High-temperature Ceramic Manganese Crystal Glaze

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Abstract: The main purpose of this paper was to produce high-temperature ceramic manganese crystal glaze made from manganese dioxide by firing at 1310 °C in reducing flame atmosphere. This paper describes the process of glaze preparation and the kiln temperature controlling during the glaze firing process in detail. For the glaze effect of the manganese crystalline glaze after firing, the super-depth-of-field three-dimensional microscope is used to observe the true depth of field of more than 20 times of the optical microscopic system.

1. Introduction:
Ceramic glaze is an important raw material of ceramics. It has a strong protective effect on the ceramic body. At the same time, the physical properties of the silicate make the glass enamel on the ceramic surface have good acid-base corrosion resistance and antibacterial properties. Since their discovery in the early 1950s, glass-ceramic materials have been widely established in many fields, such as daily life (e.g. kitchen cooktops) [1], industrial applications (e.g. abrasion resistant tiles in industrial pipes), environmental applications (e.g. reuse of wastes) [2–4], biomedical applications (e.g. prostheses for surgical implants) [5–7], architectural applications [8] and in more advanced technological applications (e.g. telescope mirrors, warheads and composite materials) [9–10]. Crystal glaze is an artificial crystal glaze used to decorate porcelain, pottery, pottery bricks, etc. It is developed on the basis of ancient Chinese traditional ceramic glaze. Ordinary ceramic glaze is coloured by adding metallic colorant into the glass enamel to achieve the effect of colour in the firing process. Such glazes tend to be in single colour, which cannot highlight the artistic beauty of the ceramic glaze itself and the special artistic effect produced in the process of high temperature firing. Manganese crystal ceramic glaze effectively overcomes these shortcomings and produces natural texture artistic effect with stable physical and chemical properties. Manganese crystalline ceramic glaze has a wide range of applications. For example, it can be applied to building exterior wall ceramics, interior decorative ceramics, utensils and tableware ceramics without containing heavy metals such as lead and chromium, on the contrary, it is environmentally friendly and has no harm to human body. In the preparation process, the mineral raw material and the non-ferrous metal raw material are separated from the ball milling time, and the crystallization effect of the non-ferrous metal is better and more stable.

2. Material and Methods
This study is concerned with the formulation and preparation method of a high temperature ceramic manganese crystalline glaze. The formulation consists of the following raw materials according to the weight ratio: potassium feldspar 60-75%, calcium carbonate 1-3%, quartz 3~5.7%, clay 3~5.7%,
manganese dioxide is 16 to 30%, iron oxide is 0.6 to 2%, and cobalt oxide is 0.8 to 5%. The preparation of the manganese crystal ceramic glaze comprises the following steps. According to the weight ratio, 60 to 75% of potassium feldspar, 1 to 3% of calcium carbonate, 3 to 5.7% of quartz, and 3 to 5.7% of clay are added into pure water with the quality of 1:1 and the ceramic fast ball mill, the speed is 450rpm, and the time is 2 ~ 3.5h. Manganese dioxide 16 to 30%, iron oxide 0.6 to 2%, cobalt oxide 0.8 to 5% are added, the rotating speed is 450 rpm, and the time is 1 to 2 h. The glaze is filtered through a 600-800 mesh ceramic filter after grinding. During the production process, the indoor temperature is controlled above 0℃ to obtain a liquid ceramic glaze. According to the relevant knowledge of thermodynamics, the glaze glass can be higher than the internal crystallization glaze with partial crystallization. Thus, the cooling of the glaze will lead to crystallization, and the difference between the melt energy and the crystal energy is large, and the crystallization is more likely to occur. Because the melt viscosity increases rapidly during cooling, the resistance to crystallization increases, and the glaze melt may not crystallize and directly form a supercooled liquid, it is necessary to control viscosity strictly. Crystallization is carried out during the cooling process, including nucleation and nucleation growth. For most silicate melts, the temperature is relatively high when the crystal grows fastest. The fastest nucleation rate is in the low temperature stage, and finding a suitable temperature is inseparable from the crystallization process. In order to ensure the quality of crystallization, the system of the firing process of crystalline glaze products is generally "slow cold". During the firing of the crystal glaze, cold air is prevented from entering the kiln, resulting in a sharp drop in the temperature inside the kiln. In addition, other factors may also cause a sharp drop in the temperature of the ceramic kiln. As long as it can meet the requirements of perfect glazing vitrification, the shorter the holding time, the better the effect, so as to avoid a large amount of glaze outflow and avoid melting of the crystallization agent. In order to obtain a good crystallization effect, the incubation time should be as long as possible in the optimum crystallization zone and then slowly cooled. The purpose is to make the crystallization the most complete and the crystal form optimal. When naturally cooling down in the kiln to cool the product, the most critical thing is to determine the highest firing temperature and the optimum holding temperature.

