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Original Article

Study on the copper and iron coexisted coloring glaze and the mechanism of the fambe

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ABSTRACT

With copper and iron oxides as colorants, reddish and bluish purple glazes were prepared by changing the raw material ratio at the same firing schedule. Based on the primary factor experiments and the analyses of XRF and SEM/EDS, the fambe mechanism was proposed. The results indicated that glaze colors were related to multiple factors. The difference in copper red and purple glazes was merely caused by the later ingredient containing $Ca_3(PO_4)_2$, in which liquid-liquid phase separation structures were developed and formed structural colors, while the accumulated Fe_2O_3 in one phase decomposed to Fe^{2+} and bubbles to form blue stains and colorful texture. In addition, both CuO and Fe_2O_3 had a variety of coloring characteristics, which depended on the process parameter, firing temperature and base glaze compositions to make colors and hues change accordingly. In such cases, the multiple chemical colors were coupled with structural colors to form the fambe glaze.

1. Introduction

For art ceramics, the phantasmagoric and unique glaze colors are more popular than the common in the contemporary era, such as the Chinese Jun ware (AD 960-1279, located in Yuzhou, Henan Province of China). With oxides of copper and iron as colorants, Jun ware has rich glaze colors, such as red, purple, bluish purple and reddish purple. The Chinese idioms is named as “wan zi qian hong”, that is a color like blaze, and almost no one has the same colors or patterns. The feature is known as “fambe” that refers to an accidental change of glaze colors and patterns caused by variable firing temperatures and atmospheres in kiln. The firing process has been praised as “one color into kiln but full of colors out”. It is this that makes the Jun ware more charming, precious and popular.

Previous studies mostly focused on the coloring mechanism of copper red glaze and the phenomenon of iron blue in the celadon glaze. Researchers found the metallic Cu, semiconductive CuO and Cu_2O of colloidal state evenly existed throughout the glaze, causing the best red coloration. It denied the conventional theory that the red coloration was caused by metallic Cu and Cu_2O colloid [1–2]. Furthermore, researchers tried to find more stable copper coloring in the glaze [2–3]. For this purpose, Cu@SiO_2 pigment was prepared by the sol-gel method [4]. For celadon glaze, the color was mainly related to the concentration of structural iron ions. The Fe^{2+}/Fe^{3+} ratio and the glaze color depended on the firing conditions. As the Fe^{2+}/Fe^{3+} ratio gradually increased, the glaze color of celadon would change from pea green to sky green. Furthermore, the blue color was more or less caused by Rayleigh scattering [5–6]. However, seldom studies have been made to interpret the fambe mechanism of the glaze with copper and iron coexisted coloring.

In this paper, the copper red, purple, and bluish glazes were successfully prepared. In order to better control the glaze appearance of the fambe glaze, the influences of the colorants, calcium phosphate contents and the firing temperature were investigated in detail. The variation of glaze colors and the formation of patterns were also discussed. This work will throw some light on the better understanding of the fambe mechanism about the glaze of copper and iron coexisted coloring, and have good reference function for the development of the fancy glaze.

2. Experimental procedure

2.1. The samples preparation process

The technique of triangular batching was used to study the effects of quartz, feldspar and calcite contents on the glaze color. The percentage and chemical compositions of raw materials are shown in Tables 1 and 2. With a geometric segmentation method and A, B, C as triangle points, 21 samples of different compositions were prepared in a batch. Table 3 shows the chemical compositions of glazes at three vertices. In all those

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Table 1
Percentage of the raw materials at three vertices (wt%).

Code	Quartz	Feldspar	Calcite	Talc	$Ca_3(PO_4)_2$	Kaolin	CuO	ZnO	SnO_2	Fe_2O_3
A	40	45	5	3	3	4	0.4	0.5	1.5	1
B	10	70	10	3	3	4	0.4	0.5	1.5	1
C	15	45	30	3	3	4	0.4	0.5	1.5	1

Table 2
Chemical compositions of the raw materials (wt%).

Raw materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
Quartz	98.37	1.41	0.22	-	-	-	-
Feldspar	69.94	17.41	0.51	3.54	1.01	0.51	7.08
Calcite	1.28	0.66	-	90.98	0.65	-	6.43
Calcinedtalc	65.33	-	0.13	0.57	33.97	-	-
Kaolin	53.50	45.46	0.57	0.36	0.11	-	-
Analytical reagents CuO, Fe_2O_3, SnO_2, ZnO and $Ca_3(PO_4)_2$ (99.0%)							

Table 3
Chemical compositions of three vertices (wt%).

