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Characterization of Li–Zn–Fe crystalline phases in low temperature ceramic glaze

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Abstract

Ceramic glaze containing Li_2O and ZnO was prepared at a low firing temperature of 1100 °C. Addition of 0–30 wt.% iron oxide content developed brown color with a metallic sparkling effect from crystallization after soaking at 980–1080 °C. Using XRD, SEM/EDS and Raman microscopy the crystalline phases were determined as lithium zinc ferrite ($Li_xZn_{1-2x}Fe_{2+x}O_4$ where $x = 0.05–0.20$), hematite (α-Fe_2O_3) and anorthite ($CaAl_2Si_2O_8$). The most preferable metallic sparkling effect was caused by the lithium zinc ferrite phase obtained from the glaze containing 10 wt.% of iron oxide. Thermal analysis by STA after heat treatment indicated that crystallization temperature of lithium zinc ferrite and the effective soaking temperature depended on the iron oxide content in the glaze. The influence of excessive iron oxide content on the crystallization behavior of lithium zinc ferrite, anorthite and hematite phases is discussed.

Keywords: Crystalline glaze; Low firing temperature; Lithium zinc ferrite; Anorthite; Hematite

1. Introduction

Crystalline glaze is a devitrified glaze which consists of crystalline phases produced during controlled nucleation and growth processes.[1] This type of glaze is normally produced by gloss firing at high temperature above 1250 °C and subsequently soaking in the temperature range of 1100–1250 °C. Addition of colored metal oxides such as iron oxide can generate crystalline effects in glazes. However the glaze usually needs to be gloss fired in the high temperature range of 1300–1350 °C.[2] Most of the effects from iron oxide addition result from the presence of the crystalline groups of hematite (α-Fe_2O_3) under oxidizing conditions or magnetite (Fe_2O_4) under reducing conditions. Anorthite crystals ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) were reported to be formed when additions of 12–20% of Al_2O_3 were made.[3] Another effect of iron oxide crystals appears at lower temperature resulting in the so-called aventurine crystalline glaze, which is traditionally obtained when using lead oxide at lower firing temperatures. Through the use of lead-free Na_2O–B_2O_3–SiO_2 frit, the iron-aventurine glaze with a crystalline effect from hematite was reported to be obtained in the temperature range 1000–1300 °C.[4]

A low firing temperature glaze without lead oxide can be produced by adding alkali and alkaline earth oxides such as Na_2O, K_2O, Li_2O, CaO and MgO. The addition of Na_2O and K_2O decreases the glaze viscosity and facilitates crystal formation. On the other hand, MgO, CaO and BaO additions increase glaze viscosity and prevent crystal formation, hence these oxides should be kept below a certain level otherwise they can cause the glaze to develop a matt appearance.[5] Low firing temperatures could be used when small amounts of ZnO and B_2O_3 were added. In this case, under suitable conditions, a high content of zinc oxide can easily act as a nucleating agent and zinc-based crystalline phases can be obtained. The zinc-containing glaze is usually gloss fired at 1150–1300 °C.[6] It gives the well known macrocrystalline glaze due to the formation of willemite ($2ZnO{\cdot}SiO_2$) crystals which can grow up to centimeters in size.

The effects of different gloss firing temperatures in the range 1200–1250 °C on transformation of willemite to spherulite has been reported.[7] The extent of willemite crystal formation was reduced when $CaCO_3$ content increased up to 3% at 1200 °C gloss firing temperature.[8] It was considered that coloring additives such as, Fe_2O_3 did not have as much effect as alkali and alkaline earth oxides on the crystallization of willemite since crystals continued to grow in the colored matrix.[3] The effect of iron oxide content on crystallization of the glass ceramic glaze has also been studied.[9] The crystalline phases of franklinite

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($ZnFe_2O_4$) and hematite (Fe_2O_3) were obtained and their relative amounts depended on the iron content in the frit mixture.[9]

Glaze containing Li_2O may show different crystallization behavior since Li_2O is a strong flux and can influence changes in the oxidation state of Fe_2O_3 in the glaze. It has been reported that lithium metasilicate easily crystallized at low temperature in a Li_2O–Fe_2O_3–SiO_2 glass.[10] $LiFeSi_2O_6$, $LiFe_5O_8$ and $LiFeO_2$ crystalline phases were formed during crystallization in CaO–MgO (Li_2O, Fe_2O_3)–SiO_2 glasses.[11] In the LiO_2–ZnO–SiO_2 system, it was thought that Li_2ZnSiO_4 phase developed due to the reaction of ZnO with $Li_2Si_2O_5$.[12] A small addition of Li_2O changes the crystallization path by precipitation of β-quartz solid solution and willemite at low temperature (800–900 °C).[13] Doping by Li_2O also stimulated the formation of franklinite in Fe_2O_3–ZnO solid–solid interaction.[14] However, it is still not clear which phases will form when Fe_2O_3 is added to glazes containing Li_2O and ZnO.

Lead-free low temperature glaze formulations containing Li_2O and ZnO whose properties are compatible with commercial stoneware body have been developed and applied in ceramic manufacturing. Base glazes with gloss firing temperatures in the range 1000–1100 °C need to be developed in terms of color and effect to enhance the value of glazed products. Since crystallization of Fe_2O_3 possibly occurs more easily when Li_2O and ZnO are contained in the glaze, it is of interest to study the crystalline phases that develop at temperatures below 1100 °C.

