Synergistic effect of Jun porcelain glazes with cobalt and copper elements and coloring mechanism

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This study investigated the synergistic effect that the co-doping of cobalt and copper elements has on Jun porcelain glazes. The phase composition of the glazes was analyzed using X-ray diffraction (XRD). The sample morphology and phase separation structure of the glazes were examined using field emission scanning electron microscopy (FESEM). The element composition and valence state of the glazes were analyzed using X-ray photoelectron spectroscopy (XPS). The element distribution of the glazes was studied using an energy dispersive spectrometer (EDS). Our research shows that the distribution of the Co and Cu elements in the glaze layer is random, and indicates the presence of a liquid–liquid phase separation structure in the glazes. The coloring of the glazes is primarily related to the content of the cobalt and copper elements, the valence state of the coloring ions, and the micro-morphology. Additionally, there is an obvious synergistic effect between the coloring metal elements Co and Cu.

Key-words: Jun porcelain glazes, Coloring, Microscopic morphology, Phase separation, Synergistic effect

1. Introduction

The Jun kiln located in the town of Yuzhou in the Henan province of China has a long and rich history of firing Jun porcelain glazes. Jun porcelain is a famous art ceramic known for its “kiln transformation”, in which the colors change when heated in kilns, and has been described as “one color in kiln and thousands of colors leaving kiln”¹⁻⁻⁵ Due to its use in the creation of sophisticated crafts and its exquisite colors, it has been known as one of the most illustrious porcelains of the Song Dynasty. Jun porcelain has a reputation of being precious, highlighted by the following Chinese saying, “gold is valuable and Jun porcelain is priceless”, and is considered a “national treasure” with both high collection and historical value.¹⁻⁻⁹ It has been presented numerous times to international friends as a national gift and is highly regarded in the international community as well.¹⁻⁻¹⁴

Currently, the majority of the scientific research regarding Jun porcelain focuses on the identification of ancient Jun porcelain, the coloring mechanism, the firing process, and the influence of different coloring agents on its macro coloring.¹⁻⁻¹⁷ For example, F. Wang¹⁵ studied the coloring mechanism of Jun glaze with iron oxide coloring agents and determined that the sky-blue color was closely related to the phase separation structure. C. X. Zhu¹¹ studied the effect that nanometer CuO has on Jun porcelain glaze colors and they observed that the color is related to the valence state of the copper element and the phase separation structure in the glaze layer. J. Y. Hou¹⁹ studied the phase composition and microstructure of Jun ware glazes and found a correlation between the color of the glazes and the glass nanostructure. J. H. Wang²⁰ studied the mechanism of color rendering in the flambe glaze of Jun porcelain and discovered that the coloring of the flambe glaze is due to the presence of both iron oxides and CuO. The research regarding the influence of coloring agents on the Jun porcelain is mainly focused on the introduction of different proportions of single coloring materials (CuO, Fe₂O₃, etc.) into the glaze. However, this approach is unable to meet the rapid innovation and development pace of Jun porcelain. Focusing on the development of a new Jun porcelain glaze, in this study, we investigated the application of two colorants in Jun porcelain glaze.

The correlation between the glaze micro-morphology, liquid–liquid phase separation, element composition, and glaze coloring after the addition of two types of coloring agents (Co and CuO) into the glaze of Jun porcelain was
studied in depth using modern analytical characterization technology. The synergistic effect of the two coloring agents on glaze coloring was also explored.

