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COATING COMPOSITION

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ABSTRACT OF THE DISCLOSURE

A composition, which may be used, for example, as a coating on articles to be placed in molten metals such as aluminum and copper, is provided comprising a non-basic refractory such as calcium phosphate, a finely divided material which may be either aluminum or aluminum oxide or mixtures thereof, and a bonding agent such as aluminum phosphate or zirconium phosphate. The composition is used as an aqueous suspension and it may also contain a suspending agent such as kaolin and a gelling agent such as silicon.

The present invention relates to protective coatings. More particularly, the present invention resides in protective coatings for metals and ceramics used in contact with molten metals, i.e., copper, aluminum and base alloys of these metals.

In molten metal handling applications, it is desirable to use certain materials for structural parts due to their desirable properties. In the melting and casting of copper and copper alloys, for example, it is highly desirable to utilize heat resistant stainless steel or cobalt alloy structural parts, such as molten metal flow distributors, spouts, filtering screens, thermocouple protection tubes and hand tools. These materials provide savings in initial cost of structural parts, savings in reduced downtime and replacement of parts, as well as permitting the design of parts used in continuous contact with molten metals.

The properties of many heat resistant, high strength metals and alloys could be used to great advantage in nonferrous foundry equipment except for the inevitable early failure of such metals under attack and dissolution by the molten alloys being processed. For example, molten copper invariably attacks these materials causing rapid deterioration and short life.

If these structural materials could be protected from molten metal attack by a relatively inexpensive inorganic coating of attack resistant material, their properties of ductility, thermal and mechanical shock resistance and ease of fabrication could be used to good advantage in molten metal handling and casting equipment.

The attainment of such a protective coating for use under these extreme conditions presents numerous problems. For example, one must find a coating resistant to attack by the molten metal and particularly resistant to attack by metal oxides. One must find a coating which will be firmly bonded to the metal part and maintain its integrity for substantially the life of the metal part. One must find a coating which has these characteristics and maintains them in use despite strenuous conditions such as thermal cycling and so forth.

One of the major difficulties in the application of a coating to high temperature metals is that of obtaining a thermal expansion fit between the coating and the metal base. Metals have high coefficients of thermal expansion whereas most nonmetals have low coefficients. If the thermal expansion differential between coating and base is not minimized, the coating will tend to separate and spall off with repeated immersion of the coated part in molten metal followed by cooling to room temperature.

It is, therefore, a principal object of the present invention to provide a protective coating for metals and ceramics used in contact with molten metals, i.e., copper, aluminum and their alloys.

It is an additional object of the present invention to provide a coating as aforesaid which resists the attack of metal oxides.

It is an additional object of the present invention to provide a coating as aforesaid which can be readily and firmly bonded to metal parts and maintain its integrity for substantially the life of the part throughout a wide variety of strenuous conditions.

It is an additional object of the present invention to provide a nonvitreous coating as aforesaid which is not readily wet by molten copper and copper alloys and therefore easily cleaned of metal deposits and oxides after use to ready it for reuse.

It is an additional object of the present invention to provide a nonvitreous coating as aforesaid which will withstand repeated use in molten copper and copper base alloys on cycling from molten metal temperatures to room temperature without loss by spalling, peeling or flaking off.

Further objects and advantages of the present invention will be apparent from a consideration of the following specification.

In accordance with the present invention it has now been found that the foregoing objects and advantages may be readily attained.

The protective coating of the present invention comprises an aqueous suspension containing from 35 to 70% by weight of a nonbasic refractory, i.e., an acidic or neutral refractory, from 15 to 35% by weight of a finely divided material selected from the group consisting of aluminum, aluminum oxide, and mixtures thereof and from 15 to 50% by weight of a refractory bonding agent.

In accordance with the present invention it has been found that the foregoing coating protects a substrate of stainless steel, for example, from virtually any attack by molten copper and aluminum alloys for long periods of time. The coating adheres tenaciously, is thermally shock proof, non-wetting and easily cleaned after use. When applied to oxide and other refractory crucibles and ceramic bodies, it also exhibits the property of inhibiting penetration of molten metal and oxides, thus extending life and minimizing contamination of the melt.

It is particularly advantageous that the foregoing objects of the present invention are readily accomplished in accordance with the present invention. An additional advantage of the present invention is the ability of the coating composition to reduce to a substantial extent the rate of oxygen uptake by the underlying metal to which it is applied despite the exposure of the coated metal to high temperature oxidizing atmospheres.

