667039

CASE: 8252
CORPORATE

AUSTRALIAN PATENT
APPLICATION NO. 37843/93

AUSTRALIA
Patents Act 1990

NOTICE OF ENTITLEMENT

I, Edward J. Whitfield
of 235 E. 42nd Street, New York, New York
UNITED STATES OF AMERICA

being authorized by the Applicant(s)/Nominated Person(s) in respect of an application entitled:

Vibratable Refractory Composition

state the following:-

1. The Applicant(s)/Nominated Person(s) has/have, for the following reasons, gained entitlement from the actual inventor(s):-

   The Applicant/Nominated Person is the assignee of the inventors.

2. The Applicant(s)/Nominated Person(s) is entitled to rely on the basic application listed in the Declaration under Article 8 of the PCT as follows:

   The Applicant/Nominated Person is the assignee of the actual inventors.

3. The basic application(s) listed in the Declaration under Article 8 of the PCT is the application first made in a Convention Country in respect of the invention.

~~4. The Applicant(s)/Nominated Person(s) is/are~~

DATED this 24th day of February 1994.

SPECIALTY REFRACTORIES INC.

BY: E. J. Whitfield
(Signature)

EDWARD J. WHITFIELD
ASSISTANT SECRETARY
(Name & Title)

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VIBRATABLE REFRACTORY COMPOSITION

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(56) Prior Art Documents
WO 91/17969
US 4210606
US 4280844

(57) Claim

1. A dry vibratable refractory composition for forming a disposable liner comprising:

from 0.1 to 20 weight percent of a high temperature binder selected from metal powder, alloys or mixtures;

from 0.5 to 5 weight percent of a low temperature binder;

from 0.01 to 3 weight percent of a density reducing inorganic material; and

at least 72 weight percent of a refractory aggregate, said composition being substantially alkali oxide free.

12. A method of providing a disposable refractory liner in a vessel having a permanent refractory liner which comprises applying the composition of claim 4 onto the permanent lining to obtain a substantially alkali oxide free disposable liner over the permanent liner, wherein the disposable liner exhibits high temperature strength while simultaneously protecting the permanent liner from degradation and wherein the disposable liner is easily removed from the vessel.

.../2

14. A vessel for handling molten metal comprising:

means for holding molten metal therein;

a relatively permanent refractory lining disposed within the holding means for protecting the holding means against the effects of the molten metal; and

a disposable refractory lining disposed upon at least a portion of the permanent refractory lining and comprising the composition of one of claims 1 to 11.

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(54) Title: VIBRATABLE REFRACTORY COMPOSITION

(57) Abstract

A dry vibratable substantially alkali free refractory composition is disclosed for use as a disposable liner wherein the combination of a powdered metal utilized as a high temperature binder and an organic material utilized as a low temperature binder obviates the use of alkali oxides which previously caused degradation of the permanent refractory liner materials upon which the disposable lining was placed. Low density materials such as expanded inorganic materials can be added to the disclosed compositions to decrease the density. The invention also relates to a method of providing a disposable lining in a vessel having a permanent refractory lining, and to the resulting vessel thereof.

VIBRATABLE REFRACTORY COMPOSITION

Technical Field

This invention relates to refractory compositions especially useful for forming a disposable, monolithic lining on the permanent refractory lining of a molten metal vessel. Such vessels include a tundish or ladle, each of which is used in continuous molten metal casting processes. Specifically, the invention relates to a substantially alkali oxide free refractory composition which is typically applied without the addition of water and either with or without the aid of vibration.

Background of the Invention

A tundish is a large intermediate holding vessel for molten metal used in continuous casting processes, such as the continuous casting of steel. The tundish is, in effect, an intermediate process reservoir which receives a large quantity of molten metal from conveying ladles exiting a furnace in which actual smelting of the ores or refining of molten metal occurs, and which then transfers the molten metal to a casting system. A system of inlet and outlet nozzles controls the flow of molten metal into and out of the tundish.

The tundish itself is generally a

steel vessel which can be lined with several layers of various refractory compositions. A permanent lining, generally of refractory castable or brick, serves as an inner lining to protect the vessel. The permanent lining, in turn, is coated with a disposable lining, generally of a refractory composition which has been applied to the permanent lining by gunning, spraying, trowelling, or dry vibration. Alternatively, the disposable lining can be formed of refractory boards. The disposable linings ~~is~~ may be in direct contact with the due to the nature of the binders utilized in dry-type refractories of the past, they are less suitable in applications where pre-heating of the tundish is required. Dry-type refractories experience complete burn-out of low temperature binders at temperatures of 800 to 1100°F. At these temperatures, the high temperature binders have not yet reached their effective binding capabilities. Thus, failures of some disposable liners of the dry-type have occurred when they have been pre-heated prior to casting.