2. Experimental procedure

2.1 Glaze preparation

The base glaze materials include 50 wt% K-feldspar, 20 wt% calcite, 18 wt% quartz sand, and 12 wt% calcined talc. The preparation of the glaze slurry was carried out by ball milling each raw material according to the glaze formula. Meanwhile, 0.1 wt% cobalt and 0.1–1.3 wt% CuO of the base glaze slurry were added as the colorants. The cobalt metal used had an average particle size of 1000 nm and a purity of 99.9%. The CuO and cobalt metal were both purchased from Shanghai St-nano Science & Technology CO. The test pieces consisted of 58 wt% kaolinite, 28.5 wt% quartz sand and 13.5 wt% feldspar. The test piece was coated with glazes by dipping. The glaze firing temperature was 1280 degrees Celsius, and was then cooled for 20 min. The preparation of the glaze slurry was carried out by ball milling each raw material according to the glaze formula. Meanwhile, 0.1 wt% cobalt and 0.1–1.3 wt% CuO of the base glaze slurry were added as the colorants. The cobalt metal used had an average particle size of 40 nm and a purity of 99.9%. The CuO used had an average particle size of 40 nm and a purity of 99.9%. The CuO and cobalt metal were both purchased from Shanghai St-nano Science & Technology CO. The test pieces consisted of 58 wt% kaolinite, 28.5 wt% quartz sand and 13.5 wt% feldspar. The test piece was coated with glazes by dipping. The glaze firing temperature was 1280 degrees Celsius, and was then cooled for 20 min. The oxidation atmosphere of the glaze fired is firing in air, and the reducing atmosphere was the mixed atmosphere (95% Ar-5% H2). The glazes were fired using the electric kiln (SQFL-1700, Shanghai Jujing Co. Ltd., China). The chemical compositions of the raw materials are given in Table 1.

2.2 Characterization

The coloring parameters and optical characteristics of the glazes were studied using a spectrophotometer (SP, Minolta CM-2600D, Japan). The phase composition of the glazes was analyzed using X-ray diffraction (XRD, Bruker D8, Germany). The sample morphology and the phase separation structure of the glazes were examined using field emission scanning electron microscopy (FESEM, FEI Nova 450, US). In order to study the phase separation structure of the glazes, some glaze-fired samples were surface-etched using 5 vol% HF for 30 s prior to testing the FESEM. The element distribution of the glaze-fired samples was studied using the energy dispersive spectrometer (EDS). The element composition and valence state of the glazes fired were analyzed using X-ray photoelectron spectroscopy (XPS, VG Scientific, UK).

3. Results and discussion

The surface appearances of the glaze-fired samples are shown in Figs. 1 and 2. As shown in Fig. 1, the coloring effect from the addition of cobalt or CuO in the base glaze shows obvious differences in the two kinds of atmosphere. The samples fired under the air atmosphere have a light blue color with 0.1 wt% cobalt [Fig. 1(c)] and a light green color with 0.1 wt% CuO [Fig. 1(e)]. Interestingly enough, the samples fired under the reducing atmosphere have a dark blue color with 0.1 wt% cobalt [Fig. 1(d)] and a glossy vermilion color with 0.1 wt% CuO [Fig. 1(f)]. Figure 2 shows the macroscopical appearance of different glazes with various amounts of cobalt and CuO. As shown in Figs. 2(A1)–2(D1) and 2(a1)–2(d1), the glazes that were fired under the air atmosphere clearly gradually change from blue to green with the addition of increasing amounts of CuO, and the number of pores on the surface of the specimens significantly decrease and the luster of the jade texture becomes more obvious. According to Figs. 2(E1)–2(F1) and 2(e1)–2(h1), the glaze fired samples have a deep red color when firing under the reducing atmosphere. With increasing amounts of CuO, the red gradually deepens and the number of stomata on the surface of the specimens significantly decreases.

The color parameters of the glaze samples fired under an air atmosphere are shown in Table 2. L* is the lightness [black(0)–white(100)], a* is the green (−)–red(+), and b* is the blue(−)–yellow(+). The base glaze fired samples