The coating composition of the present invention is an aqueous suspension containing from 35 to 70% by weight of a nonbasic refractory. The 35 to 70% by weight range is parts by weight based on the nonaqueous components of the composition. By nonbasic refractory it is intended to contemplate acidic or neutral refractories. A refractory is a non-metallic structural material for use at high temperatures. Any non-basic refractory may be conveniently used in the coating composition of the present invention. A preferred material is tri-calcium phosphate, for example, commercial bone ash. Typical other materials which may be readily employed are not limited to but include the following: silica; zirconia; mullite; beryllium oxide; titanium oxide; fire clay; kaolinite; alumina; chromium oxide; bauxite; spinel; silicon carbide; zirconium diboride; and so forth. The refractory material acts as a filler of high refractoriness, and is nonreactive with molten nonferrous metals. The refractory material is resistant to attack by molten copper and aluminum base alloys and is compatible with the bonding agent. In general, the refractory material is non-wetting. The preferred range is 40 to 70% by weight and optimally 55 to 65% by weight.

Naturally, the present invention contemplates the use of mixtures of any of the foregoing refractories.

The coating composition of the present invention utilizes a finely divided material selected from the group consisting of aluminum, aluminum oxide, and mixtures thereof. This compound is utilized in an amount from 15 to 35% by weight based upon the nonaqueous components of the coating composition. In accordance with the present invention the aluminum powder is preferably utilized for copper or copper base alloys and the aluminum oxide is preferably utilized for aluminum or aluminum base alloys. A mixture of aluminum and aluminum oxide is preferably employed for copper-aluminum alloys.

The preferred amount of this constituent is from 20 to 30% by weight.

The aluminum powder is preferably the nonleafing, non-lubricated type of aluminum or aluminum alloy containing a minimum of 95% by weight of elemental aluminum. The powder particle size is such that 97% will pass through a 200 mesh U.S. Standard sieve.

In addition to the foregoing constituents, the coating composition of the present invention contains from 15 to 50% of a refractory bonding agent or binder. Preferred materials are aluminum phosphate or zirconium phosphate. The bonding agents or binders contemplated must be refractory, i.e., they must withstand high temperatures up to 2500° F. Other such binder materials may, of course, be employed provided they will withstand these high temperatures. In addition, the refractory binder may contain, for example, small amounts of organic bonding agents.

The refractory bonding agent is utilized in an amount from 15 to 50% by weight based on the nonaqueous components of the coating composition. It is preferred to use from 20 to 30% by weight.

In addition to the foregoing constituents, one may optionally employ from 1 to 5% by weight of a suspending or thickening agent, such as kaolin. The purpose of this compound is to keep the ingredients of the coating composition in suspension. Otherwise, the ingredients would tend to settle on standing. In addition, the suspending or thickening agent tends to improve the applicability of the coating composition by painting, that is, it makes a smoother suspension. The suspending agent should preferably be an acidic or neutral refractory material, for example, fire clay may also be utilized. Alternatively, one might use an organic suspending agent, but this is less preferred.

Another optional component is silica in an amount from 1 to 5% by weight. Alternatively, one may use any thixotropic or gelling agent preferably refractory in nature. This material acts as a control over the thixotropic or gelling properties of the coating composition.

The coating composition of the present invention is an aqueous suspension One should utilize from 25 to 40% by weight of water and preferably from 28 to 38% by weight in order to provide the proper consistency for spraying or brushing the material on the part to be coated. The coating composition is applied to the structural part in a thickness of at least 0.002 inch, normally from 0.002 to 0.006 inch, and preferably from 0.003 to 0.0005 inch.

In utilizing the coating composition of the present invention one may premix the nonbasic refractory, the aluminum or aluminum oxide powder, the thixotropic agent, and the suspending agent. These constituents may then be stored for any desired period of time without degradation and loss in properties. The refractory bonding agent or binder, e.g., aluminum phosphate, may be added prior to use and the coating composition prepared for application. The aluminum phosphate may be prepared as an aqueous suspension, if desired, or the water may be added at the time of mixing the suspension.

In general, the coating composition of the present invention should be prepared by adding the liquid ingredients to the dry materials only just prior to use. The final slurry mixture cannot be stored for more than 20 hours without loss of bonding strength. As pointed out above, however, a mixture of the dry materials may be prepared or stored indefinitely without any difficulty.

The present invention will be more readily apparent from a consideration of the following illustrative example.

Example

One method of practicing this invention is outlined in the following steps.

(1) The dry coating ingredients were prepared by mixing the following finely divided powders in a suitable blender until uniformly mixed:

	Parts by weight
Tri-calcium phosphate, (commercial bone ash,—325 particle size, 97% $Ca_3(PO_4)_2$ min.)	60
Aluminum metal powder, type "H" —200 mesh, nonleafing	30
Silica power, Si_2, —325 mesh	5
Kaolin clay, air floated, water washed	5

(2) The final coating batch was prepared by thoroughly mixing, just prior to use, three parts by weight of the above dry mix with one part by weight of an aqueous solution of aluminum phosphate having a ratio of

$$Al_2O_3:3P_2O_5$$

from 1.30 to 1.36 and a specific gravity of approximately 1.48. Mixing was accomplished in a shear type mixer to insure complete wetting and distribution of agglomerated powder particles. Sufficient clean water was added to adjust the slurry to the proper consistency for application by brushing, spraying or dipping. The water addition was 28–38% by weight calculated on the basis of the sum of all the other ingredients.