A current problem with refractory materials is that they often contain alkali oxides such as, for example, Na_2O and K_2O. It is understood that, at casting temperatures, the alkali oxides present migrate to the disposable/permanent refractory interface. These alkali oxides adsorb and/or absorb onto or into the high alumina refractory. With each successive application of conventional disposable linings, nephelite forms at the interface. Therefore, damage to the permanent lining can occur during removal of the disposable liner due to the fusion of the linings because of the nephelite formation.

Sticking of the disposable lining to the permanent refractory can cause some of the permanent refractory to be lost from the metal vessel when the skull is removed. Furthermore, in those instances where the disposable lining does not stick to the permanent refractory, contamination of the permanent liner by the alkali oxides produces an increased disparity in the thermal coefficient of expansion. This difference in thermal expansion can also result in damage to the permanent lining.

What is needed, therefore, is a substantially alkali oxide free dry vibratable refractory composition which can be used to provide a disposable lining in casting vessels. This composition should also be formulated for use in processes requiring pre-heating of the tundishes such that the material does not exhibit significant spalling, cracking or other temperature-related lining failures.

Summary of the Invention

In accordance with the present invention, a substantially alkali free dry vibratable refractory composition especially adapted for forming a disposable lining is provided. The composition exhibits high heat resistance and resistance to spalling and cracking, while also providing increased ease of removal from a permanent refractory lining to which it is applied. The composition is also compatible with pre-heating techniques when used, for example, as a disposable liner in a tundish.

The refractory composition of the present invention includes from about 0.1 to about 20, and preferably about 0.1 to 12 weight percent of a high temperature binder, from about

0.5 to about 5 weight percent of a low temperature binder, from about 0.01 to about 3 weight percent of an inorganic density reducing material and at least about 72 weight percent of a refractory aggregate.

The refractory aggregate is preferably magnesia, doloma, olivine, calcia, alumina, silica, or combinations thereof. It is preferred that the refractory aggregate be magnesia or other source which provides a total MgO equivalent of at least about 50 to 95 weight percent of the aggregate.

The high temperature binder is preferably a metal powder and is utilized to increase the high temperature strength and chemical durability of the refractory material. It is preferred that the powdered metal be aluminum; silicon; and alloy of aluminum and silicon having a weight ratio of from about 50/50 to about 95/5, a mixture of aluminum and silicon having a weight ratio of from about 50/50 to about 95/5, or an alloy of magnesium and aluminum having a weight ratio of from about 80/20 to about 20/80.

Useful low temperature binders include organic materials such as the phenolic resins, with the phenol formaldehyde polymers being especially preferred. Also, the density reducing material is preferably perlite or an expanded inorganic material, such as expanded clay.

From about 0.05 to about 5 weight percent of a volume stabilizer may also be included in the refractory compositions of the invention. The volume stabilizer is preferably a clay selected from the group consisting of bentonite, kaolin clay and ball clay.

Detailed Description of the Invention

In the description that follows, all reference to percentage or % refer to percent by weight unless otherwise noted.

As discussed above, dry vibratable refractory materials of the past have incorporated alkali oxide components which have been known to effectively degrade the permanent refractory linings onto which they had been placed. Furthermore, migration of alkalis into permanent lining materials increases the difficulty of deskulling operations, often effecting the loss of portions of the permanent lining which have fused to the disposable lining.

As noted above, the refractory composition of the present invention is a dry vibratable type. It is preferably applied to a surface utilizing vibration for uniform distribution and compaction, with at least one binder being subsequently activated thermally.

The refractory composition of the present invention is substantially alkali free and therefore does not effect the permanent liner degradation and associated problems discussed above. The term "substantially alkali free" means that the refractory composition of the present invention includes a total of less than about 0.1 weight percent of alkali or alkali oxide compounds.

Any of a wide variety of refractory aggregates may be utilized in the compositions of the present invention. These aggregates include basic refractories such as magnesia, doloma, olivine, and calcia. The term "basic" refers to the chemical behavior of these materials rather than the complexity of their

composition. In addition, other refractory materials such as alumina and silica may be used.

