

Low Firing Zn Metallic Composite Glazes for Earthenware

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Abstract

Objectives: To study the effect of Zn powder content (0-40 wt%) on low firing metallic composite glaze on earthenware fabricated at 1100°C under oxidizing and partially reducing firing atmosphere. **Methods/Statistical Analysis:** The raw glaze was characterized by TGA-DSC. The fired glaze was characterized by XRD (X-Ray Diffraction) and SEM (Scanning Electron Microscopy). The chemical resistance and water contact angle of fired glaze were also investigated. **Findings:** The glaze made with 10% Zn powder has green color and some dark green stripes of CuO and Fe₂O₃ in oxidizing firing atmosphere. Contrary, the glaze has shiny violet-green aspect of the mixture of the deep blue color of FeO and CuO, and some Zn metallic luster after firing in a reducing atmosphere. The glazes appear has rough surfaces with the greenish brown color. when more Zn powder is added (20-40 wt%) by firing in an oxidizing atmosphere, light brown and opaque appearance is observed after firing in partially reducing conditions. This was attributed to the formation of Fe₃O₄. The shiny crystals of Zn₂SiO₄ and a small amount of metallic Zn are formed in the fired glaze prepared in reducing atmosphere. The fired glaze surface can be corroded by both acidic and basic solutions. Finally, the fabricated fired glaze surface is easy-to-clean with water contact angle of ≈56°. **Application/Improvements:** These results could be applied to the local clay earthenware for luster decoration providing an added value to the products.

Keywords: Low Firing, Oxidizing Atmosphere, Partially Reducing Atmosphere, Tapoh Clay, Zn Metallic Composite Glazes.

1. Introduction

Luster is the most interesting ancient ceramic decorations¹. Its effects were achieved by the application of noble metal compounds mixed with clay or ochre and a binding agent onto the surface of a previously fired glaze followed by thermal treatment at 500-600°C in reducing atmosphere to induce the reduction of metal particles. The layers of metallic nanoparticles suspended in the dielectric glass matrix are directly responsible for the luster effect². Especially, gold ruby glass and luster ceramics are the most unique examples of physical colors in the cultural heritage³. The luster appearance achieved by a colored metallic shine of a metallic luster decoration is an observation of specular reflection. The elementary

composition of the decoration (e.g. metallic-copper-and-silver colloids) is an essential parameter determining the features of the reflectance spectra of the colored metallic shines. The properties also depend on the colloidal texture of the metallic particles and on the refractive index of the glaze⁴. The main physical effect lying at the origin of luster color is the excitation of surface plasmon modes in metal nanoparticles. The luster glaze ceramic preparation is usually produced in a reducing atmosphere. For example, luster glaze containing bismuth, cobalt, copper, and lead has been produced in H₂/N₂ reducing atmospheres on earthenware surfaces⁵. The technique for metallic luster decoration consists of metal powder deposition with a brush on top of the glaze layer of a ceramic object, followed by a layer of a metal salt and annealing these layers

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together under a reducing atmosphere at about 700 to 750 °C. Metal ions penetrate into the glaze where they precipitate and produce a composite layer about 700 nm thick and composed of metallic grains of varying size from 10 to 50 nm with a gradient of size and concentration³.

This research studies a low temperature metallic glaze produced with Zn powder in order to increase the value of local earthenware. The effects of Zn powder and transparent glaze dosages applied with firing at 1100 °C under oxidizing or partially reducing atmosphere on Tapoh clay specimens were studied. The thermal behavior of the raw glaze powder was analyzed by TGA-DSC. The fired glaze was characterized by XRD and SEM-EDS. The chemical resistance and water contact angle of the fired glaze were also tested.

2. Materials and Methods

2.1 Specimen Preparation

Tapoh clay (obtained from Tambol Tapoh, Muang District, Phitsanulok Province, Thailand) was ground and sieved (Laboratory test sieve, Retsch, Germany) to 60 meshes. The clay was wetted with 20% water by volume and pressed in plaster mould of a square form (40.0 mm x 40.0 mm x 10.0 mm). The wetted specimens were dried in an oven (SL shellab, 1350 FX, USA) at 110 °C for 24 h. The dried specimens were sintered in an electric furnace (Fisher Scientific Isotemp Muffle furnace) at 800 °C with 30 min soaking time for obtaining biscuit specimens (earthenware body). The biscuit specimens were kept in plastic bag for further experiments.

