

Composition

FIELD OF THE INVENTION

The present invention relates to a coating composition (e.g. a corrosion and erosion resistant coating composition), a kit and a method for making the composition, a method for coating substrates with the composition, and a substrate coated with the composition. The present invention also relates to the use of the coating composition to coat a substrate, and to prevent or reduce erosion and/or corrosion of a substrate and/or slag deposition on a substrate.

BACKGROUND OF THE INVENTION

Boiler systems (e.g. coal or biomass boiler systems) and other high temperature systems suffer from erosion and corrosion problems within the combustion zone.

Erosion problems are commonly caused by fly ash, which not only contacts parts of the boiler system at high velocity and causes mechanical damage but can also contribute to slagging formation. During combustion in a biomass-fired furnace, for example, alkali metals are released into the flue gas in the form of, for example, KOH, KCl, K₂SO₄, NaCl, and Na₂SO₄, and these then undergo complex chemical reactions and transformations. Partial alkali metal aerosols develop and form sub-micrometer ash particles through a series of mechanisms such as nucleation, adsorption, condensation etc. These aerosols then condense on heating surfaces and form a sticky initial slagging layer through thermophoresis and turbulent diffusion. This initial slagging layer adhesively bonds fly ash onto the heating surfaces thereby resulting in the formation of a slagging layer (see Figure 1).

Corrosion problems are commonly caused by oxidation of the metal surface of the boiler system by several types of active gases (e.g. oxygen, sulfur) present in the surrounding atmospheric gases, and by the effects of high temperature.

The above-mentioned problems have a significant impact on industry. Not only do large amounts of money need to be spent on maintenance (e.g. by repairing parts or providing replacement parts), there is also an opportunity loss whilst the boiler system is shut down for repair. As such, there exists a need to minimise and/or avoid the effects of these problems in boiler systems and other high temperature systems.

SUMMARY OF THE INVENTION

Viewed from a first aspect, the present invention provides a coating composition comprising:

a corrosion and erosion resistant metal oxide selected from silicon oxide, aluminium oxide, zirconium oxide, mica, zinc oxide, or a mixture thereof;

5 a high temperature resistant metal oxide selected from chromium oxide, titanium dioxide, or a mixture thereof; and

a binder comprising alkali metal silicate and alkali metal feldspar,

wherein the weight ratio of alkali metal silicate to alkali metal feldspar is in the range 4.0 to 10.0 : 1.

10 Viewed from a further aspect, the present invention provides a container containing a coating composition as hereinbefore described.

Viewed from a further aspect, the present invention provides a kit for preparing an aqueous coating composition as hereinbefore described, comprising:

15 (i) a first container containing a mixture of a corrosion and erosion resistant metal oxide selected from silicon oxide, aluminium oxide, zirconium oxide, mica, zinc oxide, or a mixture thereof, and a high temperature resistant metal oxide selected from chromium oxide, titanium dioxide, or a mixture thereof; and

20 (ii) instructions to mix said mixture with a binder comprising alkali metal silicate and alkali metal feldspar.

Viewed from a further aspect, the present invention provides a method for preparing a coating composition as hereinbefore described, comprising the steps of:

25 (i) preparing a mixture of a corrosion and erosion resistant metal oxide selected from silicon oxide, aluminium oxide, zirconium oxide, mica, zinc oxide, or a mixture thereof, and a high temperature resistant metal oxide selected from chromium oxide, titanium dioxide, or a mixture thereof; and

(ii) mixing said mixture with a binder comprising alkali metal silicate and alkali metal feldspar.

30 Viewed from a further aspect, the present invention provides a method for preparing a coated substrate, comprising the steps of:

(i) providing a substrate; and

(ii) applying a coating composition as hereinbefore described onto at least one surface of said substrate.

35 Viewed from a further aspect, the present invention provides a coated substrate obtainable by or obtained by the method as hereinbefore described.

Viewed from a further aspect, the present invention provides a coated substrate comprising a coating composition as hereinbefore described.

Viewed from a further aspect, the present invention provides a coated substrate, wherein said coating comprises:

- 5 a corrosion and erosion resistant metal oxide selected from silicon oxide, aluminium oxide, zirconium oxide, mica, zinc oxide, or a mixture thereof;
- a high temperature resistant metal oxide selected from chromium oxide, titanium dioxide, or a mixture thereof; and
- a binder comprising alkali metal silicate and alkali metal feldspar,
- 10 wherein the weight ratio of alkali metal silicate to alkali metal feldspar is in the range of 4.0 to 10.0 : 1, preferably 4.0 – 7.5 : 1.

Viewed from a further aspect, the present invention provides a boiler (e.g. a coal or biomass boiler) comprising a coated substrate as hereinbefore described.

- 15 Viewed from a further aspect, the present invention provides the use of a coating composition as hereinbefore defined to coat a substrate.

Viewed from a further aspect, the present invention provides the use of a coating composition as hereinbefore described to prevent or reduce erosion and/or corrosion of a substrate and/or slag deposition on a substrate.

20 DEFINITIONS

As used herein, the term “binder” refers to a material or substance that holds or draws other materials together.

- 25 As used herein, the term “high temperature resistant metal oxide” refers to a metal oxide which is able to withstand temperatures in the range 800 to 1500 °C without decomposing.

As used herein, the term “corrosion and erosion resistant metal oxide” refers to a metal oxide, preferably a metal oxide, which is able to withstand corrosive conditions (e.g. contact with oxygen-containing gases and/or sulfur-containing gases) and erosive conditions (e.g. fly ash) typically present in a high temperature boiler system.

