Synthesis of Reddish Pink Pigment by Addition of Mg^{2+} into $(Al, Cr)_2O_3$ Corundum

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Mg^{2+} 添加によるクロムアルミナ赤色顔料の合成

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It is known that the colors of inorganic pigments can be changed by adding of small amount of mineralizers. In this research, the effect of Mg^{2+} on the coloring of $(Al, Cr)_2O_3$-pigment was investigated. The Mg^{2+}-added pigments consisted of $(Al, Cr)_2O_3$ corundum and $Mg(Al, Cr)_2O_4$ spinel. It was verified that the lattice constants of the corundum phase were not affected by the addition of Mg^{2+}. The valence of Cr in $(Al, Cr)_2O_3$ and in $Mg(Al, Cr)_2O_4$ were trivalent as found by X-ray photoelectron spectroscopy. The color changing of the pigments was due to the content of Cr^{3+} in the $Mg(Al, Cr)_2O_4$.

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1. Introduction

In terms of chemical and thermal stability, inorganic pigments are generally superior to organic pigments. However, the problem of inorganic pigments is that the color variation is limited.[1] Usually, inorganic pigments are synthesized as solid solutions of mother crystal and transition metal oxides. It is known that the colors of pigment can be changed by adding small amount of mineralizers.[2] For instance, reddish ceramic pigments can be prepared by doping Cr^{3+} into alumina or zinc-aluminum spinel.[3] However, the effects of mineralizers on the coloring of $(Al, Cr)_2O_3$-pigment remain obscure. In this research, the effects of Mg^{2+} on the synthesis and coloring of $(Al, Cr)_2O_3$-pigment were systematically investigated.

2. Experiments

2.1 Synthesis

The pigments were synthesized from Al_2O_3, Cr_2O_3 and $MgCO_3$. Al_2O_3 has the 99.99 mass% purity and the others have a reagent-grade purity. The compositions of the pigments are shown in Table 1. The content of Cr in the pigments was always 10 mol%. The mixtures of the raw materials were wet-milled by ball mills for 24 h. After drying, the mixture were calcined at 1600℃ for 2 h.

2.2 Measurements

2.2.1 Reflectance

The pigments were kneaded with the solvent (T-01, TNK Screen Inks) on the basis of a weight ratio of 1 : 1. The paste passed through #200 nylon screen was printed on transparent films. Reflectance spectra were measured in the wavelength range of 400 to 780 nm with a spectrophotometer (Color Analyzer TC-1800, Tokyo Denshoku).

2.2.2 X-ray diffraction analysis

The crystalline phases of pigments were identified by powder X-ray diffraction (Rint-2000, Rigaku). Lattice constants of the constituent crystallines were determined by WPPF method.[4]

2.2.3 X-ray photoelectron spectroscopy (XPS)

The tablets of the pigment powders were sintered again at 1600℃ for 2 h, and then polished to specular gloss. The polished sample was subjected to XPS (SSX-100, SSI) to determine the valence of Cr ion. The binding energies were corrected by using the value of 284.6 eV for the C1s resulting from the contaminated carbon.[5]

Table 1. Compositions of $(Al, Cr)_2O_3$-Pigments Added Mg^{2+}

Sample No.	Al_2O_3	Cr_2O_3	$MgCO_3$
M-00	90.00	10	0
M-02	89.80	10	0.20
M-05	89.50	10	0.50
M-1	89.01	10	0.99
M-2	88.04	10	1.96
M-5	85.24	10	4.76
M-10	80.91	10	9.09
M-20	73.33	10	16.67
M-30	66.93	10	23.07
M-40	61.43	10	28.57
M-50	56.67	10	33.33

3 Results and discussion

3.1 Effects of Mg^{2+}

3.1.1 Change of color by addition of Mg^{2+}

Figure 1 shows the reflectance spectra of $(Al, Cr)_2O_3$-pigments having various contents of Mg^{2+} (Table 1). Compared with the pure $(Al, Cr)_2O_3$-pigment (M-00), the reflectance of the pigment having 0.2 mol% Mg^{2+} (M-02) decreased considerably at 480 nm. Subsequently, the color of the M-02 pigment shifted from purplish pink to reddish pink. However, the reflectance at 480 nm increased with increasing of Mg^{2+} content. The color of $(Al, Cr)_2O_3$-pigments added Mg^{2+} less than 20 mol% was reddish pink. Exaggerate addition of Mg^{2+} more than 20 mol% returned the color of the pigment from reddish pink to purplish pink.

