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Influence of the thickness of the copper glaze layer on the color and its formation mechanism

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Abstract

In this paper, the effects of glaze layer thickness on the color properties of copper glaze were investigated, and the related mechanism was also revealed. The results manifest that the glaze thickness would affect the color of copper glaze. The color properties of copper glaze are determined by the phase-separated structure, the distribution of elements and the valence state of copper species. Due to the heterogeneous distribution behavior of the elements, the copper glazes with all thicknesses have three phase-separated structures, which are spherical (top layer), worm-like (interlayer) and nano-porous network-like (bottom layer). Simultaneously, the copper glazes with all thicknesses have three colors, of which the bottom layer of all samples is red. However, the color of the top layer gradually changes from milk white (0.2 mm) to cyan (0.4–0.6 mm) and then to blue (0.8–1.0 mm) with the green body thickness increases. The color of interlayer is the result of the color mixing of the top and bottom layer. A thicker green body thickness (>1 mm) could be propitious for copper glaze to present a superior color performance. This work provides a new and an easily overlooked perspective for the investigation of copper glaze.

1. Introduction

Copper glaze is an ancient ceramic art glaze, which represents a pinnacle of Chinese porcelain making technology [1–3]. Copper glaze has two characteristics: (1) it shows abundant gorgeous color, e.g., red, blue, green, etc (2) its color properties are difficult to predict and control [4]. To reveal the secrets of copper glaze, countless craftsmen in ancient China have been exploring the craftsmanship of copper glaze. Unfortunately, it is still impossible to achieve a high-quality controlled preparation of the color properties of the copper glaze.

The color mechanism of copper glaze has attracted considerable interest from researchers over a long period of time. Meanwhile, due to the development of measurement and characterization techniques, such as SEM-EDS, HRTEM and XPS, exciting developments are taking place in copper glaze research over the past several decades [4, 5]. Research results demonstrate copper glaze could be presents different colors ascribed to the dual effects of the various copper species and the amorphous photonic structure in the glaze [6–8]. Specifically, the copper species have multifarious states in the glaze, including Cu(0), Cu(I), Cu(II), CuO and Cu₂O, etc [9]. Color variations are related to the chemical states, distribution and microstructure of the copper element [10]. The amorphous photonic structure in the glaze, a liquid-liquid phase-separate structure, allowed light scattering, diffraction and reflection, leading to abundant color variations [11, 12]. Moreover, Rayleigh scattering occurred on the glaze when the diameter of phase-separated droplet of 1–100 nm, which produces
Table 1. Chemical compositions of the mineral raw materials (wt%).

|        | SiO_2 | Al_2O_3 | Fe_2O_3 | CaO | MgO | K_2O | Na_2O | LI   |
|--------|-------|---------|---------|-----|-----|------|-------|------|
| Glass frit | 70.27 | 1.00    | 0.11    | 8.66| 4.14| 0.3  | 13.45 | 1.61 |
| Calcite | 4.35  | 1.01    | 0.15    | 52.18| 0.33| 0.11 | 0.11  | 41.48|
| Wollastonite | 51.93 | 0.14    | 0.39    | 42.79| 1.54| 0.02 | 0.1   | 2.76 |
| Talc    | 66.75 | 0.58    | 0.13    | 1.29 | 30.64| 0.06 | 0.12  | 0.67 |
| K-feldspar | 75.73 | 13.31   | 0.68    | 0.59 | 0.05| 6.03 | 2.71  | 0.20 |
| Quartz  | 59.05 | 0.60    | 0.01    | 0.02 | 0.03| 0.12 | 0.01  | 0.12 |

opalescent blue and contributes to the coloring of the glaze [5]. In this case, Yin believed the short-range ordered phase-separated structure is the source of the structural color of amorphous photonic in the glaze [8].

