(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 October 2017 (19.10.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/179969 A2

(51) International Patent Classification: Not classified

(21) International Application Number: PCT/MY2017/050026

(22) International Filing Date: 9 June 2017 (09.06.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PI 2016701334 12 April 2016 (12.04.2016) MY

(71) Applicant: UNIVERSITI PUTRA MALAYSIA [MY/MY]; Putra Science Park, Pejabat Timbalan Naib Canselor (penyelidikan Dan Inovasi), Serdang, Selangor, 43400 (MY).

(72) Inventors: MUSTAPHA, Faizal; Fakulti Kejuruteraan, Universiti Putra Malaysia, Serdang, Selangor, 43400 (MY). **MAZLAN, Norkhairunnisa**; Fakulti Kejuruteraan, Universiti Putra Malaysia, Serdang, Selangor, 43400 (MY). **MOHD BASRI, Mohd Salahuddin**; Fakulti Kejuruteraan, Universiti Putra Malaysia, Serdang, Selangor, 43400 (MY).

(74) Agent: H A RASHID, Ahmad Fadzlee; Ipvolusi SDN BHD, A-3-3a, Centrio Pantai Hillpark, No. 1, Jalan Pantai Murni, Kuala Lumpur, 59200 (MY).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *of inventorship (Rule 4.17(iv))*

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

— *with information concerning request for restoration of the right of priority in respect of one or more priority claims (Rules 26bis.3 and 48.2(b)(vii))*

(54) Title: FIRE RETARDANT COATING COMPOSITION

(57) Abstract: The present invention relates to an intumescent fire retardant coating composition. The fire retardant coating composition comprises alkali metal hydroxide, alkali metal silicate, rice ash husk and water.

WO 2017/179969 A2

FIRE RETARDANT COATING COMPOSITION

FIELD OF INVENTION

The present invention relates to a fire retardant coating composition. More particularly, the present invention relates to an intumescent fire retardant coating composition.

BACKGROUND OF THE INVENTION

Steel are largely used in many areas such as in building construction, offshore structure, ships, railways, bridges and airports due to its exceptional strength. Steel, while obviously very strong, is not immune to the effects of fire. It starts to lose its strength at temperatures exceeding 540 °C and eventually collapses. This is why all steel structures should be protected from fire and heat to help maintain their strength and create adequate egress time for those inside the structure.

Fire retardant coating is an example of a means to shield and protect steel structures. For example, United States Publication No. 2006/0079612 A1 discloses a fire retardant coating composition comprising a resin based coating, an effective flame retarding compound selected from the group consisting of sterically hindered nitroxyl stabilizers, sterically hindered hydroxylamine stabilizers and sterically hindered alkoxyamine stabilizers and at least one conventional flame retardant. However, in the case of exposure to direct fire for a prolonged period of time, the fire may fully burn through the coating thus exposing the inner steel structure. Therefore, the prior art above may not be able provide adequate protection from prolonged fire exposure.

Intumescent fire retardant coatings have been developed to provide protection from prolonged fire exposure. In case of a fire, intumescent fire resistant coatings will expand greatly, creating a char layer that further protects the steel structure. The char layer is considerably more effective than traditional insulating and fire retarding materials in minimizing the exposure of the underlying steel structure to temperatures that would allow for further combustion. As a result, the rates of combustion and generation of smoke are substantially reduced, increasing egress time. In addition, the fire is usually contained to the room of origin which helps to maintain structural integrity and minimizes property damage. An example of an intumescent fire retardant coating composition is disclosed in Chinese Patent No. CN 1380368 A. This prior art discloses a fire retardant coating composition comprising acrylic resin, catalyst, char-forming agent, foaming agent, reinforced flame retardant, agents fillers, solvent, additives and smoke suppressants. However, the prior art as well as any other resin based fire retardant coatings, have low ignition temperature and contain chemicals capable of causing damage to health by inhalation of vapour or dust. Furthermore, when come into contact with skin, resin based coatings may cause irritant contact dermatitis and allergic reactions. Moreover, the combustion products emitted upon the exposure of resin based fire retardant coatings to fire may be even more harmful to humans.

Therefore there is a need for a fire retardant coating composition that addresses the abovementioned limitations of the existing fire retardant coating compositions.

SUMMARY OF INVENTION

In a first aspect of the present invention, there is provided a fire retardant coating composition, characterized by comprising alkali metal hydroxide; alkali metal silicate; and rice ash husk.

The provision of the rice ash husk as an aluminosilicate source and the alkali metals, which the aluminosilicate source and alkali metals provide an intumescent geopolymer coating with the addition of water as the coating is capable of expanding and forming a char layer when exposed to fire to further protect a coated structure.

In the first aspect of the present invention, said alkali metal hydroxide is preferably selected from a group comprising sodium hydroxide, potassium hydroxide and any mixture thereof. In addition, said alkali metal silicate is preferably selected from a group comprising sodium silicate, potassium silicate and any mixture thereof. Further, the weight ratio of said alkali metal hydroxide to said alkali metal silicate preferably ranges between 1:3.5 to 1:5.5.

In addition, in the first aspect of the present invention, the weight ratio of said rice husk ash to a mixture of said alkali metal hydroxide and said alkali metal silicate ranges between 0.3:1 to 0.7:1. The particle size of said rice ash husk preferably ranges between 3.4 to 59.5 µm while the silica content of said rice ash husk preferably ranges between 81 to 97 percentage by weight.

Further, in the first aspect of the present invention, the fire retardant coating composition further comprises water. The amount of said water preferably ranges between 70 to 73 percentage by weight.

In a second aspect of the present invention, there is provided a method for producing fire retardant coating. The method is characterized by the steps of mixing of alkali metal hydroxide, alkali metal silicate, rice husk ash and water to obtain a homogeneous mixture (step **101**); reducing entrapped air bubbles inside the homogeneous mixture to obtain a slurry mixture (step **102**); coating the slurry mixture onto an area to be insulated and protected (step **103**); vacuum drying the coating at room temperature to remove any air pockets (step **104**); drying the vacuum dried coating under moderate heating (step **105**); subjecting the dried coating to pressure to obtain uniform coating thickness (step **106**); curing the dried coating (step **107**); and air curing the cured coating to obtain a fire retardant coating (step **108**).

Additionally, in the second aspect of the present invention, said alkali metal hydroxide is preferably selected from a group comprising sodium hydroxide, potassium hydroxide and any mixture thereof. In addition, said alkali metal silicate is preferably selected from a group comprising sodium silicate, potassium silicate and any mixture thereof. Further, the weight ratio of said alkali metal hydroxide to said alkali metal silicate preferably ranges between 1:3.5 to 1:5.5.

Furthermore, in the second aspect of the present invention, the weight ratio of said rice husk ash to a mixture of said alkali metal hydroxide and said alkali metal silicate ranges between 0.3:1 to 0.7:1. The particle size of said rice ash husk preferably ranges between 3.4 to 59.5 µm while the silica content of said rice ash husk preferably ranges between 81 to 97 percentage by weight.

Moreover, in the second aspect of the present invention, the fire retardant coating composition further comprises water. The amount of said water preferably ranges between 70 to 73 percentage by weight.

In addition, in the second aspect of the present invention, the step of reducing entrapped air bubbles inside the homogeneous mixture is preferably done using means by either; sieving or vibrating the homogeneous mixture.

Furthermore, in the second aspect of the present invention, the step of coating the slurry mixture onto an area to be insulated and protected is preferably done by either; doctor-blade, brush-coating, dip-coating, spray-coating or spin-coating.

Moreover, in the second aspect of the present invention, the step of vacuum drying is preferably conducted for a period of 10 to 20 minutes.

Further, in the second aspect of the present invention, the step of drying is conducted at a temperature ranging between 40 to 55 °C for a period of 20 to 40 minutes.

Additionally, in the second aspect of the present invention, the step of curing is conducted at a temperature ranging between 40 to 75 °C for a period of 18 to 30 hours.