- 30 As used herein, the term “feldspar” refers to an aluminosilicate mineral that contains a metal. As used herein, the term “alkali metal feldspar” refers to an aluminosilicate mineral that contains an alkali metal, preferably sodium or potassium.

- 35 As used herein, the term “mica” refers to a sheet phyllosilicate mineral having the repeating unit general formula $XY_{2-3}Z_4O_{10}(OH, F)_2$, wherein X = K, Na, or Ca; Y = Al, Mg, Fe, or mixtures thereof; and Z = Si, Al or mixtures thereof.

As used herein, the term "room temperature" refers to temperatures in the range 20 to 35 °C.

As used herein, the term "wt%" is based on the total weight of the composition, unless otherwise specified.

As used herein, the term "weight ratio" refers to the ratios of the solid weights of the specified components. Thus, if a component is present in the composition as a solution (e.g. as an aqueous solution), any weight ratio including this component refers to the weight of the solid component present in that solution, not the weight of the solution.

As used herein, a weight ratio of A:B:C which is specified as (a1 to a2) : (b1 to b2) : (c1 to c2), means that the value of A in the ratio can range from a1 to a2, that the value of B in the ratio can range from b1 to b2, and that the value of C in the ratio can range from c1 to c2.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a coating composition comprising:
a corrosion and erosion resistant metal oxide selected from silicon oxide, aluminium oxide, zirconium oxide, mica, zinc oxide, or a mixture thereof;
a high temperature resistant metal oxide selected from chromium oxide, titanium dioxide, or a mixture thereof; and
a binder comprising alkali metal silicate and alkali metal feldspar,
wherein the weight ratio of alkali metal silicate to alkali metal feldspar is in the range 4.0 to 10.0 : 1.

The present invention advantageously provides a corrosion and erosion resistant coating composition that yields coatings that can withstand erosive and corrosive conditions at high temperatures. Thus, the coatings of the present invention display a range of desirable properties, including high strength and durability and a low surface roughness. These properties make the coating compositions of the present invention particularly suitable for coating the surfaces of boiler tubes and other boiler parts in order to ensure they perform efficiently and have a prolonged lifetime.

Without wishing to be bound by theory, it is thought that the application of the coating compositions to the surface of a metal substrate (e.g. a boiler tube) results in the active metal surface being protected by an inert, ceramic surface, which not only prevents initial slagging formation and thereby reduces the slag deposition rate, but also provides a protective barrier for the underlying substrate and therefore provides erosion

and corrosion resistance. The ceramic nature of the applied coating is believed to be a result of the weight ratio of the specific components present in the composition. Similarly, application of the coating compositions to the surface of a cement substrate (e.g. a cement substrate, or a substrate (e.g. a metal substrate) coated with a layer of cement) results in the surface being protected by an inert, ceramic surface, which not only prevents initial slagging formation and thereby reduces the slag deposition rate, but also provides a protective barrier for the underlying ceramic substrate and therefore provides erosion resistance.

In preferred compositions of the present invention, the weight ratio of alkali metal silicate to alkali metal feldspar is in the range 4.0 to 7.5 : 1 (e.g. 4.5 to 7.5 : 1), more preferably 4.0 to 7.0 : 1 (e.g. 4.5 to 7.0 : 1), even more preferably 4.0 to 6.5 : 1 (e.g. 4.5 to 6.5 : 1), even more preferably 4.0 to 6.0 : 1 (e.g. 4.5 to 6.0 : 1), even more preferably 4.0 to 5.5 : 1 (e.g. 4.5 to 5.5 : 1), even more preferably 4.0 to 5.0 : 1 (e.g. 4.5 to 5.0 : 1). At these ratios, the coatings of the present invention have been demonstrated to have a low mass gain (in mg/cm²), and to also undergo minimal, if any, cracking when subjected to high temperature corrosive conditions. The coatings of the present invention are therefore corrosion-resistant.

In preferred compositions of the present invention, the alkali metal silicate is selected from sodium silicate, potassium silicate, or a mixture thereof. More preferably, the alkali metal silicate is a mixture of sodium silicate and potassium silicate.

In preferred compositions of the present invention, the alkali metal feldspar is selected from potassium feldspar, sodium feldspar, or a mixture thereof. More preferably, the alkali metal feldspar is potassium feldspar.

In preferred compositions of the present invention, the alkali metal silicate is a mixture of sodium silicate and potassium silicate, and the alkali metal feldspar is potassium feldspar.

In preferred compositions of the present invention, the weight ratio of sodium silicate to potassium silicate to potassium feldspar is in the range (2.1 to 5) : (1.5 to 5) : 1, preferably (2.1 to 3.5) : (1.5 to 5) : 1, more preferably (2.1 to 3.3) : (1.5 to 5) : 1, even more preferably (2.1 to 3.1) : (1.5 to 5) : 1, even more preferably (2.1 to 2.9) : (1.5 to 5) : 1, even more preferably (2.1 to 2.7) : (1.5 to 5) : 1, even more preferably (2.1 to 2.5) : (1.5 to 5) : 1, even more preferably (2.1 to 2.3) : (1.5 to 5) : 1.