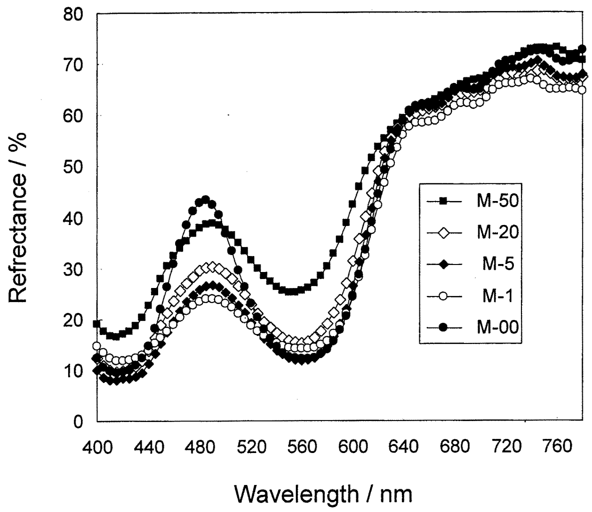

Fig. 1. Reflectance spectra of $(Al, Cr)_2O_3$-pigments added Mg^{2+}.

3.1.2 Crystalline phase of the pigment

Figure 2 shows X-ray diffraction patterns of $(Al, Cr)_2O_3$-pigments added Mg^{2+}. The structure of M-00 without Mg^{2+} was a single phase of $(Al, Cr)_2O_3$ corundum. On the contrary, another pigments involving Mg^{2+} consisted $(Al, Cr)_2O_3$ corundum and $Mg(Al, Cr)_2O_4$ spinel phases. No change of lattice constants of the $(Al, Cr)_2O_3$ corundum was found by the addition of Mg^{2+}.

3.1.3 Valence of Cr ion

Figure 3 shows XPS spectra of M-00, M-5 and M-20. For all the pigments the binding energies of 3p, $2p_{3/2}$ and $2p_{1/2}$ of Cr were 43, 576 and 586 eV, respectively. The electronic structures of Cr oxides can be dentified from the binding energies.[6] Ren et al.[7] reported that the valence of Cr in the chromium-based reddish pigments such as Cr-doped $CaSnSiO_5$ and Cr-doped $CaTiSiO_5$ is tetravalent. However, the valence of Cr of $(Al, Cr)_2O_3$ corundum and $Mg(Al, Cr)_2O_4$ spinel phases in the pigments obtained by this experiment could be determined to be trivalent.

3.2 Mechanism of color changing

As shown in Fig. 2, $(Al, Cr)_2O_3$-pigments involving Mg^{2+} were mixtures of $(Al, Cr)_2O_3$ and $Mg(Al, Cr)_2O_4$. The colors of $(Al, Cr)_2O_3$ and $Mg(Al, Cr)_2O_4$ change with increasing of the content of Cr^{3+} from purplish pink to brown, and finally to green.[7] Therefore, the contents of Cr^{3+} in the $(Al, Cr)_2O_3$ and $Mg(Al, Cr)_2O_4$ phases should be investigated in order to clear the color changing of the pigments. The content of Cr^{3+} in $(Al, Cr)_2O_3$ does not

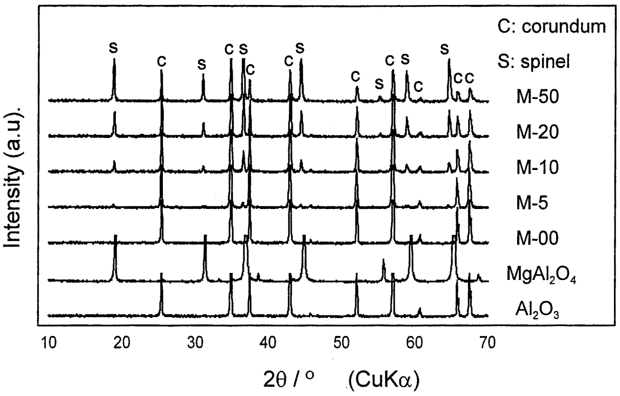

Fig. 2. X-ray diffraction patterns of $(Al, Cr)_2O_3$-pigments added Mg^{2+}.