2.2 Glaze Preparation and Firing Condition

Zn powder (size 80 mesh, lab grade), transparent glaze (commercial grade), CuCO₃ (lab grade), bentonite (commercial grade), and Fe₂O₃ (lab grade) were mixed according to 5 formulae, which are shown in Table 1.

They were then mixed with 70% H₂O by volume in a porcelain mortar. This was followed by the addition of 5 wt% sodium silicate (as suspension and binder agent) for all formulae (No. 1-5). The purpose for the addition of Fe₂O₃ to the glaze composition was to obtain the metallic effect as iron in glasses stimulates a darkness of the glassy matrix. The presence of a dark background is a key point for obtaining the bright metallic effect⁶. Furthermore, iron oxide also acted as a flux and phase-separation accelerator during firing⁷. The suspension of the raw mixtures was applied to the biscuit Tapoh clay specimens by dipping about 2 mm layer of glaze thickness. Three replicates of specimens were prepared in all experiments. After glazing, the specimens with the glaze layer were dried at 110 °C for 2 h and then fired in an electric furnace in an oxidizing atmosphere or partially reducing atmosphere at a heating rate of 2 °C/min and reaching 1100 °C. The firing step was followed by soaking for 30 min. For the partially reducing conditions, the dried glazed specimens were placed in a ceramics box and covered with lid.

2.3 Materials Analysis

2.3.1 TGA and DSC Analysis (Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA))

Simultaneous thermal and differential thermal analyses (TGA-DSC-1, Mettler) were carried out on formula 2 raw glaze powder dried at 100 °C. The measurements were performed in the conditions of glaze powder weight 6.3559 mg at a heating rate of 10 °C/min from 50°C to 1200 °C under an N₂ 50 mL/min flow.

2.3.2 XRD Characterization

The fired glaze surface powder of formula 2 was characterized by X-ray powder Diffractometer (XRD, PW 3040/60, X' Pert Pro MPD) with a Cu tube anode, 10–80° 2θ range with step size of 0.02° and 3 s time/step.

Table 1. The ratios (wt%) of raw materials for low firing metallic glaze preparation.

Formula	Zn powder (wt%)	Transparent Glaze (wt%)	CuCO ₃ (wt%)	Bentonite (wt%)	Fe ₂ O ₃ (wt%)	Sodium silicate (wt%)
1	0	91	5	4	1.5	5
2	10	81	5	4	1.5	5
3	20	71	5	4	1.5	5
4	30	61	5	4	1.5	5
5	40	51	5	4	1.5	5

2.3.3 SEM-EDS Analysis

Scanning electron microscope equipped with energy dispersive spectrometer (SEM-EDS, LEO 1455 VP) was used to observe the morphology and elemental composition of formula 2 fired glaze on specimen surface after firing at 1100 °C in partially reducing atmosphere.

2.3.4 Chemical Resistance

The chemical resistance of the fired glaze on specimen surfaces was tested in solution of 3% HCl by volume and 3% NaOH by weight using the modified method⁸. The specimens were cleaned with methyl alcohol and then immersed in 3% HCl or 3% NaOH solution for 6 days. After the immersion, the specimens were dried and images of the glaze surface were acquired using both binocular microscopy (Olympus BH2) and photography (Digital camera, Motic Image, +2.0 ML) with 400 X magnification power.

2.3.5 Water Contact Angle Measurement

The hydrophilic properties of the fired on specimen surface was evaluated by measuring the contact angle of a distilled water droplet (diameter 2-6 mm) placed on the surface of the fired glaze using contact angle analyzer (Dataphysics, OCA20).

3. Results and Discussions

3.1 The Effects of Firing Atmosphere and Zn Powder Dosage

Figure 1 (a-j) shows the appearance of fired glazes with 0-40 wt% Zn metal powder prepared in oxidizing and partially reducing firing atmospheres at 1100 °C. The transparent glaze without Zn powder contains big bubbles on the glaze surface in the case both firing atmospheres. The big bubbles appearing on the glaze of the specimens are attributed to the liberation of CO₂ gas from CuCO₃ during high firing rate and also during the rapid cooling. The CO₂ gas escaping from the surface causes craters on the surface, while the gas trapped inside the glaze forms bubbles⁹. Furthermore, it was observed that more and larger bubbles formed in glaze prepared by firing in reducing atmosphere than in oxidizing atmosphere. This correlates with good solubility in glaze of metal compounds under oxidizing firing conditions. On the other hand, the reduc-