Furthermore, in the second aspect of the present invention, the step of air curing is preferably conducted at room temperature for a period of 6 to 20 days.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate embodiments of the invention and, together with the description, serve to explain the principles of the invention.

FIG. 1 illustrates a flowchart of a method for producing a fire retardant coating using the fire retardant composition according to an embodiment of the present invention.

FIG. 2 illustrates a fire retardant test set up.

FIG. 3 illustrates ISO-834 standard temperature-time fire curve.

FIG. 4 illustrates particle size distribution histogram of sieved rice husk ash.

FIGS. 5(a-b) illustrate Pareto charts showing the effect of main factors and interaction between main factors on the fire retardancy responses of the fire retardant coatings prepared using the method of **FIG. 1**.

FIGS. 6(a-b) illustrate contour plots showing the effect of water/solid ratio and silica/alumina (Si/Al) ratio on the fire retardancy responses of the fire retardant coatings prepared using the method of **FIG. 1**.

FIG. 7 illustrates fire retardant test curves for bare mild steel and fire retardant coatings prepared using the method of **FIG. 1**.

FIGS. 8(a-b) illustrate real images of fire retardant coatings prepared using the method of **FIG. 1**.

FIGS. 9(a-d) illustrate scanning electron microscope (SEM) images of fire retardant coatings prepared using the method of **FIG. 1**.

FIG. 10 illustrates thermal gravimetrical analysis curves of fire retardant coatings prepared using the method of **FIG. 1**.

FIGS. 11(a-b) illustrates fire retardant test curves of an alternative fire retardant coating composition.

FIGS. 12(a-b) illustrate real and thermal images of an alternative fire retardant coating with 10 mm thickness.

FIGS. 13(a-b) illustrate real and thermal images of an alternative fire retardant coating with 1 mm thickness.

DESCRIPTION OF THE PREFERRED EMBODIMENT

A preferred embodiment of the present invention will be described herein below with reference to the accompanying drawings. In the following description, well known functions or constructions are not described in detail since they would obscure the description with unnecessary detail.

It is an objective of this invention to provide an intumescent fire retardant coating composition. The fire retardant coating composition comprises alkali metal hydroxide, alkali metal silicate and rice ash husk. The composition may be provided in powder form for easy transportation. Alternatively, the composition may be prepared into a fire retardant slurry or a readymade coating by the addition of water to form a geopolymer coating.

Geopolymers comprises chains or networks of mineral molecules linked with covalent bonds. They are intumescent, strong, light-weight and are considered to be environmentally friendly due to the lack of volatile organic compounds. They may be synthesized using two synthesis routes; namely in alkaline medium and in acidic medium. They are amorphous at ambient and medium temperatures but become crystalline at temperatures exceeding 500 °C. These properties make them useful material to be used in fire- and heat-resistant coatings, adhesives and tiles.

The geopolymer of the present invention is an alkali-activated aluminosilicate prepared by reacting an alkaline activator solution with an aluminosilicate source. The geopolymerization process involves a substantially fast chemical reaction under alkaline condition on aluminosilicate that results in a three-dimensional polymeric chain and ring structure consisting of -Si-O-Al-O bonds.

The alkaline activator solution of the present invention is prepared from a mixture of sodium silicate solution and sodium hydroxide solution while the aluminosilicate source of the present invention is rice husk ash (RHA). Unlike most fire retardant coating materials, RHA is non-toxic and environmental-friendly. RHA is generated from burning rice husk at temperatures lower than 700 °C. Rice husk contains about 50 % cellulose, 25 to 30 % lignin and 15 to 20 % silica. When rice husk is burnt, cellulose and lignin are removed, leaving behind silica ash which constitutes more than 80 to 85 % of the RHA. At burning temperatures up to 700 °C, silica in RHA maintains in an amorphous form.

Insulating and protecting an area from fire using the fire retardant composition of the present invention may be performed using the method as illustrated in **FIG. 1**. Initially, alkali metal hydroxide, alkali metal silicate, RHA and water are mixed to obtain a homogeneous mixture as in step **101**. The alkali metal hydroxide is preferably selected from a group comprising sodium hydroxide, potassium hydroxide and any mixture thereof while the alkali metal silicate is preferably selected from a group comprising sodium silicate, potassium silicate and any mixture thereof. Preferably, the weight ratio of alkali metal hydroxide to alkali metal silicate ranges between 1:3.5 to 1:5.5. The weight ratio of RHA to a mixture of alkali metal hydroxide and alkali metal silicate preferably ranges between 0.3:1 to 0.7:1. Preferably, the particle size of RHA ranges between 3.4 to 59.5 μm. Additionally, the silica content of RHA preferably ranges between 81 to 97 percentage by weight. Preferably, the amount of water ranges between 70 to 73 percentage by weight.

Next, entrapped air bubbles inside the homogeneous mixture are reduced to obtain a slurry mixture as in step **102**. The entrapped air bubbles inside the homogeneous mixture are reduced using means that includes but is not limited to sieving and vibrating the homogeneous mixture.

Thereon, the slurry mixture is coated onto an area to be insulated and protected as in step **103**. The slurry mixture is coated using means that includes but is not limited to doctor-blade, brush-coating, dip-coating, spray-coating and spin-coating.

Next, the coating is vacuum dried at room temperature to remove any air pockets as in step **104**. Preferably, the step of vacuum drying is conducted for a period of 10 to 20 minutes.

Then, the vacuum dried coating is further dried under moderate heating as in step **105**. Preferably, the step of drying is conducted at a temperature ranging between 40 to 55 °C for a period of 20 to 40 minutes.

Next, the dried coating is subjected to pressure to obtain uniform coating thickness as in step **106**. The subjected pressure depends on the desired thickness and the viscosity of the dried coating. Due to the subjected pressure, excess dried coating may spill over the edges of the area to be insulated and protected. Optionally, the excess dried coating on the edges may be cut.

Next, the dried coating is cured as in step **107**. Preferably, the step of curing is conducted at a temperature ranging between 40 to 75 °C for a period of 18 to 30 hours.

Finally, the dried coating is air cured as in step **108** to obtain a fire resistant coating. Preferably, the step of air curing is conducted at room temperature for a period of 6 to 20 days.

The examples used herein are intended merely to facilitate an understanding of ways in which the embodiments herein may be practiced and to further enable those of skill in the art to practice the embodiments herein. Accordingly, the examples should not be constructed as limiting the scope of the embodiment herein.

Examples of the Experiments are illustrated as follows:

Materials and Experimental details

Preparation of rice husk ash

Rice husk was burnt at a temperature below 700 °C for 24 hours to produce RHA. The burnt RHA was then grounded using a planetary mill and sieved in order to obtain RHA in particle sizes ranging between 3.4 to 59.5 μm.

Preparation of fire retardant coating

The fire retardant coating was first prepared by mixing sodium hydroxide (NaOH) solution and sodium silicate (Na_2SiO_3) solution at various ratios to produce an alkaline activator (AA) solution. A ready-made Na_2SiO_3 solution was used which comprises 30.3 wt. % of water (H_2O), 11.9 wt. % of sodium oxide (Na_2O) and 57.8 wt. % of silica oxide (SiO_2). NaOH solutions (97 % purity) of concentrations 8 M and 12 M were prepared by dissolving NaOH pellets in deionized water (DIW). Sieved RHA was added to the AA solution and the mixture was gently stirred for 30 seconds. Thereon, the mixture was transferred into a mechanical stirrer and stirred for an additional 30 minutes until a homogenous mixture was obtained. The homogeneous mixture was strained through a small sieve in order to reduce air bubbles entrapped inside the mixture. The obtained slurry mixture was poured directly onto a mild steel plate substrate having a width of 10 cm, length of 10 cm and a thickness of 0.1 cm. The slurry mixture was made to evenly coat the substrate. Prior to coating, the mild steel plate substrate was cleaned using sand paper and degreased with acetone. The coated substrate was left for a minute for the coat to self-level. Then, the coated substrate was placed in a vacuum oven for degasification at room temperature to remove remaining entrapped air bubbles. Thereon, the coated substrate was dried in an oven for approximately 40 minutes at 40 °C. The coated substrate was then pressed using a press machine to obtain a uniform thickness throughout the substrate. Next, excess coat on the edges of the substrate was cut off and the coated substrate was placed again in the oven for a curing process for 24 hours at 50 °C. This was followed by 6 to 20 days of air curing at room temperature. The thickness of the air cured fire retardant coat was around 1.0 ± 0.3 mm.

