EXOTHERMIC SLEEVE MIXES
CONTAINING FINE ALUMINUM

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ABSTRACT
The invention relates to an exothermic sleeve composition comprising (a) an oxidizable metal where the oxidizable metal comprises fine aluminum as the major component, and (b) an oxidizing agent capable of generating an exothermic reaction. The invention also relates to the use of the sleeve composition to prepare sleeves, the sleeves prepared with the sleeve compositions, and the use of the sleeves to prepare metal castings.
EXHIBIT 4
EXOTHERMIC SLEEVE MIXES CONTAINING FINE ALUMINUM

FIELD OF THE INVENTION

The invention relates to an exothermic sleeve composition comprising (a) an oxidizable metal where the oxidizable metal comprises fine aluminum as the major component, and (b) an oxidizing agent capable of generating an exothermic reaction. The invention also relates to the use of the sleeve composition to prepare sleeves, the sleeves prepared with the sleeve compositions, and the use of the sleeves to prepare metal castings.

BACKGROUND OF THE INVENTION

A casting assembly typically consists of a pouring cup, a gating system (including downsprue, choke, and runner), riser, sleeve, mold, core, and other components. To produce a metal casting, metal is poured into the casting assembly and passes through the gating system to the mold and/or core assembly where it cools and solidifies. The metal part is then removed by separating it from the core and/or mold assembly.

Risers or feeders are reservoirs that contain excess molten metal. The excess molten metal is needed to compensate for contractions or voids of metal that occur during the casting process. Metal from the riser fills such voids in the casting when the casting metal contracts. Thus the metal from the riser needs to remain in a liquid state for a longer period of time, so it can provide metal to the casting as it cools and solidifies. Sleeves are used to surround or encapsulate the riser and other parts of the casting assembly in order to keep the molten metal in the riser hot and maintain it in the liquid state for a longer time.

In order to serve their function, sleeves have exothermic and/or insulating properties. Exothermic sleeves function by liberating heat. This liberated heat satisfies some or all of the specific heat requirements of the riser and limits the temperature loss of the molten metal in the riser, thereby keeping the metal hotter and liquid longer. Insulating sleeves, on the other hand, maintain the heat of the molten metal in the riser by insulating it from the surrounding mold assembly.

For years sleeves were produced by “ramming”, “vacuuming”, and “blowing or shooting”, methods well known in the art. More recently, it was discovered that sleeves could be made by chemically curing a shaped sleeve mix with a curing catalyst by the no-bake and cold-box process. See published application WO 97/35677, which hereby incorporated by reference. These processes provide sleeves with improved dimensional accuracy.

Typical exothermic sleeve formulations contain aluminum as a fuel, metal oxides and nitrates as oxidizers, and fluorocarbon containing compounds as fluxing agents. The aluminum is typically used in granular and/or a powder, having a broad particle size distribution, and is considered “coarse” in nature. The exothermic sleeves prepared with this coarse aluminum produce an acceptable exothermic reaction in most cases, but the surface finish of the casting metal against the sleeve material is often “rough” because the massive heat produced by the exotherm of the sleeve. This is a concern to foundries because a rough casting surface finish requires extra cleaning time and machining before the casting can be used effectively. In some cases the surface finish is so rough that the casting is defective and scrapped.

One method used to prevent the exotherm from the sleeve from causing a poor surface finish is to move the riser sleeve away from the casting assembly. By doing this, the casting is exposed to less heat, and the risk of a poor surface finish is decreased. The disadvantage of this remedy is that it increases the amount of riser metal used, which lowers the casting yield.

An example of a method used to move the sleeve away from the riser sleeve is the so-called “spring thorn”. The spring thorn is a “spring-loaded locator” that creates a gap between the riser sleeve and the casting that allows sand to build-up between the riser sleeve and the surface of the casting. This molding sand acts as a barrier between the sleeve and the surface casting and keeps the exotherm created by the riser away from the casting surface. The spring thorn is particularly useful for mounting riser sleeves used with high pressure, green sand molding equipment to cast metals. Another way to reduce the negative impact of the sleeve’s exotherm on the surface finish of the casting is by adding a protective layer of metal (a riser “pad”) between the riser sleeve and the casting assembly. After the casting is made and the riser is removed from the casting, this additional pad of metal must be removed from the casting. The disadvantage of this technique is that it adds processing steps, which increases the cost of the casting.

SUMMARY OF THE INVENTION

The invention relates to an exothermic sleeve mix comprising:

(a) an oxidizable metal where the oxidizable metal comprises fine aluminum as the major component, and
(b) an oxidizing agent capable of generating an exothermic reaction.