ing conditions may cause a decrease in solubility of metal compounds¹⁰. For firing in oxidizing atmosphere, the brown color of the glaze is due to the presence of iron(III) oxide particles inserted in the glass matrix¹¹ or copper(II) oxide in presence of iron oxides¹². However, the glaze has a deep blue color with big bubbles for specimens prepared in partially reducing firing atmosphere (Figure 1f). This is attributed to the color of iron(II) oxide¹³ and copper(II) oxide in the presence of sodium or potassium oxide¹². No bubbles were observed for specimens containing Zn powder and prepared by firing at 1100 °C in either of the atmospheres. However, a little pin holes can still be found in the glazes. This is because of ZnO, which is formed from Zn metal by oxidation or partial oxidation, is effective in viscosity reduction and dissolves readily in glaze at higher temperatures¹⁴. The pin holes on the glazes are also attributed to rapid cooling. The gas escaping in the form of bubbles will leave holes at the surface, which will not have enough time to fill⁹. Thus, in firing processing, more soaking and cooling times are necessary to remove all the escaping gases from the glaze. For the addition of 10 wt% Zn powder, the glaze has green color and some dark green stripes with little pinholes for the specimens prepared by firing in oxidizing atmosphere (Figure 1). The specimens are shiny violet-green with little pinholes for firing in reducing atmosphere (Figure 1g). Zn does not contribute any color on its own¹⁴. Thus the colors in the glazes prepared by firing in both types of atmosphere are related to other compounds. The greenish-brown color of glaze formed by firing in oxidizing atmosphere results from mixing the characteristics of copper(II) and iron(III) oxides⁶. On the other hand, violet-green color of glaze produced by firing in reducing atmosphere is attributed to the mixture of the deep blue colors of iron(II)¹³ and copper(II) oxides¹⁵. It seems that the glaze prepared in reducing atmosphere exhibits some luster. This may be originating from the bright Zn metallic effect. Further Zn powder addition (20-40 wt%) results in glazes that are matt and have rough surfaces. The matt and rough characteristics of the glazes increase with increasing dosage of the Zn powder (Figure 1 c-e and h-j). These observations showed that matt metallic effects correspond with rough surfaces. The matt appearance and roughness of glaze surfaces were attributed to the segregation of zinc and ZnO from the glassy matrix because of its saturation¹⁵ while transparent glaze dosage lowers. The color of glazes is greenish brown (Figure 1 c-e) and light brown (Figure

1 h-j) for specimens fired in oxidizing and reducing conditions, respectively. The greenish brown color observed after firing in oxidizing atmosphere is also a result of mixture of a copper(II) oxide¹⁴ and iron(III) oxide⁶ in zinc containing glaze. For firing in partially reducing conditions, the light brown and opaque characteristics are attributed to the formation of magnetite (Fe₃O₄) or mixed iron(II, III) oxides¹¹.