![Fig. 1. The surface appearances of the Jun porcelain glazes: (a–b) matrix glaze; (c–d) adding 0.1 wt% Co; (e–f) adding 0.1 wt% CuO; (a) and (c) and (e) fired under an air atmosphere; (b) and (d) and (f) fired under a reducing atmosphere; (g) and (h) show enlarged images of (c) and (d) respectively.](image-url)
clearly exhibited the highest $L^*$ (90.09), and the $L^*$ values significantly decrease when doping with 0.1 wt % Co. The $L^*$ values of the glazes containing 0.1 wt % Co gradually decrease with an increasing amount of CuO, indicating that the brightness of the glazes would make a transmutation when co-doping with Co and CuO. The $L^*$ values decrease from 62.42 to 57.89, when the content of CuO in the glaze increases from 0.1 to 1.3 wt %. In terms of the co-doped glazes, the negative values of $a^*$ and $b^*$ are acquired. With an increase in the CuO content from 0.1 to 1.3 wt %, the $a^*$ values gradually decrease from 1.62 to 4.81 and the $b^*$ values progressively increase from −24.88 to 4.81. The color values of the glazes fired under the reducing atmosphere are shown in Table 3. The $L^*$ values of the co-doped glazes gradually decrease with an increase in the amount of CuO from 0.1 to 1.0 wt %, and the maximum value is achieved when the concentration of CuO is 1.3 wt %. The positive $a^*$ values and negative $b^*$ values are acquired, which indicates the color values are primarily in the red–blue region.

The corresponding ultra violet–visible (UV–vis) reflectance spectra of the Jun porcelain glazes fired under different atmospheres are shown in Fig. 3. Circular area with a diameter of 3 mm of glaze would be measured in the UV–vis reflectance spectra test. According to Fig. 3(a), the position of the reflectance peaks of the glazes shift from...
410 to 474 nm with an increase in the CuO content, and the corresponding color of light changes from blue to green. In light of previous reports, cobalt appears blue in the glaze and divalent copper appears green. Therefore, in light of the above experimental results, we can conclude that the color rendering effect of the co-doped glazes fired under an air atmosphere is due to the competition of the content ratio of cobalt and copper. From Fig. 3(b), two reflectance peaks (390 and 550 nm) corresponding to blue–green appeared in the spectrum of the sample without CuO. Furthermore, the spectrum of Jun porcelain glazes with 0.1–1.3 wt% CuO has reflection peaks at 615 and 725 nm, these two peaks correspond to red.

The XRD patterns of glaze fired samples under different atmospheres are shown in Fig. 4. Some crystallization peaks, corresponding to alpha-quartz (JCPDS card NO. 79-1911), and cristobalite (JCPDS card NO. 82-1406) were detected in all of the samples fired under an air atmosphere [Fig. 4(a)]. The intensity of the characteristic peaks of the quartz crystal of the glazes is obviously heightened with increasing amounts of CuO. Additionally, Fig. 4(b) shows the diffraction peaks of Jun porcelain glazes that are indexed to elemental copper (JCPDS card NO. 4-836) when the glazes contained CuO contents greater than 0.5 wt% CuO. The quartz phase gradually disappears with an increase in the amount of CuO from 0.9 to 1.3 wt%.

The phase separation structures of the glaze fired samples were further analyzed and the response of the glaze layer to light was determined by etching the glaze samples. The SEM morphology and micro-porous size statistics of the samples with 0.1 wt% cobalt and 0.5 wt% CuO after using 5 vol% HF to etch are shown in Fig. 5. The glaze samples fired under different atmospheres include discrete phase separation structures. Additionally, compared to the glazes fired under an air atmosphere, the average diameter of the phase-separated structures of the glaze samples fired under the reducing atmosphere decreased from 226.78 to 108.16 nm and the density of the phase-separated structures significantly increased. According to the results of the above analysis, we know that the viscosity of the glazes is different and the growth of quartz in the glaze is affected because of the synergistic effect of cobalt and copper. A schematic diagram of the formation of different phase-separated structures is shown in Fig. 6. Compared with the fired glazes under the reducing atmosphere, more ions that can destroy the silicon tetrahedron may exist in the glaze layer of the fired glazes under an air atmosphere. This may cause the viscosity of the glaze layer to decrease during the firing process, which is beneficial to the further growth of
the phase-separated structures in the glaze layer. Because the size of the scattering particles is much larger than 100 nm, the scattering effect of the glaze layer on incident light is mainly diffuse scattering, which has little dependence on the wavelength. Thus, the change in the coloration of the glaze samples mainly depends on the coloration ion, that is, the change from blue to green with an increase in the amount of CuO (as shown in Figs. 2(A1)–2(D1)).

