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Development of gold-bronze metallic glazes in a clay-based system for stoneware bodies

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ABSTRACT

In this study, a triaxial glaze system consisting of red clay, kaoline, quartz, MnO, CuO and CoO is systematically developed to produce gold-bronze raw metallic glazes for stoneware bodies. At first, all of the glazed samples in the developed system were fired in an electrically-heated kiln at 1160 °C. Then, the selected successful gold-bronze metallic glazes were applied onto 3-D forms of stoneware bodies and fired at the same conditions. Microstructural characterizations of the glazes are done with scanning electron microscopy (SEM) and energy dispersive x-ray analyses (EDS). This study revealed that triaxial blending of the ceramic raw materials is a beneficial method for glaze production and gold-bronze surfaces are obtained in glazes G 9, G 26, and G 34. It is observed that chemical composition of the glazes directly influence the color and the amount of CuO is more significative than MnO for achieving gold-bronze effect.

1. Introduction

Oxide coatings are commonly used for ceramics with a high decorative effect and metallic glazes are one of the most attractive glaze types in ceramic industry. They enhance the surface aesthetic properties with a brilliant metallic shine as lusters usually do [1,2]. Bronze luster on the surface of a glaze can be achieved with chromium and lead compounds in a special reduction firing. Bronze-effect glazes can be obtained in oxidized stoneware and porcelain using the fluxing action of manganese oxide with or without copper oxide, feldspar and/or clay [3].

Reduction luster is a highly decorative traditional glazing technique. However, it is necessary to control the furnace temperature, atmosphere and time during the reduction process in order to achieve successful results and this is quite difficult for traditional kilns [4]. Therefore, reduction technique is not appropriate for industrial production in terms of instability surface properties and generation of undesirable gases [5].

Nowadays, metallic glazed products exhibit many innovations for the decoration of ceramics, compared with decorations made by adding noble metals, reduction techniques or specific firings at lower temperatures (third fire) [6]. Generally, metallic glazes are produced using different raw materials such as clays, feldspars, Al-based phosphates, ceria, metallic oxides and frits [1,7]. As opposed to fritted compositions, raw glaze is a cost effective and time consuming alternative for ceramics [8,9]. Golden or bronze metallic effect is generally obtained by luster technique by using noble metals or lead in glaze compositions as well as introducing high amounts of frits in glaze batches [2,10]. Unlike luster glazes, it is necessary to use a different preparation method for metallic glazes and that the final surfaces exhibit the characteristics of the chemical ingredients [2]. Among all clay body types with artistic potters, stoneware is the most important with its fired strength and the character of the finished product. Firing atmosphere, inherent metallic oxides in clay and chemical glaze composition are the main factors that affect the colors of the fired stoneware objects [11]. When developing a new glaze composition, it is of a great importance to perform a systematic study which is most effectively ensured using blending systems and constructions. There are different types of methods such as line blend, triaxial and quadraxial blends. Triaxial blending of the ceramic raw materials is an important process, mainly used to create a new glaze. They are very useful systems for mixing raw materials, glazes, or colorants [12]. Generally, they give thoroughly comprehensive scans of mixtures including two, three and four components [13]. In the present study, the gold-bronze raw metallic glazes are designed by employing a triaxial blend system in order to explore the combinations of selected components that are suitable for stoneware decorations. For this purpose, a glaze system consisting of red clay, kaoline, quartz, MnO, CuO and CoO is developed and characterized in terms of surface properties and microstructure.

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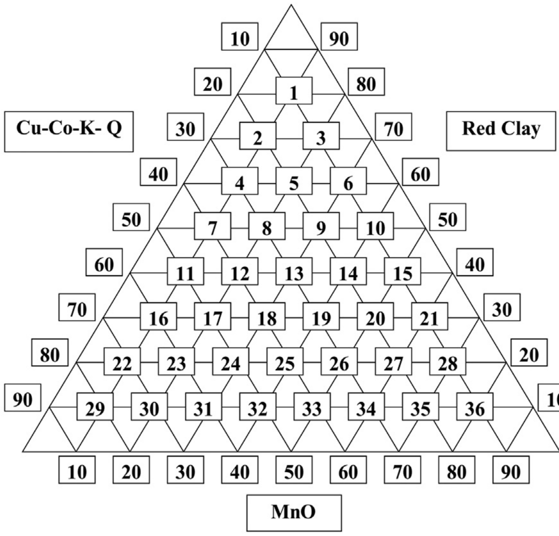

Fig. 1. Triaxial glaze system (Cu:CuO, Co:CoO, K:Kaolin, Q:Quartz).

Table 1
Raw material ratios of the glazes.