The surface finish of the casting that is in contact with the heat produced by the burning of the exothermic sleeve is improved, if fine aluminum is used in the exothermic sleeve mix. Smoother castings are made, similar to or better than that of cores and molds made with sand. The sleeve compositions are used to make castings from metals, e.g. iron, ductile iron, steel, aluminum, etc.

A smoother finish reduces the need for cleaning and machining the casting. As a result, the exothermic riser sleeve can be placed directly in contact with the surface of the casting. Special mounting techniques, such as the so-called “spring thorn locator” that increase the cost of making the casting, are not required.

DEFINITIONS AND ABBREVIATIONS

The following definitions and abbreviations are stipulated:

\( \mu m \) - microns.

Casting assembly - assembly of casting components such as pouring cup, gating system (downsprue,
The exothermic sleeve composition comprises (a) fine aluminum and (b) an oxidizing agent. The sleeve compositions are used to make sleeve mixes that contain (1) an exothermic sleeve composition, and (2) an effective amount of a chemically reactive inorganic or organic binder. The sleeve mix is shaped and cured by contacting the sleeve with an effective amount of a curing catalyst.

The fine aluminum, typically a powder, is defined as aluminum having a particle distribution such that 95 weight percent of the aluminum passes through 100 mesh as determined by the US Standard Screen Test, preferably a particle distribution such that more than 95 percent of the aluminum passes through the 140 mesh.

Aluminum can be used as a pure metal, as an alloy with magnesium, silicon, copper, or possibly a component of a waste material. Although not preferred for achieving the best surface finish, minor amounts of coarse aluminum can be mixed with the fine aluminum to reduce the cost of the sleeve composition, for instance up to 15 weight percent based on the amount of aluminum, preferably less than 5 weight percent. Coarse aluminum is aluminum having a particle distribution outside the definition stipulated for fine aluminum.

Existing commercial formulations contain large amounts of coarse Al, up to 300 weight %, where the weight percent is based upon the total weight of aluminum used. But the surface finish of casting is usually very poor, resulting in excessive machining.

The oxidizing agent used for the exothermic sleeve includes iron oxide, manganese oxide, nitrates, potassium permanganate, etc. Oxides do not need to be present at stoichiometric levels to satisfy the metal aluminum fuel component since the riser sleeves and molds in which they are contained are permeable. Thus oxygen from the oxidizing agents is supplemented by atmospheric oxygen when the aluminum fuel is burned. Typically the weight ratio of aluminum to oxidizing agent is from about 10:1 to about 1:1, preferably about 5:1 to about 1.5:1.

Depending upon the degree of exothermic properties wanted in the sleeve, the amount of fine aluminum in the sleeve composition will range from 5 weight percent to 45 weight percent, typically 20 weight percent to 35 weight percent, based upon the weight of the sleeve composition.

Insulating materials can be added to the sleeve composition. Such materials include refractory materials (e.g. magnesia, alumina, sand, and aluminosilicate), hollow microspheres, and fibers. The amount of insulating material in the sleeve composition ranges from 30 weight percent to 85 weight percent, typically 30 weight percent to 70 weight percent, where the weight percent is based upon the weight of the sleeve composition. Preferably used as the insulating material are hollow aluminosilicate microspheres such as those described in WO 97/35677, which is hereby incorporated by reference.

The sleeve mixes can also contain refractories such as silica, sand, magnesia, alumina, olivine, chromeite, aluminosilicate, and silicon carbide among others. Those refractories are preferably used in amounts less than 60 weight percent based upon the weight of the sleeve composition, more preferably less than 25 weight percent based upon the weight of the sleeve composition.

In addition, the sleeve composition may contain fillers, additives, and fluxes, such as cryolite (Na$_3$AlF$_6$), potassium aluminum tetrafluoride, potassium aluminum hexafluoride.

The sleeve compositions are mixed with chemical binders to form a sleeve mix. Any inorganic or organic foundry binder, that sufficiently holds the sleeve mix together in the shape of a sleeve and polymerizes in the presence of a curing catalyst, will work. Examples of such binders include inorganic binders such as sodium silicate binders cured with carbon dioxide (see U.S. Pat. No. 4,985,489 which is hereby incorporated into this disclosure by reference), and organic binders such as phenolic resins, phenolic urethane binders, furan binders, alkaline phenolic resole binders (see U.S. Pat. No. 4,750,716 which is hereby incorporated by reference), and epoxy-acrylic binders among others. Preferred binders include epoxy-acrylic binders sold by Ashland Inc. under the ISOSET® trademark. The epoxy-acrylic binders, cured with sulfur dioxide in the
presence of an oxidizing agent, are described in U.S. Pat. No. 4,526,219, which is hereby incorporated into this disclosurereference. Most preferred of the binder are amine curable phenolic urethane binders, as described in U.S. Pat. No. 3,485,497, U.S. Pat. Nos. 3,409,579, and 3,676,392, which are hereby incorporated into this disclosure by reference. These binders are based on a two-part system, one part being a phenolic resin component and the other part being a polyisocyanate component.