Analysis, measurement and characterization

Five factors were considered in the experimental design based on their probable influence on fire retardancy responses, namely, the temperature at equilibrium (TAE) and the time taken to reach 300 °C (TTR300). The considered factors are; weight of Na_2SiO_3/weight of NaOH (A), weight of RHA/weight of Na_2SiO_3 and NaOH (B), curing temperature (C), curing period (D) and concentration of NaOH solution (E). A two level-five factors fractional factorial (2-5 FFD) experiment was designed. The effect of each factor was studied on two levels, low and high. Other influencing factors such as coating thickness (1.0 ± 0.3 mm) and particle size of RHA were kept constant for this experiment.

Experimental data were analyzed using a statistical analysis software. The values for R-squares and predicted R-squares from the statistical analysis were ensured to be close 1.0 in order to guarantee that the results generated are accurate and reliable. Chemical composition of RHA was analyzed using an X-ray fluorescence (XRF) spectrometer. The RHA sample was dried in an oven at 35 to 45 °C for 24 hours prior to the analysis to remove any moisture. Scanning electron microscope (SEM) was used to analyze the microstructure of selected fire retardant coated substrate. Thermogravimetry analysis (TGA) was conducted to study the thermal behaviour of the resultant coatings. TGA was carried out using a thermogravimetric analyzer equipped with ultra-micro balances under nitrogen gas atmosphere in alumina crucibles at a heating rate of 10 °C/min over a temperature range of 50 to 1000 °C.

Fire retardant test

Fire retardant test set up is shown in **FIG. 2**. The fire retardant test was conducted using a non-contact method involving an infrared camera and a blow torch. Distance between the infrared camera and coated substrate sample, x_1, was kept constant at 60 cm while the distance between the coated substrate sample and blow torch, x_2, was kept constant at 7 cm throughout the test. Bare and coated substrates were exposed to fire for at least 20 minutes or until equilibrium temperature was reached. Temperature on the back of the coated substrate was plotted as a function of time. The recorded maximum non-exposed temperature of the samples were ensured to follow as closely as possible to the ISO-834 standard temperature-time fire curve shown in **FIG. 3**. ISO 834 standard temperature-time fire curve is a standard curve used for fire resistance tests of materials that are subjected to a category "A" fire hazard i.e. with the fire hazard rating based on the burning rate of general combustible building materials and building contents.

Result and discussion

The particle size distribution histogram of RHA is shown in **FIG. 4**. The step of sieving burnt RHA successfully retrieved RHA in particle sizes ranging between 3.4 to 59.5 µm, with an average size of approximately 22.8 µm to be utilized in the fire retardant coating composition.

The result of the chemical composition analysis of RHA is shown in **TABLE 1**.

TABLE 1

Component	Mass %
SiO_2	87.4
PdO	6.0
Al_2O_3	3.0
Fe_2O_3	1.49
CaO	1.40
K_2O	0.49

Cr_2O_3	0.27
MnO	0.19
NiO	0.068
CuO	0.045
ZnO	0.035

From the chemical composition analysis, SiO_2 was found to be the major constituent in RHA. Other major constituents present include palladium (II) oxide (PdO), aluminium oxide (Al_2O_3) and iron (III) oxide (Fe_2O_3).

Using a design matrix of the factors and fire retardancy responses, the experimental data was analyzed using a statistical analysis software. The uncoded or actual value of the design matrix for all factors and the corresponding responses for 32 experimental runs including replications are shown in **TABLE 2**.

TABLE 2

Sample	A	B	C	D	E	TAE	TTR300
S09	3.5	0.7	70	21	8	471.4	234
S05	3.5	0.7	70	7	12	442.0	260
S02	3.5	0.7	50	21	12	434.3	300
S23	3.5	0.3	50	7	12	564.6	218
S22	3.5	0.7	50	7	8	471.6	215
S12	5.5	0.3	70	7	12	438.2	405
S16	5.5	0.7	50	7	12	491.5	208
S19	5.5	0.3	50	21	12	452.8	432
S06	3.5	0.3	70	21	12	515.1	297
S14	3.5	0.3	70	7	8	417.2	767
S29	3.5	0.3	70	21	12	510.9	292
S32	3.5	0.7	50	7	8	473.9	263
S20	3.5	0.3	70	7	8	417.4	750
S04	5.5	0.3	50	7	8	424.1	991
S30	5.5	0.7	70	21	12	506.9	236
S28	5.5	0.7	50	7	12	497.6	152
S40	5.5	0.3	70	21	8	451.5	488
S15	3.5	0.3	50	21	8	487.6	438
S24	3.5	0.3	50	7	12	555.1	263
S25	3.5	0.7	70	21	8	462.3	227
S17	3.5	0.7	70	7	12	440.0	263
S13	5.5	0.7	70	7	8	473.9	214
S33	5.5	0.3	70	7	12	444.8	400
S03	3.5	0.7	50	21	12	430.0	305
S34	5.5	0.3	70	21	8	451.8	508
S26	5.5	0.7	70	7	8	487.7	399
S39	5.5	0.3	50	21	12	443.6	474
S11	5.5	0.7	50	21	8	490.7	180
S21	3.5	0.3	50	21	8	492.0	441
S41	5.5	0.7	50	21	8	498.7	200
S07	5.5	0.3	50	7	8	398.3	1025
S42	5.5	0.7	70	21	12	497.1	213

Notes: A = weight of Na_2SiO_3/weight of NaOH; B = weight of RHA/weight of Na_2SiO_3 and NaOH; C = curing temperature; D = curing period; E = concentration of NaOH solution; TAE = Temperature at equilibrium (in °C); TTR300 = Time taken to reach 300 °C (in a second).

During the fire retardant test, the samples did not release any smoke or ignite when come into contact with fire. From **TABLE 2**, it can be seen that coated sample S24 recorded the highest TAE and took a relatively short time to reach 300 °C. It can be concluded that S24 is the poorest performing fire retardant composition. Coated sample S07 recorded the slowest TTR300 and the lowest TAE, making it the best performing fire retardant composition.

FIG. 5a and **FIG. 5b** are Pareto charts showing the effect of main factors and interaction between main factors on TAE and TTR300, respectively. A reference line, determined from the value of margin of error (ME), was drawn on each chart which if exceeded will identify the factor as potentially important and could have a strong effect on the fire retardancy responses. From both charts, factor E was found to be the most influential factor as the effect extends the most beyond the reference line. With the exception of factor C, which had no effect on TTR300, other factors are statistically significant at 95 % confidence level. In comparison to the other interactions, those occurring between factors B and E has the strongest effect on both responses. Factors B and E were thus selected for optimization.

FIG. 6a and **FIG. 6b** are contour plots showing the effect of water/solid ratio and silica/alumina (Si/Al) ratio on TAE and TTR300, respectively. According to the contour plots, the highest ratios of Si/Al at approximately 140 produced fire retardant coating with the greatest fire retardancy. This is attributed to the improved adhesion strength facilitated by the increase of silica content. The high degree of dissolved silica creates rougher surface. Rougher surface provides good adhesion bonding, thus, fire retardant coatings with higher Si/Al ratio are able to provide better fire retardancy. Fire retardant coating having a water/solid ratio ranging between 1.35 and 1.50 have the best fire retardancy. It can be seen that the fire retardancy increases for samples having a water/solid ratio higher than 1.50. However, the degree of dehydration and rate of shrinkage increase along with it, leading to delamination of fire retardant coating. On the other hand, a lower water/solid ratio will lead to low workability and a less than homogenous mixture. A heterogeneous mixture will produce a coating with weaker adhesion strength to the steel substrate and higher expansion rate. Coating with good adhesion bonding can effectively protect the steel substrate without experiencing major cracks due to expansion and shrinkage during a fire.