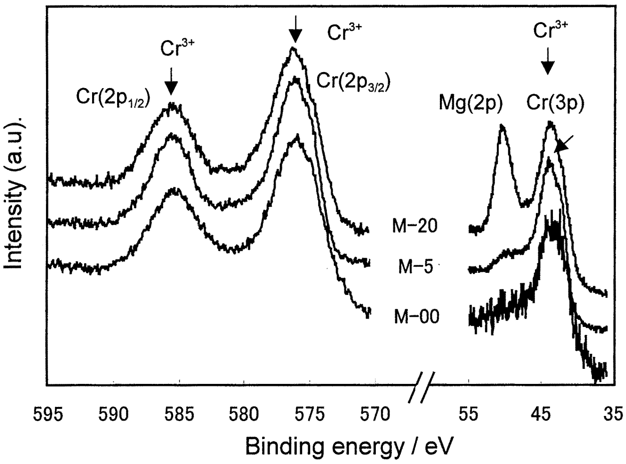

Fig. 3. X-ray photoelectron spectra of Cr2p, Cr3p and Mg2p peaks of $(Al, Cr)_2O_3$-pigments added Mg^{2+}.

Table 2. Contents of Al_2O_3, Cr_2O_3 and MgO in $(Al, Cr)_2O_3$-Pigments

	$(Al,Cr)_2O_3$ (C)			$Mg(Al,Cr)_2O_4$ (S)					Color
	Al_2O_3	Cr_2O_3	Cr/(Al+Cr)	MgO	Al_2O_3	Cr_2O_3	Cr/(Mg+Al+Cr)	S/C	-
Sample No.	mol%	mol%	-	mol%	mol%	mol%	-	-	-
M-00	90.00	10.00	0.10	0.00	0.00	0.00	0.00	0.000	Purplish pink
M-02	89.80	9.80	0.10	0.20	0.00	0.20	0.50	0.002	Reddish pink
M-05	89.26	9.74	0.10	0.50	0.24	0.26	0.26	0.005	Reddish pink
M-1	88.37	9.65	0.10	0.99	0.64	0.35	0.18	0.010	Reddish pink
M-2	86.63	9.46	0.10	1.96	1.42	0.54	0.14	0.020	Reddish pink
M-5	81.58	8.91	0.10	4.76	3.67	1.09	0.11	0.053	Reddish pink
M-10	73.77	8.05	0.10	9.09	7.14	1.95	0.11	0.111	Reddish pink
M-20	60.10	6.56	0.10	16.67	13.23	3.44	0.10	0.250	Reddish pink
M-30	48.56	5.30	0.10	23.07	18.37	4.70	0.10	0.428	Purplish pink
M-40	38.64	4.22	0.10	28.57	22.79	5.78	0.10	0.667	Purplish pink
M-50	30.06	3.28	0.10	33.33	26.61	6.72	0.10	1.000	Purplish pink

change by the addition of Mg^{2+} because the lattice constants of $(Al, Cr)_2O_3$ were constant as described in Section 3.1.2. Thus, the composition of $(Al, Cr)_2O_3$ was determined to be $Al_{0.9}Cr_{0.1}O_3$. Based on the assumption that all of the Mg^{2+} added into $(Al, Cr)_2O_3$-pigment converts to $Mg(Al, Cr)_2O_4$, the content of Al and Cr in $(Al, Cr)_2O_3$ and $Mg(Al, Cr)_2O_4$ could be calculated from the composition of the raw materials in Table 1. Similarly, the ratio of $Mg(Al, Cr)_2O_4$ to $(Al, Cr)_2O_3$, (S/C), could be calculated. The calculated results are shown in **Table 2**. Increasing Mg^{2+}, the apparent content of Cr^{3+} in $Mg(Al, Cr)_2O_4$ increased. However, the ratio of Cr^{3+} to $Mg(Al, Cr)_2O_4$ as $Cr/(Mg+Al+Cr)$ decreased. Thus, the color of $Mg(Al, Cr)_2O_4$ changes from green, to brown, and finally to purplish pink. On the contrary, the content of Cr^{3+} in the $(Al, Cr)_2O_3$ phase was 10% which is equal to the content of Cr^{3+} in M-00. The color of $(Al, Cr)_2O_3$ phase was always purplish pink as shown in Fig. 1.