Obviously, the state variation of copper species and the formation of phase-separated structure are controlled by the preparation process parameters, such as glaze formulation, firing atmosphere and calcination temperature. In general, copper glaze fired in air shows a green hue, whose coloring mechanism is divalent copper cations (Cu^{2+}) and monovalent copper cations (Cu^+) dissolving in the glass phase. Cu^2+ is colorless, while Cu^{2+} tints the glaze a green [10]. In comparison, a strong reducing atmosphere is an essential for copper glaze presents a red hue because CuO were reduced to the metallic Cu and Cu_2O [13, 14]. Meanwhile, the red hue gradually darkens with the increase of the CuO content in the glaze formulation, and eventually turns to blue-green [15]. Phosphorus (P) is a crucial component of the copper glaze to form a phase-separated structure, which could increase the content of non-bridging oxygen and the spatial density of oxygen atoms around Cu^{2+} in the glaze [3]. Coupling of color produced by both mechanisms of phase-separated structure and copper species gives the glaze a blue hue [5, 12]. In addition, a stronger base glaze is easier to convert copper ions to a high valence state [10].

To sum up, relevant research of copper glaze mainly focuses on two aspects: (1) stable preparation technology of high-quality copper red glaze, i.e., to develop a suitable glaze formulation and to determine the best firing process. (2) to investigate the color mechanism of copper glaze. In simple terms, composition regulation of glaze formulation, e.g., the content of copper, phosphorus and alkali metal, is the most common thoughts for studying the color properties and mechanism of copper glaze by scholars [5, 15]. Whereas, the effects of glaze thickness on the color properties of copper glaze seems to be neglected. Generally, porcelain craftsmen believed that the glaze thickness should not be too thin based on a mass of practical experience, otherwise the glaze surface will be colorless because of the volatilization of copper species [2, 4]. The pity is that they cannot scientifically explain the deeper mechanism. Therefore, the relationship between the glaze thickness and color properties of copper glaze needs to be systematically investigated, and the related mechanism needs to be revealed.

In the present work, a series of copper glaze samples were synthesized by altering the glaze thickness. The effects of glaze thickness on the valence state and distribution of copper species have been studied. Meanwhile, the structural evolution of copper glaze and the element distributed behavior was also investigated.

2. Experimental procedure

2.1. Materials

The copper glaze compositions were made by 25.43 wt% glass frit, 15.26 wt% calcite, 10.17 wt% wollastonite, 5.09 wt% talc, 25.43 wt% K-feldspar, 15.26 wt% quartz, 1.32 wt% copper oxide (CuO) and 2.03 wt% tin oxide (SnO). CuO, SnO, sodium carboxyl methyl cellulose (CMC) and sodium tripolyphosphate (STPP) were purchased from Shanghai Titan Scientific Co., Ltd. Besides, chemical compositions of the mineral raw materials are given in table 1.

2.2. Glaze preparation

The glaze slurry was prepared by ball milling the raw materials, 50 wt% water, 0.3 wt% CMC and 0.2 wt% STPP at a rate of 400 r min⁻¹ for 30 min, and sieved through 80 sieve meshes. Then, the glaze slurry was applied to the test piece (Ø 5 cm) by dipping method. After dried, the test pieces were polished by an abrasive paper to obtain test pieces with thickness of approximately 0.2, 0.4, 0.6, 0.8 and 1.0 mm (green body thickness), respectively. The green body thickness is adjusted by controlling the dipping time and polishing together. Afterwards, the test pieces were fired from room temperature to 1050 °C at a heating rate of 4 °C min⁻¹ under an air atmosphere and then increased to 1280 °C at a heating rate of 0.67 °C min⁻¹ under a weak reducing atmosphere. Subsequently, these specimens were held for 20 min at this temperature under a weak reducing atmosphere. Finally, the test pieces were cooled down to room temperature naturally in the kiln to obtain copper glaze samples. It should be
noted that the thickness of all copper glaze samples (glaze thickness) was reduced after firing due to high temperature melting.