In alternative preferred compositions of the present invention, the weight ratio of sodium silicate to potassium silicate to potassium feldspar is in the range (2.1 to 5) : (1.8 to 3.5) : 1, preferably (2.1 to 5) : (1.8 to 3.2) : 1, more preferably (2.1 to 5) : (1.8 to 3.0) :

1, even more preferably (2.1 to 5) : (1.8 to 2.8) : 1, even more preferably (2.1 to 5) : (1.8 to 2.6) : 1, even more preferably (2.1 to 5) : (2.0 to 4.0) : 1, even more preferably (2.1 to 5.0) : (2.0 to 3.5) : 1, even more preferably (2.1 to 5.0) : (2.0 to 3.2) : 1, even more preferably (2.1 to 5.0) : (2.0 to 2.8) : 1, even more preferably (2.1 to 5.0) : (2.0 to 2.6) : 1.

In alternative preferred compositions of the present invention, the weight ratio of sodium silicate to potassium silicate to potassium feldspar is in the range (2.1 to 3.5) : (2.4 to 4.0) : 1, preferably (2.1 to 3.5) : (2.4 to 3.5) : 1, more preferably (2.1 to 3.5) : (2.4 to 3.2) : 1, even more preferably (2.1 to 3.5) : (2.4 to 3.0) : 1, even more preferably (2.1 to 3.5) : (2.4 to 2.7) : 1.

In alternative preferred compositions of the present invention, the weight ratio of sodium silicate to potassium silicate to potassium feldspar is in the range (2.2 to 2.7) : (2.4 to 4.0) : 1, preferably (2.2 to 2.7) : (2.4 to 3.5) : 1, more preferably (2.2 to 2.7) : (2.4 to 3.2) : 1, even more preferably (2.2 to 2.7) : (2.4 to 3.0) : 1, even more preferably (2.2 to 2.7) : (2.4 to 2.7) : 1.

Preferred compositions of the present invention comprise 50 to 75 wt%, more preferably 55 to 70 wt%, even more preferably 57 to 69 wt% aqueous binder based upon the total weight of composition.

Preferred compositions of the present invention comprise 15 to 40 wt%, more preferably 20 to 35 wt%, even more preferably 20 to 30 wt%, even more preferably 23 to 30 wt% solid binder based upon the total weight of composition.

In preferred compositions of the present invention, the alkali metal silicate is in the form of an aqueous solution. In preferred compositions of the present invention, the alkali metal silicate is in the form of a 20 to 50 wt% aqueous solution, more preferably a 25 to 45 wt% aqueous solution, even more preferably a 30 to 40 wt% aqueous solution.

Preferred compositions of the present invention comprise 20 to 35 wt%, more preferably 22 to 30 wt%, even more preferably 25 to 29 wt% aqueous sodium silicate solution based upon the total weight of composition.

Preferred compositions of the present invention comprise 20 to 45 wt%, more preferably 25 to 40 wt%, even more preferably 29 to 35 wt% aqueous potassium silicate solution based upon the total weight of composition.

Preferred compositions of the present invention comprise 1 to 7 wt%, more preferably 2 to 6 wt%, even more preferably 3 to 5 wt% alkali metal feldspar based upon the total weight of composition.

In preferred compositions of the present invention, the weight ratio of the binder to the high temperature resistant metal oxide is 3.0 to 8.0 : 1 (e.g. 4.0 to 8.0 : 1) , more preferably 3.0 to 7.0 : 1 (e.g. 4.0 to 7.0 : 1), even more preferably 3.0 to 6.0 : 1 (e.g. 4.0 to 6.0 : 1), even more preferably 3.0 to 5.0 : 1 (e.g. 4.0 to 5.0 : 1, such as 4.0 to 4.5 : 1).

5 In preferred compositions of the present invention, the weight ratio of the corrosion and erosion resistant metal oxide to the high temperature resistant metal oxide is 3.0 to 10.0 : 1, preferably 3.0 to 8.0 : 1 (e.g. 4.0 to 8.0 : 1, such as 4.5 to 8.0 : 1), more preferably 3.0 to 7.0 : 1 (e.g. 4.0 to 7.0 : 1, such as 4.5 to 7.0 : 1), even more preferably 3.0 to 6.0 : 1 (e.g. 4.0 to 6.0 : 1, such as 4.5 to 6.0 : 1), even more preferably to 3.0 to 5.5 : 1 (e.g. 4.0 to 5.5 : 1, such as 4.5 to 5.5 : 1), even more preferably to 3.0 to 5.3 : 1 (e.g. 4.0 to 5.3 : 1, such as 4.5 to 5.3 : 1). In alternative preferred compositions of the present invention, the weight ratio of the corrosion and erosion resistant metal oxide to the high temperature resistant metal oxide is 5.0 to 7.0 : 1, preferably 5.0 to 6.0 : 1, more preferably 5.0 to 5.5 : 1, even more preferably 5.0 to 5.3 : 1. At these ratios, the coatings of the present invention have been demonstrated to have a high abrasion resistance, meaning that the coatings are able to withstand continued impact by falling/moving particles. Such an environment is typically found within a high temperature boiler system. The coatings of the present invention are therefore erosion-resistant.

20 Preferred compositions of the present invention comprise 20 to 40 wt%, more preferably 30 to 40 wt%, even more preferably 30 to 35 wt%, of a corrosion and erosion resistant metal oxide based upon the total weight of the composition.

25 In preferred compositions of the present invention, the corrosion and erosion resistant metal oxide is selected from silicon oxide, aluminium oxide and zirconium oxide, or mixtures thereof. More preferably, the corrosion and erosion resistant metal oxide is selected from silicon oxide and aluminium oxide, or mixtures thereof. Even more preferably, the corrosion and erosion resistant metal oxide is a mixture of silicon oxide and aluminium oxide.