The most preferred refractory aggregate for the composition is magnesia or other sources which provide at least 50 to 99% MgO, and it is present in an amount of at least about 72 weight percent of the composition. The various particle size ranges of the aggregate may be selected and combined. One skilled in the art is aware of the fact that control of the particle size distribution is important to get efficient packing of the dry vibratable composition. Otherwise, it is possible that laminations of the different size fractions will occur during installation of the lining. These laminations are detrimental to the performance of the lining because, if present in sufficient amounts, they can be penetrated by the molten metal. The components (and in particular, the refractory aggregate) can be crushed or ground with the appropriate particle sizes selected to achieve the desired distribution. If necessary, routine tests can be conducted to select the optimum particle size distribution of the composition.

The present invention utilizes a high temperature binder comprised of a metal powder which is essentially inert to reaction with permanent refractory linings. The metallic powders of the present invention provide satisfactory high temperature strength without causing the above-discussed alkali related degradation.

As noted above, any of a wide range of metal powders, alloys or mixtures may be used, with aluminum, silicon, any alloy or mixture of

aluminum and silicon, or any alloy of magnesium and aluminum being typical. Advantageous weight ratios of these alloys and mixtures are set forth above. Optimum performance has been found when aluminum/silicon alloys having a greater proportion of aluminum to silicon are used. The most preferred metal powder is an 88Al/12Si alloy having a particle size of 8 microns.

The particle size distribution of the metal powder is selected to be commensurate with the size of the aggregate so that efficient packing of the composition occurs during installation. If necessary, routine tests can be conducted to select the optimum particle size distribution for any particular metal powder.

Although amounts as high as 20% can be used, the amount of metal powder is typically less than about 6%, with optimum amounts shown in the Examples. The amount of powdered metal effectively adds durability and increased strength to the composition and disposable liner formed therefrom over a temperature range of from about 1100 to 3000°F. More importantly, these powdered metals eliminate the need for binders of alkali bearing compounds.

The composition of the present invention ~~may advantageously~~ include a density reducing inorganic material, such as perlite or expanded clay. A preferred expanded clay is an expanded fire clay having a bulk density of about 25-35 pounds per cubic foot ("p.c.f."). These inorganic additives are preferred compared to organic additives such as paper fibers because it is easier to maintain them in a homogenous blend or dispersion throughout the aggregate.

The low temperature binder is utilized

to hold the composition together once installated and before the high temperature binder is activated. Phenolic resins are preferred for use as this component.

Also, a volume stabilizer is included to enhance the ability of the composition to shrink upon cooling to facilitate deskulling. Preferably, this component is a clay, such as bentonite or air-floated ball clay.

EXAMPLES

Table 1 lists six compositions which illustrate preferred embodiments of the invention. Composition A and B include an aluminum/silicon alloy as the high temperature binder, and differ only in that composition B includes 1 percent weight additional expanded fire clay and 0.5 percent weight less for each of the metal powder and MgO compared to Composition A.

Composition C utilizes a magnesium/aluminum alloy powder as the high temperature binder, while compositions D, E and F illustrate the use of a high temperature binder of aluminum powder, silicon powder, and a mixture of these powders, respectively.

TABLE 3

Material	A	B	C	D	E	F
MgO	92	91.5	92	92	89	91
Phenolic Resin	3	3	3	3	3	3
Expanded Fire Clay	1	2	1	1	1	1
Air Floated Ball Clay	1	1	1	1	1	1
88 Al/12 Si alloy	3	2.5	-	-	-	-
50Mg/50 Al	-	-	3	-	-	-
Al	-	-	-	3	-	2.25
Si	-	-	-	-	6	0.75
1500°F. Qualitative Hot Strength Rating	4.0	4.0	2.8	2.0	2.0	2.0

* Rating Scale: 1-5 with 5 being the most resistant.

Table 2 indicates that the qualitative high temperature test resistance results (which are representative of hardness) for compositions A and B are essentially the same. Both compositions were also found to possess good hot strength and superior slag/steel resistance.

Compared to the single element or powder mixture, the magnesium/aluminum alloy has a better hot strength rating, so that compositions A, B and C are preferred for more aggressive applications. Composition D, E and F possess lower hot strength ratings, but are useful in processing less aggressive (or relatively lower temperature) molten metals.

Refractory compositions made according to this invention, for all modes of application, also demonstrate excellent thermal properties including rapid heat up without spalling.

The claims defining the invention are as follows:

1. A dry vibratable refractory composition for forming a disposable liner comprising:

from 0.1 to 20 weight percent of a high temperature binder selected from metal powder, alloys or mixtures;

from 0.5 to 5 weight percent of a low temperature binder;

from 0.01 to 3 weight percent of a density reducing inorganic material; and

at least 72 weight percent of a refractory aggregate, said composition being substantially alkali oxide free.