Code	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	SnO_2	ZnO	CuO	Fe_2O_3
A	73.78	10.01	6.05	1.48	3.45	0.23	1.34	1.47	0.49	0.39	1.31
B	62.03	13.99	11.37	1.77	5.54	0.23	1.34	1.47	0.49	0.39	1.38
C	49.92	9.91	28.31	1.64	5.04	0.23	1.34	1.47	0.49	0.39	1.26

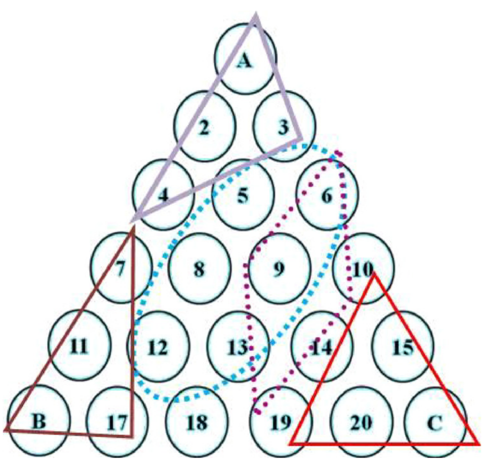

Fig. 1. Triangular batching diagram and the coloring effect area.

Table 4
Chemical composition of the base glaze B# (wt%).

SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	SnO_2	ZnO
60.55	11.76	17.37	1.69	5.02	0.26	1.36	1.49	0.50

samples, the best sample was selected as the basic composition for further experiments.

The glaze slurries (1.6 g/cm^3) of A, B and C in Table 1 were made of formular raw materials, 60 wt% water, 0.4 wt% sodium carboxyl methyl cellulose (CMC) and 0.2 wt% sodium tripolyphosphate (STPP). Then, the mixtures were grinded at a rate of 300 r/min for 35 min and sieved through 80 sieve mesh. The biscuit pieces were glazed by dipping. After dried, the test pieces were fired from room temperature to 1030 °C at a heating rate of 3.4 °C/min under oxidizing atmosphere and then increased to 1260 °C, 1280 °C, 1310 °C and 1320 °C at a heating rate of 1 °C/min under reducing atmosphere. Subsequently, the samples were held for 20 min at this temperature under reducing atmosphere. Finally, the samples were cooled down to room temperature naturally in the furnace.

2.2. Characterization

The color parameters (L*, a*, b*) of the fired specimens were measured by WSD-3C colorimeter using CIE Standard Illuminant D_{65}, following the CIE-L*a*b* colorimetric method recommended by the CIE. On this method, L* is the lightness axis (black (0) - white (100)), a* is the green (-) - red (+) axis, and b* is the blue (-) - yellow (+) axis. The Aigo GE-5 Digital Microscope (DM, China) was used for photomicrography. The X-ray data was collected by using an X-ray diffractometer (XRD, D/max 2200 PC, Japan) based on Cu-Ka radiation (λ = 1.5406 Å). The chemical composition of samples was determined by X-ray fluorescence (XRF, XGT-7200V, Japan). Meanwhile, the microstructure was investigated by scanning electron microscopy (SEM, Hitachi S-4800, Japan) equipped with energy dispersive spectrometry (EDS). Before the testing, the surface of sample was etched using 1 vol% HF for 20 s to expose the crystals and phase separation structures. Transmission electron microscopy (TEM, Tecnai G2 F20, America) at 200 kV was used to study the microstructure of unetched powder samples.

3. Results and discussion

3.1. Base glaze composition and colorant content with glaze color

Fig. 1 shows the triangular batching diagram with the coloring effect. From Table 1, only quartz, feldspar and calcite were variables, and talc, kaolin, calcium phosphate ($Ca_3(PO_4)_2$), ZnO, SnO_2, CuO and Fe_2O_3 were consistent. The firing result revealed that glaze surfaces appeared copper red (10-19-C triangular area), dark grayish purple (A-4-3 oblique triangular area), brownish purple (7-B-17 oblique triangular area), bluish purple (blue line circled area) and reddish purple (6-13-19-10 rhombus area) at 1280 °C. In fact, there was no strict demarcation line between color areas, because it had strong temperature dependence. Increasing the firing temperature to 1320 °C, the gray and brown areas would shrink toward A and B respectively, while the red area moved toward A-B line. Moreover, 15-20-C area would transform into