30 Preferred compositions of the present invention comprise 1 to 20 wt%, more preferably 3 to 15 wt%, even more preferably 5 to 10 wt%, of a high temperature resistant metal oxide based upon the total weight of the composition.

In preferred compositions of the present invention, the high temperature resistant metal oxide is chromium oxide. In alternative preferred compositions of the present invention, the high temperature resistant metal oxide is titanium dioxide.

In particularly preferred compositions of the present invention, the corrosion and erosion resistant metal oxide is a mixture of silicon oxide and aluminium oxide, and said high temperature resistant metal oxide is chromium oxide.

5 In preferred compositions of the present invention, the weight ratio of silicon oxide to chromium oxide to aluminium oxide is in the range (0.1 to 0.9) : (0.1 to 0.9) : 1, preferably (0.1 to 0.5) : (0.1 to 0.5) : 1, more preferably (0.2 to 0.5) : (0.1 to 0.4) : 1, even more preferably (0.3 to 0.5) : (0.1 to 0.3) : 1.

10 In alternative preferred compositions of the present invention, the corrosion and erosion resistant metal oxide is a mixture of silicon oxide and aluminium oxide, and said high temperature resistant metal oxide is titanium oxide.

In alternative preferred compositions of the present invention, the corrosion and erosion resistant metal oxide is a mixture of silicon oxide and zirconium oxide, and said high temperature resistant metal oxide is chromium oxide.

15 Preferred compositions of the present invention comprise 1 to 15 wt%, more preferably 5 to 15 wt%, even more preferably 7 to 11 wt%, of SiO_2 based upon the total weight of the composition.

20 Preferred compositions of the present invention comprise at least 15 wt% of Al_2O_3 based upon the total weight of the composition. More preferably, the compositions of the present invention comprise 15 to 35 wt%, more preferably 20 to 35 wt%, even more preferably 20 to 25 wt%, of Al_2O_3 based upon the total weight of the composition.

Preferred compositions of the present invention comprise 1 to 10 wt%, more preferably 2 to 8 wt%, even more preferably 4 to 8 wt%, of Cr_2O_3 based upon the total weight of the composition.

25 Preferred compositions of the present invention comprise 1 to 15 wt%, more preferably 5 to 15 wt%, even more preferably 7 to 11 wt%, of zirconium oxide based upon the total weight of the composition.

Preferred compositions of the present invention comprise 1 to 15 wt%, more preferably 5 to 15 wt%, even more preferably 7 to 11 wt%, of mica based upon the total weight of the composition.

30 Preferred compositions of the present invention comprise 1 to 15 wt%, more preferably 5 to 15 wt%, even more preferably 7 to 11 wt%, of zinc oxide based upon the total weight of the composition.

35 Preferred compositions of the present invention comprise 1 to 10 wt%, more preferably 2 to 8 wt%, even more preferably 4 to 8 wt%, of titanium dioxide based upon the total weight of the composition.

Preferably, the average particle size of the TiO_2 , Cr_2O_3 , SiO_2 and Al_2O_3 employed in the compositions of the present invention is equal to or less than 100 micron, preferably equal to or less than 65 micron, more preferably equal to or less than 45 micron, even more preferably equal to or less than 35 micron.

5 Preferably, the average particle size of the alkali metal feldspar employed in the compositions of the present invention is equal to or less than 125 micron, preferably equal to or less than 120 micron, more preferably equal to or less than 115 micron, even more preferably equal to or less than 110 micron.

10 Preferred compositions of the present invention do not comprise silicon carbide (SiC).

 Preferred compositions of the present invention do not comprise titanium dioxide (TiO_2).

 A particularly preferred composition of the present invention comprises:

15 1 to 15 wt%, preferably 7 to 11 wt% of SiO_2 ;
 15 to 35 wt%, preferably 20 to 25 wt% of Al_2O_3 ;
 1 to 10 wt%, preferably 4 to 8 wt% of Cr_2O_3 ;
 20 to 35 wt%, preferably 25 to 29 wt% of aqueous sodium silicate solution;
 20 to 45 wt%, preferably 29 to 35 wt% of aqueous potassium silicate solution;
 and

20 1 to 7 wt%, preferably 3 to 5 wt% of potassium feldspar,
 wherein each of the specified wt% values are based upon the total weight of the composition.

25 Preferably, the coating composition of the present invention is an aqueous coating composition. Preferably, the coating composition of the present invention comprises less than 5 wt%, more preferably less than 3 wt%, even more preferably less than 2 wt%, most preferably less than 1 wt % (e.g. less than 0.5 wt %) of organic solvent.

 The present invention also provides a container containing a coating composition as hereinbefore described. Containers of the present invention include drums, bottles, boxes, tins, jars, sachets etc.

30 The present invention also provides a kit for preparing an aqueous coating composition as hereinbefore described, comprising:

- (i) a first container containing a mixture of a corrosion and erosion resistant metal oxide selected from silicon oxide, aluminium oxide, zirconium oxide, mica, zinc oxide, or a mixture thereof, and a high temperature resistant metal

oxide selected from chromium oxide, titanium dioxide, or a mixture thereof;
and

- (ii) instructions to mix said mixture with a binder comprising alkali metal silicate and alkali metal feldspar.

