Preparation of copper-red glazes by in-situ reductive process and its coloring research

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1. Introduction

Copper-red glazes have a strong presence in Chinese history. Much attention has been focused on copper-red glazes due to their elegant color and ruby-like appearance.1-3 Indeed, copper-red glazes are highly regarded in contemporary society, and they are often given as gifts from China to other national leaders.4) Copper-red glazes have a strong presence in Chinese history. Much attention has been focused on copper-red glazes due to their elegant color and ruby-like appearance.1-3 Indeed, copper-red glazes are highly regarded in contemporary society, and they are often given as gifts from China to other national leaders.4) Copper-red glazes have a strong presence in Chinese history. Much attention has been focused on copper-red glazes due to their elegant color and ruby-like appearance.1-3 Indeed, copper-red glazes are highly regarded in contemporary society, and they are often given as gifts from China to other national leaders.4) Copper-red glazes have a strong presence in Chinese history. Much attention has been focused on copper-red glazes due to their elegant color and ruby-like appearance.1-3 Indeed, copper-red glazes are highly regarded in contemporary society, and they are often given as gifts from China to other national leaders.4) Copper-red glazes have a strong presence in Chinese history. Much attention has been focused on copper-red glazes due to their elegant color and ruby-like appearance.1-3 Indeed, copper-red glazes are highly regarded in contemporary society, and they are often given as gifts from China to other national leaders.4) Copper-red glazes have a strong presence in Chinese history. Much attention has been focused on copper-red glazes due to their elegant color and ruby-like appearance.1-3 Indeed, copper-red glazes are highly regarded in contemporary society, and they are often given as gifts from China to other national leaders.4) Copper-red glazes have a strong presence in Chinese history. Much attention has been focused on copper-red glazes due to their elegant color and ruby-like appearance.1-3 Indeed, copper-red glazes are highly regarded in contemporary society, and they are often given as gifts from China to other national leaders.4) Copper-red glazes have a strong presence in Chinese history. Much attention has been focused on copper-red glazes due to their elegant color and ruby-like appearance.1-3 Indeed, copper-red glazes are highly regarded in contemporary society, and they are often given as gifts from China to other national leaders.4)

A unique preparation method for copper-red glaze is investigated by using nano-SiC to reduce CuO nano-materials in an oxidizing environment. X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy, and fourier-transform infrared spectroscopy were used to investigate the influence of nano-SiC content on the crystalline phase evolution and phase separation of the copper-red glaze. The results indicate that the added nano-SiC can promote the crystallization of SiO2 and increase the average diameter of phase separation in the glaze. The color of the samples containing 0.01 to 0.3 mass % SiC become redder in hue after calcination in an oxidizing atmosphere. Interestingly, the structural color forms due to Rayleigh scattering, which may account for the slightly blue hue of glaze-fired samples containing different amounts of nano-SiC. The viscosity of the molten glazes decreases with increasing nano-SiC content. A possible in-situ reductive mechanism is proposed to explain how the red color is generated and changes with the amount of nanosized SiC.

2. Experimental procedure

The matrix glaze materials included 53.7 mass % K-feldspar, 18.9 mass % quartz sand, 16.8 mass % calcite, 0.6 mass % copper oxide, and 10 mass % tale. The copper oxide had an average particle size of 40 nm and was 99.9% pure (Shanghai St-nano Science & Technology CO). The silicon carbide had an average particle size of 30 nm and 99.9% purity. It was added as the reducing agent in amounts ranging from 0–0.3 mass % of the matrix glaze materials. The raw glaze slurry was prepared by milling the starting material mixture, which was first weighted with 65 mass % water, and then milled for 6 h at 300 r/min. The matrix glaze slurry was formed by passing the raw glaze slurry through a 200 mesh screen. Its density was then adjusted to 1.5 g/cm³ by water.

The chemical compositions of the matrix glaze materials are provided in Table 1. The glaze slip was applied to the square test pieces (3 cm × 3 cm) by dipping. After they dried, the test pieces were calcined at 3 K/min from room temperature to 1553 K, where they dwellled for 20 min under an oxidizing atmosphere. The electric kiln (SQFL-1700, Shanghai Jujing Co. Ltd., China) has been used to prepare calcined samples, and the internal

Table 1. Chemical compositions of the raw glaze materials (mass %)

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>K₂O</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>97.61</td>
<td>1.83</td>
<td>0.56</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Feldspar</td>
<td>68.32</td>
<td>16.89</td>
<td>8.96</td>
<td>1.55</td>
<td>3.68</td>
<td>0.60</td>
</tr>
<tr>
<td>Talc</td>
<td>64.52</td>
<td>0.09</td>
<td>34.97</td>
<td>0.35</td>
<td>0.35</td>
<td>0.07</td>
</tr>
<tr>
<td>Calcite</td>
<td>0.86</td>
<td>—</td>
<td>—</td>
<td>0.59</td>
<td>98.55</td>
<td>—</td>
</tr>
</tbody>
</table>

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dimensions of the kiln are length-350 mm and width-250 mm and height-250 mm.