2.3. Characterization

In this work, chemical composition of mineral raw material was determined by x-ray fluorescence spectrometer that was equipped with a Rh target (XRF; Axios Advanced, PANalytical, Holland). Chromatic parameters of the glaze samples were measured by WSD-3C colorimeter using CIE Standard Illuminant D65, following the CIE-L*a*b* colorimetric method recommended by the CIE. Here, L* is the lightness axis (black (0) ~ white (100)), a* is the green (−) ~ red (+) axis, and b* is the blue (−) ~ yellow (+) axis. The Digital Microscope (XJ-HU380, China) was used for photomicrography. Phases compositions present in the glaze samples were analyzed using an x-ray diffractometer (XRD; D8 Advance, Bruker AXS GmbH, Germany) using Cu Kα radiation (λ = 0.15418 nm). The XRD data were collected using a step-scan mode with a step size of 0.02° and a scanning range (2θ) of 5°–80°. Microstructure of the glaze samples was observed by a scanning electron microscopy (SEM; SU8010, Hitachi, Japan) equipped with energy dispersive spectrometry (EDS). Before the SEM analysis, the glaze samples were etched by 5vol.% HF solutions for 20 s. Sizes of the phase-separated droplets were performed by using Nano Measurer software. The contents and valence states of copper ions in the glaze sample with different thickness were determined by x-ray photoelectron spectrometer (XPS; PHI-5000versaprobeIII, Japan) using AlKα radiation. The binding energy values were calibrated based on the Cls peak that was measured at 284.8 eV. Phase-separated structure in glaze was observed by transmission electron microscope (TEM, JEOL JEM-F200, Japan) equipped with energy dispersive spectrometry (EDS).

3. Results and discussion

Figure 1 exhibits the optical photographs and SEM images of glaze samples with the green body thickness from 0.2 to 1.0 mm. It can be seen from SEM images that the thickness of glaze layer was reduced to about 0.20, 0.30, 0.45, 0.60 and 0.68 mm after firing, respectively. Interestingly, there are significant differences in the color behavior of glaze specimens of different green body thicknesses. It can be seen from figure 1(a) the glaze sample with a green body thickness of 0.2 mm shows a milk white and has some slightly pink spot. As the green body thickness increased to 0.4 mm [figure 1(b)], a cyan spot was observed, and a large pink area surrounds the cyan spot. For the sample with a green body thickness of 0.6 mm, a significant increase in the area of cyan spot, and the pink area turned to fuchsia. What is interesting is that the samples with a green body thickness greater than 0.8 mm [as seen in figures 1(d) and (e)] all show blue, as well as the greater the thickness, the darker the blue hue.

Compared with visual observation, chromatic parameters are a more objective index to describe the color evolution of glaze with thickness. Table 2 lists the chromatic parameters of glazes with different thicknesses. As the green body thickness increases from 0.2 to 1.0 mm, L*- and b*-value of the glaze samples all decrease continuously with an increase in the thickness, suggesting that the glaze gradually appears dark blue with the development of thickness. Specifically, chromatic value of the 1.0mm-sample is L* = 30.59, a* = 7.78 and b* = 23.77. Obviously, chromatic parameters evolution is consistent with the observation in figure 1. To sum up, glaze thickness has great influence on the color of copper glaze.
In order to reveal the relationship between the color properties and glaze thickness, a series of measurements and characterizations were implemented on glaze samples with different thicknesses. Figure 2 presents the XRD patterns of the glaze samples with different green body thicknesses. The main crystalline phases observed in the glaze sample of a green body thickness of 0.2 mm are cristobalite (PDF# 39–1425) and tridymite (PDF# 16-0152). With the increase of thickness, the peak of tridymite phase disappeared first, and the intensity of cristobalite phase significantly decreased. Meanwhile, a significant broad scattering peak located at a 2θ of 20°−30° was observed in the XRD patterns of the glaze samples with the green body thickness greater than 0.4 mm, which indicates the formation of an amorphous phase. Moreover, no crystalline phase can be detected in samples with a green body thickness greater than 0.8 mm. According to the XRD patterns of raw materials (figure 1S), the cristobalite and tridymite detected are unlikely to come from inherent components in the raw materials. Lundin has confirmed that the cristobalite phase tends to form in systems with excess quartz. Moreover, the formation of cristobalite is a solid-state reaction starting from the surface of the quartz grain [16]. Schneider also manifested that cristobalite may be formed from a silica-rich amorphous phase [17]. Consequently, the detected cristobalite phase is a phase transition product [18]. Besides, the detected tridymite is an associated product of cristobalite, because they both are formed by planar sequences of six-membered rings of silica tetrahedra. Hence, the strong similarities between tridymite and cristobalite allow the growth of mixed-layered sequences and tridymite could act as a support for the development of cristobalite [19]. Based on the chemical composition of the raw materials and the formulation of the copper glaze, it is clear that the copper glaze studied in this work is a system with a high silica and quartz content. Moreover, in thinner samples (0.2 and 0.4 mm), the SiO₂ content of the copper glaze will be considerably increased due to the cation diffusion effect (cation diffusion effect will be discussed in detail in figure 4 section.). In contrast, the chemical composition of the glaze is relatively stable in thicker samples (0.6, 0.8 and 1.0 mm). In summary, the cristobalite and tridymite phases can be detected in the thinner samples, while the thicker samples show an amorphous phase. Additionally, in the case of the thicker glaze samples, the centre of the amorphous broad peaks did not change, indicating the phase compositions of the glaze were not affected by the thickness. Therefore, phase composition is not the critical factor in the color change of the glaze samples.