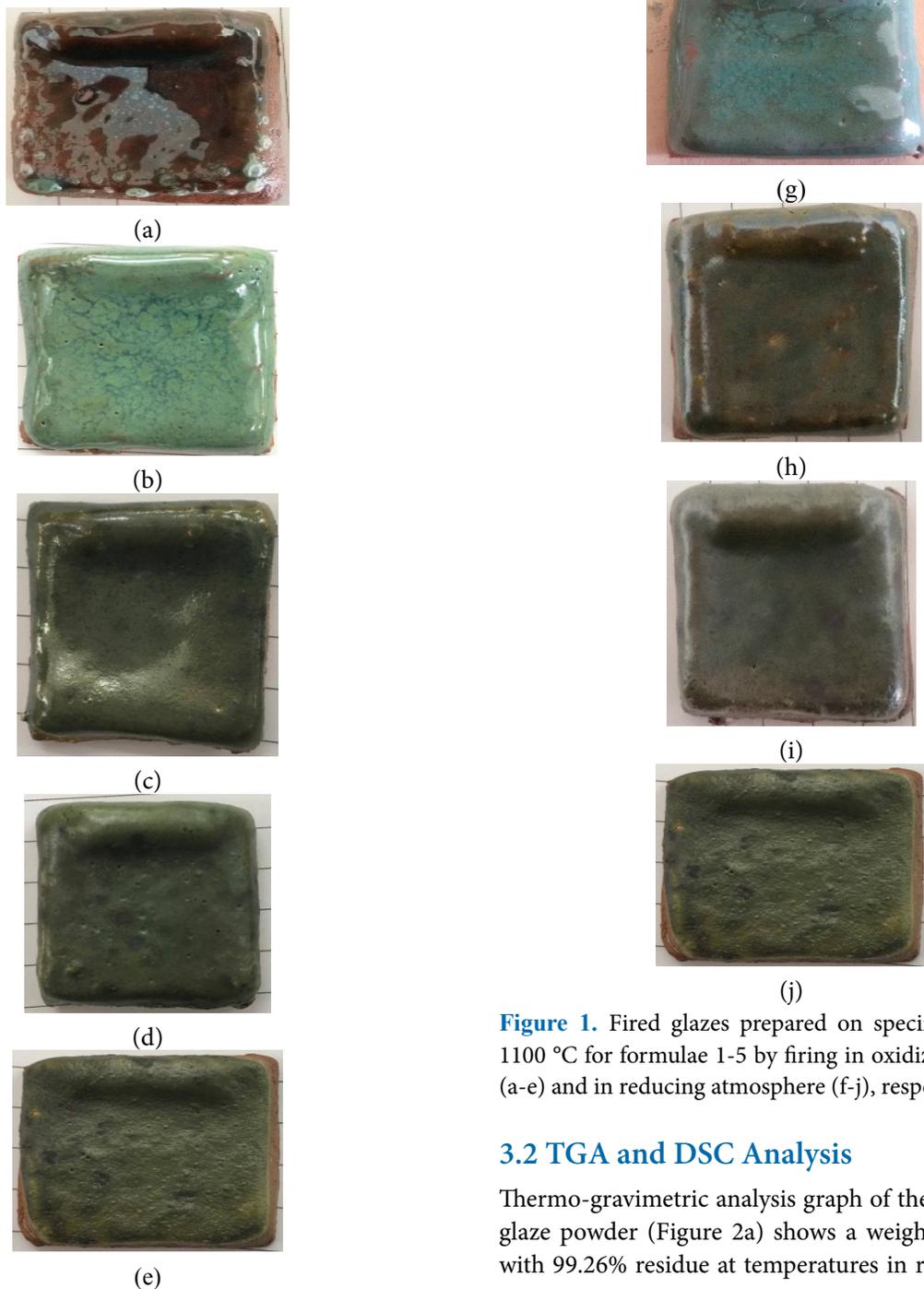


Figure 1. Fired glazes prepared on specimen surfaces at 1100 °C for formulae 1-5 by firing in oxidizing atmosphere (a-e) and in reducing atmosphere (f-j), respectively.

3.2 TGA and DSC Analysis

Thermo-gravimetric analysis graph of the formula 2 raw glaze powder (Figure 2a) shows a weight loss of 0.74% with 99.26% residue at temperatures in range of 50–230

°C. This is attributed to the evaporation of the physically adsorbed water on the surface of particles¹⁶. The weight loss of 1.33% with 97.92% residue at temperatures in the range of 290 °C to 410 °C, is attributed to the complete decomposition of CuCO₃¹⁷ and strongly bonded water molecules that are present in the first coordination sphere of the interlayer ions of the clay sheet¹⁸. From 430°C until 1150 °C a weight increase of 0.98% with 98.09-98.91% residue. It was due to the rearrangements of the chemical bonds of metal and C or N during pyrolysis under nitrogen atmosphere¹⁹. In addition, sodium silicate, which was used as a suspension agent, is exposed to CO₂ gas, which is liberated from CuCO₃, and then the formation of Na₂CO₃ and SiO₂ is observed as is shown in equation (1)⁹:

$$\text{Na}_2\text{SiO}_3 + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{SiO}_2 \text{ (colloidal)}$$

(1)

Beyond 1150 °C, weight loss of 0.11% with 98.80% residue is observed. This is caused by the decomposition of nitrogen from the metal²⁰ and Na₂CO₃⁹.