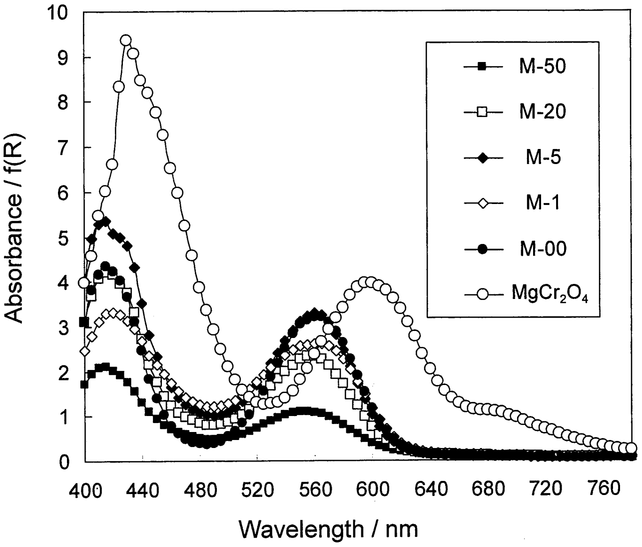

Fig. 4. Reflectance spectra of $(Al, Cr)_2O_3$-pigments added Mg^{2+}.

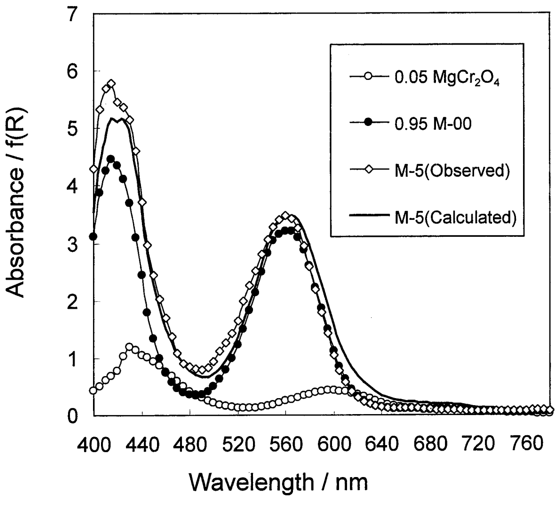

Fig. 5. Calculated reflectance spectra of 0.95M10-00 and 0.05 $MgCr_2O_4$.

Figure 4 shows the absorbance of the $(Al, Cr)_2O_3$-pigments represented by the remission function $f(R)=(1-R)^2/2R$ where R is reflectance.[8] According to Duncan,[9] the absorbance $f(R)$ of a pigment mixture can be expressed by Eq. (1).

$$f(R)_{\mathrm{mix}}=C_1\cdot f(R_1)+C_2\cdot f(R_2)+\cdots C_n\cdot f(R_n) \qquad (1)$$

where C_i is the mole ratio of the component i, and $f(R_i)$ is the remission function of the component i.

Using Eq. (1), the coloring mechanism of M-5 with a fair reddish pink was examined. It is difficult to know the color of $Mg(Al, Cr)_2O_4$ phase in M-5. Then color was approximated with that of $MgCr_2O_4$. The ratio of $Mg(Al, Cr)_2O_4$ to $(Al, Cr)_2O_3$ in M-5 was shown in Table 2 as S/C. The reflectance curve of M-5 was calculated by summation of the reflectance spectra of $(Al, Cr)_2O_3$ and $MgCr_2O_4$. The calculated reflectance curve in **Fig. 5** was almost consistent with the observed one.

4. Conclusions

The phases of the $(Al, Cr)_2O_3$-pigments added Mg^{2+} consisted of $(Al, Cr)_2O_3$ corundum and $Mg(Al, Cr)_2O_4$ spinel. The valence of Cr of both the $(Al, Cr)_2O_3$ and $Mg(Al, Cr)_2O_4$ was trivalent. Only 0.2 mol% addition of Mg^{2+} could change the color of the $(Al, Cr)_2O_3$-pigment from purplish pink to reddish pink. The color changing of the pigment depends on the content of Cr^{3+} in the $Mg(Al, Cr)_2O_4$ phase.

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