As shown in figures 1(a)–(c), the presented color of glaze samples is a superimposition of multiple colors. Accordingly, it is speculated that these copper glaze samples are composed of glaze layers with different colors. To investigate the properties of these glaze layers, Digital Microscope and SEM-EDS measurement were performed. Figures 3(b), (g), (l), (q) and (v) show the cross-section magnified photographs of glaze samples with different thicknesses, respectively, suggesting that the copper glaze reported in this paper does have a multilayer

![Figure 2. XRD patterns of the glaze samples with different green body thicknesses.](image)

| Green body thickness (mm) | Glaze thickness (mm) | L⁺ | a' | b' | Color                        |
|--------------------------|----------------------|----|----|----|------------------------------|
| 0.2                      | 0.20                 | 76.15 | 0.19 | 3.21 | Milk white-slightly pink spot |
| 0.4                      | 0.30                 | 62.25 | -0.77 | -2.89 | Pink- slightly baby cyan     |
| 0.6                      | 0.45                 | 56.93 | -3.51 | -8.25 | Cyan- slightly lilac         |
| 0.8                      | 0.60                 | 48.08 | -3.54 | -20.68 | Wateth blue                 |
| 1.0                      | 0.68                 | 30.59 | 7.78  | -23.77 | Dark blue                   |
structure. Specifically, the copper glazes with green body thickness of 0.2, 0.4 and 0.6 mm are composed of a white layer (top layer, contact with the air) and a red layer (bottom layer, contact with the body). The copper glazes with green body thickness of 0.8 and 1.0 mm are composed of a blue layer (top layer), a purple layer (interlayer) and a red layer (bottom layer). Moreover, the thickness of both the red and purple layers increased with the increase of the entire glaze thickness. Figures 3(a), (f), (k), (p) and (u) exhibit the microstructures of the top layer of glaze samples with different thicknesses, respectively. It can be obviously seen from figure 3(a) that there is a huge crystal particle embedded in the glaze layer, which is presumed to be a cristobalite crystal based on the XRD analysis in figure 2. Moreover, the spherical phase-separated structures were formed in the top layer of every copper glaze samples. Meanwhile, the average size of these spherical particles decreases with the increase of the entire glaze thickness. The structure unit of copper glaze system is \([\text{SiO}_4]\) tetrahedron, and the viscosity of this system is proportional to the silicon content \([20]\). Due to the crystallization of a large number of cristobalite and tridymite crystals, it speculated that the viscosity of a thinner glaze sample is less than that of the thicker glaze sample. In the system of low-viscosity, the phase-separated structures were easier to grow, so the average size of phase-separated particles in the thinner glaze sample is larger than that of the thicker glaze sample \([5]\).
The microstructures of the interlayer of copper glaze samples are shown in figures 3(d), (i), (n), (s) and (x). It demonstrated the worm-like phase-separated structures appeared in the interlayer of every copper glaze samples. Similarly, the average size in the glaze pattern was larger than that of the gap due to the phase-separated structures is easier to grow in a low-viscosity copper glaze system (i.e., the glaze samples with small thickness), as shown in figures 3(d), (i) and (n). Correspondingly, in thicker glaze samples, e.g., figures 3(s) and (x), the average size in the glaze pattern was close to that of the gap.