The DSC-curve is shown in Figure 2b of glaze powder consists of an endothermic peak at 259.38 °C (in the range 247.65 °C to 272.48 °C) and a little exothermic peak at 414.75 °C (in the range 410.09 °C to 420.91 °C). The endothermic peak at 259.38 °C is related to the decomposition of copper carbonate and desorption of bonded water molecules, which are accompanied by weight loss from 240 to 270 °C in the TGA curve. On the other hand, a little exothermal peak at 414.75 °C relates to the dehy-

droxylation²¹ and the evolution of NO_x, CO, and CO₂ gases²². This exothermic peak also indicates the formation of a metal nitride compound²³. This behavior could be attributed to the high extent of nitrogen dissolution as indicated by the relative mass gain in the corresponding TGA curve (Figure 2a). It was seen that the glaze powder only loses weight corresponding to 1.20% of the initial mass. This is because all of the raw materials in the glaze powder mixture, except CuCO₃ are thermally stable.

3.3 XRD Pattern of Fired Glaze

Figure 3 shows the XRD spectrum of the fired glaze from formula 2 prepared by firing in a reducing atmosphere at 1100 °C. The spectrum shows a broad peak pattern in the range of 2θ from 20° to 40°, which is typical of amorphous silica⁶. It also exhibits some typical amorphous halo of the glassy phase with the presence of two very weak peaks at 2θ of 31.5° and 44°²⁴. Furthermore, some morphology of the Zn-ortho silicate composition can be observed at 2θ of 21.5°, 25.8°, 32°, 35°, 40.5°, 45.5°, 50°, and 65°²⁵ in this XRD pattern. It can also be seen that the formation of the metallic Zn is very limited, as evidenced by the very weak peaks at about 55 and 70°²⁶. Zn metal can also be easily changed to ZnO by oxidation or partial oxidation and dissolve readily in glaze at higher temperatures¹⁴. This can be deduced from peaks occurring at 2θ of 32°, 34°, 36°, 57°, and 63°²⁷, which are also very weak. The XRD peaks of CuO appear at 32.5° and 40°²⁸. For Fe₃O₄, the characteris-

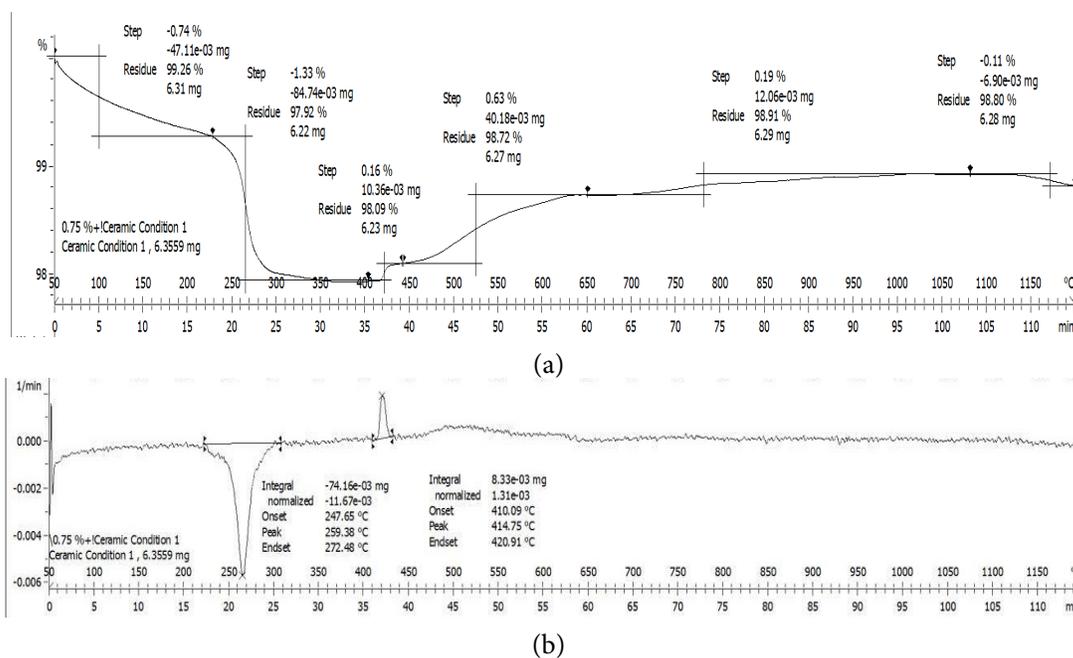


Figure 2. TGA (a) and DSC (b) graphs of raw glaze powder from formula 2.

