Synthesis of Sphene-pink Pigment under Various Firing Conditions

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ABSTRACT

The present research was performed to determine the optimal firing condition and holding time for malayaite crystal, which is responsible for the stable pink-red coloration in glaze at high temperatures, using CrCl_3 as chromophore for the synthesis of Cr_2O_3 - SnO_2 - CaO - SiO_2 system pigments. The malayaite crystal was influenced by the raw materials used for synthesis, firing temperature, and holding time. Thus there are differences in the crystal phase and in the coloration according to the condition of synthesis. When CrCl_3 was used as chromophore, the pigment could be synthesized at lower temperatures, because CrCl_3 melts at 1150°C , which is much lower than the temperature at which Cr_2O_3 melts (higher than 2435°C). And the employed Cr ion showed a change in oxidation state. When a mineralizer was used to improve the employment of malayaite and the Cr ion, and the low temperature was maintained at which the malayaite crystal is produced, the production of malayaite crystal was promoted and the employment of chromophore was also promoted in the oxidation state of Cr (IV). The results of the experiment showed that the optimal firing condition was 18 h of holding time at 800°C , using CrCl_3 as chromophore, followed by 2 h at the raised temperature of 1150°C . The change in coloration of the Cr (IV) employed by malayaite showed a very rich color of red. Thus it was possible to effectively synthesize sphene-pink pigments with more red tint at a low temperature.

Key words : Malayaite, Sphene, CrCl_3 , Pink, Pigment

1. Introduction

For a long time many attempts were made to achieve red coloration in ceramic glaze, but obtaining pure red coloration was not possible. Therefore colors like pink, purple, brick red, and maroon were usually accepted as the coloration of red type colors.¹⁾ Accordingly, it is necessary to develop red type pigments for glaze that show stable coloration at a high temperature. When Cr_2O_3 is used as chromophore, colors like pink, red, or green appear.²⁾ If Cr_2O_3 is used together with SnO_2 and CaO in the glaze, the coloration becomes deep purple, which is mainly due to malayaite. Such a crystal lattice, known also as sphene, involves the binding of metal ions as chromophore such as transition metal ions.³⁾ In this case, it is known that the substitution of the Sn ion by Cr in the crystal structure results in the coloration of reddish brown. The malayaite crystal has been known to be very stable against heat, which makes it a very good raw material for the main lattice of the pigments used for ceramics.⁴⁾

Because of such merits, the Cr_2O_3 - SnO_2 - CaO - SiO_2 composition is widely utilized as pigments for ceramic glazes. It is attracting attention in the ceramic industry as the only alternative red type pigment that does not contain cad-

mium, and can be used at temperatures up to 1300°C .¹⁾ When the CaSnSiO_5 composition was synthesized, malayaite was produced with cassiterite.

The oxidation states of the Cr ions employed by the produced crystal are mixed, mostly Cr (III) and Cr (IV), each of which gives different coloration when employed by crystal.^{1,5)} In particular, it has been known that malayaite gives brown coloration and cassiterite a purple type coloration.^{6,7)} When CrCl_3 was used as chromophore, it was shown that Cr ions were employed mostly in the oxidation state of Cr (IV).⁸⁾

The present research aimed to obtain the optimal synthetic condition for red coloration, by making Cr ions employed as chromophore by the malayaite being produced during the synthesis of the SnO_2 - CaO - SiO_2 system pigments. In order to maximally promote the employment of Cr ions by malayaite, changes were made in the firing step and firing time at the temperature malayaite was produced. CrCl_3 was used for this purpose as chromophore in place of Cr_2O_3 . By using CrCl_3 as the raw material for coloration, in order to promote the reaction between crystal and chromophore at a low temperature during the synthesis of pigment, it may be possible to lower the synthetic temperature. In addition, a change in the oxidation state of Cr ion can be anticipated, which may result in the promotion of the employment of Cr (IV) by malayaite. For this reason an attempt was made to obtain the condition for the synthesis of the pigment which gives an optimal red coloration.

