Analysis Of Influence Of Colourant And Firing Temperature On Self-Reduction Celadon Glaze

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Abstract

The formation of traditional celadon is inseparable from the control of reduction atmosphere, which greatly increases the cost and affects the ecological balance. The self-reduction celadon glaze is prepared by adding a reduction material that can reduce the variable valence metal oxygen ions in the ceramic raw material, so as to achieve a firing technique, that not use of the reducing gas for reduction control. Although there are some reports about self-reduction porcelain technology, at present manufacturers have not carried out comprehensive research on self-reduction porcelain technology. This experiment based alkali raw lime glaze ($K_2O - Al_2O_3 - CaO - SiO_2$),and imitated the ancient celadon glaze , in the oxidization atmosphere, celadon glaze was prepared by adding reducing agent into the basic glaze formula. On this basis,the colourant and firing temperature were used as variables to study the celadon glaze preparation process by reduction method and analyzed the change rule and reason of celadon glaze preparation.

Keywords: celadon glaze; reduction atmosphere; self-reduction glaze; Colourant; iring technique; glaze preparation

I. Introduction

Celadon glaze has been promoting the development of ceramic history since the appearance of ancient China. In the thousands of years, it has been loved by people, among which there are many representative celadons, including the powder celadon of Song Dynasty, celadon of Guan ware, Longquan celadon, Ru ware celadon and so on (Hitoshi Ojima &Takeshi Matsukawa ,2022). As is known to all, celadon glaze is mostly iron glaze system, which needs to be fired in addition to reduction atmosphere. In ancient times, the kiln furnace was filled with appropriate amount of firewood, bamboo and other fuels to form a reduction atmosphere, which leads to high instability of the atmosphere strength (Cheng X, et al. 2015; H. Hashimoto, 2016).Since the adoption of electric kiln for firing ceramics in modern times, a large number of CO, H2 and other strong reducing gases are introduced to form the reduction atmosphere(Y. Wang, et al. 2018; Y.-Y. Chen, 2020; A. K. Yadav, 2021). The improvement of modern technology makes the atmosphere controllable, but there are still problems such as excessive energy consumption, destruction of the ecological environment and low comprehensive benefits. which affect greatly the development of ceramics(Fatih Apaydın,2020; H. Zaitouni,L. Hajji,2022). Based on this, some scholars have begun to focus on the preparation of ceramics by oxidation atmosphere self-reduction method. Li Jiake, Zhang Junkui et al. (2021) conducted imitation research on hightemperature raw copper red glaze by using the added silicon carbide as the reducing agent, indicating that carbon is not suitable for reducing agent. Li Xiaochi et al.(2016) used the reducing agent SiC and the aid colorant SnO2 to prepare the celadon glaze, and its intrinsic self-reduction mechanism was simply described

The application of self-reduction method in ceramics has only recently entered the ceramic field, and the original selfreduction method was widely used in glass, Such as in ancient times, the production of copper ruby glass, usually with tin (Sn) as reducing agent in the glass, it is because of tin oxide activation energy is higher, so it can

Glaze raw	material	XRF	test	comp	osition
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be used to restore copper oxide in the glass (Zhu J, Shi P, Wang F, et al.), so as to make the present a copper red glass. Most scholars (xiao-chi li,2013; Li Qijiang2021; Li Jiake, 2011; Li Jianfeng 2013) mainly focus in the preparation of copper red glaze in the fields of the reduction ceramics prepared, for example, studied the preparation of copper red glaze by self-reduction method with different reducing agents. Wang Fen and Wang Jing et al.(2014) studied the imitation of ancient transparent celadon glaze by adding silicon carbide and silicon powder. Spay(2018) studied celadon glaze and phase separation glaze by adding silicon carbide. According to a number of previous studies, it has been proved that the manufacturing cost of self-reduction celadon is lower than that of traditional celadon, and it is environmentally friendly. In the experiment, the variables such as colorant and firing temperature are the research bullet point of celadon glaze preparation process by self-reduction method.

2. Experiment

2.1 materials

The experiment mainly uses natural mineral raw materials, and the chemical composition of raw materials through XRF test is shown in Table Fig.1.