5 Preferred kits further comprise a second container containing said binder.

The present invention also provides a method for preparing a coating composition as hereinbefore described, comprising the steps of:

- (i) preparing a mixture of a corrosion and erosion resistant metal oxide selected from silicon oxide, aluminium oxide, zirconium oxide, mica, zinc oxide, or a
10 mixture thereof, and a high temperature resistant metal oxide selected from chromium oxide, titanium dioxide, or a mixture thereof; and
- (ii) mixing said mixture with a binder comprising alkali metal silicate and alkali metal feldspar.

15 In preferred methods of the present invention, the step (ii) mixing is at room temperature.

The present invention also provides a method for preparing a coated substrate, comprising the steps of:

- (i) providing a substrate; and
- (ii) applying a coating composition as hereinbefore defined onto at least one
20 surface of said substrate.

In preferred methods of the present invention, the substrate is made from metal and/or cement. Preferably, the substrate is made from metal. More preferably, the substrate is made from carbon steel (e.g. carbon steel SS400) or stainless steel.

25 In preferred methods of the present invention, the substrate is a boiler tube, fire tube, a plug tube, a wall tube, a superheater tube or a coverguard. In boiler systems, plug tubes are attached to boiler tubes and fire tubes to help protect them from high temperature erosion and corrosion. In boiler systems, a wall tube is a tube on the wall in the combustion zone, which may or may not be covered with a layer of cement. In boiler systems, a superheater tube is a tube in the superheater zone. In boiler systems, a
30 coverguard (e.g. a coverguard made from stainless steel) is used to cover all or part of a superheater tube in order to protect the superheater tube.

In preferred methods of the present invention, the substrate has a surface roughness of 2.5 to 5.5 micron, preferably 3.0 to 5.0 micron (e.g. 4.0 micron) as determined by profilometry.

In preferred methods of the present invention, the coating composition is applied in step (ii) by a method selected from spray coating, brush coating, dip coating or combinations thereof. More preferably, the coating composition is applied in step (ii) by spray coating, even more preferably by air spray coating or airless spray coating.

5 In preferred methods of the present invention, step (ii) provides a layer of coating composition having a thickness (i.e. a wet thickness) of 300 to 400 microns, more preferably 320 to 380 microns (e.g. 350 microns).

Preferred methods of the present invention further comprise an initial step of preparing the substrate for coating. Preferably, the substrate is prepared for coating by
10 cleaning and/or blasting with sand or garnet.

Preferred methods of the present invention further comprise a drying step that follows step (ii). Preferably, the coated substrate is air-dried at room temperature for 1 to 24 hours, more preferably 1 to 12 hours, even more preferably 1 to 7 hours (e.g. 6 hours). In preferred methods of the present invention, the dried layer of coating composition has
15 a thickness of 100 to 200 microns, more preferably 120 to 180 microns (e.g. 150 microns).

Preferred methods of the present invention further comprise a sintering step that follows the drying step. Preferably, the dried coated substrate is sintered for 1 to 10 hours, more preferably 2 to 8 hours, even more preferably 3 to 6 hours (e.g. 5 hours).
20 Preferably, the dried coated substrate is sintered at 500 to 700 °C, more preferably 550 to 650 °C, even more preferably 580 to 620 °C (e.g. 600 °C). Preferably, the dried coated substrate is sintered at a heating rate of 1 to 10 °C/minute, more preferably 2 to 8 °C/minute, even more preferably 3 to 7 °C/minute.

The present invention also provides a coated substrate obtainable by or obtained
25 a method as hereinbefore described.

The present invention also provides a coated substrate comprising a coating composition as hereinbefore described.

The present invention also provides a coated substrate, wherein said coating comprises:

- 30 a corrosion and erosion resistant metal oxide selected from silicon oxide, aluminium oxide, zirconium oxide, mica, zinc oxide, or a mixture thereof;
a high temperature resistant metal oxide selected from chromium oxide, titanium dioxide, or a mixture thereof; and
a binder comprising alkali metal silicate and alkali metal feldspar,

wherein the weight ratio of alkali metal silicate to alkali metal feldspar is in the range of 4.0 to 10.0 : 1, preferably 4.0 to 7.5 : 1.

Preferred coatings are as set out above in relation to the coating compositions. It will be noted that the coatings of the present invention (i.e. the dry coatings after the solvent has been evaporated away) have the same ratios of components as the coating compositions, because the weight ratios employed in the coating compositions of the present invention refer to the ratios of the solid weights of the specified components.

Preferred coatings of the present invention have a weight loss of less than 50 mg, more preferably less than 40 mg, even more preferably less than 30 mg, even more preferably less than 20 mg when tested for abrasion resistance according to ASTM-D968. The coatings of the present invention perform well in abrasion resistance tests, indicating that they have a high strength and are able to withstand continued impact.

Preferably, the coated substrate of the present invention is a boiler tube, a fire tube, wall tube, superheater tube, coverguard or a plug tube.

The present invention also provides a boiler (e.g. a coal or biomass boiler) comprising a coated substrate as hereinbefore described.

The present invention also provides the use of a coating composition as hereinbefore described to coat a substrate.

The present invention also provides the use of a coating composition as hereinbefore described to prevent or reduce erosion and/or corrosion of a substrate and/or slag deposition on a substrate.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows a schematic diagram of slag formation in a biomass boiler.

Figure 2 shows the surface roughness (Ra) results of profilometry tests taken on the top surfaces of coatings of the present invention and of comparative coatings.

Figure 3 shows the weight loss of coatings of the present invention and of comparative coatings after having been subjected to an abrasion resistance test.

