.

6. The refractory composition of Claim 3 wherein the calcium hydroxide concentration is from
20 about 3.0 percent to about 5.0 percent by weight of the total refractory composition.

7. The refractory composition of Claim 3 wherein the calcium hydroxide concentration is from
about 3.5 percent to about 4.5 percent by weight of the total refractory composition.

- 25 8. The refractory composition of Claim 4 wherein the calcium oxide concentration is from about
1.0 percent to about 8.0 percent by weight of the total refractory composition.

9. The refractory composition of Claim 4 wherein the calcium oxide concentration is from about
3.0 percent to about 5.0 percent by weight of the total refractory composition.

10. The refractory composition of Claim 4 wherein the calcium hydroxide concentration is from about 3.5 percent to about 4.5 percent by weight of the total refractory composition.
- 5 11. The refractory composition of Claim 1 wherein the sulfamic acid is from about 1.0 percent by weight to about 5.0 percent by weight of the total refractory composition.
12. The refractory composition of Claim 1 wherein the sulfamic acid is from about 2.0 percent by weight to about 4.0 percent by weight of the total refractory composition.
- 10 13. The refractory composition of Claim 1 wherein the sulfamic acid is from about 2.5 percent by weight to about 3.5 percent by weight of the total refractory composition.
14. The refractory composition of Claim 1 wherein the sulfamic acid is from about 1.0 percent to
15 about 5.0 percent by weight of the refractory composition and the calcium hydroxide is from about 1.0 percent to about 8.0 percent by weight of the total refractory composition.
15. The refractory composition of Claim 1 wherein the sulfamic acid is from about 2.0 percent to
20 about 4.0 percent by weight of the refractory composition and the calcium hydroxide is from about 3.0 percent to about 5.0 percent by weight of the refractory composition.
16. The refractory composition of Claim 1 wherein the sulfamic acid is from about 2.5 percent to about 3.5 percent by weight of the refractory composition and the calcium hydroxide is from about 3.5 percent to about 4.5 percent by weight of the refractory composition.
- 25 17. The refractory composition according to Claim 1 wherein the sulfamic acid is from about 1.0 percent to about 5.0 percent by weight of the refractory composition and calcium oxide is from about 1.0 percent to about 8.0 percent by weight of the refractory composition.

18. The refractory composition according to Claim 1 wherein the sulfamic acid is from about 2.0 percent to about 4.0 percent by weight of the refractory composition and calcium oxide is from about 3.0 percent to about 5.0 percent by weight of the refractory composition.
- 5 19. The refractory composition according to Claim 1 wherein the sulfamic acid is from about 2.5 percent to about 3.5 percent by weight refractory composition and calcium oxide is from about 3.5 percent by weight to about 4.5 percent by weight of the refractory composition.
20. A refractory gunning composition consisting essentially of:
- 10 a) a magnesia-based refractory;
b) sulfamic acid;
c) calcia; and,
d) a wetting agent.
- 15 21. The refractory gunning composition according to Claim 20 wherein the calcia is calcium hydroxide or calcium oxide.
22. The refractory gunning composition according to Claim 21 wherein the calcia is calcium hydroxide.
- 20 23. The refractory gunning composition according to Claim 21 wherein the calcia is calcium oxide.
24. The gunning composition according to Claim 20 wherein the sulfamic acid is from about 1.0 percent to about 5.0 percent by weight of the gunning composition; calcia is from about 1.0 percent to about 8.0 percent by weight of the gunning composition; and, the wetting agent is from about 0.05 percent to about 0.5 percent by weight of the gunning composition.
- 25 25. The gunning composition of Claim 20 wherein the sulfamic acid is from about 1.0 percent by weight to about 5.0 percent by weight gunning composition; from about 1.0 percent to about 8.0