[0035] The amount of binder needed is an effective amount to maintain the shape of the sleeve and allow for effective curing, i.e. which will produce a sleeve which can be handled or self-supported after curing. An effective amount of binder is greater than about 4 weight percent, based upon the weight of the sleeve composition. Preferably the amount of binder ranges from about 5 weight percent to about 15 weight percent, more preferably from about 6 weight percent to about 12 weight percent.

[0036] Curing the sleeve by the no-bake process takes place by mixing a liquid curing catalyst with the sleeve mix, shaping the sleeve mix containing the catalyst, and allowing the sleeve shape to cure, typically at ambient temperature without the addition of heat. The preferred liquid curing catalyst is a tertiary amine and the preferred no-bake curing process is described in U.S. Pat. No. 3,485,797, which is hereby incorporated by reference into this disclosure. Specific examples of such liquid curing catalysts include 4-alkyl pyridines wherein the alkyl group has from one to four carbon atoms, isoquinoline, arylpyridines such as phenyl pyridine, pyridine, acridine, 2-methoxy pyridine, pyridazine, 3-chloro pyridine, quinoline, N-methyl imidazole, N-ethyl imidazole, 4,4'-dipyrildine, 4-phenylpropyridine, 1-methylbenzimidazole, and 1,4-thiazine.

[0037] Curing the sleeve by the cold-box process takes place by blowing or ramming the sleeve mix into a pattern and contacting the sleeve with a vaporous or gaseous catalyst. Various vapor or vapor/gas mixtures or gases such as tertiary amines, carbon dioxide, methyl formate, and sulfur dioxide can be used depending on the chemical binder chosen. Those skilled in the art will know which gaseous curing agent is appropriate for the binder used. For example, an amine vapor/gas mixture is used with phenolic-urethane resins. Sulfur dioxide (in conjunction with an oxidizing agent) is used with an epoxy-acrylic resin. Carbon dioxide (see U.S. Pat. No. 4,985,489, which is hereby incorporated by reference) or methyl esters (see U.S. Pat. No. 4,750,716 which is hereby incorporated into this disclosure by reference) are used with alkali phenolic resole resins.

[0038] Preferably sleeves are prepared by a cold-box process with a phenolic urethane binder by passing a tertiary amine gas, such as triethylamine, through the molded sleeve mix in the manner as described in U.S. Pat. No. 3,409,579; or with an epoxy-acrylic binder cured with sulfur dioxide in the presence of an oxidizing agent as described in U.S. Pat. No. 4,526,219. Typical gassing times are from 0.5 to 3.0 seconds, preferably from 0.5 to 2.0 seconds. Purge times are from 1.0 to 60 seconds, preferably from 1.0 to 10 seconds.

EXAMPLES

(General Procedure)

[0039] The exothermic sleeves were prepared with phenolic-urethane binder using cold-box technology. The exothermic composition contained aluminosilicate microspheres, aluminum powder, iron oxide, manganese dioxide, potassium nitrate and cryolite. Those components were mixed with an ISOCURE® Part I and Part II binder and then cured with an amine catalyst using conventional cold box technology. The sleeves were then tested for casting performance in a ductile iron test casting. Evaluation of the resulting castings included the safety margin of the riser and an analysis of the surface finish of casting. All parts are by weight and all percentages are weight percentages based upon the weight of the sleeve composition unless otherwise specified.

Example A, B, 1, and 2

(Preparation of sleeve compositions)

[0040] Sleeve compositions were prepared by mixing the following components with the aluminum powder described in Table I. The “fine aluminum” and “coarse aluminum” used in the examples are described in Table II.

<table>
<thead>
<tr>
<th>TABLE I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>Microspheres</td>
</tr>
<tr>
<td>Potassium nitrate</td>
</tr>
<tr>
<td>Cryolite</td>
</tr>
<tr>
<td>MnO₂</td>
</tr>
<tr>
<td>Fe₃O₄</td>
</tr>
<tr>
<td>Aluminum powder (Table II)</td>
</tr>
</tbody>
</table>

[0041] TABLE II

<table>
<thead>
<tr>
<th>PARTICLE SIZE DISTRIBUTION OF THE COARSE AND FINE ALUMINUM USED IN THE SLEEVE COMPOSITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight % particle retained on Mesh</td>
</tr>
<tr>
<td>Aluminum Composition</td>
</tr>
<tr>
<td>-----------------------</td>
</tr>
<tr>
<td>40</td>
</tr>
<tr>
<td>70</td>
</tr>
<tr>
<td>100</td>
</tr>
<tr>
<td>140</td>
</tr>
<tr>
<td>200</td>
</tr>
<tr>
<td>325</td>
</tr>
<tr>
<td>Pan</td>
</tr>
</tbody>
</table>

²Where g/w is based upon the total parts of components used in the sleeve mix.
³Sleeve composition B was a 50/50 weight percent mixture of mix A (coarse aluminum) and B (fine aluminum).