FIG. 7 shows fire retardant test curves for bare mild steel and coated samples, S24 and S07. Mild steel was chosen for the experiment as mild steel is the type of steel widely used in the construction field. Coated samples, S24 and S07, were selected as they recorded the poorest and the best fire retardant performance, respectively. A reference line is drawn on the test curve at 500 °C as it is the failure temperature for mild steel, the point when mild steel loses its strength and collapses. Uncoated mild steel collapsed rapidly after only 28 seconds while coated sample S24 collapsed after 5 minutes following exposure to direct fire. The back temperature of the mild steel plate of coated sample S07, which is the best coating composition, reached 300 °C after at least 17 minutes. Additionally, S07 achieved an equilibrium temperature at about 398 °C, which is well below mild steel's failure temperature, after about 25 minutes. The equilibrium temperature is expected to remain unchanged for at least one hour.

FIG. 8a and **FIG. 8b** show real images of coated samples, S24 and S07, respectively after the fire retardant test. In the case of S24, due to improper coating expansion and poor adhesion bonding between fire retardant coating and mild steel substrate, fire was able to reach the substrate faster resulting in poor fire retardant performance. Coated sample S07 showed the best fire retardant performance in terms of adhesion in comparison to S24. In addition, the central part of the sample, where the coating had direct contact with the fire, is believed to undergo crystallization as evident from the glassy structure. This crystalline state will probably remain unchanged with longer fire exposure, thus providing longer-lasting protection.

The surface morphology of coated sample S07 was further analysed using SEM. **FIG. 9a** and **FIG. 9b** show microstructure images of S07 before the exposure to fire. **FIG. 9a** shows a microstructure image with continuous crystalline surface within a gel matrix, which is a characteristic of geopolymer. A closed up view of coated sample S07, in **FIG. 9b**, depicts uniform plate-like layered structures with angular edges. Micro cracks or wrinkles believed to be shrinkage cracks are clearly observed on the surface of the sample. This is attributed to water evaporation during curing process. **FIG. 9c** and **FIG. 9d** show microstructure images of coated sample S07 after the exposure to fire. Wide and deep cracks are observed following exposure of the sample to fire at approximately 800 °C for more than 30 minutes. The cracks are a result of additional removal of hydrogen bonded water. A closed up view of sample S07 after exposure to fire, as seen in **FIG. 9d**, exhibit a surface morphology covered with small and large needle-like structures. The presence of such crystalline structures indicate that more oligomers are generated as a result of fire exposure. The generated oligomers trigger the release of more reactive Si- and Al-tetrahedra. The formation of crystalline structures, which indicates a high degree of geopolymerization in the fire retardant coating, provided the improved fire retardant performance.

FIG. 10 shows TGA curves of samples S07 and S24. Weight loss beginning at around 55 °C and ending at around 112 °C for both samples is attributed to the loss of absorbed water. A total weight loss of approximately 2.5 % is associated with the loss of absorbed water. The onset of rapid weight loss occurring at around 127 °C is associated with the removal of free water, water bonded to hydrogen bonds and water bonded to silicate molecules. Water loss through the endothermic dehydration will leave a thermally stable residue. From **FIG. 10**, it can be observed that S07 has a higher rate of dehydration in comparison to S24 with a recorded 6 % difference at 150 °C. S07 reached thermal stability faster and at a lower temperature, 514.4 °C, in comparison to S24 which reached thermal stability at 522.5 °C. The overall weight loss was 27.7 % and 22.6 % for S07 and S24, respectively.

As a conclusion, after considering the interaction between all the factors, factors B and E were found to be the most influential. With the exception of factor C which has no effect on TTR300, other factors were found to be statistically significant. Fire retardant coating composition with a Si/Al ratio of around 140 and a water/solid ratio ranging between 1.35 and 1.50 showed better fire retardant performance. Of all the coated samples, S07 prepared with weight of Na_2SiO_3/weight of NaOH of 5.5, weight of RHA/weight of Na_2SiO_3 and NaOH of 0.3, curing temperature of 50 °C, curing period of 7 days and concentration of NaOH solution of 8 M, showed the best fire retardant performance. Small and large needle shaped structures formed on S07 following the fire retardant test attributes to the improved fire retardant performance. The back temperature of mild steel plate of coated sample S07 reached 300 °C after 17 minutes and took around 25 minutes to reach equilibrium temperature. S07 achieved an equilibrium state at 398 °C. The results proved that RHA with the optimized coating composition has the potential to be an alternative silica source for geopolymer fire retardant coating.

Taking into consideration the results of the optimized coating composition, an alternative coating composition was formulated as follows;

A: ranging between 4.5 to 5.5
B: ranging between 0.4 to 0.55
C: ≤ 50 °C
D: ranging between 1 to 7 days
E: ranging between 8 to 10 M

The alternative coating composition was coated on mild steel substrate using a similar preparation method as the previous experiment. However, the thickness of the air cured fire retardant coat of the alternative coating composition was varied to be 1 mm and 10 mm thick. Fire retardant test was similarly conducted and the obtained fire retardant test curves for coating with 10 mm thickness and 1 mm thickness are shown in **FIG. 11a** and **FIG. 11b**, respectively. As observed in **FIG. 11a**, coating with 10 mm thickness only reached equilibrium at approximately 87 °C after 4000 seconds. On the other hand, coating with 1 mm thickness reached equilibrium much faster after 1800 seconds at around 340 °C as observed in **FIG. 11b**.

FIG. 12a and **FIG. 12b** show real image and thermal image of coating with 10 mm thickness after the fire retardant test while **FIG. 13a** and **FIG. 13b** show real image and thermal image of coating with 1 mm thickness after the fire retardant test. Both samples showed outstanding fire retardant performances. Moreover, both samples exhibited intumescent behaviour with an optimum expansion. The samples only expanded between 3 to 5 times its original thicknesses. The thermal images proved that the heat did not spread to another parts of the coating which resulted in the expansion of only the central part of the coating. It shows that the alternative coating composition has a lower thermal diffusivity. This is one of the main characters of good intumescent material which is able to block heat from spreading to the other parts of the material.

While embodiments of the invention have been illustrated and described, it is not intended that these embodiments illustrate and describe all possible forms of the invention. Rather, the words used in the specifications are words of description rather than limitation and various changes may be made without departing from the scope of the invention.

CLAIMS

1. A fire retardant coating composition, characterized by comprising:
    alkali metal hydroxide;
    alkali metal silicate; and
    rice ash husk.

2. The fire retardant coating composition as claimed in claim **1**, wherein the particle size of said rice ash husk ranges between 3.4 to 59.5 µm.

3. The fire retardant coating composition as claimed in claim **1**, wherein the silica content of said rice ash husk ranges between 81 to 97 percentage by weight.

4. The fire retardant coating composition as claimed in claim **1**, wherein said alkali metal hydroxide is selected from a group comprising sodium hydroxide, potassium hydroxide and any mixture thereof.

5. The fire retardant coating composition as claimed in claim **1**, wherein said alkali metal silicate is selected from a group comprising sodium silicate, potassium silicate and any mixture thereof.

6. The fire retardant coating composition as claimed in claim **1**, wherein the weight ratio of said alkali metal hydroxide to said alkali metal silicate ranges between 1:3.5 to 1:5.5.

7. The fire retardant coating composition as claimed in claim **1**, wherein the weight ratio of said rice husk ash to a mixture of said alkali metal hydroxide and said alkali metal silicate ranges between 0.3:1 to 0.7:1.

8. The fire retardant coating composition as claimed in claim **1**, wherein the fire retardant coating composition further comprises water.

9. The fire retardant coating composition as claimed in claim **8**, wherein the amount of said water ranges between 70 to 73 percentage by weight.