Figure 4a shows the measured sample weight of substrates coated with coatings of the present invention and comparative coatings after having been subjected to up to 15 cycles of a thermal shock resistance test.

Figure 4b shows the visual appearance of the coated substrates after having been subjected to the thermal shock resistance test of Figure 4a, alongside a blank substrate subjected to the same test conditions.

Figure 5 shows the mass gain (in mg/cm²) of substrates coated with coatings of the present invention and comparative coatings after having been subjected to a high temperature corrosion test.

Figure 6a shows the appearance of a plug tube coated with the composition of Example 2 prior to being subjected to a slag resistance test in a fire tube in a biomass boiler.

Figure 6b shows the appearance of a plug tube coated with the composition of Example 2 after having been subjected to a slag resistance test in a fire tube in a biomass boiler.

Figure 7a shows the appearance of an uncoated plug tube prior to being subjected to a slag resistance test in a fire tube in a biomass boiler.

Figure 7b shows the appearance of an uncoated plug tube after having been subjected to a slag resistance test in a fire tube in a biomass boiler.

EXAMPLES

Materials

All starting materials were commercially available from Sigma Aldrich.

Measurement methods

The coatings of the present invention were tested according to a variety of methods, as outlined below:

- The surface roughness of the coatings were assessed using a Mitutoyo: SURFTEST SV-3000 profilometer.
- Coating adhesion to the substrate was measured according to ASTM-D4541, wherein a dolly comprising a layer of glue is brought into contact with a coated substrate to determine how strongly the coating is attached to the substrate.
- Abrasion resistance of the coatings was measured according to ASTM-D968, wherein a 10 kg load of SiC particles (size 1.4 to 2.0 mm) is dropped onto the coating and resultant weight loss from the coating is measured.
- Thermal shock resistance was measured by heating a coated sample up to 800 °C in a furnace, using a heating rate of 8 °C/min. The sample was then held at 800 °C for 15 min before being taken out of the furnace and being allowed to cool at room temperature. The sample weight was then measured. This process was

repeated for 15 cycles, with the sample weight being measured, and the appearance of the coating being observed, at the end of each cycle.

- High temperature corrosion properties were measured by heating a coated sample up to 800 °C in a furnace at atmospheric pressure over a period of 40 min. The coated sample was left at a temperature of 800 °C for 24 h, before allowing to cool and measuring the mass gain (in mg/cm²) of the coated substrate.
- Slag resistance was observed by placing a coated plug tube into an operating stoker fire tube boiler and conducting a visual inspection of the plug tube after three months.

Coating preparation method

SiO₂, Cr₂O₃, Al₂O₃, and SiC as required (see below) were introduced into a mixing tank at room temperature. Potassium feldspar, a 37.5 wt% aqueous solution of sodium silicate and/or a 37.5 wt% aqueous solution of potassium silicate were then added to the mixing tank as binders. The resultant mixture was stirred at 25 rpm at room temperature for several minutes to obtain the coating compositions. Uniform mixing was evidenced by the absence of residue larger than about 250 microns. The coating compositions are further described below, and the weight ratios of various components are specified in Table 1 below.

Ratio	Comparative Example 1	Comparative Example 2	Comparative Example 3	Example 1	Example 2
Weight ratio alkali metal silicate : alkali metal feldspar	3.50 : 1	3.83 : 1	3.83 : 1	4.09 : 1	4.88 : 1
Weight ratio sodium silicate : potassium silicate : potassium feldspar	1.75 : 1.75 : 1	2.03 : 1.80 : 1	2.03 : 1.80 : 1	2.29 : 1.80 : 1	2.30 : 2.59 : 1
Weight ratio binder : high temperature resistant metal oxide	1.35 : 1	2.19 : 1	N/A	4.24 : 1	4.41 : 1
Weight ratio corrosion and erosion resistant metal oxide :	1.2 : 1	2.41 : 1	N/A	5.59 : 1	5.17 : 1

high temperature resistant metal oxide					
Weight ratio silicon oxide : chromium oxide : aluminium oxide	1 : 1.67 : 1	3.08 : 1.7 : 1	N/A	0.43 : 0.26 : 1	0.41 : 0.28 : 1

Table 1

Example 1

5 The aqueous coating composition of Example 1 consists of SiO_2 : Cr_2O_3 : Al_2O_3 in a weight ratio of 0.43 : 0.26 : 1, sodium silicate : potassium silicate : potassium feldspar in a weight ratio of 2.3 : 1.8 : 1, binder : Cr_2O_3 in a weight ratio of 4.24 : 1, and water to obtain a total weight of 100 g. The amount of SiO_2 , Cr_2O_3 and Al_2O_3 is 39.5 %wt of total weight of the aqueous coating composition.

10 Example 2

The aqueous coating composition of Example 2 consists of SiO_2 : Cr_2O_3 : Al_2O_3 in a weight ratio of 0.41 : 0.28 : 1, sodium silicate : potassium silicate : potassium feldspar in a weight ratio of 2.3 : 2.6 : 1, binder : Cr_2O_3 in a weight ratio of 4.4 : 1, and water to obtain a total weight of 100 g. The amount of SiO_2 , Cr_2O_3 and Al_2O_3 is 37 %wt of total weight of the aqueous coating composition.

Comparative Example 1

20 The aqueous coating composition of Comparative Example 1 consists of SiO_2 : Cr_2O_3 : SiC : Al_2O_3 in a weight ratio of 1 : 1.67 : 5 : 1, sodium silicate : potassium silicate : potassium feldspar in a weight ratio of 1.75 : 1.75 : 1, binder : Cr_2O_3 in a weight ratio of 1.35 : 1, and water to obtain a total weight of 100 g. The amount of SiO_2 , Cr_2O_3 , SiC and Al_2O_3 is 52 %wt of total weight of the aqueous coating composition.