Figures 3(e), (j), (o), (t) and (y) present the microstructures of the bottom layer (i.e., red layer) of glaze samples with different thicknesses, respectively. Apparently, the nano-porous network-like phase-separated structures were formed in the bottom layer of every copper glaze samples. In contrast to the top layer and interlayer, the average size of phase-separation droplets in the bottom layer of all samples is similar. The reason is that the chemical composition of the bottom layer of all samples is similar, so their viscosities are close, which is proved from the EDS results in table S1 (available online at stacks.iop.org/MRX/9/085001/mmedia).

Based on the above analysis, the copper glaze reported in this work has three phase-separated structures, which are spherical, worm-like and nano-porous network-like phase-separated structures, respectively. Insets of figures 3(u), (x) and (y) demonstrate the corresponding ring-shaped 2D FFT images, suggesting that these three phase-separated structures are all belonged to the amorphous photons structure [11]. As a result, the difference in the microstructure of the glaze layers is believed to be caused by the variation in chemical compositions.

Table S1 lists content of each ion measured by EDS in different glaze layers in figure 3. Simultaneously, figures 4 and 2S summarize the distribution rule of these ions. Obviously, many ions are heterogeneously
distributed in the direction perpendicular to the glaze surface, such as copper, calcium and silicon, etc. Figure 3(a) shows the content of copper cations in different glaze layer. It can be observed that the copper content in the top layer is higher than that in the bottom layer in all samples, which are ascribed to the volatility of CuO during the firing process [2, 4, 21]. Considering that copper is the only colorant in this system and that the volatilization of CuO is inevitable, a thicker glaze layer is more beneficial for color development of copper glaze. Similarly, figures 3(b) and (d) suggest that network modifier species (i.e., Na, K, Mg and Ca) are enriched within the top layer, especially Ca. On the contrary, the content of network former species (i.e., Al and Si) gradually increase from the top layer to the bottom layer. Accordingly, the modifier/former species ratio [i.e., (Na+K + Mg+Ca)/(Al+Si)] of the top glaze layer is greater than that of the bottom glaze layer, as shown in figure 4(e). The heterogeneous distribution behavior of modifier and former species could be caused by the cation diffusion from glaze to body, in which the diffusion driven force is concentration difference of modifier ions between glaze and body, since the proportion of modifier species in the body is lower than that in the glaze [22]. As previously mentioned, the fact that the crystallization of cristobalite and tridymite crystals in a thinner glaze sample is another reason for the higher modifier/former species ratio in the top layer. In brief, there are three reasons for the heterogeneous distribution of metal ions in the direction perpendicular to the glaze: (1) cation diffusion (dominant); (2) volatilization of CuO (secondary); and (3) crystallization of a large number of cristobalite and tridymite crystals (only appears in the thinner samples).

Based on the above analysis of the chemical composition, it can be concluded that the viscosity of glaze layer gradually increases from the top layer to the bottom layer [23, 24]. Obviously, a lower viscosity is more suitable for phase separation [25–27]. Consequently, the phase-separated structures of the top layer, interlayer and bottom layer are zero-, two- and three-dimensional, respectively.