10. A method for producing fire retardant coating is characterized by the steps of:
    a) mixing of alkali metal hydroxide, alkali metal silicate, rice husk ash and water to obtain a homogeneous mixture (step **101**);
    b) reducing entrapped air bubbles inside the homogeneous mixture to obtain a slurry mixture (step **102**);
    c) coating the slurry mixture onto an area to be insulated and protected (step **103**);
    d) vacuum drying the coating at room temperature to remove any air pockets (step **104**);
    e) drying the vacuum dried coating under moderate heating (step **105**);
    f) subjecting the dried coating to pressure to obtain uniform coating thickness (step **106**);
    g) curing the dried coating (step **107**); and
    h) air curing the cured coating to obtain a fire retardant coating (step **108**).

11. The method as claimed in claim **10**, wherein the particle size of said rice ash husk ranges between 3.4 to 59.5 μm.

12. The method as claimed in claim **10**, wherein the silica content of said rice ash husk ranges between 81 to 97 percentage by weight.

13. The method as claimed in claim **10**, wherein said alkali metal hydroxide is selected from a group comprising sodium hydroxide, potassium hydroxide and any mixture thereof.

14. The method as claimed in claim **10**, wherein said alkali metal silicate is selected from a group comprising sodium silicate, potassium silicate and any mixture thereof.

15. The method as claimed in claim **10**, wherein the weight ratio of said alkali metal hydroxide to said alkali metal silicate ranges between 1:3.5 to 1:5.5.

16. The method as claimed in claim **10**, wherein the weight ratio of said rice husk ash to a mixture of said alkali metal hydroxide and said alkali metal silicate ranges between 0.3:1 to 0.7:1.

17. The method as claimed in claim **10**, wherein the amount of said water ranges between 70 to 73 percentage by weight.

18. The method as claimed in claim **10**, wherein the step of reducing entrapped air bubbles inside the homogeneous mixture is done using means by either; sieving or vibrating the homogeneous mixture.

19. The method as claimed in claim **10**, wherein the step of coating the slurry mixture onto an area to be insulated and protected is done by either; doctor-blade, brush-coating, dip-coating, spray-coating or spin-coating.

20. The method as claimed in claim **10**, wherein the step of vacuum drying is conducted for a period of 10 to 20 minutes.

21. The method as claimed in claim **10**, wherein the step of drying is conducted at a temperature ranging between 40 to 55 °C for a period of 20 to 40 minutes.

22. The method as claimed in claim **10**, wherein the step of curing is conducted at a temperature ranging between 40 to 75 °C for a period of 18 to 30 hours.

23. The method as claimed in claim **10**, wherein the step of air curing is conducted at room temperature for a period of 6 to 20 days.

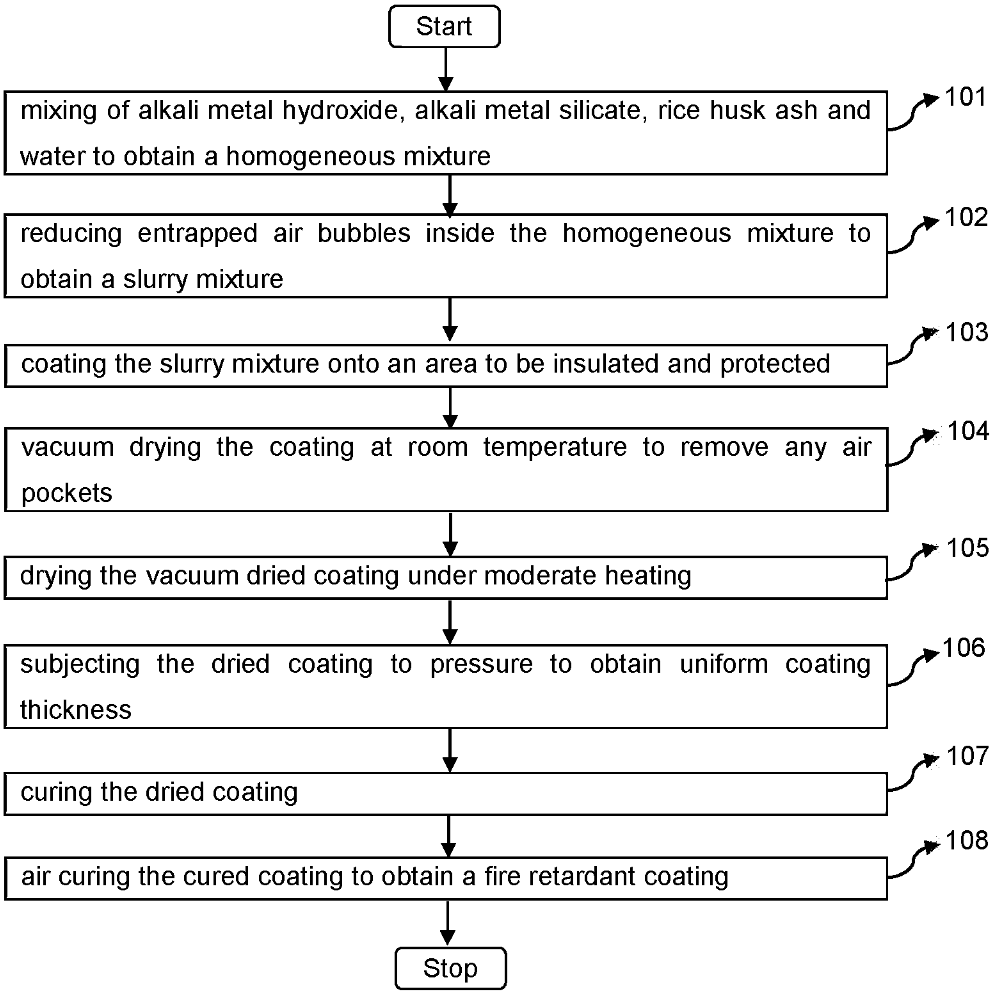

Start
mixing of alkali metal hydroxide, alkali metal silicate, rice husk ash and water to obtain a homogeneous mixture
101
reducing entrapped air bubbles inside the homogeneous mixture to obtain a slurry mixture
102
coating the slurry mixture onto an area to be insulated and protected
103
vacuum drying the coating at room temperature to remove any air pockets
104
drying the vacuum dried coating under moderate heating
105
subjecting the dried coating to pressure to obtain uniform coating thickness
106
curing the dried coating
107
air curing the cured coating to obtain a fire retardant coating
108
Stop

