Effect of iron content and annealing temperature on the color characteristics of Fe-ZrSiO₄ coral pink pigments synthesized by Sol–gel method

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To investigate color properties by inclusion of hematite in the iron zircon pigments, different samples were prepared by the sol–gel method without mineralizer. The starting amount of the ferric salt in the sol–gel reacting mixture was varied in order to obtain Fe₂O₃/Zr molar ratio in the range of 5–30%. Fe-ZrSiO₄ pigments of the sol–gel reaction were calcined in the range 600–1300°C. The crystalline phases were determined by using X-ray diffraction(XRD). The process of inclusion of hematite in iron zircon pink color was studied by UV-Vis-NIR spectroscopy and FT–IR spectroscopy. It was found that the coral pink and reddish color in the iron zircon pigments is due to α-Fe₂O₃ particles incorporated in the zircon matrix.©2009 The Ceramic Society of Japan. All rights reserved.

Key-words : Fe-ZrSiO₄ pigment, Zircon, Inclusion, Hematite, Sol–gel, Color properties

1. Introduction

The inorganic pigments used in ceramics are homogeneous mixtures. The colouring of the pigments in ceramic body or glazes is due to the intravitrail dispersion of the main crystalline phases. Therefore, the crystalline phases require structural and chemical stability in order not to be solubilized during firing: (1) thermal stability at high temperatures above 1200°C, (2) chemical stability towards the vitreous phases colored by the pigment, (3) low toxicity for health and environments. Especially red pigments development has been restricted to Pb₃O₄, CdS, Se₁–x, etc. new red pigments need to be developed. Very limited number of pigments are available which satisfy such requirements, among which ZrSiO₄ pigments have the strong points of high thermal stability, anti-corrosion and environment-friendliness. Thus, the ZrSiO₄ pigments are very important for the ceramic industry, due to not only its structural and chemical properties but also the excellent and stable coloring at high firing temperatures. Among the red inorganic pigments used in ceramics, the pigment doped with iron (Fe-ZrSiO₄, DCMA 14–44–5) is called coral pink, which belongs to the 3 major ZrSiO₄ pigments along with praseodymium yellow and vanadium blue. During the synthesis of ZrSiO₄, the metal iron(Fe) used as a chromophore is included as a guest ion in the structure of ZrSiO₄, which causes pink colouring. The metal ion used for doping has been reported to not only form a solid solution in the ZrSiO₄ matrix but also exist as a separated phase in the structure (that is, capsule or inclusion). The sol–gel process was introduced in the mid-19th century for the study about silica gel, but active research has begun since glass was prepared using metal alkoxide. That is economical method as ZrSiO₄ can be synthesized at relatively low temperatures without a special equipment. Moreover, products with a wide range of composition and homogeneous mixed phases can be obtained, as well as with high purity if starting solution is pure because of the simple purification process.

Thus the sol–gel process is a very important method of low temperature synthesis. It also has many elements that can be applied to the preparation of Fe-ZrSiO₄ pigments. It is very difficult to control the coloring by Fe-ZrSiO₄ pigments compared to other pigments, so there must be very careful fine grinding of starting materials (zirconia and silica). In case of Fe-ZrSiO₄ pigments, finer particles can give better coral pink color that is more reddish and yellowish. In addition, inclusion of higher amount of Fe ion can be expected by the ceramic method. That is, the finer particles prepared through the homogeneous mixing of liquid sample has higher reactivity, and the consequent maximization of inclusion improves the quality of pigment not only in color but also in reflectance property. Thus the inclusion of chromophoric iron into host crystal is a very important process that affects the quality of the coloring and durability of zircon pigments. Therefore, in order to develop Fe-ZrSiO₄ pigments for high-temperature firing, the present research employed the sol–gel process, to synthesize more homogeneous and finer pigments at low temperature without using mineralizer. By varying the iron content and analyzing the characteristics of the pigments at different calcination temperatures, the optimum condition for the synthesis of best-coloring coral pink pigments was studied, as well as the process of iron inclusion during the crystallization of zircon.