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Raw material	CaO	SiO ₂	A1 ₂ O ₃	K_2O	Fe ₂ O ₃	MgO	Na ₂ O	
Feldspar	-	74.68	15.5	6.02	0.08	0.07	3.64	
Quartz	0.53	98.43	0.22	0.04	0.04	0.67	0.07	
Calcite	96.8	1.58	-	-	0.07	1.19	0.36	
Talcum	0.24	64.64	-	0.06	0.06	34.96	0.04	
Kaolin	0.09	60	37.62	0.42	0.23	-	1.49	

Frit	11.39	75.13	10.31	-	0.13	2.91	-

Fig.1. Glaze raw material XRF test composition

The celadon glaze foundation formula was determined through the four-angle batching method in the experiment, it as shown in Fig.2.

F	Formulas of the azure and pale green colors in imitating Yaozhou glazes (wt%)							
Quartz	Frit	Feldspar	Calcite	Talcum	Kaolin	Tin oxide	Zinc oxide	
30	24	24	8	3	5	2	4	

Fig.2. Formulas of the azure and pale green colors in imitating Yaozhou glazes (wt%)

In this experiment, iron trioxide (Fe_2O_3) was used as colourant for celadon glaze. As a common ceramic colorant in ancient and modern China, iron raw materials are also the earliest materials used in ceramic glazes as colorants. Due to its variable valence, iron glaze colors are diverse, and the ceramic glaze colors formed by it like: cyan, blue, emerald green, brown-yellow and black. Therefore, the addition amount of colorant(Fe₂O₃) deserves further study. Based on the celadon base formula, the amount of reductant silica powder was fixed at 0.4wt% by single factor variable method, and the amount of colorant Ferric trioxide (Fe₂O₃) was changed to 0-5wt%. The specific scheme is shown in Fig.3.

Reducing agent silicon powder addition amount design (wt%)							
Number	a	b	с	d	e		
addition	0	1	C	2	1		
amount	0	1	2	3	4		

Fig.3. Reducing agent silicon powder addition amount design (wt%)

2.2 Firing temperature

In the experiment, the single factor variable method was used to change the firing temperature of celadon glaze (1130 °C-1280 °C) by adding a fixed amount of reducing agent silica powder at 0.4wt %, on the basis of celadon basic glaze formula. The specific scheme is shown in Fig.4

Firing temperature design (°C)								
Number a b c d e f								
Firing temperature	1130	1160	1190	1220	1250	1280		

Fig.4. Firing temperature design (°C)

The heating system oxidation in the atmosphere was as follows: at low temperature (less than 300°C), heating at 5°C/min to dry the sample; In the middle temperature section (300-900°C), the temperature increases rapidly at 3°C/min to reduce energy consumption; In the high



Fig. 5. Sample firing temperature rise graph (a) shuttle gas furnace; (b) high temperature box resistance furnace

3. Methods

3.1 Glaze effect test

The glaze effect test uses the microscope to enlarge the sample quickly to obtain the micrograph to analyze the glaze color (Model : GE-5; China, Maximum magnification :720 X), and uses the whiteness meter instrument to measure the chroma value of the glaze color (Model : Wsd-3c, China), so as to obtain the relationship between variables and the glaze color, the method mainly measuring the temperature section (more than 900°C), the temperature is slowly raised at 1.5 °C/min to ensure the firing of ceramic products; After reaching the firing temperature, keep it warm for 20 minutes and close the furnace. After cooling the fired samples, open the furnace for sampling. The temperature rise curve of the furnace is shown in Fig.5.



spatial color coordinate L* A * B * value. The value of $L^* A * B *$ was used to characterize the color of glaze. The range of L* value was 0-100, indicating the change of A * represents the process of brightness, red-green gradual change, the higher of a* value is, the glaze colour is more redder, the lower of a* is, the colour is higher degree of green, b* represents the process of blueyellow gradual change, the higher value of b* is, the colour is more yellow, when the the lower of B^* is, the degree of blue colour is more higher, the color coordinate space is shown in Fig.6. The ceramic samples are slice dimensions of round with 50mm(diameter) ×3mm(thickness)



Fig. 6. Spatial color coordinate system

3.2 XRD test

XRD test includes XRD analysis and Raman spectrum analysis, the purpose is to study the type of crystal phase in the sample and the change of crystal phase content in different samples. This experiment uses X-ray diffractometer to analyses the samples (Model : D/max-2200PC, Japan). The specific measurement parameters are: tube voltage :40 kV, tube current :100 mA, target material :Cu target, scanning range :5° ~80°, scanning 8° per minute).