Examples C, D, and 3, and 4

(Preparation of sleeves and sleeve mixes from aluminum compositions A, B, 1, 2)

[0042] Sleeves (C, D, 3, and 4) were prepared by mixing the aluminum compositions (A, B, 1, and 2) with 8.8 parts of ISOCURE® cold-box binder. Test sleeves (6"x3") were prepared by the ISOCURE® cold-box process along the lines described in WO 97/35677, which is hereby incorporated by reference.
Example E, F, and 5, and 6

(Preparation of castings from the sleeves C, D, 3, and 4)

Ductile iron castings were prepared from casting assemblies where sleeves C, D, 3, and 4 were used to surround the top riser of the casting assembly respectively. The test casting made is an impeller casting having a weight of about 5.5 kg and uses a 2.5 x 3.5 riser to feed the casting. The metal is poured down the sprue from the side, filling the casting cavity first and then the riser. The pouring temperature was 1600° C. The surface finish of the castings in contact with the sleeve was compared. The results of the casting experiments are summarized in Table III below. The safety margin of all the cast sleeves was measured and was more than adequate.

### TABLE III

<table>
<thead>
<tr>
<th>EXAMPLE</th>
<th>SLEEVE</th>
<th>AI</th>
<th>CASTING RESULTS/SURFACE FINISH</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>C</td>
<td>Coarse (A)</td>
<td>Poor</td>
</tr>
<tr>
<td>H</td>
<td>D</td>
<td>Mix (B)</td>
<td>Poor</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>Fine (1)</td>
<td>Excellent</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>Fine (2)</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

The observations recorded in Table III indicate that the ductile iron castings made with the sleeves that contained the fine aluminum had excellent surface finish, while the castings prepared with the sleeves that contained the coarse aluminum had poor surface finish.

1. An exothermic sleeve composition comprising:
   (a) an oxidizable metal where the oxidizable metal comprises fine aluminum as the major component, and
   (b) an effective amount of an oxidizing agent capable of generating an exothermic reaction.

2. The composition of claim 1 wherein the fine aluminum comprises a particle distribution such that 95 weight percent of the aluminum passes through a 100 mesh as determined by the US Standard Screen Test.

3. The sleeve composition of claim 2 wherein the fine aluminum comprises a particle distribution such that 95 weight percent passes through a 140 mesh as determined by the US Standard Screen Test.

4. The composition of claim 3 wherein the fine aluminum comprises at least 5 to 45 weight percent of the sleeve composition.

5. The sleeve composition of claim 4 wherein the sleeve composition contains from 30 weight percent to 80 weight percent of hollow alumina microspheres, where said weight is based upon the total weight of the sleeve composition.

6. The sleeve composition of claim 4 wherein the sleeve composition contains sand as a refractory in an amount of 30 weight percent to 70 weight percent based upon the total weight of the sleeve composition.

7. A sleeve mix comprising the sleeve composition of claim 1, 2, 3, 4, 5, or 6 and an effective binding amount of an organic foundry binder.

8. A cold-box process for making an exothermic sleeve comprising:
   (A) introducing the sleeve mix of claim 7 into a sleeve pattern to prepare an uncured sleeve;
   (B) contacting said uncured sleeve prepared by (A) with a vaporous curing catalyst;
   (C) allowing said sleeve resulting from (B) to cure until said sleeve becomes handleable; and
   (E) removing said sleeve from the pattern.

9. The process of claim 8 wherein the binder is selected from the group of phenolic urethane binders and epoxy-acrylic binders.

10. The process of claim 9 wherein the binder level is from about 4 weight percent to about 12 weight percent based upon the weight of the sleeve composition.

11. A sleeve prepared by the process of claim 10.

12. A process for casting a metal part which comprises:
   (1) using an exothermic sleeve of claim 11 in a mold assembly of a casting assembly;
   (2) pouring metal, while in the liquid state, into said casting assembly;
   (3) allowing said metal to cool and solidify; and
   (4) then separating the cast metal part from the casting assembly.

13. A metal part prepared in accordance with claim 12.