2. Experimental procedures

2.1 Synthesis of Fe-ZrSiO₄ pigments

For the synthesis of ZrSiO₄, high purity reagent grade Si(OCH₃)₄ (Aldrich, TEOS, 98%) and ZrOCl₂·8H₂O(Junsei Chemical Co., Ltd., ZOC) were used as starting materials, FeCl₃·6H₂O(Duksan Pure Chemical Co., Ltd.) as a chromophore, and double distilled water for hydrolysis. EtOH was used as a solvent, and HCl as a catalyst. First, for homogeneous mixing of dopant ion, FeCl₃·6H₂O solutions (0.01/0.015/0.02/0.03/0.05/0.06 mol) were diluted in 40 times volume (76 ml) of H₂O,
respectively, under stirring at 60°C for 30 min, to which Si(OCH3)4 (0.1 mol) was slowly added drop by drop. This 1st solution was stirred for 30 min, to which then 0.2 mol of EtOH and 0.04 mol of the reaction catalyst HCl were slowly added drop by drop. The resulting solution was stirred for 2 h for 1st hydrolysis. Then the 2nd hydrolysis was carried out by slowly adding the ZrOCl2·8H2O solution (0.1 mol) diluted in 76 ml of H2O that had been prepared already. The ZrO2–SiO2 gels were subjected to 1st drying at room temperature, and then to 2nd drying at 70°C in a dryer, followed by ball milling. Each of them were calcinated at 600, 800, 1000, 1200, and 1300°C (2°C/min, 3 h soaking), respectively. The experimental compositions are shown in Table 1.

### 2.2 Characteristics of Fe-ZrSiO4 pigments

The crystallization of the samples was followed by X-ray diffractometer using a Ni-filtered Cu Kα radiation (Shimadzu Co., XRD 7000). The fraction of ZrSiO4 (αZrSiO4 = I61200 + I61111 + I63111 + I63111) was obtained based on the relative intensity calculated using the 4 peak areas - ZrSiO4 (200), (Monoclinic) M-ZrO2 (111, 111) and (Tetragonal) T-ZrO2 (111) - that appeared in the 2θ range of 26–32° in the X-ray diffraction pattern of sample powder heat-treated at each temperature. During the course of the pigment synthesis (600–1300°C), the process of inclusion was examined by analyzing the changes in the characteristic hematite bands using a FT–IR (Shimadzu Co., IR Prestige–21) and an UV-Vis-NIR scanning spectrophotometer (Shimadzu Co., UV–3101 PC). The FT–IR spectra were obtained in the transmission mode in the range of 26–32°C. When ZrSiO4 began to form, to 1300°C, the crystalline hematite inclusion and the consequent coloring.

The crystalline phases formed and the changes in the characteristic bands were expressed numerically by means of an U.V PC optical color analysis software (P/N 206–67449), as in Table 1. The crystalline phases formed and the changes in the characteristic bands were observed by the analytical methods described above, to examine the process of hematite inclusion and the consequent coloring.

### 2.3 Application of underglazes and glazes under high-temperature firing

The scope of the application of the Fe-ZrSiO4 pigments synthesized in the present research is the range of the ceramics made by high-temperature firing (SK 8–SK 10). For final evaluation of the coloring of the synthesized pigments, experiments were conducted by applying them to the glazes used for the ceramics made by high-temperature firing. Lime-barium glaze was used because it has the best fluidity and widest transparent and glossy area of all the basic components of basic glaze; and its seger formula is as follows:

- 0.297 KNaO
- 0.157 CaO 0.734 Al2O3 4.682 SiO2
- 0.018 MgO
- 0.528 BaO

Each of the synthesized pigments was added to lime-barium glazes (10%), followed by wet-mixing; the resulting glazes were applied to tile-type bisque samples (4 cm × 4 cm). Firing was performed in an electric furnace by raising temperature up to 1265°C at the rate of 3°C/min, followed by 30 min of firing at 1265°C and then cooling. The characteristics of the colors of the high temperature firing glazes using the synthesized Fe-ZrSiO4 pigments were measured by UV-Vis spectroscopy, which were then expressed numerically based on the CIE L*a*b* color order system.