To examine the valence states of the coloring metal elements in the Jun porcelain glazes, the binding states of Cu and Co were investigated using XPS. The high-resolution XPS of Jun porcelain glaze samples, recorded in the energy region of the Cu-2p and Co-2p transition, is shown in Fig. 7. The Jun porcelain glaze samples fired under different atmospheres, show only a few weak Co-2p signal peaks, which corresponds to Co$^{2+}$ and Co$^{3+}$. Additionally, a few obvious Cu-2p signal peaks are observed on the glaze surface samples fired under an air atmosphere, which corresponds to Cu$^{1+}$ and Cu$^{2+}$. Interestingly, three chemical states of copper exist in the Jun porcelain glaze samples fired under the reducing atmosphere: Cu$^{0}$ and Cu$^{1+}$ and Cu$^{2+}$.

The FESEM image and the EDS mapping analyses of the surface of the Jun porcelain glazes fired under the air atmosphere are shown in Fig. 8. As shown in Fig. 8, all of the glazes include Cu and Co that are randomly distributed.
Fig. 7. XPS fitting spectra of Co-2P and Cu-2P of the sample with 0.1 wt % Co and 1.3 wt % CuO: (a) and (b) samples fired under an air atmosphere; (c) and (d) samples fired under a reducing atmosphere.

Fig. 8. FESEM image and EDS mapping analyses of the surface of the glaze containing 0.1 wt % Co and 1.3 wt % CuO, fired under the air atmosphere.
throughout the Jun porcelain glazes. This may be a result of the stochastic diffusion of Cu and Co during the glaze-firing processes. The FESEM image and EDS mapping analyses of the surface of the Jun porcelain glazes fired under the reducing atmosphere are shown in Fig. 9. As shown in Fig. 9, all of the glazes include Co that are randomly distributed throughout the Jun porcelain glazes. Additionally, we can infer the presence of agglomerates of elemental copper in Jun porcelain glazes from the EDS element mapping images of copper and oxygen.

The valence of copper in the Jun porcelain glazes fired under the reducing atmosphere is mainly Cu$^0$, which is determined using XPS [Fig. 7(d)] and XRD [Fig. 4(b)]. Thus, the red color in Fig. 2(H1) is primarily due to the coloration of the copper in the glaze. Combined with the statistical results shown in Figs. 5(b) and 5(d), the scattering particles in the glaze are spherical with a diameter of about 100 nm, achieving the conditions of Rayleigh scattering.\textsuperscript{22)-25) Considering that the intensity of Rayleigh scattering is inversely proportional to the quadratic of the wavelength of the incident light, and the blue light, with a shorter wavelength, is stronger than the red light in Rayleigh scattering, we can observe the presence of blue surrounding the red area from the Figs. 2(e1)–2(h1). As shown in Fig. 3(b), the reflectivity of the samples at different wavelengths is observed to gradually increase with a decrease in the wavelength, which also confirmed that the color of the glaze with the two synergistic elements, copper and cobalt, under the reducing atmosphere followed the Rayleigh scattering mechanism.

4. Summary

The split-new Jun porcelain glazes were successfully fired by co-doping with cobalt and copper. The color of the glazes gradually changed from blue to green with increasing amounts of CuO when the glaze samples were fired under an air atmosphere. The red color of the Jun porcelain glazes gradually deepens and the number of stomata on the surface of the specimens significantly decreases with an increasing copper content when the glazes were fired under a reducing atmosphere. The quartz phase gradually disappears with an increasing amount of CuO from 0.9 to 1.3 wt % when the Jun porcelain glazes were fired under a reducing atmosphere. Due to the different viscosity of the glazes containing cobalt and copper, the average particle size of the phase-separated structures of the Jun porcelain glazes fired under an air atmosphere is obviously larger than those fired under a reducing atmosphere. The valence state of the coloring metal elements in the glazes and the micro-structure of glazes have an important influence on the coloration of the Jun porcelain glazes.

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