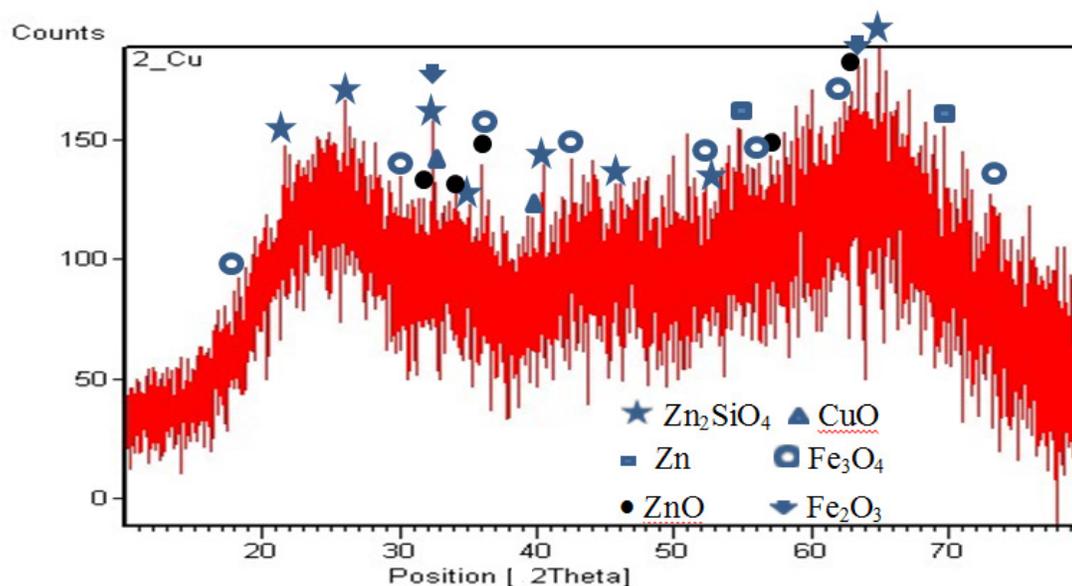


Figure 3. XRD pattern of low firing Zn composite glaze from formula 2.

tic peaks are located at 18°, 30°, 35°, 36°, 42.5°, 52.5°, 56°, 62°, and 73.5°²⁹. Furthermore, Fe₂O₃ (hematite) exhibits peaks at 33° and 63°². These compounds were formed in the fired glaze made in partially reducing atmosphere and correlate with colors and appearance.

3.4 Morphology and Elemental Composition of Fired Glaze

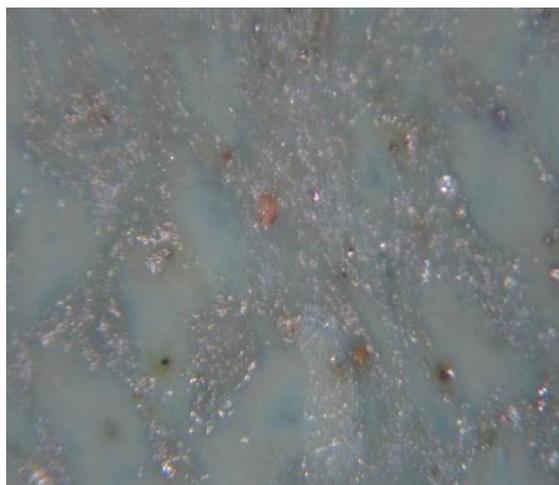
The morphology analysis based on the image from digital camera is shown in Figure 4a detects shiny crystals on glaze surface. This may be attributed to zinc silicate (Zn₂SiO₄) crystals containing a small amount of metallic Zn on the fired glaze. The Zn₂SiO₄ crystals have diameters in the range 69.08-78.76 nm as detected in the SEM image is shown in Figure 4b. This crystal was well developed at 1080 °C¹⁴. SEM also showed that the porosities within the fired glaze have disappeared. This revealed that the raw materials in the glaze mixture are well melted during firing at 1100°C. In addition, the bubbles in the glaze matrix have also disappeared, and only small pin holes remain. However, the SEM image shows that the glaze surface is relatively rough and heterogeneous due to the nanoparticles of Zn₂SiO₄ being dispersed within a glass matrix. Generally, the crystalline material is constituted of a dominant amorphous phase⁸. The EDS analysis results show that the glaze component by wt% are 23.17% O, 36.02% Si, 11.49% Zn, 7.93% Al, 7.62% Cu, 6.69% Na, 2.71% K, 2.76% Ca, and 1.60% Fe. The contents of these elements

correlated well with the dosage of each raw material in raw glaze mixtures as shown in Table 1. These materials then formed the oxide, silicate, or aluminosilicate compounds during firing at 1100°C. The formation of these compounds is confirmed by the XRD pattern shown in Figure 3.