### 3. Results and discussions

#### 3.1 Color properties of pigments

**Figure 1** shows the analysis of UV-Vis spectroscopy spectra for FeCl3 0.2 M synthetic pigments at different calcination temperatures. At the temperatures below 600°C, when the crystallization of hematite had not yet begun, the band was around 500 nm. Then as the calcination temperature was raised above 600°C, the band moved from the short wavelength to the long wavelength in the range of 570–600 nm. Accordingly, the color of the pigment also changed from an orange tone to a reddish brown tone. As the temperatures change from 1000°C, when ZrSiO4 began to form, to 1300°C, when inclusion was completed, the color of the pigment changed to coral pink colors due to the inclusion of iron; while the band moved to the wavelength of 600–620 nm with higher intensity.

The coloring of the synthesized pigments was measured according to iron contents by UV-Vis spectroscopy, and the results were expressed numerically using the U.V PC optical color analysis software (P/N 206–67449) as in Table 2. The

<table>
<thead>
<tr>
<th>Wavelength (λ × mm)</th>
<th>Absorbance a.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.2</td>
</tr>
<tr>
<td>400</td>
<td>0.9</td>
</tr>
<tr>
<td>600</td>
<td>0.7</td>
</tr>
<tr>
<td>800</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**Fig. 1.** Diffuse reflectance spectra for FeCl3 0.2 M samples at different temperatures in the range from 800 to 200 nm.
colors developed by the pigments synthesized at 1300°C with different iron contents and added to lime-barium glazes are as follows: The sample with 0.1 M or 0.15 M of FeCl₃ had very bright pink color, while that with 0.2 M excellent coral pink color. The sample with 0.3 M had a little deep coral pink color with somewhat poor saturation. The coloring of the pigments became deeper as the iron content of pigment increased from 0.3 M to 0.5 M and then to 0.6 M, and the color developed in glaze also changed from a coral pink tone with a tint of orange to a deep red brown tone with a tint of reddish brown.

Figures 2, 3 and 4 show the \( L^* \), \( a^* \) and \( b^* \) values of the colors developed by the synthetic pigment specimens doped with different iron concentrations and those of the glaze specimens to which the pigments were applied. The colors of the synthetic pigments had the most reddish tone at 0.3 M of FeCl₃. When the synthetic pigments were applied to lime-barium glazes, the \( L^* \) value was 55.73 with 0.3 M of FeCl₃. The color of 0.2 M was most similar to that when a commercially available pigment and \( L^* \) value was 68.63. \( L^* \) values with 0.1 M and 0.15 M were 76.60 and 78.39, respectively, which are very bright color tones, and \( a^* \) and \( b^* \) values has similar tendency. With 0.2 M, \( a^* \) and \( b^* \) were 17.5 and 24.2, respectively, and the color was a very clear and excellent coral pink tone. As the concentration of FeCl₃ varied from 0.3 M to 0.5 M and then to 0.6 M, the \( L^* \) value of the developed color dropped to 54.83 and 44.09, respectively, while \( a^* \) increased in the range of 17.49–18.89, and also \( b^* \) in the range of 20.40–22.91; while the colors changed to deep reddish brown.

Based on the results above, the best condition for the development of coral pink color in glaze was 10% of Fe₂O₃, which is less amount compared with the commercially available pigments containing 15–35% of Fe₂O₃; thus the developed color can be considered excellent. Therefore, in the present research, FeCl₃ 0.2 M was selected as a condition for adding iron to Fe-ZrSiO₄ pigment to obtain the best coral pink color, in an effort to study the relationship between the colors and crystalline phases of the pigments according to varying calcination temperatures, as well as to study the process of hematite inclusion.

### Table 2. UV Analysis of Calcined Powders and Glazes with Fe 0.1–0.6 M Samples at 1300°C

<table>
<thead>
<tr>
<th>samples</th>
<th>pigment powders</th>
<th>glazed tiles (10%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( L^* )</td>
<td>( a^* )</td>
</tr>
<tr>
<td>Commercial</td>
<td>54.33</td>
<td>15.68</td>
</tr>
<tr>
<td>1M–1300</td>
<td>60.31</td>
<td>12.71</td>
</tr>
<tr>
<td>1.5M–1300</td>
<td>59.63</td>
<td>13.11</td>
</tr>
<tr>
<td>2M–1300</td>
<td>59.31</td>
<td>8.68</td>
</tr>
<tr>
<td>5M–1300</td>
<td>41.31</td>
<td>11.56</td>
</tr>
<tr>
<td>6M–1300</td>
<td>47.74</td>
<td>8.94</td>
</tr>
</tbody>
</table>