Due to the opacifying effects of the phase-separated structure, the final color performance of copper glazes was mainly determined by the color of the top layer. In order to further investigate the color properties and microstructure of the top glaze layer, Digital Microscope and SEM-EDS measurement were also performed on the glaze surface. Figure 5 presents the Digital Microscope photos and SEM images of the glaze samples with different thicknesses. It can be confirmed from figure 5(a) that the top layer of the 0.2mm-sample is milky white, instead of colorless. Additionally, the top layers of the glaze samples from 0.4 to 1.0 mm are light cyan, cyan, blue-green and blue-purple, respectively. As shown in figures 5(b), (e) and (h), there are many cristobalite round crystals with a size of about 100/nm were also observed in the samples with the green body thicknesses from 0.2 to 0.6 mm, which is consistent with the analysis in figures 2 and 3. In addition to the crystallized cristobalite particles and phase-separated structures, a third structure (figure 3(S)) was detected in the glaze samples with the green body thickness of 0.2 and 0.4 mm, namely transparent transition region. In these regions, there are some red areas in the bottom layer can be observed so easily. However, EDS spectra (figure 4S) did not demonstrate an obvious difference in the chemical composition of the transparent transition and phase-separated structure region. In contrast, although many dark color spots can be observed [figures 5(g), (j) and (m)], the transparent transition region was not detected in the glaze samples with a green body thickness greater than 0.6 mm. Combined with the interface shape between the top layer and interlayer is a wavy line (instead of a straight line), it is believed that the reason for the observation of dark color spots is caused by the uneven thickness of the top layer. In other words, the place where dark color spots can be seen should be the thinner area of the top layer.

Figures 3(e), (j), (o), (t) and (y) exhibit the microstructures of glaze surface in all thickness samples. Obviously, glaze surfaces have the same phase-separated structures as the corresponding surface fracture surface. Similarly, the average size of the phase-separated droplets is decreasing with the thickness of the glaze layer increases. Based on the measurement of Nano Measurer software, it can be calculated that the average sizes of the phase-separated droplets for the samples with the green body thicknesses from 0.2 to 1.0 mm are 358, 211, 175, 115 and 109 nm, respectively.

According to the principles of colloidal chemistry, phase-separated structure can produce structural color, and the type of structural color is related to the size of phase-separated droplets. Specially, when the droplet size is about 100 nm, Rayleigh scattering could be formed, which give rise to the blue opalescence [12, 28]. In contrast, Mie scattering could be formed when the droplet size is larger than 100 nm, which generates the milk white [12]. For instance, the 0.2mm-sample, whose phase-separated droplets size is 358 nm and shows milk white. As for the samples with a green body thickness greater than 0.4 mm, the opacifying effects caused by the phase-separated structures can also be observed. Nevertheless, the corresponding structural colors are not obvious due to the tainting effect of copper ions.

To investigate the mechanism of phase separation, TEM-EDS analysis was performed on the surface of the 1.0mm-sample, as shown in figure 6. It can be obviously seen from the TEM image that the particle size of the spherical particles formed by phase separation is about 100 nm, which is in agreement with the SEM results in figure 5(o). The EDS mapping images of Ca, Cu and Mg elements, particularly Ca, suggesting that these metal elements are enriched around the area of phase-separated droplets. Nevertheless, the EDS mapping images of Si and Al elements manifest that these elements are uniform distributed in the glaze surface. The enrichment
Figure 5. Digital Microscope photos (a), (d), (g), (j), (m) and SEM images of the glaze samples with different green body thicknesses (mm): (a)–(e) 0.2; (f)–(j) 0.4; (k)–(o) 0.6; (p)–(t) 0.8; (u)–(y) 1.0.

Figure 6. TEM micrograph and EDS mapping images of glaze sample (top layer) with the green body thickness of 1.0 mm.
behavior of Ca, Cu and Mg elements is ascribed to the phase separation behavior \[22\]. Ca, Cu and Mg cations have higher ion potential, while the ion potential of Si cation is lower. Consequently, compared with Si cation, Ca, Cu and Mg cations have greater ability to bond oxygen, which is responsible for the liquid-liquid immiscibility of glaze phase (i.e., phase separation) \[4, 11, 12\]. The heterogeneous distribution of the elements will lead to the difference in refractive index between the spherical areas (i.e., phase-separated structure) and the non-spherical areas \[27\]. Apparently, the combined effects of the difference in refractive index and nano-scale phase-separated droplets could make the glaze have an excellent opacifying effect and a soft luster. Additionally, many non-bridging oxygens would be produced during the competing for oxygen ions, which will be easy to generate a blue hue after bonding with copper species \[3\].