Besides X-ray diffractometer, Raman Spectrometer is also used to prove the XRD analysis result, the working principle of Raman scattering is under the incident light, different molecular vibrations are generated inside the sample, which will produce characteristic peaks, and this is the only corresponding with variable, so it can be used for qualitative molecular structure. In this experiment, a confocal laser Raman spectrometer was used (Model: Renishaw-Invia, England). The ceramic samples are round slice with dimensions of 50mm(diameter) $\times 3$ mm(thickness), this test is non-destructive test, fired ceramics can be directly tested and its test parameters: test range of 100-3200 cm⁻¹, test time is 60 s.

3.3 Micro-Structure Analysis

Micro-Structure analysis via scanning electron microscopy (SEM) to test microstructure and characterization of the celadon glaze (model: S-4800 SEM, Japan). The sample was cut into thin blocks with dimension of 2 mm (length)×2 mm (width)×1 mm (thickness) by low-speed diamond cutter and cleaned by ultrasonic for 2 hours. It was eroded in hydrofluoric acid solution(0.1 mol/L) for 60 s, then removed deionized water and cleaned in into ultrasonic equipment for 2 hours, then dried at 60°C; Because of the poor electrical conductivity of ceramic glaze, it is necessary to spray with a very thin layer of gold on its surface for 45 s.

4. Results and Discussions

4.1 The influence of colourant on self-reduction celadon Glaze

4.1.1 Glaze effect

Fig.7 shows samples firied at 1250°C with oxidizing atmosphere, and the glaze with 0-5wt % addition of ferric oxide (Fe2O3). From the Fig.7, when the content of Fe2O3 is 0 wt %, glaze color is basically the grey-light colour with a little green, mainly

because other ceramic material also contains a small amount of iron compounds, and glaze is extremely uneven. As intake colourant of Fe2O3 increased from 1 to 5 wt %, the glaze color from blue to green, to brown, and black, And the brightness of the glaze is gradually rising.



Fig. 7. Glaze surface with different amounts of Fe2O3 added

(a) –(f) different Fe2O3 contents of 0, 1, 2, 3, 4and 5 wt%

In order to further study the glaze chromaticity in a more scientific way, Fig.8 shows the value changes of a*, b*and L* of samples' glaze, which were measured by colorimeter for different ferric trioxide (Fe2O3) contents. The glaze increased with the addition of ferric trioxide (Fe2O3) from 1wt% to 5wt%, the overall trend of b* value is decreasing, which indicates that with the increase of the amount of colorant added, the overall yellow of glaze is decreasing. The glaze a * value increased gradually with the addition of Ferric trioxide (Fe2O3) from 1 wt% to 5 wt%, indicating that the green color of the sample glaze decreased with the increase of colorant. With the increase of the addition amount of Fe2O3 from 1 wt% to 5 wt%, the overall L* value of glaze decreased, indicating that with the increase of the addition amount of colorant, the overall blackness of the glaze is increasing, but the L* value tends to be stable after the addition of iron trioxide (Fe2O3) is more than 3 wt%, so if the celadon glaze will be prepared, the addition of colorant should be controlled at 1 wt%.



The amount of iron oxide added

Fig. 8. Glaze color analysis chart of different Fe2O3 powder addition amount (a)-(e) different Fe2O3 contents of 1, 2, 3, 4and 5 wt%

4.1.2 XRD analysis

Fig. 9 shows the X-ray diffraction (XRD) patterns of the glaze sample with the addition of iron trioxide (Fe2O3) at 0 wt%, 2 wt% and 4 wt%. It can be seen from the figure that when the addition of iron trioxide (Fe2O3) at 0 wt%, the main crystals in the XRD patterns of the glaze sample are residual quartz peaks, and the peak value is very high; It can be seen that with the increase of colorant Ferric trioxide (Fe2O3), the characteristic peak of Ferric trioxide (Fe₃O₄) appears in the XRD pattern of sample glaze, and the intensity of characteristic peak of Ferric trioxide (Fe₃O₄) increases. This is mainly because with the increase of iron trioxide (Fe₂O₃), the amount of reduced silicon (Si) in the glaze is insufficient, resulting in incomplete oxidation of the glaze, and its reaction formula is 6Fe2O3(s)+Si (s) $\square \square \square 4Fe2O3(s) + SiO_2(s)$.

