The Effect of Phosphorus on Iron Based Crystallization Glazes

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Abstract: Iron crystallization glaze is one of the ceramic glazes, which has attracted the attention of the ceramic industry for its unique crystallization effect and various decorative effects. Among them, the phosphorus content is a key parameter, which can affect the crystallization behavior, crystal size and morphology of the iron system crystallization glaze. In order to better control the preparation process of ferrocrystalline glaze, the effect of phosphorus on ferrocrystalline glaze was studied. Kaolin, potassium feldspar, calcite, talc powder and quartz are used as the main raw materials to prepare iron-based crystalline glaze. By adjusting the content of P, the amount, size and shape of crystal precipitation on the glaze are controlled, so as to obtain iron-based crystalline glaze with different decorative effects. Through XRD, SEM and other analytical means to carry out the experiment, it is found that in the absence of phosphorus, the glaze presents a large number of triangular crystals, giving the metal decoration effect. After addition of P, the growth of magnetic hematite crystals was inhibited, and the morphology of magnetic hematite crystals changed into pine branches, pine whiskers and small clusters. Iron ions enter the glaze layer, causing the glaze to change from metallic to brownish yellow, with a decorative effect.

Keywords: Iron based crystallization glaze; Calcium phosphate; Decorative effect

1. Introduction

Glaze is widely used in the field of ceramic materials for its excellent optical decoration effect, mechanical properties, stain resistance, corrosion resistance and so on. Among them, the crystal glaze has been loved by the majority of consumers because of its unique decorative effect caused by the absorption and reflection of light. Among them, the iron crystallizing glaze has a long history, and the rabbit hair glaze, oil drop glaze and other historical precious glaze species of Jian kiln [1].

The reason for this special decorative effect in iron based crystallization glaze is the reflection of light falling on the glaze surface, which is influenced by the size, shape, quantity, arrangement, and observation angle of metal particles or crystals on the glaze surface [2-3]. Ancient craftsmen only created artistic glazes that still amaze the world today through the accumulation of glaze making techniques and experience. At present, scholars have prepared various iron based crystallization glazes by adjusting the formula and firing temperature [4-6]. However, in the study of ancient glazes, it was found that there are many phase separation structures in the base glaze of iron based crystallization glazes [7-8]. However, the effect of phase separation agents on the crystal growth and distribution in iron based crystallization glazes is relatively small.

In this paper, according to the current development trend of ferric crystallizing glaze, a kind of ferric crystallizing glaze with excellent decorative effect, low price, simple process and adjusting the number and size of surface crystals was successfully prepared by using ferric oxide as color agent and phosphorus to control crystal crystallization in the glaze. The effect of phosphorus on the crystallization of iron oxide was analyzed by means of XRD and SEM.

2. Experiment

2.1 Experimental materials

The raw materials are kaolin, potassium feldspar, calcite, talc powder and quartz, and the chemical composition is shown in Table 1. During the preparation, pure iron oxide (purity ≥99%, TCM reagent)

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and calcium phosphate (purity 95%, TCM reagent) were used to carry out the analysis.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	I.L.
Kaolin	50.16	35.76	0.44	0.02	0.06	0.62	0.09	12.77
Feldspar	73.01	14.67	0.07	0.37	0.05	8.62	2.68	0.20
Calcite	3.16	0.99	0.14	52.86	0.38	0.19	0.08	42.03
Talc	64.46	0.70	0.18	0.94	33.18	0.04	0.01	0.31
Quartz	99.07	0.50	_	0.01	0.05	0.16	0.01	0.14

Table 1: Raw Material Composition Table

I. L.=Loss on ignition

2.2 Sample preparation

Table 2 shows the composition of each formula, in which BG is the basic formula, and PG-1 to 4 is the glaze with different calcium phosphate addition amounts. The raw materials were milled in 30wt% water ball for 30min according to the formula, and the glaze paste was made through the 200-mesh screen. The glaze is then impregnated onto a 5cm diameter body. After drying, the sample was calcined in a Muffle furnace at 10°C/min to 1320°C, held for 1h, then cooled to 1150°C naturally, then held for another 2h, and finally cooled to room temperature naturally to obtain the final sample.

	BG	PG-1	PG-2	PG-3	PG-4
Feldspar	48	48	48	48	48
Quartz	36	36	36	36	36
Calcite	11	11	11	11	11
Talc	10	10	10	10	10
Tricalcium phosphate	0	3	6	9	12
Iron	16	16	16	16	16

Table 2: Formula Composition

2.3 Sample performance analysis

The pigment and glaze color were measured for chromaticity (L*, a*, b*) using a WSD-3C whiteness colorimeter.

The morphology of the pigments and glaze color were observed using a scanning electron microscope equipped with an energy-dispersive spectrometer (JSM-7500F, JEOL Ltd., Japan).

The powder's phase composition was analyzed using X-ray diffraction (D8Advance, Bruker, Germany).