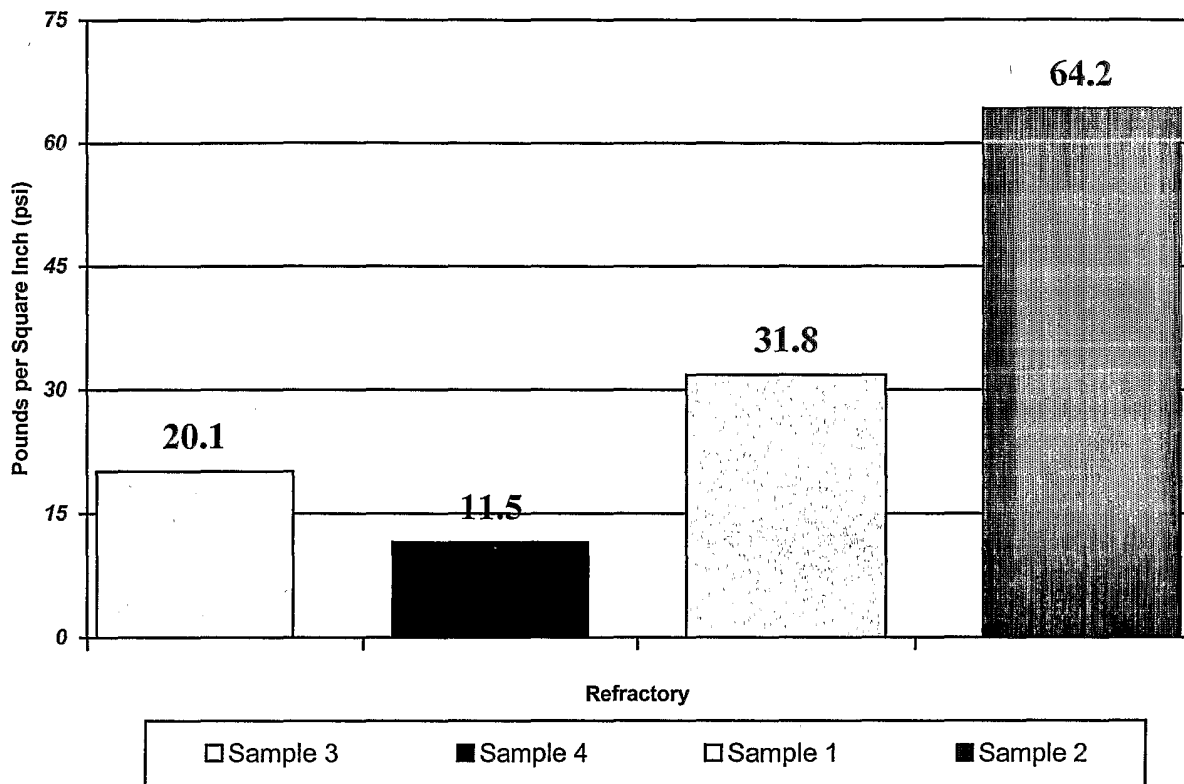
percent by weight of the gunning composition is calcium hydroxide; and, from about 0.05 percent to about 0.5 percent by weight of the gunning composition is a wetting agent.

26. The gunning composition according to Claim 20 wherein the sulfamic acid is from about 2.0
5 percent to about 4.0 percent by weight of the gunning composition; calcium hydroxide is from about 3.0 percent to about 5.0 percent by weight of the gunning composition; and, a wetting agent from about 0.05 percent to about 0.5 percent by weight of the gunning composition.
27. The gunning composition according to Claim 20 wherein the sulfamic acid is from about 2.5
10 percent to about 3.5 percent by weight of the gunning composition; calcium hydroxide from about 3.5 percent to about 4.5 percent by weight of the gunning composition; and, a wetting agent from about 0.05 percent to about 0.5 percent by weight of the gunning composition.
28. The gunning composition according to Claim 20 wherein the sulfamic acid is from about 1.0
15 percent to about 5.0 percent by weight of the gunning composition; calcium oxide is from about 1.0 percent to about 8.0 percent by weight of the gunning composition; and, a wetting agent from about 0.05 percent to about 0.5 percent by weight of the gunning composition.
29. The gunning composition according to Claim 20 wherein the sulfamic acid is from about 2.0
20 percent to about 4.0 percent by weight of the gunning composition; calcium oxide from about 3.0 percent to about 5.0 percent by weight of the gunning composition; and, a wetting agent from about 0.05 percent to about 0.5 percent by weight of the gunning composition.
30. The gunning composition according to Claim 20 wherein the sulfamic acid is from about 2.5
25 percent to about 3.5 percent by weight of the gunning composition; calcium oxide from about 3.5 percent to about 4.5 percent by weight of the gunning composition; and, a wetting agent from about 0.05 percent to about 0.5 percent by weight of the gunning composition.

31. The gunning composition according to Claim 20 wherein the wetting agent is selected from the group consisting of a superplasticizer, anionic surfactant, cationic surfactant, nonionic surfactant and dispersant.
- 5 32. The gunning composition according to Claim 31 wherein the superplasticizer is selected from the group consisting of a sulfonated naphthalene condensate, polycarboxylic ether and maleic acid copolymer.
- 10 33. The gunning composition according to Claim 32 wherein the superplasticizer is a sulfonated naphthalene condensate.
34. A method of forming a monolithic refractory lining on a metallurgical vessel, comprising gunning onto at least a portion of the inside surface of the vessel the composition of Claim 20.