surface



when the amount of colorant added is different

Figure 10 is the Raman spectra of different amounts of iron trioxide (Fe2O3). It can be seen intuitively from the figure that in the absence of iron trioxide (Fe2O3), a characteristic peak appears at 520cm-1 in the Raman spectrogram of the sample glaze, which is the characteristic peak of quartz crystal, that is consistent with the XRD pattern of the sample above, further indicating the presence of residual quartz crystal in the sample prepared without iron trioxide (Fe2O3). When the amount of ferric trioxide (Fe2O3) is 5 wt%, it can be found from the Raman diagram that a characteristic peak appears at 672.1 cm-1, which corresponds to the crystal of Ferric trioxide (Fe₃O₄), that further proves that with the increase of ferric trioxide (Fe2O3), reduced silicon (Si) in glaze is insufficient amount of iron oxide, resulting in incomplete oxidation, the formation of iron oxide (Fe₃O₄)



Fig. 10. Different Fe2O3 addition glaze Raman spectra

4.1.3 Micro-Structure Analysis

Figure 11 shows the GE-5 microstructure of the glaze with different iron trioxide (Fe₂O₃) addition amount. It can be seen from the figure that with the increasing iron trioxide (Fe₂O₃) addition amount, the bubbles on the glaze gradually decrease, and the glaze turns from green to black while the gloss increases.

Figure 12 is the SEM microscopic structure of samples with different amount of ferric oxide (Fe2O3). From the figure, when the oxidizing atmosphere firing glaze with no addition of the ferric oxide (Fe2O3) in the sample, there were more residual quartz crystal in the sample surface, and glaze

appeared crack in the quartz crystal surrounding , that shows that the residual quartz samples were too much and grown too large (size: $1.5\mu m \times 0.5\mu m \times 0.5\mu m$), those caused glaze cracking, which also successfully explained the above mentioned, when the iron trioxide (Fe2O3) adding amount of 0 wt% , the glaze is not smooth

this phenomenon; When the amount of ferric trioxide (Fe2O3) is up to 5 wt%, the glaze is basically uniform phase separation, and under the same corrosion time, the sample is more difficult to corrosion than the sample with small amount of ferric trioxide (Fe2O3).



Fig. 11. Glazed GE-5 diagram with different amounts of ferric oxide added (a)–(d) different Fe2O3 contents of 1,2, 4and 5 wt%



Fig. 12. SEM image of glaze with different amounts of ferric oxide added (a)0 wt%; (b) 5 wt%

4.2 The influence of firing temperature on self-reduction celadon Glaze

4.2.1 Glaze effect

Fig. 13 is the glaze surfaces at different firing temperatures under oxidizing atmosphere, from the fig.13, with the increase of the firing

temperature, the surface colour of celadon glaze samples prepared by self-reduction method gradually changed from gray green to cyan ; When the temperature reaches 1280°C, the glaze is bright cyan but the glaze is defective and uneven, which is mainly because the glaze forms are too much glass phase at too high temperature and under the redox reaction of high temperature, the redox reaction iron of trioxide (Fe₂O₃) and silicon powder (Si) is more violent, and in the short firing holding time (20 min), the inner glaze is not smooth from melting to forming.



Fig. 13. Glazed surface with different firing temperatures (a)1130°C; (b) 1160°C; (c) 1190°C; (d) 1220°C; (e) 1250°C; (f) 1280°C

indicating that the whiteness of sample glaze

did not change with the change of firing

temperature; With the increase of the firing

temperature from 1130°C-1220°C, glaze b *

value remains unchanged overall that stable

at about 3, when the firing temperature from

1220°C to 1280°C, glaze b * value showed a

Figure 14 shows the changing trend of glaze, a * value, b * value and L* value measured by the colorimeter at different firing temperatures. As the firing temperature increases from 1130°C-1280°C, the overall trend of the a * value is decreasing, but they are all negative value, which indicates that with the increase of the amount of phase separating agent, the overall blue color of the glaze is weakening; The L* value of glaze remained stable at about 49 with the increase of firing temperature from 1130-1280,



phase downward trend and a negative number, this of the data shows that the glaze with the increase of glaze the firing temperature is stabilized in yellowish system, and than turning to blue 1280, system.