2. A refractory composition according to claim 1, for forming a disposable liner comprising:

from 0.1 to 12 weight percent of a powdered metal binder;

from 0.5 to 5 weight percent of a low temperature organic binder;

from 0.01 to 3 weight percent of a density reducing inorganic material;

from 0.05 to 5 weight percent of a volume stabilizer; and

at least 75 weight percent of a refractory aggregate.

3. The composition of claim 1, wherein the high temperature binder is a powdered metal or metal alloy selected from aluminum; silicon; mixtures of aluminum and silicon; and alloy combinations of aluminum with silicon or magnesium.

4. The composition of any one of the preceding claims, wherein the refractory aggregate is selected from magnesia, doloma, olivine, calcia, alumina, silica, and combinations thereof, and wherein the composition contains less than about 0.1 weight percent of alkali oxides.

5. The composition of any one of the preceding claims, wherein the high temperature binder is a powdered metal selected from aluminum; silicon; and alloy of aluminum and silicon having a weight ratio of aluminum to silicon of from

50/50 to 95/5; a mixture of aluminum and silicon having a weight ratio of aluminum to silicon of from 50/50 to 95/5; and an alloy of magnesium and aluminum having a weight ratio of magnesium to aluminum of from 80/20 to 20/80.

6. The composition of any one of the preceding claims, wherein the low temperature binder is a phenolic resin.

7. The composition of claim 6, wherein the phenolic resin is a phenol formaldehyde polymer.

8. The composition of any one of the preceding claims, wherein the density reducing inorganic material comprises perlite or expanded clay.

9. The composition of claim 6, further comprising a volume stabilizer in an amount of from 0.05 to 5 weight percent.

10. The composition of claim 9, wherein the volume stabilizer is a clay selected from the group consisting of bentonite, kaolin clay and ball clay.

11. The composition of any one of the preceding claims, wherein the organic binder is a phenolic resin and the refractory aggregate comprises magnesia.

12. A method of providing a disposable refractory liner in a vessel having a permanent refractory liner which comprises applying the composition of claim 4 onto the permanent lining to obtain a substantially alkali oxide free disposable liner over the permanent liner, wherein the disposable liner exhibits high temperature strength while simultaneously protecting the permanent liner from degradation and wherein the disposable liner is easily removed from the vessel.

13. The method of claim 12, wherein said composition is adapted for application in a dry state by vibration into place and which hardens by thermal activation of at least one of the binders.

14. A vessel for handling molten metal comprising:

means for holding molten metal therein;

a relatively permanent refractory lining disposed within the holding means for protecting the holding means against the effects of the molten metal; and

a disposable refractory lining disposed upon at least a portion of the permanent refractory lining and comprising the composition of one of claims 1 to 11.

15. A dry vibratable refractory composition substantially as hereinbefore described in any of the Examples.

16. A method for providing a disposable refractory liner in a vessel substantially as hereinbefore specifically described.

DATED this Third Day of January 1996
Minteq International Inc
Patent Attorneys for the Applicant
SPRUSON & FERGUSON

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 93/01861

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C04B 35/66 // C04B 35/04
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)

IPC5: C04B, C22C, F27D

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.

DIALOG: WPI, CLAIMS, QUESTEL: EDOC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO, A1, 9117969 (QUIGLEY COMPANY, INC.), 28 November 1991 (28.11.91), claims 1-3,6-8	1,2,5,7-12, 17
Y	US, A, 4201606 (FRANK NEAT), 6 May 1980 (06.05.80), column 2, line 9 - line 14	1,2,4-17
Y	US, A, 4280844 (HIROSHI SHIKANO ET AL), 28 July 1981 (28.07.81), column 2, line 15 - line 39, claims 1,2, example 4	1,2,4-9, 12-17
A	DE, B2, 2744486 (TAIKO ROZAI CO.,LTD.), 29 January 1981 (29.01.81), claims 1,2	1-17

[X] Further documents are listed in the continuation of Box C. [X] 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 document 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	Date of mailing of the international search report
23 June 1993	19. 07. 93

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. + 31-70) 340-2040, Tx. 31 651 epo nl, Fax: + 31-70) 340-3016	Mårten Hulthén

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNA .ONAL SEARCH REPORT

	l. .rnational application No. PCT/US 93/01861

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

28/05/93

International application No.
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