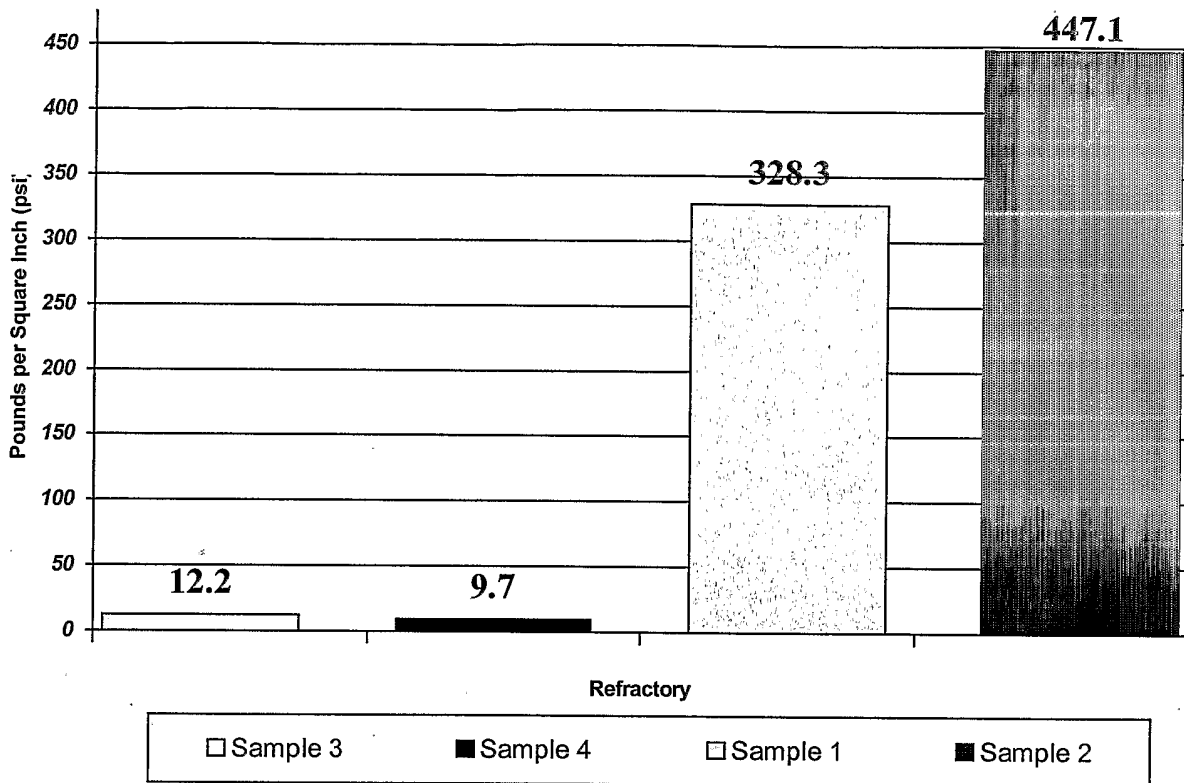
1370 Degree Celsius Hot Breaking Strength

FIGURE 1



1510 Degrees Fahrenheit Hot Breaking Strength

FIGURE 2



INTERNATIONAL SEARCH REPORT

International Application No
PC1/US2004/032154

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C04B35/66 C04B35/03 C04B35/04

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 7 C04B

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 practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 383 045 A (NAGLE ET AL) 10 May 1983 (1983-05-10) Table 3, Mix. 3 abstract; claims 1,7,11	1-4, 11, 12
Y	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 10, 31 October 1997 (1997-10-31) & JP 09 165271 A (HARIMA CERAMIC CO LTD; NIPPON STEEL CORP), 24 June 1997 (1997-06-24) abstract	1-4, 11, 12
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Further documents are listed in the continuation of box C.

Patent family members are listed in 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 document but published on or after the international filing date
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- *P* document published prior to the international filing date but later than the priority date claimed

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- * & * document member of the same patent family

Date of the actual completion of the international search

2 February 2005

Date of mailing of the international search report

15/02/2005

Name and mailing address of the ISA

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Vathilakis, S

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/US2004/032154

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 075 (C-1163), 8 February 1994 (1994-02-08) & JP 05 286771 A (SHINAGAWA REFRACT CO LTD), 2 November 1993 (1993-11-02) abstract -----	1
A	DATABASE WPI Section Ch, Week 198732 Derwent Publications Ltd., London, GB; Class L02, AN 1987-224275 XP002315965 & JP 62 148377 A (SHINAGAWA FIRE BRICK) 2 July 1987 (1987-07-02) abstract -----	1
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 06, 30 June 1997 (1997-06-30) & JP 09 040470 A (HARIMA CERAMIC CO LTD; NIPPON STEEL CORP), 10 February 1997 (1997-02-10) abstract -----	1-10

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/032154

Information on patent family members

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4383045	A	10-05-1983	BR 8302022 A CA 1192230 A1 DE 3360349 D1 EP 0094171 A1 JP 1006143 B JP 1525347 C JP 58208169 A MX 159567 A	27-12-1983 20-08-1985 08-08-1985 16-11-1983 02-02-1989 30-10-1989 03-12-1983 06-07-1989
JP 09165271	A	24-06-1997	NONE	
JP 05286771	A	02-11-1993	JP 1961029 C JP 6088840 B	10-08-1995 09-11-1994
JP 62148377	A	02-07-1987	NONE	
JP 09040470	A	10-02-1997	NONE	