Fig. 14 Glazed chroma analysis chart with different firing temperatures

(a)1130°C; (b) 1160°C; (c) 1190°C; (d) 1220°C; (e) 1250°C; (f) 1280°C

According to the variation trend of a* value, b * value and L* value of the sample glaze, the higher the firing temperature is, the better the color formation will be. However, combined with the glaze effect picture, when the firing temperature is 1280°C, the glaze effect will be worse, so the more reasonable firing temperature is 1250°C.

4.2.2 XRD analysis

Fig15 is the X-ray diffraction (XRD) pattern of glaze samples at different firing temperatures. It can be seen from the figure that the XRD pattern of celadon samples prepared by self-reduction method, when the firing temperature increases from 1130°C to 1220°C,the characteristic peak intensity of silica (SiO2) increases gradually, which indicates that with the increase of firing temperature, the redox of Fe2O3 and Si becomes more complete, and more SiO2 is produced, which is mostly crystal. When the firing temperature changes from 1220°C to 1280°C, the characteristic peak intensity of SiO2 in the XRD patterns of the celadon samples prepared by the self-reduction method gradually decreases. When the firing temperature reaches 1280°C, the glass phase like steamed bread appears, indicating that after the firing temperature reaches 1220° C and than increasing the firing temperature, the glaze surface of celadon samples prepared by self-reduction method will form more glass phase, resulting in the reduction of SiO₂ crystal glaze layer.



Fig. 15. XRD of the sample at different firing temperatures

Figure 16 is the Raman spectra of different firing temperatures. It can be seen intuitively from the figure that when the firing temperature is 1130° C, the characteristic peaks appear at 125.599 cm-1 \times 189.502cm-1 \times 459.455 cm-1 and 520.914 cm-1, the strong peak at 459.455Cm-1 and 520.914 cm-1 is consistent with the Raman peak of α quartz , which means that the glaze of celadon samples prepared by self-reduction method at this firing temperature is mainly α quartz. When the firing temperature reaches 1220°C, characteristic peaks appear at 125.599 cm-1, 189.502cm-1 and 459.455

cm-1, and the intensity of α quartz characteristic peak increases compared with that at 1130°C, indicating that with the increase of firing temperature, α in the sample glaze, quartz becomes more; When the firing temperature is 1280°C, there is no obvious characteristic peak in the Raman spectrum, which indicates that the celadon samples prepared by self-reduction method at this firing temperature have less α quartz content or no α quartz content in the glaze surface, which is consistent with the above XRD patterns.



Fig. 16. Glazed Raman spectra of different firing temperatures

4.2.3 Micro-Structure Analysis

Figure 17 shows the GE-5 microstructure of ceramic glaze at different firing temperatures. It can be seen from the figure that with the increasing of firing temperature from 1130°C to 1250°C, the bubbles on the glaze of celadon sample prepared by self-reduction

method basically did not change, but the color changed from ink to blue. At the sintering temperature of 1280°C, there are large glass forms on the surface of the sample, and the size of bubbles increases as well as the number decrease of bubbles.



Fig. 17. Glazed surface GE-5 with different firing temperatures

(a) –(f) different firing temperature of 1130, 1160, 1190, 1220, 1250and 1280 °C
(b)

Figure 18 shows the SEM microstructure of celadon glaze prepared by self-reduction method at different firing

temperatures. It can be seen from the figure that there is a small amount of residual quartz in the sample glaze when the firing temperature is 1130°C. When the firing temperature is 1190°C, the residual quartz in the glaze becomes more and larger in size. When the firing temperature is 1250°C, the size of residual quartz in the sample glaze decreases. When the firing temperature is 1250°C, a layer of glass phase covering the

sample glaze that is difficult to corrode off, and from the corroded surface glass, it can be found that the internal phase is divided and there are cracks and uneven phenomenon, which is consistent with the previous glaze analysis and phase analysis.



Fig.18. Sample glaze scan of different firing temperatures (f) different firing temperature of 1130°C, 1190°C, 1250°Cand 1280 °C

5. Conclusion

- With the increase of the amount of colorant (Fe₂O₃), an incomplete oxidation reaction took place between silicon powder and ferric oxide and generated the ferric oxide(Fe₃O₄), that lead to the development of black glaze, at the same time, the amount of residual quartz in the glaze decreased
- 2. With the increase of firing temperature, the glaze color changes to blue color with the redox reaction of silica powder and ferric oxide
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