Comparative Example 2

25 The aqueous coating composition of Comparative Example 2 consists of SiO_2 : Cr_2O_3 : Al_2O_3 in a weight ratio of 3.08 : 1.7 : 1, sodium silicate : potassium silicate : potassium feldspar in a weight ratio of 2 : 1.8 : 1, binder : Cr_2O_3 in a weight ratio of 2.2 : 1, and water to obtain a total weight of 100 g. The amount of SiO_2 , Cr_2O_3 and Al_2O_3 is 37.5 %wt of total weight of the aqueous coating composition.

Comparative Example 3

The aqueous coating composition of Comparative Example 3 consists of SiO_2 : Cr_2O_3 : Al_2O_3 in a weight ratio of 0 : 0 : 1, sodium silicate : potassium silicate : potassium feldspar in a weight ratio of 2 : 1.8 : 1, binder : Al_2O_3 in a weight ratio of 0.64 : 1, and water to obtain a total weight of 100 g. The amount of Al_2O_3 is 37.5 %wt of total weight of the aqueous coating composition.

The compositions of Comparative Examples 1 to 3 fall outside the scope of the invention because the weight ratio of alkali metal silicate to alkali metal feldspar is not within the range 4 to 10 : 1. Furthermore, Comparative Example 3 does not comprise a high temperature resistant metal oxide selected from chromium oxide, titanium dioxide, or a mixture thereof.

Substrate coating method

The coating compositions were then coated onto a substrate prior to being tested for various properties.

For surface roughness, abrasion resistance, thermal shock resistance and high temperature corrosion resistance tests, the selected substrate was a carbon steel plate SS400. For the slag resistance tests, the selected substrate was a plug tube.

The substrate was prepared for coating by cleaning and then blasting with garnet or sand until the substrate had a surface roughness of 30 to 50 micron.

The coating composition was prepared as described above.

The coating composition was then applied directly to the surface of the prepared substrate using a spray gun system at a pressure of 5 bar to a thickness of 300 to 400 micron. The coated substrates were air-dried for at least 6 hours prior to any testing. The dried coating had a thickness of 100 to 200 microns.

Coating testing

The coated substrates were tested for various properties and the results are discussed in more detail below.

- Top surface investigation

Figure 2 shows the results of profilometry tests taken on the top surfaces of each of the applied coatings, wherein each bar shows the measured roughness (R_a) of the surface of each sample in microns as recorded by the profilometer. Example 1, and

particularly Example 2, was found to have a low surface roughness compared to the comparative examples. The low surface roughness of the coatings of the present invention means that they have a smaller surface area for slag to form upon, which reduces the slag deposition rate.

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- Adhesion test

The coatings were subjected to an adhesion test as described above. As outlined in Table 2 below, Examples 1 and 2 showed visible separation of the glue from the coating into which it has been brought into contact (i.e. that there is no coating visible on the dolly face after testing, i.e. little peel off), indicating that the coatings are both strong and securely attached to the underlying substrate.

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- Abrasion resistance test

The coatings were subjected to an abrasion resistance test as described above. As shown in Figure 3, Examples 1 and 2 experienced a low weight loss following impacting with falling SiC particles compared to the majority of the comparative coatings. The low weight loss of the coatings of the present invention under these conditions further confirms that the coatings have a high strength and are able to withstand continued impact, as is the case for boiler tubes in a boiler system, for example.

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- Thermal shock resistance test

The coatings were subjected to a thermal shock resistance test as described above. As shown in Figures 4a and 4b, the coatings of Examples 1 and 2 survived the thermal shock test without breaking or cracking and remained a constant weight even after 15 repeated cycles. In comparison, the coating of Comparative Example 3 failed after the first cycle. The results show that the coatings of the present invention are able to withstand high temperature conditions (e.g. such as temperatures achieved within a CFB boiler system) for extended periods, indicating they are durable and will likely have a long lifetime if subjected to similar conditions..

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- High temperature corrosion test

The coatings were subjected to a high temperature corrosion test as described above. As shown in Figure 5, the substrates coated with coatings of Examples 1 and 2 only experienced a very small mass gain following the test. In comparison, the mass gain for an uncoated substrate when subjected to the same test was found be significantly

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increased. The results indicate that not only are the coatings of the present invention able to withstand corrosion at high temperatures, but also that they act as a protective barrier to prevent the underlying metal surface (e.g. a metal boiler pipe) from corroding under these conditions (e.g. as a result of oxidation by the oxygen present in the surrounding atmospheric gases).

- Slag resistance test

The coating of Example 2 was subjected to a slag resistance test as described above. As shown in Figures 6a and 6b, the plug tube coated with the coating composition of Example 2 still had an intact coating present after three months in a fire tube of a biomass boiler and was found to have experienced little, if any, corrosion. Furthermore, only a small amount of slag had been deposited on the coating and this was easily removed. In comparison, Figures 7a and 7b show that an uncoated plug tube subjected to the same test experienced a high level of corrosion due to the formation of oxide scale on the surface of the plug tube, as well as some corrosion-related damage. Large amounts of slag were also found to have deposited on the plug tube, which was very difficult to remove. The results show that the coatings of the present invention help to prevent slag formation on the surface of components in boiler systems. It is estimated that the coatings of the present invention result in around a 10-fold reduction in the slag deposition rate compared to uncoated substrates.