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Fig. 1. Firing step diagrams by time and temperature. (a) First step firing at 800°C/0~72 h and second step at 1200°C/2 h, (b) First step firing at 800°C/18 h and second step at 1050~1200°C/2 h.

2. Experiments

2.1. Starting material

In order to synthesize the pigments, CrCl_3 (Junsei, Extra Pure, Japan), SnO_2 (Junsei, Chemical Pure, Japan), and borax (Duksan, Extra Pure, Korea) were selected as starting materials. The basic composition was $\text{CaCr}_{0.02}\text{Sn}_{0.98}\text{SiO}_5$,⁹⁾ which had shown the best employment of Cr ions by the malayaite crystal, with CrCl_3 as the coloring material in place of Cr_2O_3 , and with 4% of borax added as mineralizer.

The changes in firing condition are shown in Fig. 1. In the case of (a), the condition for the synthesis of pigment was maintenance at 800°C for 0~72 h as the first firing step and 2 h at 1200°C as the second firing step. In the case of (b), the optimum holding time of the first firing step and the elevated highest temperature of the second firing step were adapted for the synthesis of pigment.

2.2. Sample analysis

In order to identify the crystal phase of the synthesized pigment, X-ray diffractometer using a Ni-filtered $\text{CuK}\alpha$ radiation (XRD-7000, Shimadzu, Japan) analysis was carried out with CaF_2 added as standard material. The characteristic malayaite phase bands and employment of Cr ions in malayaite were analyzed by FT-IR (IR Prestige-21, Shimadzu, Japan). The FT-IR spectra were obtained in the reflectance mode using DRS-8000A in the range of 200~4000 cm^{-1} . Raman spectroscopy (Lambda Solutions, Inc., U.S.A.) analysis was carried out using Vector Raman Probe (RP 532-US). The shape and size of the synthesized pigment particles were observed using SEM (SS-550, Shimadzu, Japan).

The colors of the synthesized pigments and their coloring in lime glaze were analyzed using UV-vis spectroscopy (Shimadzu, UV-2410 PC). The UV-vis spectra were obtained in the range of 200~800 nm and the result was represented as a spectral reflection curve. The result was also expressed numerically by means of optical color analysis software (P/N 206-67449), using the CIE $L^*a^*b^*$ color system, with L^* representing the brightness in the range from black ($L^*=0$) to

white ($L^*=100$). a^* is the axis representing the colors in the range from green ($-a^*$) to red ($+a^*$), while b^* is the axis representing the colors on the range from blue ($-b^*$) to yellow ($+b^*$).

For final evaluation of the coloring of the synthesized pigments, experiments were conducted by applying them to the lime glaze. The seger formula for the lime glaze can be referred to below:

Each of the synthesized pigments was added to lime glaze (6%) and then fired in an electric furnace by raising the temperature up to 1260°C at the rate 3°C/min, followed by 40 min of firing at 1260°C.

3. Results and Discussion

3.1. Influence of holding time at the first firing step

Fig. 2 shows the result of the XRD analysis of the samples obtained by varying the holding time from 3 to 72 h at 800°C. A comparison between the single peak of the malayaite phase appearing at 33.6° of the 2θ value and the peak of the mixed malayaite and cassiterite phases at 33.95° shows that the relative intensity of the single peak and mixed peak is high as the holding time increases. The reason is that, in the course of synthesis, the formation of malayaite crystal is very much affected by the holding time at the temperature where the crystal began to be formed.

The FT-IR analysis (Fig. 3) of the synthesized pigment showed that the longer holding time resulted in the appearance of a more intensive band of cassiterite. This indicates that the amount of cassiterite increased as the holding time increased, which is in accordance with the XRD analysis. Of the 6 kinds of pigment shown in Fig. 3, the pigment 18 h shows the smallest band at 345, 367 cm^{-1} , which is part of the absorption band of cassiterite. This indicates that the pigment of 18 h of holding time contains the least amount of cassiterite. The pigment of 18 h showed bands at 675, 705 cm^{-1} ,

Fig. 2. (a) XRD patterns of samples of the first fired step at 800°C for 3~72 h and second step at 1200°C/2 h, (b) Magnification of interesting peaks (32.5~36.5°).