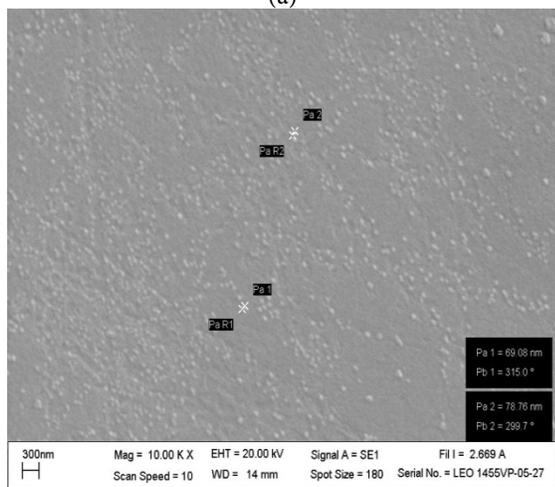
3.5 Chemical Resistance

Figure 5 shows the effects of acid and base exposure of fired glaze on specimen made by firing in a reducing atmosphere. It can be seen that glaze surfaces after both acid (Figure 5b) and base (Figure 5c) treatments have become more clear and smooth in comparison to the specimen without chemical treatment (Figure 5a). This is because some crystalline materials on the glaze surface were removed during both chemical treatments. This indicates that the glazes were corroded by both the acidic and the basic solution. However, it was observed that the glaze shows lower degree resistance to the acid than to the base. This is confirmed by glaze surface after the acid corrosion being more clear than after base corrosion. This is attributed to some zinc metal particles or zinc compounds being oxidized to Zn(II) ions in acidic solution, which were removed from glaze surface. However, Zn(II) ions react with OH⁻ in basic solution to form Zn(OH)₂ near the glaze surface, which can precipitate on the surface and form a protective film, resulting in the reduction of the rate of corrosion³⁰. Another possible reason

is that acids readily release hydrogen ions that can easily exchange alkali ions in the intermolecular network of fired glaze, changing them gradually into hydrated silicates. As the glass network becomes low in alkali ions, the free silica-hydrate gel forms on the surface and can be easily removed³¹.



(a)

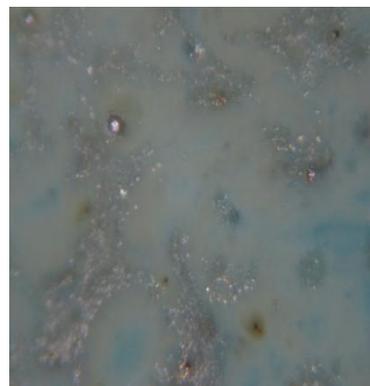


(b)

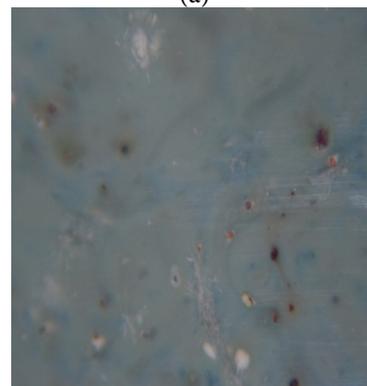
Figure 4. Morphology of formula 2 fired glaze made by firing in reducing atmosphere: (a) photography by digital camera with 400 X magnification power and (b) photography by SEM with 10000 X magnification power.

3.6 Water Contact Angle

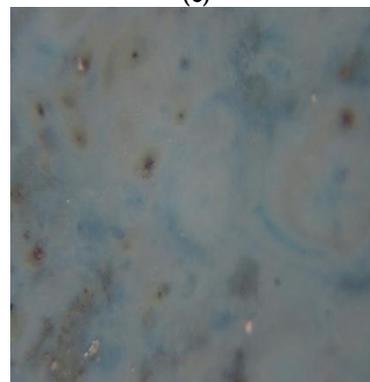
The contact angle is shown in Figure 6 of a water drop on the glaze surface of fired composite glaze from formula 2 was 56.2° (left angle) and 55.2° (right angle), which is similar to a standard glaze ($\approx 60^\circ$)⁶. It was shown that this glaze surface is hydrophilic (water contact angle $< 90^\circ$)¹⁵ which is easy-to-clean³².