(3) The metal test strips were prepared for coating by the following procedure. The metal strips were degreased with solvent. They were then lightly etched in 50 volume percent hydrochloric acid, HCl, for 10 minutes followed by water rinse. They were then passivated in 30 volume percent nitric acid, HNO_3, for 20 minutes followed by a water rinse. The surfaces were oxidized in air atmosphere at 1750° F. for 6 minutes and air cooled to room temperature.

(4) The coating was applied to the metal substrate by spraying. The use of a spraying technique is preferred because it permits better control of the thickness of the coating, although brushing or dipping may be used. The coating slurry is applied to such a thickness as to produce a deposit of 20 to 50 m./cm.^{2}, which is small enough to avoid a flaky deposit while on the other hand insuring a coherent coating of adequate covering power.

(5) The coated metal part was permitted to air dry at a temperature not to exceed 40° C. for at least 15 minutes. Twenty minutes is generally sufficient. The coated part may then be oven baked, if desired, to a temperature of 200° C. for 10 minutes to render the aluminum phosphate bond permanently resistant to water. If the need for this property is not important, the baking procedure may be omitted and the coated article is ready for use after the air drying period. In this example the oven baking was omitted.

(6) Samples of sheet and rod forms of wrought 400 series stainless steels coated as described and subjected to immersion in induction stirred crucible melts of electrolytic tough pitch copper, deoxidized copper, 70–30 brass, 12% nickel silver, phosphor-bronze and other copper alloys at temperatures up to 1200° C. and times to

4 hurs. The test specimens were removed from the molten bath at half-hour intervals for visual observation and reinserted after cooling nearly to room temperature. The results showed no loss of material from the basis metal. Control samples of the 400 series stainless steels, subjected to the same test conditions without benefit of this protective coating showed the following typical results.

Grade of steel	Test medium	Temperature, ° C.	Time (hr.)	Percent wt. loss
AISI 430	70-30 brass	1, 093	1	12. 50
AISI 430	do	1, 093	1½	34. 70
AISI 446	do	1, 093	1½	15. 40
AISI 430	ETP copper	1, 200	1	49. 00

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

What is claimed is:

1. A composition for use in contacting molten metals consisting essentially of:

(a) 35–70% by weight of a non-basic refractory which is non-reactive with molten non-ferrous metals consisting essentially of calcium phosphate;

(b) 15–35% by weight of a finely divided material selected from the group consisting of aluminum, aluminum oxide, and mixtures thereof; and

(c) from 15–50% of refractory bonding agent selected from the group consisting of aluminum phosphate, zirconium phosphate and mixture thereof.

2. A composition according to claim **1** including from 1 to 5% by weight of a suspending agent.

3. A composition according to claim 1 including from 1 to 5% by weight of a gelling agent.

4. A composition according to claim **1** in which the composition is an aqueous suspension.

5. A composition according to claim **1** which contains from 25–40% by weight water.

6. A composition consisting essentially of:

(a) 35–70% by weight of non-basic refractory consisting essentially of calcium phosphate;

(b) 15–35% by weight of a finely divided material selected from the group consisting of aluminum, aluminum oxide, and mixture thereof; and

(c) from 15–50% of refractory bonding agent selected from the group consisting of aluminum phosphate, zirconium phosphate and mixtures thereof.

7. A protectively coated structural part for contact with molten metal, said structural part coated to a thickness of at least 0.002 inch with a protective coating composition consisting essentially of:

(a) 35–70% by weight of a non-basic refractory which is non-reactive with molten non-ferrous metals consisting essentially of calcium phosphate;

(b) 15–35% by weight of aluminum, aluminum oxide, and mixtures thereof; and

(c) from 15–50% of refractory bonding agent selected from the group consisting of aluminum phosphate, zirconium phosphate, and mixtures thereof.

8. A process for protecting articles to be in contact with molten metals and oxides associated therewith comprising coating said articles with a composition consisting essentially of:

(a) 35–70% by weight of a non-basis refractory which is non-reactive with molten non-ferrous metals consisting essentially of calcium phosphate;

(b) 15–35% by weight of a finely divided material selected from the group consisting of aluminum, aluminum oxide, and mixtures thereof; and

(c) from 15–50% of refractory bonding agent selected from the group consisting of aluminum phosphate, zirconium phosphate, and mixtures thereof.

9. A composition according to claim **1** in which said non-basic refractory is commercial bone ash.

10. A protectively coated structural part according to claim **7** in which said non-basic refractory is commercial bone ash.

11. A process according to claim **8** in which the non-basic refractory is commercial bone ash.

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