As discussed above, the structural evolution of copper glaze with thickness has been systematically analyzed. Simultaneously, the effects of the phase-separated structure on the structural color of copper glaze have been also explained. However, the valence state of the copper species is the decisive factor for the color properties of copper glaze \[15\]. Take the 1.0 mm-sample for instance, figure 7 shows the XPS spectra of blue (top layer) and red layer (bottom layer). The two XPS spectra show similar characteristics, indicating that the blue and red layers are built by identical elements, i.e., Si, Al, O, Ca, Mg, Na, K, Cu, Sn elements (C element is come from reference substrate of measuring equipment.) \[29\].

Figure 8 exhibits the high resolution XPS spectra of Cu species in red and blue layer of 1.0mm-sample, respectively. On account of the Cu 2p peak has notably split-orbit components (\(\Delta = 19.7\)), it is possible to distinguish the valence states of copper species using satellite features of the Cu 2p peak \[15, 30\]. As shown in figures 8(a) and (c), peaks located at approximately 932.7 and 952.5 eV were observed, which correspond to the Cu 2p\(_{3/2}\) and Cu 2p\(_{1/2}\) levels, respectively. After peak fitting, three kinds of copper species were detected in the red layer, which corresponds to Cu(0), Cu(I) and Cu(II). In contrast, only Cu(I) and Cu(II) were observed in the blue layer. Similarly, the Cu Auger spectra (LMM) of red and blue layer present the same state information of Cu species. Specifically, three peaks located at approximately 916.7, 917.7 and 918.6 eV are assigned to the Cu(I), Cu(II) and Cu(0), respectively \[15, 31, 32\]. Combined with literature, the Cu(0) and Cu(I) are corresponding to the metallic Cu and Cu\(_2\)O, respectively, both of which show red hue \[1, 15, 33\]. In this glaze system, i.e., silicate glass, Cu(II) usually bonding with O\(^{2-}\) to form [CuO\(_2\)]\(^4-\) octahedron, of which present blue or green hue \[5, 34\]. Based on the semiquantitative analysis of Cu species, it is found that Cu(I) is dominant in the red layer, whereas Cu(II) is dominant in the blue layer. Obviously, the color of copper species corresponding to the color of glaze layer. As a result, the source for the color difference of different glaze layers is that the copper species exhibit different valence states. Nevertheless, it should be pointed out that the state of copper species is controlled by various processing parameters, including viscosity, glaze thickness, position, and so on.

Based on the above analysis of the structure and valence state, the schematic representation of the color and structural evolution of copper glaze is illustrated, as shown in figure 9. It should be emphasized that the copper glaze samples are fired in a reducing atmosphere and cooled in an air atmosphere. During the firing in a reducing atmosphere, the CuO in the copper glaze is reduced to Cu\(_2\)O and metallic Cu, thereby copper glaze shows a red hue \[35, 36\]. Meanwhile, both the upward diffusion of copper species (including volatilize into the air) and the downward diffusion of alkali species (including ion exchange between glaze and body) occurred in this stage.
Therefore, the viscosity of glaze gradually increases from the top layer to the bottom layer because of the heterogeneous distribution of alkali species. The lower viscosity of the top layer improved the elemental diffusion at high temperatures, which allowed copper species to more easily contact CO. During the cooling in an air, partially low-valent copper species in the top layer are oxidized into Cu(II), and constitute to \([\text{CuO}_6]\) octahedron with O\(^{2-}\), thereby the top layer of copper glaze shows a blue or green hue. Analogously, highly concentrated alkali species broke up the silica network and increased the number of non-bridging oxygen, thus aggrandized the spatial density of oxygen atoms in the glass network structure, which helps to intensify the blue hue\[^5\]. On this basis, the blue opalescence produced by the phase-separated structure will further strengthen the blue hue of the top layer, at the same time increase the three-dimensional presentation of the color. In contrast, the bottom layer of copper glaze still maintains red on account of it is not in contact with air. Besides, the interlayer is a transition layer, which has both top and bottom layer characteristics. Accordingly, the purple interlayer is attributed to the color mixing of the top and bottom layer\[^{37}\].