The results of the above tests are summarised in Table 2 below.

Test/property	Comparative Example 1	Comparative Example 2	Comparative Example 3	Example 1	Example 2
Adhesion	peel-off < 5% of testing area	peel-off < 5% of testing area	peel-off > 50% of testing area	peel-off < 5% of testing area	peel-off < 5% of testing area
Abrasion resistance (weight loss in mg)	90	40	20	20	<20
Thermal shock resistance	> 15 cycles	> 15 cycles	Fail at 1 st cycle	> 15 cycles	> 15 cycles
High temperature corrosion test:					
- mass gain in mg/cm ²	3	2	7	2	0.5
- appearance	30% of total area cracked	20% of total area cracked	100% of total area cracked	20% of total area cracked	No cracking

Slag resistance test (appearance)	-	-	-	Coating intact; small amount of slag deposition	-
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Table 2

The results show that the coatings of the present invention have superior properties in terms of strength, durability and surface roughness compared to the comparative coatings tested, and that they are able to better withstand high temperatures and corrosive conditions. As such, the coatings of the present invention are well-suited for environments in which corrosion, erosion and slagging are common problems (e.g. in boiler systems etc.) and can help to prevent the undesirable effects of these problems.

CLAIMS:

1. A coating composition comprising:

a corrosion and erosion resistant metal oxide selected from silicon oxide, aluminium oxide, zirconium oxide, mica, zinc oxide, or a mixture thereof;

a high temperature resistant metal oxide selected from chromium oxide, titanium dioxide, or a mixture thereof; and

a binder comprising alkali metal silicate and alkali metal feldspar,

wherein the weight ratio of alkali metal silicate to alkali metal feldspar is in the range 4.0 to 10.0 : 1;

the alkali metal silicate is a mixture of sodium silicate and potassium silicate, and the alkali metal feldspar is potassium feldspar; and

the weight ratio of sodium silicate to potassium silicate to potassium feldspar is in the range (2.1 to 5.0) : (1.5 to 5.0) : 1.

2. A coating composition according to claim 1, wherein the weight ratio of alkali metal silicate to alkali metal feldspar is in the range 4.0 to 7.5 : 1.
3. A coating composition according to claim 1 or claim 2, wherein the weight ratio of sodium silicate to potassium silicate to potassium feldspar is in the range (2.1 to 3.5) : (1.5 to 5.0) : 1.
4. A coating composition according to any one of claims 1 to 3, wherein the weight ratio of said binder to said high temperature resistant metal oxide is 3.0 to 8.0 : 1.
5. A coating composition according to claim 4, wherein the weight ratio of said binder to said high temperature resistant metal oxide is 3.0 to 7.0 : 1.
6. A coating composition according to any one of claims 1 to 5, wherein said corrosion and erosion resistant metal oxide is a mixture of silicon oxide and aluminium oxide, and said high temperature resistant metal oxide is chromium oxide.

7. A coating composition according to claim 6, wherein the weight ratio of silicon oxide to chromium oxide to aluminium oxide is in the range (0.1 – 0.9) : (0.1 – 0.9) : 1.
8. A coating composition according to claim 7, wherein the weight ratio of silicon oxide to chromium oxide to aluminium oxide is in the range (0.1 to 0.5) : (0.1 to 0.5) : 1.
9. A coating composition according to any one of claims 1 to 8, wherein the coating composition is an aqueous coating composition.
10. A container containing a coating composition according to any one of claims 1 to 9.
11. A kit for preparing a coating composition as claimed in any one of claims 1 to 9, comprising:
 - (i) a first container containing a mixture of a corrosion and erosion resistant metal oxide selected from silicon oxide, aluminium oxide, zirconium oxide, mica, zinc oxide, or a mixture thereof, and a high temperature resistant metal oxide selected from chromium oxide, titanium dioxide, or a mixture thereof;
 - (ii) a second container comprising a binder comprising alkali metal silicate and alkali metal feldspar, wherein the alkali metal silicate is a mixture of sodium silicate and potassium silicate, and the alkali metal feldspar is potassium feldspar; and
 - (iii) instructions to mix said mixture of said first container with said binder of said second container.
12. A method for preparing a coating composition as defined in any one of claims 1 to 9, comprising the steps of:
 - (i) preparing a mixture of a corrosion and erosion resistant metal oxide selected from silicon oxide, aluminium oxide, zirconium oxide, mica, zinc oxide, or a mixture thereof, and a high temperature resistant metal oxide selected from chromium oxide, titanium dioxide, or a mixture thereof; and
 - (ii) mixing said mixture with a binder comprising alkali metal silicate and alkali metal feldspar, wherein the alkali metal silicate is a mixture of sodium

silicate and potassium silicate, and the alkali metal feldspar is potassium feldspar.

13. A method for preparing a coated substrate, comprising the steps of:
 - (i) providing a substrate; and
 - (ii) applying a coating composition as defined in any one of claims 1 to 9 onto at least one surface of said substrate.
14. A coated substrate comprising a coating composition as defined in any one of claims 1 to 9.
15. A boiler (e.g. a coal or biomass boiler) comprising a coated substrate according to claim 14.
16. Use of a coating composition as defined in any one of claims 1 to 9 to coat a substrate.
17. Use of a coating composition as defined in any one of claims 1 to 9 to prevent or reduce erosion and/or corrosion of a substrate and/or slag deposition on a substrate.