FIG. 1

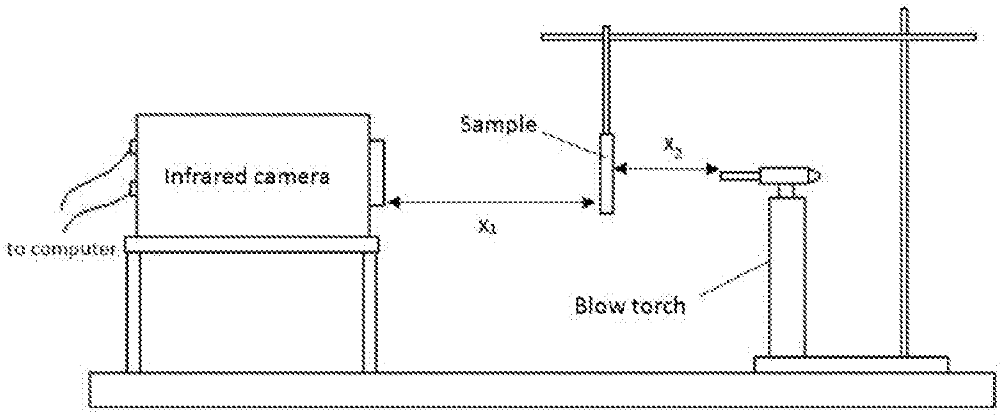
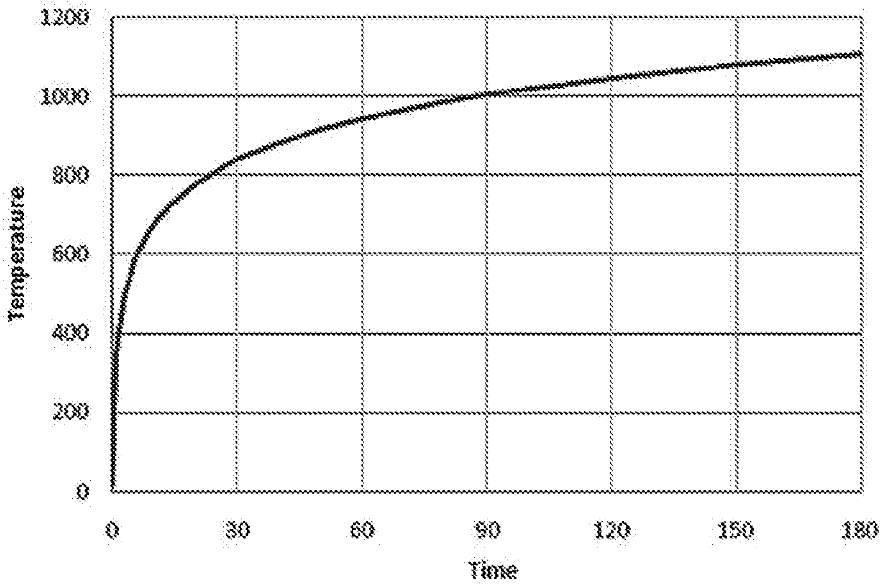
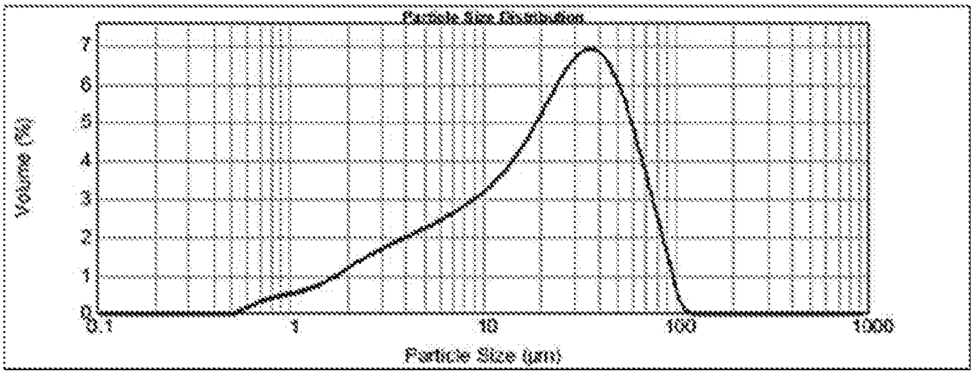

Sample
x_2
Infrared camera
x_1
to computer
Blow torch

FIG. 2



Temperature
1200
1000
800
600
400
200
0
0
30
60
90
120
150
180
Time

FIG. 3



Particle Size Distribution
Volume (%)
7
6
5
4
3
2
1
0
0.1
1
10
100
1000
Particle Size (µm)

FIG. 4

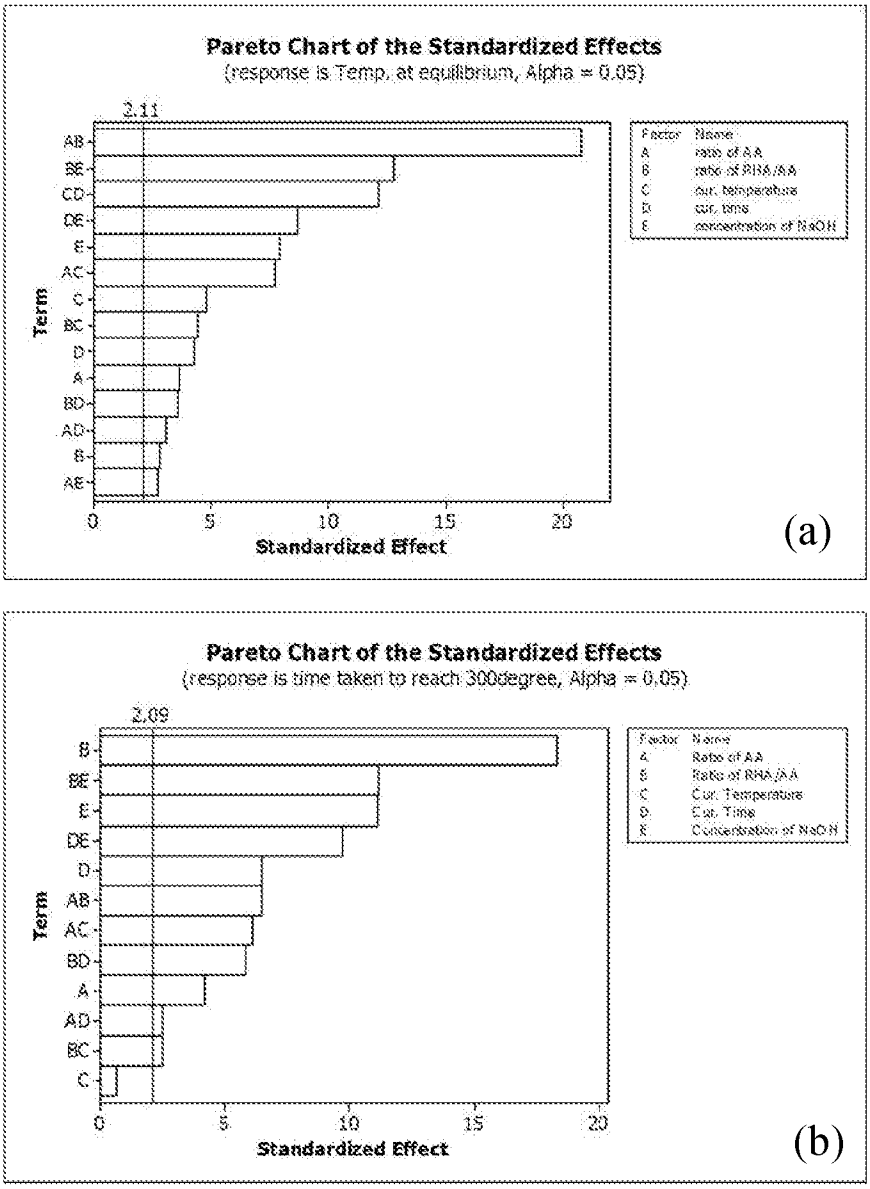

Pareto Chart of the Standardized Effects
(response is Temp. at equilibrium, Alpha = 0.05)
2.11
AB
BE
CD
DE
E
AC
C
BC
D
A
BD
AD
B
AE
Term
0
5
10
15
20
Standardized Effect
Factor Name
A ratio of AA
B ratio of RHA/AA
C cur. temperature
D cur. time
E concentration of NaOH
(a)
Pareto Chart of the Standardized Effects
(response is time taken to reach 300degree, Alpha = 0.05)
2.09
B
BE
E
DE
D
AB
AC
BD
A
AD
BC
C
Term
0
5
10
15
20
Standardized Effect
Factor Name
A Ratio of AA
B Ratio of RHA/AA
C Cur. Temperature
D Cur. Time
E Concentration of NaOH
(b)