The color parameters ($L^*, a^*, b^*$) of the glazes were measured using a CM-2600 colorimeter with CIE (Commission Internationale de L’Eclairage) standard illuminate D65. The CIE-L\textsuperscript*$ a\textsuperscript* b\textsuperscript*$ colorimetric method was followed, as recommended by the CIE. According to this method, $L^*$ is the lightness value [black(0)-white(100)], $a^*$ is the green(−)red(+) value, and $b^*$ is the blue(−)yellow(+) value. X-ray diffraction with monochromatic Cu K\textalpha\ radiation was used to obtain the diffraction patterns of the samples. The microstructure of the samples was examined by EDX and SEM. Before testing, the sample surfaces were etched using 10 vol% HF for 30 s to expose the crystal and phase separation structures. XPS measurements were performed on an ESCALAB 250 high performance electron spectrometer using a monochromatized Al K\textalpha\ excitation source. The samples’ bonding structure was investigated using a FT-IR spectrometer (NICOLET 6700) with KBr as the standard pellet in the range 400–1500 cm\textsuperscript{−1}.

3. Results and discussion

Figures 1(a)–1(f) shows the appearance of the representative glazes after adding 0–0.3 mass % nano-SiC. The sample containing 0 mass % nano-SiC calcined under an oxidizing atmosphere is blue-green in color, as seen in Fig. 1(a). The samples containing 0.01 to 0.3 mass % silicon carbon are darker in hue and take on a red color after being calcined under oxidizing conditions [Figs. 1(b)–1(f)]. However, the most traditional copper-red glaze color appeared on the glaze surfaces when the content of silicon carbide was 0.03 mass % [Fig. 1(c)].

The color parameter values ($L^*, a^*, b^*$) of the glazes with different nano-SiC content are shown in Table 2. For glaze-calcined samples containing 0.01–0.3 mass % nano-SiC contents, positive values of $a^*$ and near-zero values of $b^*$ were obtained. This suggests that the values mainly lie in the region beneath red. For comparison, the $L^*$ values first increase and then decrease with increasing nano-SiC content. Local maxima are presented at 0.03 mass % nano-SiC.

The XRD patterns of glaze-calcined samples with 0.03, 0.05, 0.1 and 0.3 mass % SiC content, are shown in Fig. 2. The characteristic amorphous hump can be observed within the 2theta ≈ 20–35 degree range in all samples, which is associated with aluminosilicate glass.\textsuperscript{16} It is also possible to determine peaks that correspond to SiO\textsubscript{2} ($\alpha$-quartz) in the X-ray patterns. The intensities of the diffraction peaks corresponding to SiO\textsubscript{2} ($\alpha$-quartz) increases with rising nano-SiC content from 0.03 to 0.3 mass %. This indicates that the chemical reactions occur during the firing process, where SiO\textsubscript{2} ($\alpha$-quartz) phases form as a result of the reaction between the matrix glaze and nano-SiC.

An SEM image of the glaze surface containing 0.3 mass % SiC is shown in Fig. 3(a) and the corresponding EDX elemental mapping image of Cu Ka is in Fig. 3(b). As can be seen in Fig. 3(b), the glaze surface contains elemental copper, which formed small aggregates randomly distributed throughout the glaze. This may be a result of stochastic diffusion of copper during the glaze-calcined process.