### 3.2 Synthesis of Fe-ZrSiO₄ pigments

#### 3.2.1 Phase changes depending on iron contents

Figure 5 shows the change in the phases of synthetic pigments according to varying iron contents at 1300°C. The observation of the synthesized pigments revealed that the first phase was zircon, with traces of M-ZrO₂ and hematite as the second phase. There was no big growth of hematite phase when the concentration of FeCl₃ was up to 0.3mol, while the samples with 0.5 M–0.6 M showed the growth of hematite phase, along with the remarkable reduction of M-ZrO₂ phase and the growth of zircon phase. Such a process of ZrSiO₄ expansion by the solid solution of T-ZrO₂ and Fe³⁺ species in the synthesis of Fe-ZrSiO₄ is considered due to the role of iron as a mineralizer. We can see that at the concentrations of FeCl₃ above 0.3 mol, a portion of the iron was not included, existing as excess hematite and affecting the coloring of pigment.
3.2.2 Phase changes depending on different calcination temperatures

The changes in phase were analyzed with FeCl₃ 0.2 M pigment, which shows best development of coral pink color, according to varying calcination temperatures. Figure 6 shows the change in the crystalline phases of the FeCl₃ 0.2 M pigment according to varying calcination temperatures. The formation of T-ZrO₂ began at 600°C and was promoted at 800°C. Whereas the formation of ZrSiO₄ began at 1000°C and was promoted at 1200°C. The formation of ZrSiO₄ rapidly progressed at 1300°C due to the Hedvall Effect of T-ZrO₂ and SiO₂.⁹

In the present research, the temperature range for the beginning and promotion of ZrSiO₄ formation was 1000–1300°C. This is remarkably lower than 1400°C, at which the formation of ZrSiO₄ begins when the single synthesis of ZrSiO₄ is carried out by the sol–gel process without using a mineralizer. Thus, we can see that iron acted as a mineralizer in the process of ZrSiO₄ crystallization. Regarding the correlation between the crystalline phases and the coloring of pigments in glazes, the sample calcinated at 1300°C developed the brightness and best coral pink color. Assuming that the excellent coral pink color of the Fe-ZrSiO₄ pigment synthesized under the optimum condition was due to the inclusion of hematite(α-Fe₂O₃), the process of the inclusion during the ZrSiO₄ formation was as follows: Crystallization of hematite began at 800°C, when hematite crystal began to be detected, and there was active crystallization at 1000°C. Crystallization of hematite was promoted along with that of ZrSiO₄ at 1200°C, and the hematite peak decreased at 1300°C, when the formation of ZrSiO₄ became rapid. Therefore, we can see that iron acted as a mineralizer in the process of ZrSiO₄ crystallization.

Llusar et al.¹³,¹⁰ proposed the Coarsening-Oclusion model, in which the coloring of ZrSiO₄ pigments is due to the attraction of transition elements, which are chromophores, into crystal structure during the process of ZrSiO₄ synthesis. They also mentioned: Hematite, which is used as a chromophore for coral pink pigments, may stay in a certain place or may grow through expansive coarsening process during the formation of ZrSiO₄. Therefore, the inclusion of hematite showed an important characteristic that it proceeded along with hematite crystallization at the final stage of ZrSiO₄ crystallization.

Figure 8 shows the yield of zirconia and zircon, and the change in the relative intensity of the hematite peak at different calcination temperatures. In the course of raising calcination temperature, T-ZrO₂ increased at low temperatures and its amount began to decrease due to its reaction with SiO₂ to form ZrSiO₄. Accordingly, M-ZrO₂ also decreased at 1300°C, the highest temperature, along with the growth of zircon. This pattern is same as the pattern of hematite peak intensity. Therefore, it is considered as an inclusion in which hematite is incorporated into or surrounded by the growing ZrSiO₄ crystal. Thus, the inclusion of hematite showed an important characteristic that it proceeded along with hematite crystallization at the final stage of ZrSiO₄ crystallization.