![Figure 1 Crystal growth rate K1 nucleation rate K2, viscosity η, relationship with temperature T](image-url)
In Figure 1, firing is one of the key processes of crystallization. It is very important to formulate a reasonable firing system to ensure the formation of crystal nucleation and the growth of crystals. When the crystal glaze is fired, the curve of temperature rise rate needs to be kept at 980°C for 30 minutes. After the glaze is completely melted, it is necessary to carry out the heat preservation operation at a temperature stage suitable for crystallization in order to control the cooling rate, and the size of the crystal glaze flower is related to the holding time and the cooling rate. If the furnace temperature is cooled too fast, the shape of the crystal flower is extremely small, showing the appearance of the glaze. If the cooling rate is too slow, the artistic rhyme is lost due to the coarse crystal flower and the rough surface of the glaze. According to the thermodynamic principle, when the melt cools to the crystallization temperature, the close-range order of the particles in the liquid is extended, and the nucleus is formed intermittently due to the decrease of the kinetic energy of particles. If the cooling continues, the nucleus can be stabilized. The seed crystal, which then centers on the seed crystal, develops into a crystal. The two processes of nucleation and grain growth are affected by two contradictory factors.

On the one hand, with the increase of cooling degree, the temperature decreases, the kinetic energy of the liquid particle decreases, the attraction force increases relatively, and thus it is easy to coalesce and attach to the surface of the crystal nucleus, which is favorable for crystal nucleation and crystal growth. On the other hand, with the increase of cooling degree, the viscosity of the liquid increases, and particle moves with difficulty. The coincidence zone slope (shaded area) of the nucleation rate $K_2$ (temperature curve) and the crystal growth rate $K_1$ (temperature curve) is the most suitable region for crystallization and crystal growth, as shown in Figure 1.

When the crystallization holding temperature deviates, the viscosity of the glaze is small, the nucleation is less, the development is fast, and the crystal form is unstable. When the holding temperature is low, there are more crystals and the crystal flower is small. The calcination temperature of most crystalline glazes is lower than 100°C, but it needs to be experimentally determined. The firing range of the crystal glaze is quite narrow (generally only ± 5°C). Therefore, the requirements for the firing curve are very strict.

3. Results and Discussion
The crystal glaze melts at 1230 ℃ ± 50°C, exhibits good fluidity, and forms a uniform glass on the surface of the ceramic body. The characteristics of the vitreous surface can be observed under a super-depth microscopic microscope, showing a typical band of a wide range of glass materials and dark brown. The colour is mainly related to MnO₂ and Co₂O₄ in the glaze formula. In other experiments, the addition of trace of high-purity cobalt oxide plays a very important role in the development of glaze colour. The pure MnO₂ showed a brown colour even when the amount used reached 20% ± 5% by weight. Figure 3 shows the effect of the glaze under reducing flame conditions.

Figure 2 Not insulated at 980 ℃, manganese crystal, super depth of field three-dimensional microscope
The reducing atmosphere flame is shown in Figure 2, and the glaze effect under the condition of 980°C heat preservation is not performed. The glazed surface under the low-magnification microscope of the super depth of field 3D microscope shows several crystals (Fig. 4). Background light is dark brown in strong light and close to black in natural light. The surface has a silver metal flaky spot of 0.2×0.25 mm, and the spots are evenly distributed on the experimental test piece, which produces strong reflection and metallic luster under sunlight irradiation. We can observe that the crystals have a very pronounced silvery luster and form a radial growth. Under the condition of reducing flame, the black background of glaze presents valley-like details at 400 magnification of three-dimensional ultra-deep field microscope. It can be seen that the silver crystals grow radially. It was confirmed by EDS analysis that the metal component contained in the crystal was Mn. Metal crystallization produces a strong reflection. Because its crystal area affects the interaction with visible light (scattering phenomenon) and changes the aesthetic properties, the gloss effect may be due to this special microstructure. Fig. 2 shows that the crystal area of the test piece is about 2.0 mm × 2.5 mm under the condition of holding temperature at 980°C for 30 minutes under a reducing flame. The crystals were magnified and it was found that when the crystal was enlarged at 100 times, the crystals had a tendency to grow radially, while the surface of the crystal showed signs of liquid material flow.
Through the observation of Fig. 5, it is found that there are tiny cracks in the glazed surface around the crystal nucleus. It can be considered that a strong external force is generated during the growth of the crystal nucleus, and the crystal nucleus is still growing and changing after the surrounding crystals have cooled and solidified. Therefore, tiny cracks are generated on the surface of the crystal. This observation proves that the growth time of the crystal nucleus lags behind the growth time of the crystal as shown in Fig. 6.

4. Conclusions
After a lot of experiments on high temperature manganese crystal glaze, the following conclusions are drawn. Previous literature studies on crystalline glazes have focused on oxidized flame atmospheres and a discussion of crystalline glazes of zinc oxide. This paper focuses on the preparation and firing of crystalline glaze of manganese oxide under reducing flame atmosphere. When the glaze contains more than 15% manganese oxide by weight, the reduction flame combustion produces the crystallization effect of metallic selenium. The heat preservation during the heating process has an important influence on the area of the manganese crystal. In the experiment, the 980°C heat preservation plays an important role in the growth of the crystal body. In the process of crystallization of manganese oxide, the crystal body and the crystal nucleus respectively exhibit different growth curves. After the crystal nucleus is formed, the crystal grows radially as the center of the crystal nucleus. During the cooling process, the crystal stops growing first, followed by the crystal nucleus.

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