2. Materials and methods

The test glazes were produced at low firing temperature by a crystallization technique. The base glaze was prepared from commercial grade raw materials (the suppliers) as follows: nepheline syenite (Cernic International Co., Ltd.), pottery stone (C.K. Ceramics Co., Ltd.), colemanite and silica sand (Amarin Ceramic Corp. Co., Ltd.). Chemical compositions of the raw materials were analyzed by X-ray fluorescence (XRF, Philips PW-2404). The Sager formula was used to calculate the trial glaze formulation. 5 wt.% of commercial grade Li_2CO_3 (Ceramic R Us Co., Ltd.) and ZnO (Cernic International Co., Ltd.) were used to reduce gloss firing temperature. Commercial grade iron oxide (Amarin Ceramic Corp. Co., Ltd.) 5–30 wt.% was added to develop crystalline effects in the glazes which are referred as Fe5–Fe30 formulas. The raw material mixture was mixed with 80% water and milled by rapid milling for 10 min. The glaze slip was sieved and 0.3 wt.% of commercial grade dispersive agent Na_2SiO_3 (Cernic International Co., Ltd.) was added. The density was adjusted to 1.5 g/cm^3 by water. The glaze slip was applied to the biscuit test piece (stoneware body, ϕ 4.5–5 cm) by dipping. The test piece was fired at a heating rate of 2 °C/min to 1100 °C followed by soaking for 1 h. It was cooled down at a cooling rate of 0.5 °C/min to 1080 °C, soaked for 3 h, and consequently cooled down at a rate of 1 °C/min to 980 °C, then soaked for 1 h. The crystalline glaze materials were obtained after cooling down to room temperature. The experimental procedure is shown in Fig. 1.

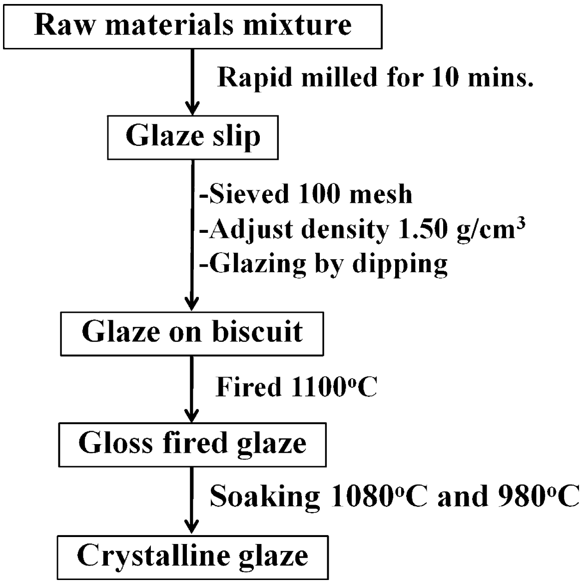

Fig. 1. Preparation of the crystalline glaze.

The crystalline phases formed in each glaze were identified by X-ray diffraction (XRD, JEOL JDX-3530, Cu-Kα radiations, 30 kV, 40 mA, scan rate 0.04 s^{-1}). Microstructures and elemental compositions were examined by scanning electron microscopy (SEM, Hitachi S-3400N, at 20 kV, WD = 9–10 mm) and energy dispersive X-ray spectrometry (EDS, EDAX Genesis 6.04, live time 100, dead time 15–20%). Crystallization behavior was observed by simultaneous thermal analysis (STA, Netzsch STA 449C, heating rate 10 K/min). XRD and Raman microscopy (Senterra Dispersive Raman Microscope, Bruker Optics, 785 nm, 25 mW) were used to study the crystallization changes after the heat treatment at temperature range 820–1100 °C.

3. Results and discussion

After the gloss firing at 1100 °C, the glazes have yellowish to brown and dark brown color with increase in iron oxide content. Crystalline effects were found in all glazes in which the iron oxide content was 5–30 wt.% (Fe5–Fe30) after soaking at 1080 and 980 °C as shown in Fig. 2. There was a small crystalline effect in the glaze when the iron oxide content was 5 wt.% (Fe5). The degree of crystallinity increased with an outstanding sprinkling metallic effect when iron oxide contents were 10 and 15 wt.% (Fe10–Fe15). However this effect was decreased as the content of iron oxide increased to 20 wt.% and above (Fe20–Fe30).

The XRD patterns in Fig. 3 showed that the main crystalline phase was lithium zinc ferrite ($Li_xZn_{1-2x}Fe_{2+x}O_4$ where $x = 0.05$–0.20) when the iron oxide content was 5–15 wt.% (Fe5–Fe15) but the peak intensity of this phase was decreased when the iron oxide content was increased. The main phases became anorthite ($CaAl_2Si_2O_8$) and hematite (α-Fe_2O_3) when the iron oxide content was more than 20 wt.% (Fe20–Fe30).

Back scattered images from SEM in Fig. 4 showed equiaxed shaped crystals in bright contrast and rod shaped crystals, the equiaxed crystals being observed in every sample. The rod shaped crystals and some smaller particles were observed when the amount of the equiaxed crystals decreased especially in