Fig. 5. XRD patterns of the (Fe)x–ZrO₂–SiO₂ gel with different Fe concentrations at 1300°C. Z: zircon, m: monoclinic ZrO₂, t: tetragonal ZrO₂, H: hematite, C: crystobalite.

Fig. 6. Change of XRD pattern of the (Fe)0.2–ZrO₂–SiO₂ gel with different temperatures. (left) Z: zircon, m: monoclinic ZrO₂, t: tetragonal ZrO₂, H: hematite, C: crystobalite.

Fig. 7. Magnified XRD pattern of the (Fe)0.2–zircon pigments with different temperatures. The symbol present ZR: zircon, H: hematite, T: tetragonal zirconia, M: monoclinic zirconia (right).
inclusion did not occur even if the mixture of iron and synthesized zircon was calcinated, and that the addition of calcinated sample to glazes never brought about red coloring.

3.3 Characteristics of the IR spectra

3.3.1 IR spectra depending on different calcination temperatures

It has been reported that inclusion of hematite in Fe-ZrSiO₄ pigments occurred simultaneously with ZrSiO₄ crystallization, which has also been confirmed by the result of the present XRD experiment.

FT–IR analysis was carried out for clearer interpretation of the result. The process of the hematite inclusion was analyzed by varying the calcination temperature. Pure ZrSiO₄ was calcinated at 1300°C to be used as standard material. The characteristic absorption band of hematite was quoted from existing literatures. The spectral change that the characteristic absorption band of hematite was gradually replaced by that of pure ZrSiO₄ was interpreted as the process of inclusion.

The characteristic bands of ZrSiO₄ are 1025, 920, 640, 420 and 360 cm⁻¹. Figure 9 shows the IR spectra at different calcination temperatures. The process of hematite formation was analyzed by varying the calcination temperature. Pure ZrSiO₄ was calcinated at 1300°C to be used as standard material. The characteristic absorption band of hematite was quoted from existing literatures. The spectral change that the characteristic absorption band of hematite was gradually replaced by that of pure ZrSiO₄ was interpreted as the process of inclusion.

3.4 Characteristics of the UV-Vis-NIR spectra

Figure 10 shows the result of the UV-Vis-NIR Spectroscopy. FeCl₃ 0.3 M pigments synthesized at different temperatures were subjected to the spectroscopy in order to measure the changes in bands during the crystallization of hematite and the consequent process of inclusion. The bands around 290–330 nm, 470–535 nm and 850 nm, which are the characteristic peaks of hematite, show obvious shift as the temperature changes from 800°C to 1000°C. This means that the iron in the sample had not been included but existed separately as hematite. During the course of raising the calcination temperature of the samples, the spectra of the samples begin to show change from 1200°C, when the zircon formation began to be promoted. The spectra of the samples calcinated at 1200°C and 1300°C show that the characteristic bands of hematite are remarkably weakened in every domain of the UV-Vis-NIR. It is interpreted that the characteristic absorption wavelengths are weakened because hematite had been included into the crystal. This agrees to the XRD data in Fig. 6, as well as the IR data in Fig. 9.
4. Conclusion

Fe-ZrSiO₄ pigments were synthesized by the sol–gel process to be applied to lime-baryum glazes. The results are as follows:

(1) Fe-ZrSiO₄ pigments were synthesized using Si(OC₂H₅)₄ and ZrOCl₂·8H₂O as starting materials and FeCl₃·6H₂O as a chromophore at 1200–1300°C. The optimum condition for the synthesis of coral pink pigments was 0.2 M (Fe₂O₃ 10%) of FeCl₃·6H₂O at 1300°C.

(2) Hematite(Fe³⁺), as colorant of the synthesized pigment, began to be crystallized at 800°C, and the crystal grew until the temperature reached 1300°C, when it formed almost a single phase to be incorporated in ZrSiO₄.

(3) The value of color in 0.2 M of FeCl₃·6H₂O synthetic pigments were \( L^* = 59.31, a^* = 8.68, b^* = 5.64 \). It’s color was reddish brown. When the pigments were applied to lime-baryum glazes (10%), the value of color were \( L^* = 68.63, a^* = 17.13, b^* = 24.09 \), and it was excellent coral pink.

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