The FT-IR absorbance spectra of the glazes are shown in Fig. 4. All spectra reveal three characteristic peaks located at 1056, 789 and 465 cm\textsuperscript{−1}. The band at 789 cm\textsuperscript{−1} corresponds with bending vibrations of two type of bridge bonds, Si–O–Si and Si–O–Al, while the band at 465 cm\textsuperscript{−1} is associated with O–Si–O bending vibrations.\textsuperscript{17} The absorption band at 1056 cm\textsuperscript{−1} is linked to the stretching vibration of Si–O.\textsuperscript{18} Comparing the decomposition of the investigated glazes, the intensity of all characteristic bands increases with an increase in nano-SiC content. It is possible that the addition of nano-SiC leads to the breakdown of

<table>
<thead>
<tr>
<th>Nano-SiC content (mass %)</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>63.32</td>
<td>−6.53</td>
<td>−7.65</td>
<td>blue-green</td>
</tr>
<tr>
<td>0.01</td>
<td>65.59</td>
<td>3.86</td>
<td>−0.38</td>
<td>red-slightly blue</td>
</tr>
<tr>
<td>0.03</td>
<td>73.68</td>
<td>8.75</td>
<td>−0.06</td>
<td>red</td>
</tr>
<tr>
<td>0.05</td>
<td>65.28</td>
<td>5.06</td>
<td>−0.19</td>
<td>red-slightly blue</td>
</tr>
<tr>
<td>0.1</td>
<td>63.28</td>
<td>3.28</td>
<td>−0.46</td>
<td>red-slightly blue</td>
</tr>
<tr>
<td>0.3</td>
<td>58.67</td>
<td>2.19</td>
<td>−0.23</td>
<td>red-slightly blue</td>
</tr>
</tbody>
</table>
(SiO₄)⁴⁻ tetrahedra in the copper-red glaze, which destroys the covalent network. As a result, the viscosity of the molten glazes decreases gradually with increasing nano-SiC.

To examine the chemical composition and the valence state of copper in the glaze surface, survey spectra and binding states were investigated using XPS. The XPS survey spectra of the fired glaze containing 0−0.3 mass% CuO are shown in Fig. 5(a). The O1s, Si2s, Si2p, C1s, K2s, Ca2s, Al2p and Cu2p peaks are easily detectable and the six spectra have similar spectral features and peak positions.

The high-resolution XPS spectra of the glazes containing 0.3 mass% nano-SiC, recorded in the Cu-2p transition energy region, is shown in Fig. 5(b). The Cu2p peak has significantly split spin–orbit components (Δ = 19.73 eV). It is possible to distinguish the copper oxidation states using the satellite features of Cu2p.¹⁹) For the glaze-fired samples with 0.03 mass% nano-SiC contents, few satellite peaks can be detected at 945 eV. This may correspond to Cu⁺. However, the possibility that the peaks correspond to Cu metal is not excluded from the result of Cu2p XPS spectra [Fig. 5(b)].

For elemental copper, chemical state identification can be difficult using solely XPS. Cu LMM spectra of the glaze samples containing 0.03 mass% nano-SiC were obtained [Fig. 5(c)]. These were used, as a result of the bigger chemical shifts observed for Cu LMM compared to Cu2p.²⁰) And the standard peak positions of LMM spectra of Cu¹⁺, Cu²⁺ and Cu⁰ are 916.8, 917.7 and 918.6 eV, respectively. It was found that the Lorentzian-fitted peak of the fired samples containing 0.03 mass% nano-SiC is 916.5 eV, which corresponds to the LMM spectra peak of Cu¹⁺. Combined with the XPS, LMM, and color analysis of the samples, it was determined that the copper oxidation state in the copper-red porcelain samples is mainly Cu¹⁺.

Figures 6(a)–6(f) presents the SEM micro-graphs of etched glaze surfaces containing different nano-SiC content. It can be observed that the discrete droplet phase separation structures reside in every calcined glaze. Additionally, the average diameter of the phase separation droplets increases with increasing nano-SiC content in the glaze. The reason for this is that the viscosity of the molten glazes decreases when nano-SiC content increases. It is generally understood that glaze coloring is influenced by discrete droplet phase separation structures. When the average diameter of the scattering particles is 1−100 nm, Rayleigh scattering likely takes place in the glaze.²¹) Furthermore, the scattering intensity is inversely proportional to the biquadrate of the
I react with Cu layer can be represented by [SiO4]4+
which is reduced from Cu2+. Copper oxide
incorporated into the glass network.25) The reaction between nano-SiC and nano-CuO occurs. Copper oxide
during the calcination process, the in-situ
formation of SiC. The viscosity of molten glazes decreases
gradually with the introduction of larger amount of nano-SiC.

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References

4. Conclusions

The copper-red glaze was successfully produced by using
nano-SiC as a reducing agent to reduce CuO in an oxidizing
environment. The most genuine copper-red glaze color appears on the
glaze surface when the silicon carbon is 0.03 mass %. The SiO2
phases form in the glaze as a result of the reaction between the
matrix glaze and SiC. The viscosity of molten glazes decreases
gradually with the introduction of larger amount of nano-SiC.