FIG. 5

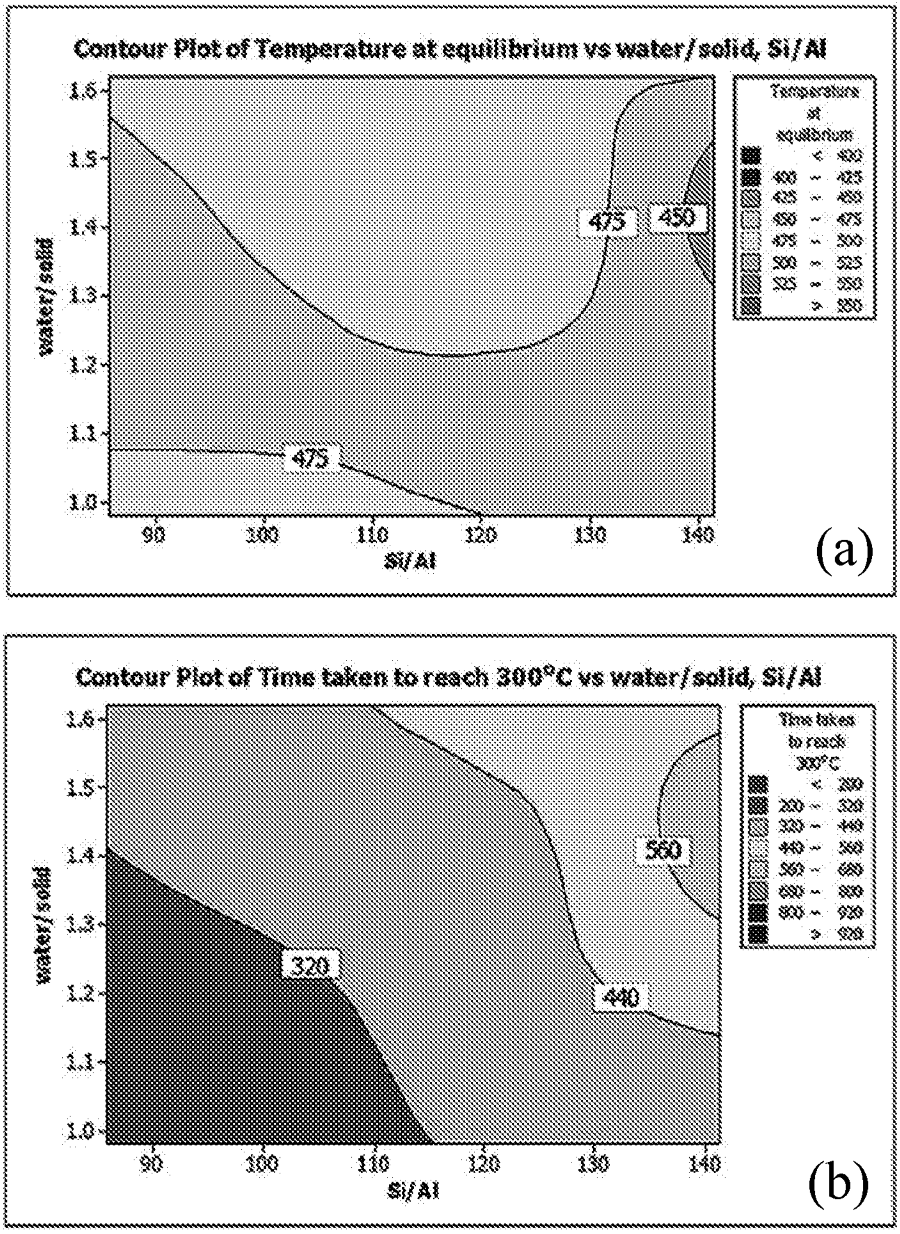

Contour Plot of Temperature at equilibrium vs water/solid, Si/Al
water/solid
1.6
1.5
1.4
1.3
1.2
1.1
1.0
Si/Al
90
100
110
120
130
140
475
450
475
Temperature at equilibrium
< 400
400 – 425
425 – 450
450 – 475
475 – 500
500 – 525
525 – 550
> 550
(a)
Contour Plot of Time taken to reach 300°C vs water/solid, Si/Al
water/solid
1.6
1.5
1.4
1.3
1.2
1.1
1.0
Si/Al
90
100
110
120
130
140
560
320
440
Time taken to reach 300°C
< 200
200 – 320
320 – 440
440 – 560
560 – 680
680 – 800
800 – 920
> 920
(b)

FIG. 6

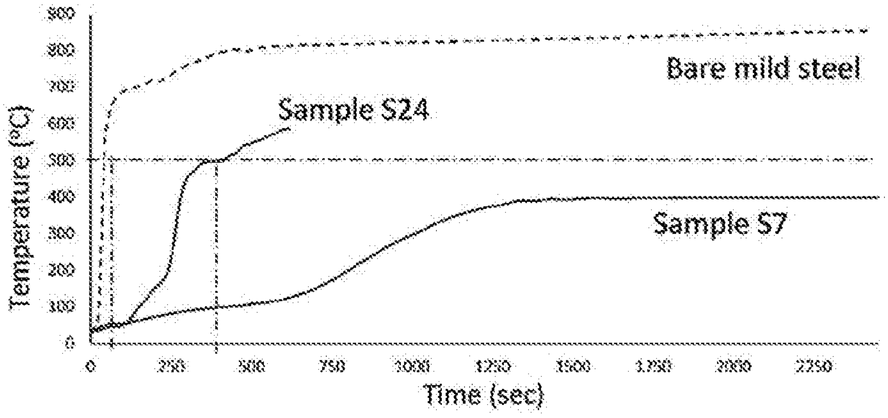

900
800
700
600
500
400
300
200
100
0
Temperature (°C)
0
250
500
750
1000
1250
1500
1750
2000
2250
Time (sec)
Bare mild steel
Sample S24
Sample S7

FIG. 7

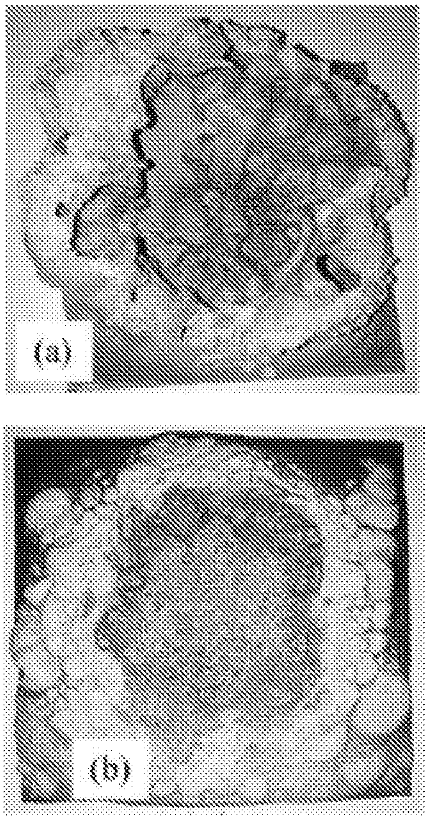

(a)
(b)