Figure 8. High resolution XPS spectra of Cu 2p (a), (c) and Cu LMM (b), (d) of red (a), (b) and blue layer (c), (d) in figure 7.

Figure 9. Schematic representation of the color and structural evolution of copper glaze.
As for the copper glaze sample with a green body thickness less than 0.2 mm, it shows milk white due to the large amount of volatilization of the copper species in the top layer and the structural color produced by the Mie scattering \(^{38}\). As for the copper glaze samples with the thicknesses from 0.4 to 0.6 mm, they show cyan because of a mass of copper species in the top layer are oxidized to green Cu(II) and the structural color (milk white) produced by the Mie scattering. Besides, the red from bottom layer also can be observed in the thinner glaze samples. As for the copper glaze samples with the thicknesses from 0.8 to 1.0 mm, they present blue on account of the oxidized Cu(II) in the top layer and non-bridging oxygen constitute to blue \([\text{CuO}_6]\) octahedron and the structural color (blue opalescence) produced by the Rayleigh scattering. As the glaze thickness increases, the residual content of the copper species increases, thus the deepening of the blue hue of the top layer. Simultaneously, the size of the phase-separated droplets of the top layer decreases, which lead to the increases of transmittance. Consequently, the purple from the interlayer can be observed in the thicker copper glaze samples, such as the glaze thickness need greater than 1.0 mm.

In the present work, the color properties of copper glaze could be controlled by the green body thickness. Glaze thickness would affect the elements distribution, copper ions valence state and organizational structure of the copper glaze. In brief, a thicker thickness could be propitious to copper glaze shows an abundant, bright and three-dimensional color effect.

4. Conclusion

To summarize, this article reported the relationship between the glaze thickness and color properties of copper glaze. Furthermore, the elements distribution behavior and the structural evolution of copper glaze, as well as the valence state evolution of copper species were systematically investigated. The main conclusions are as following:

(1) The color of copper glaze with green body thickness of 0.2, 0.4, 0.6, 0.8 and 1.0 mm are milk white-slightly pink spot, pink-slightly baby cyan, cyan-slightly lilac, wathet blue and dark blue, respectively.

(2) Copper glaze samples of each thickness are also composed of three different colors. The color of the bottom layer is red regardless of the glaze thickness. Nevertheless, as the green body thickness increases from 0.2 to 1.0 mm, the colors of the top layer are milk white (0.2 mm), light green (0.4–0.6 mm) and blue (0.8–1.0 mm) in proper order. The color of interlayer is the result of the color mixing of the top and bottom layer. The final color of copper glaze is mainly determined by the color of the top layer, while the interlayer and bottom layer play a lesser role.

(3) Copper glaze is not a homogeneous material, which consists of three phase-separated structures, namely spherical (top layer), worm-like (interlayer) and nano-porous network-like (bottom layer). Meanwhile, there are many elements are heterogeneously distributed in the glaze. For instance, the content of Al and Si elements gradually increases from the top layer to the bottom layer, while Na, K, Mg, Ca and Cu elements show contrary distribution behavior.

(4) The mechanism of the bottom layer presents a red hue is due to Cu(II) was reduced to Cu(I) and Cu(0). The mechanism of the toper layer shows a blue hue is due to Cu(II) and a large number of non-bridge oxygen constitute to \([\text{CuO}_6]\) octahedron. In contrast, the toper layer presents a green hue, when the content of non-bridge oxygen is lower.

(5) The color properties of copper glaze are the result of the coupling of the phase-separated structure, the distribution of elements and the valence state of copper species.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
Declaration of interest statement

The authors declare that they have no conflict of interest.

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