Recipe no	Red Clay	MnO	Cu-Co-K-Q			
			CuO	CoO	Kaolin	Quartz
1	80	10	2.5	2.5	2.5	2.5
2	70	10	5	5	5	5
3	70	20	2.5	2.5	2.5	2.5
4	60	10	7.5	7.5	7.5	7.5
5	60	20	5	5	5	5
6	60	30	2.5	2.5	2.5	2.5
7	50	10	10	10	10	10
8	50	20	7.5	7.5	7.5	7.5
9	50	30	5	5	5	5
10	50	40	2.5	2.5	2.5	2.5
11	40	10	12.5	12.5	12.5	12.5
12	40	20	10	10	10	10
13	40	30	7.5	7.5	7.5	7.5
14	40	40	5	5	5	5
15	40	50	2.5	2.5	2.5	2.5
16	30	10	15	15	15	15
17	30	20	12.5	12.5	12.5	12.5
18	30	30	10	10	10	10
19	30	40	7.5	7.5	7.5	7.5
20	30	50	5	5	5	5
21	30	60	2.5	2.5	2.5	2.5
22	20	10	17.5	17.5	17.5	17.5
23	20	20	15	15	15	15
24	20	30	12.5	12.5	12.5	12.5
25	20	40	10	10	10	10
26	20	50	7.5	7.5	7.5	7.5
27	20	60	5	5	5	5
28	20	70	2.5	2.5	2.5	2.5
29	10	10	20	20	20	20
30	10	20	17.5	17.5	17.5	17.5
31	10	30	15	15	15	15
32	10	40	12.5	12.5	12.5	12.5
33	10	50	10	10	10	10
34	10	60	7.5	7.5	7.5	7.5
35	10	70	5	5	5	5
36	10	80	2.5	2.5	2.5	2.5

2. Experimental procedure

Firstly, a literature review is done in order to prepare metallic glazes [3,5,6,14–20] and then a new triaxial glaze system is developed for a systematic study (Fig. 1). Table 1 indicates how compositions were selected and what the amounts of constituents are respectively. Compositional triaxial system was studied in the glaze synthesis. In this system (CuO + CoO + Kaoline + Quartz) side, the amount of each constituent is kept equal and 36 glaze recipes are prepared (Table 1).

At first, all glazes are applied on the stoneware substrates and after that, 9, 14, 25, 26 and 34 coded recipes are chosen for the application of 3-D stoneware forms. Starting batches as 100 g were wet ball milled for 15 min and liter weights of glazes were arranged as 1550 g. Glaze application onto stoneware bodies were made by pouring method on plaques that are biscuit fired at 1000 °C and all of the samples were fired in a laboratory type electrically-heated kiln (Nabertherm N100/14) at 1160 °C. The coloring parameters L*, a*, and b* of the samples were measured using a Minolta CR-300 series chromo-meter. L*, a*, b* analyses were made three times for every glazed bodies. Then, the mean values and standard deviations were calculated. Color differences (ΔE*) were also calculated as $\Delta E = ([\Delta L^*]^2 + [\Delta a^*]^2 + [\Delta b^*]^2)$ [21]. Glaze microstructures were examined by scanning electron microscopy (FEI NANO SEM 650), fitted with an energy dispersive X-ray analyzer (EDS). Coating is not applied onto the surfaces of the glaze samples before SEM and EDS analyses.

Table 2
Color (L*, a*, b*) and ΔE* values of some studied glazes.

Glazes	L*	a*	b*	ΔE*
G 26[a]	54.81 ± 0.25	8.96 ± 0.02	22.48 ± 0.25	–
G 9	45.28 ± 0.33	8.01 ± 0.39	16.60 ± 0.68	11.23
G 14	45.50 ± 0.72	0.25 ± 0.47	3.98 ± 0.39	22.46
G 25	53.20 ± 1.21	0.29 ± 0.05	4.36 ± 0.27	20.15
G 34	48.16 ± 1.13	8.14 ± 0.31	20.88 ± 0.86	6.88

[a] G 26 is selected as the reference for ΔE* calculations.

3. Results and discussion

Color (L*, a*, b*) and ΔE* of some studied glazes are represented in Table 2. According to CIELAB model L* = 0 represents black and L* = 100 shows white, a* is green-red at horizontal axis, and b* is yellow-blue at vertical axis [22]. With respect to Table 2, L* values of the glazes are ranged from 45.28 to 54.81. Generally G 9, G 26 and G 34 glazes exhibited higher a* and b* values when compared to G 14 and G 25. It is observed that, this significant increment caused a color transformation in glazes and metallic black and gray surfaces turned into gold-bronze color. L*, a*, and b* of the G 26 glaze is 54.81, 8.96, and 22.48, respectively. The total color difference between two objects is characterized by ΔE*. This difference is a single value which considers the difference between L*, a*, and b* of the sample and standard [21,22]. Amongst the studied glazes, gold-bronze G 26 which has the highest L*, a*, and b* values is selected as the reference sample of the studied system and ΔE* is controlled according to this glaze. In Table 2, it is seen that ΔE* of the G 14 and G 25 glazes are 22.46 and 20.15, respectively. On the contrary to these metallic black and gray glazes, the total color difference is decreased to 11.23 in G 9 and 6.88 in G 34 gold-bronze samples.

Glaze maturation is generally achieved in most of the glazes with a glossy, sateen matt or matt appearance. When designing a glaze composition, clays are one of the most important raw materials as they are not only colloidaly dispersed materials but also constitute the large amounts and activity in glaze batch [23]. It is determined that increasing amounts of MnO resulted in more glossy surfaces in final products. Chromium, cobalt, iron, manganese, nickel, copper, vanadium and titanium are from transition metal group and generally used as colorants in glaze. Manganese acts as fluxes, increases the fluidity and produces clusters of colored crystals [23]. G 14 glaze exhibited a silky matte metallic black color with a smooth surface texture while the