FIG. 8

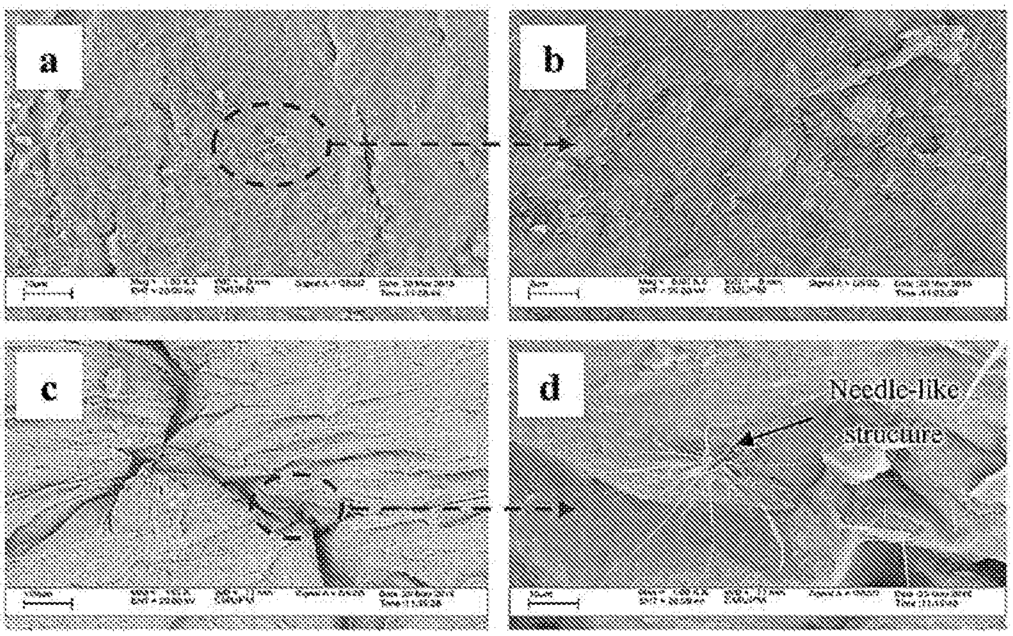

a
b
c
d
Needle-like structure

FIG. 9

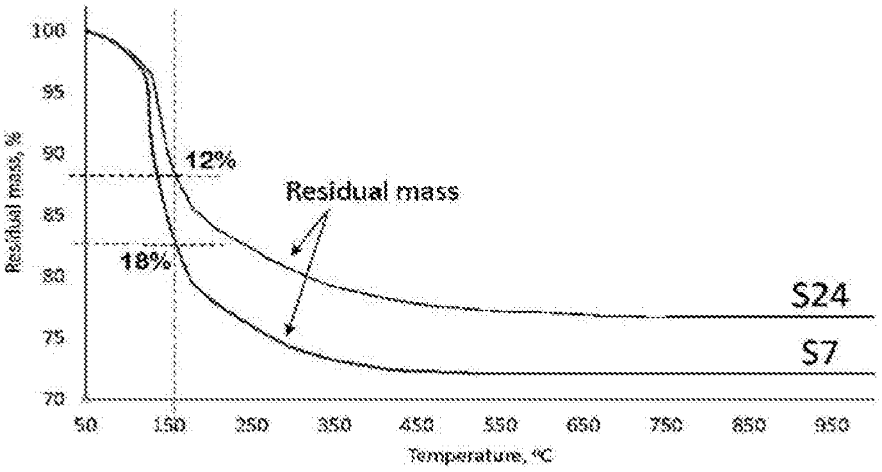

100
95
90
85
80
75
70
Residual mass, %
50
150
250
350
450
550
650
750
850
950
Temperature, °C
12%
18%
Residual mass
S24
S7

FIG. 10

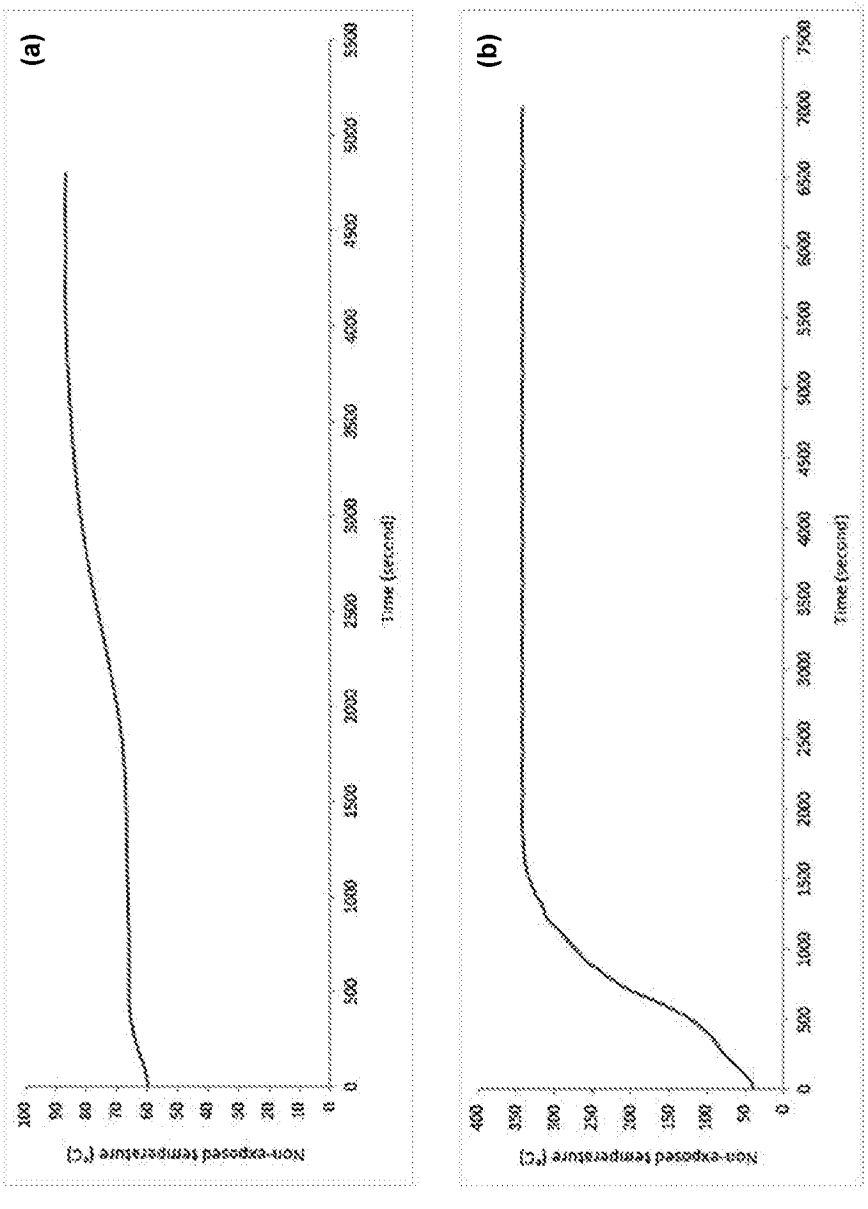

(a)
Non-exposed temperature [°C]
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
Time (second)
(b)
Non-exposed temperature [°C]
400
350
300
250
200
150
100
50
0
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
7500
Time (second)

FIG. 11

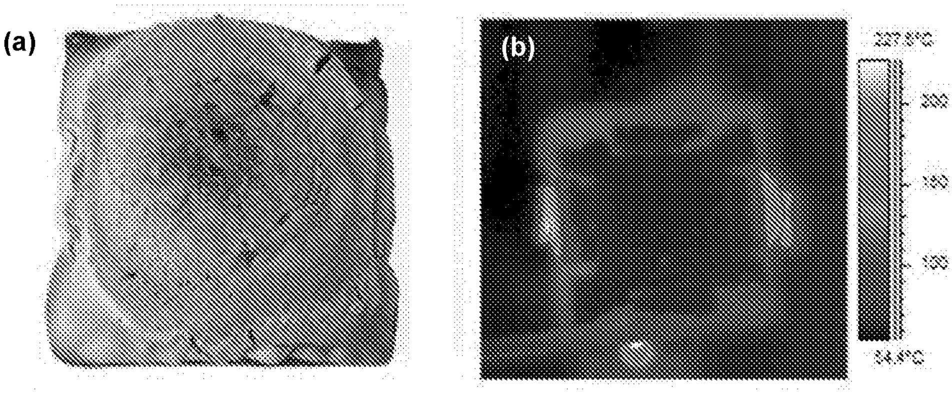


FIG. 12

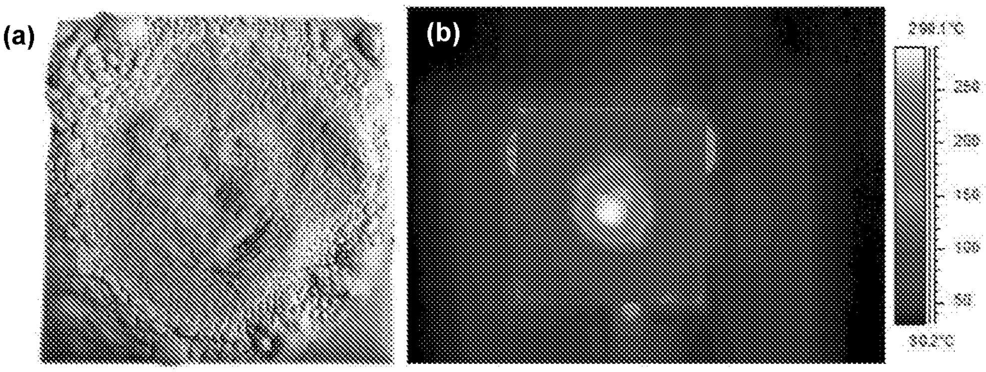


FIG. 13