3. Experimental results and analysis

3.1 Sample appearance

Figure 1 shows optical photos of BG and PG1-4 samples. All glaze surfaces are smooth and free from obvious defects. There are small and dense crystalline particles on the surface of the BG sample, which exhibit a significant reflection effect. When phosphorus is added, the number of crystalline particles on the surface of PG-1~4 gradually decreases. It is worth noting that crystal particles cannot be directly observed on the surfaces of PG-3 and PG-4, but rather exhibit a mixture of brown and yellow colors.



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Figure 1: Optical photo of the sample

3.2 Effect of P on the crystallization behavior of glaze

3.2.1 XRD analysis

Figure 2 shows the XRD patterns of all samples. As can be seen from the figure, the glaze of BG is mainly composed of magnehematite crystals (JCPDS: 25-1402), and contains some hematite residue. At this time, the diffraction peak intensity is very high, indicating that the BG sample contains a large number of magnehematite crystals, and directional crystallization along the (311) face appears. The content of magnehematite in PG-1 ~PG-4 decreased gradually with the increase of P, and finally disappeared completely. However, in PG-4, the diffraction peaks of both magnehematite and hematite have basically disappeared, which may be due to the introduction of calcium phosphate, which makes the crystals melt into the glaze during heating.



Figure 2: XRD pattern of the sample

3.2.2 SEM analysis

In order to further analyze the influence of crystals on glaze spots, the crystal morphology and size of the sample surface were observed through SEM photographs. From Figure 3, it can be seen that in the sample BG without P, magnetite exhibits a triangular layered distribution with crystal sizes ranging from 200 to 1000 μ . The dense directional growth of these crystals enables the sample to exhibit strong reflection effects, with varying degrees of m. Combining Figures 1 and 3, it can be observed that as the phosphorus content increases, the crystal in the sample changes from a complete triangular structure to a morphology composed of crisscrossing whiskers. And as the phosphorus content increases, this

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triangular crystal becomes more loose and less abundant. It is worth noting that as the phosphorus content further increases, the crisscrossing crystal structure gradually disappears, becoming medium-sized crystals with sizes ranging from 20 to 50 microns, newly developed whisker structures, and a large number of amorphous phase structures.



Figure 3: Microstructure of samples with different P Content



Figure 4: Surface crystal microstructure and energy spectrum analysis of sample BG

In order to further study the composition of crystal particles on the surface of sample BG, EDS spectrum analysis was performed on the surface of sample BG where triangular lamellar crystals were grown, and the results were shown in Figure 4. It can be seen from Figure 4 that the detected surface mainly contains Si, Al, Fe and O elements, among which O elements contain the most, while the triangular lamellar area mainly contains Fe and O elements. Combined with Figure 2 and Figure 3, it is considered that the crystals precipitated from sample BG are magnehematite crystals and the crystals are distributed on the surface of the sample in a triangular lamellar shape.

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Figure 5: Localized magnified microstructure of PG-4

Using SEM to observe the surface of PG-4 sample, as shown in Figure 5a, different regions of the sample surface exhibit different crystal distributions. After zooming in on the regions with different morphologies, it was observed that, as shown in Figure 5b, this region has a size range of 20-50 μ Medium crystal m, some areas as shown in Figure 5d show sizes below 20 μ M is a small crystal with a large number of amorphous phases appearing in the region, as shown in Figure c. Based on Figures 1 and 3, it can be seen that as the addition of P ions increases, the crystal size gradually decreases, the content of magnetite crystals gradually decreases, the number of crystal particles on the glaze decreases, and the reflection effect weakens. At the same time, the content of iron in the amorphous glaze in the sample increases, and the glaze matrix turns dark brown. Among them, the crystallization areas of medium and small crystals leave "dots" on the glaze, presenting different decorative effects.

In order to further understand the principle of P addition on the precipitation of iron crystalline glaze crystals, SEM was used to further observe the crystallization region in PG4, and the results were shown in Figure 6. It can be seen from the figure that a large number of phase separation structures are found in the crystal crystal region of the glaze, which is caused by P competing with Si for oxygen in the glass network after the addition of P. Meanwhile, phase separation structures will inhibit crystal growth during firing due to the formation of diffusion barriers [9].

Figure 6: Localized magnified microstructure of PG-4

4. Conclusion

This study is based on raw glaze, with iron as the main color oxide, and supplemented by special firing methods to prepare a series of iron based crystallization glazes by regulating the content of P. When P is not present, there are a large number of sizes up to 200-1000 on the glaze surface μ . The triangular

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crystal of m endows the glaze with a metallic decorative effect. Subsequently, the addition of P inhibits the growth of magnetic hematite crystals, causing the hematite crystals to change from triangular to pine branched, pine whiskered, and finally to small clusters. At the same time, as the crystal size and content decrease, a large amount of iron ions enter the glaze layer, and through ion coloring, the glaze gradually transforms from a metallic texture to a decorative effect of brown yellow spots.

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