(a)



(c)



(c)

Figure 5. Optical microscope images of specimens after chemical challenge treatment by acid (b) and base (c) compared to sample without chemical treatment (a). The images were acquired with 400 X magnification power.

4. Conclusion

Zn metal dosage in fired glaze is prepared by firing at 1100°C in oxidizing and partially reducing atmospheres has a profound effect on the properties of the glaze. Big bubbles are observed on the glaze surface for both firing atmospheres in the cases of specimen containing 0%

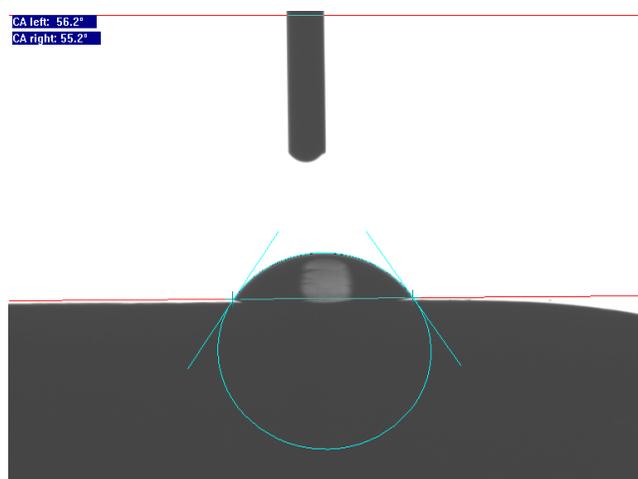


Figure 6. Water contact angle of fired composite glaze from formula 2.

Zn powder. However, these bubbles are not present in specimen made with added Zn powder. The bubbles on glaze surface are attributed to the liberation of CO_2 gas from CuCO_3 due to high firing rate and rapid cooling. The bubbles disappeared after firing at 1100°C for both atmospheres when Zn powder was added to the mixture of the starting materials. The glazes in these cases still contained little pin holes. This is because ZnO is effective in viscosity reduction and readily dissolves in the glaze. As for the pin holes, the firing processing requires high temperatures and long holding and cooling times to remove all the escaping gases from the glaze. The brown color of the glaze, which occurred with firing under an oxidizing atmosphere, is due to the presence of iron(III) oxide or copper(II) oxide particles. In the case of firing under a partially reducing atmosphere, the glaze has a deep blue color with big bubbles. This is attributed to the color of iron(II) oxide and copper(II) oxide in the presence of sodium or potassium oxide. The glaze made with the addition of 10% Zn powder has a green color with some dark green stripes, which is due to the mixing of characteristics of copper(II) and iron(III) oxides. In the case of firing in a reducing atmosphere, the glaze is shiny and violet-green, which is attributed to the mixing of the deep blue color of iron(II) and copper(II) oxides. The glaze prepared under these conditions also exhibits and some luster due to metallic Zn nanoparticles. The glazes become matt with rough surfaces with further more Zn powder addition (20-40 wt %). These characteristic were attributed to the segregation of zinc and ZnO from the glassy matrix because of its saturation. The greenish brown color of fired glaze in oxidizing firing atmosphere

is due to the properties of the mixture of a copper(II) oxide and iron(III) oxide in zinc containing materials. On the other hand, the light brown and opaque appearance observed for glazes made by firing in partially reducing conditions are attributed to the presence of a mixture iron(II) and iron(III) oxides. The results of TGA-DSC, XRD, and EDS analyses correlate well with the color and appearance of the fired glaze materials. The fired glaze made in reducing atmosphere contains shiny crystals, which are characteristic of zinc silicate (Zn_2SiO_4) crystal containing small amounts of metallic Zn. The fired glaze surface is corroded by both acidic and basic solutions. The materials show better resistance to base than to acid. Finally, the fired glaze surface is hydrophilic with a water contact angle of about 56° , which means the materials are easy-to-clean. This research results could be applied to the local clay earthenware for luster decoration providing an added value to the products.

5. Acknowledgment

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