Fig. 3. FT-IR spectra of samples fired in the first step at 800°C for 3~48 h and second step at 1200°C/2 h.

Fig. 4. Raman Spectra of Samples fired in the first step at 800°C for 3~48 h and second step at 1200°C/2 h.

Fig. 5. SEM Analysis of Samples fired in the first step at 800°C/3~72 h and second step at 1200°C/2 h. (a) 3 h, (b) 6 h, (c) 12 h, (d) 18 h, (e) 24 h, (f) 36 h, and (g) 72 h.

indicating that the Cr (IV) ion was employed by the malayaite crystal.¹⁰ That means malayaite employed more of the Cr (IV) ion than cassiterite, which is the main factor

of red coloring.

The reason for such a phenomenon is clearly explained by the Raman spectra analysis shown in Fig. 4. As for the first

Fig. 6. CIE $L^*a^*b^*$ colorimetric parameters of glaze application samples fired in the first step at $800^\circ\text{C}/3\sim 72\text{ h}$ and second step at 1200°C .

Fig. 7. UV-VIS spectra of glaze application samples fired at the first step at $800^\circ\text{C}/3\sim 72\text{ h}$ and second step at 1200°C .

3~18 h of holding time the intensity of the characteristic peak of malayaite increased as the holding time increased, the pigment 18 h showed the most intense peak at $940, 1212\text{ cm}^{-1}$.¹¹⁾ But when the holding time was increased to 24~48 h, the intensity of the peak of malayaite decreased; while a new peak of CaO appeared, accompanied by an increase in the intensity of the peak of cassiterite. This indicates that when the holding time is longer than 24 h, part of the malayaite phase is decomposed, resulting in the increase in the amount of cassiterite and the appearance of the peak of CaO.

The observation by SEM of the pigments in Fig. 5 reveals that the bar type means the malayaite phase existed in all the samples, especially pigment (d), which underwent 18 h of holding time and contained the largest amount of the malayaite phase produced. As the holding time was extended up to 72 h, there was severe coagulation of particles, with the appearance of a glass phase formed by the reaction between CaO and SiO_2 from the decomposition of malayaite.

Fig. 8. XRD patterns of samples fired in first step at $800^\circ\text{C}/18\text{ h}$ and second step at $1200\sim 1050^\circ\text{C}/2\text{ h}$.

The changes in color as the result of applying 6 wt% of the synthesized pigments to lime glaze were expressed as CIE $L^*a^*b^*$ values. The pigment synthesized without intervening the holding time, the pigment 0 h, showed the lowest a^* and b^* values, but the a^* value became larger as the holding time increased. The a^* value was largest when the intervening holding time was 18 h, resulting in the best red color. When the holding time was increased over 18 h, however, the a^* value became rather low; whereas when the holding time was 72 h, there was a drastic decrease in both the a^* and b^* values. This is due to the influence of the CaO, SiO_2 , and SnO_2 (cassiterite) produced as the result of the decomposition of malayaite.

Both Cr (III) and Cr (IV) ions are employed by the malayaite crystal, and Cr (IV) has been reported to exert an influence on the red coloration in glaze. In order to determine the oxidation state of the Cr ions employed by the malayaite crystal of the synthesized pigments, UV-vis analysis was carried out on the pigments applied to glaze. The result is shown in Fig. 7.

The absorption bands reflect the oxidation state of Cr ions. The absorption band at 520 nm originated from the employed Cr (IV) ions in the malayaite crystal is explained by diagram of Tanabe-Sugano as $^3A_{2g}(\text{F}) \rightarrow ^3T_{1g}(\text{F})$.^{7,12)} The relative strong band of sample 18 h is shown at 520 nm. This result indicates that the majority of the employed ions are Cr (IV). Whereas the pigments of the 0 h and the 24 and 72 h of holding time showed an increase in the intensity of the band at 600 nm, indicating increased employment of Cr (III).^{7,12)} As shown in Fig. 6, the pigment 18 h has the largest a^* value, since it has the largest amount of employed Cr (IV), which exerts the greatest effect on the color of glaze.

The observation by SEM revealed coagulation in all the pigments, as shown in Fig. 5, and thus an attempt was made to lower the synthetic temperature.

3.2. Influence of temperature at the second firing step

The new firing condition was 18 h at 800°C , as in the case

Fig. 9. Raman spectra of samples fired in the first step at 800°C/18 h and second step at 1200~1050°C/2 h.

of (b) in Fig. 1, followed by 2 h at the highest temperature that was lowered in a stepwise manner from 1150°C to 1100°C and 1050°C. The results of the XRD analysis of the synthesized pigments are shown in Fig. 8. The result shows that the main peak of the pigments synthesized at the firing temperature of 1050~1100°C corresponded to cassiterite, indicating that malayaite had not been sufficiently produced. Whereas the main peak of the pigment synthesized at 1150°C corresponded to malayaite. This is almost the same result as in the case where pigment was synthesized at 1200°C, indicating that the synthetic temperature could be lowered according to the changes in the length of the intervening holding time.

Fig. 9 shows the result of the Raman spectroscopy analysis, carried out to compare the crystal phases produced in the pigments synthesized at 1150°C and 1200°C. The result shows that the peaks of cassiterite, very weak peaks appearing at 616, 778, 956, and 1013 cm^{-1} , are relatively more intensive in the case of the pigment synthesized at 1200°C than in the case of the pigment synthesized at 1150°C, whereas the peak of malayaite was most intensive in the case of the pigment synthesized at 1150°C. Thus the optimum synthetic temperature might be 1150°C.

Fig. 10 shows the result of the overvation by SEM of the

Fig. 11. UV-VIS spectra of samples fired at the first step at 800°C for 18 h and second step at 1200~1050°C/2 h

pigments synthesized at 1050~1200°C. The result confirmed that a larger amount of the particles of the malayaite crystal were produced in the pigments synthesized at 1150°C and 1200°C than in the pigment synthesized at 1050°C, whereas the pigment synthesized at 1200°C showed more agglomerative than the pigment synthesized at 1150°C. Thus the optimum synthetic temperature of the pigment was expected at 1150°C.

Fig. 11 shows the result of the UV analysis of the fired specimens that contains 6 wt% of pigments added to lime glaze. The pigment synthesized at 1150°C showed the most intensive absorption band at 520 nm,^{7,12)} with the most vivid and richest coloration. Thus the optimal firing condition for the synthesis of pink pigment was shown to be 18 h of holding time at 800°C, followed by 2 h at 1150°C.

4. Conclusions

Pink pigment was synthesized using the composition $\text{CaCr}_{0.02}\text{Sn}_{0.985}\text{SiO}_5$ with CrCl_3 as the substitute for Cr_2O_3 and 4 wt% of borax as mineralizer. In the case of synthesizing sphene-pink pigments at 1200°C, cassiterite and CaO phases appeared due to decomposition of malayaite over a holding time of 24 h at 800°C. The optimum condition for synthesis of sphene-pink pigments was a holding time of 18 h at 800°C and malayaite was produced by maintaining

Fig. 10. SEM analysis of samples fired at the first step at 800°C/18 h and second step at 1050~1200°C/2 h, (a) 1050, (b) 1150, and (c) 1200°C.

2 h at 1150°C. At the optimum condition, employment of Cr (IV) which exerts a great effect on the red coloration of pigments gave the best chromaticity (a^*) value of pigment in glaze.

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