Effect of planetary ball millings for oxide precursors on chromaticity of tantalum(V)-based oxynitrides

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Ta(V)-based oxynitrides have been prepared by heat-treatment for mixed powders of Ta(V)-based oxide precursors, aluminum nitride and potassium fluoride in nitrogen atmosphere without flowing ammonia. This method is an eco-friendly and cost-effective way suitable for an industrial scale production of the pigments containing Ta(V)-based oxynitrides with the brilliant color of reddish yellow–yellow, as compared to the conventional method such as ammonolysis with flowing large amounts of ammonia. They have a potential to be employed as non-toxic ceramic pigments, and to substitute pigments containing harmful elements. Effect of planetary ball milling time for oxide precursors on chromaticity of the tantalum(V)-based oxynitrides was evaluated. Results showed that the planetary ball millings of oxide precursors for longer time decreased the particle size of Ta(V)-based oxynitride and improved the chroma ($C^\ast$) of the oxynitride.

Key-words : Tantalum oxynitride, Pigment, Aluminum nitride, Non-toxic, Planetary ball milling, Chroma

1. Introduction

Inorganic pigments are widely used for color materials. However, most inorganic pigments contain transition metals or heavy metals such as Cd, Cr, Pb, Sb, Se and V. The use of them containing such toxic elements is restricted in many countries to protect human health and the environment.

Ta-based oxynitride pervoskites ($Ca_xLa_xTaO_{2+x}N_{1+x}$, etc.) are generally obtained as yellow to deep red powders by ammonolysis of tantalum-based oxide precursor powders using ammonia.¹,² The powders have been considered promising replacements that could eliminate toxic metals emissions (e.g. Cd and Se from cadmium-based pigments) to the environment, because tantalum compounds are non-toxic. Their colors can be tuned from yellow to deep red by chemical composition adjustments (according to a change of the nitrogen content). It is also reported that they are visible light-responsive photocatalysts, which can be employed for overall water splitting at wavelength of up to 600 nm.³

The oxynitrides are non-toxic, but are produced with flowing large amounts of ammonia which is toxic and flammable. In addition, the ammonolysis of the tantalum-based oxide precursors is very sluggish. They make it difficult to promote mass production of the oxynitride pigments.

We have synthesized tantalum oxynitrides using aluminum nitride (AIN) as nitrogen source for nitridation of Sr–La–Ta oxide precursors without flowing ammonia. This synthetic technique leads to a safer preparation of Ta-based oxynitrides in a shorter time as compared to the preparation by ammonolysis. In this study, effect of the particle size of the oxide precursors on chromaticity of the tantalum(V)-based oxynitrides was evaluated. The planetary ball millings for the oxide precursors decreased the particle size of Ta(V)-based oxynitride ($Sr_1-xLa_xTaO_{2+x}N_{1+x}$) and improved the chroma ($C^\ast$) of the pigments.

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2. Experimental

The Ta$_2$O$_5$ powder (TAO02PB, Kojundo Chemical Lab. Co., Ltd., Saitama, Japan), the La$_2$O$_3$ powder (LAO01PB, Kojundo Chemical Lab. Co., Ltd., Saitama, Japan) and the SrCO$_3$ powder (Yoneyama Chemical Industries Ltd., Osaka, Japan) were used for the synthesis of LaTaO$_4$–Sr$_2$Ta$_2$O$_7$ mixture which was the precursor of Sr$_{1-x}$La$_x$TaO$_{2+x}$N$_{1+x}$, (the solid solution of the pervoskites SrTaO$_2$N and LaTaON$_2$). The LaTaO$_4$–Sr$_2$Ta$_2$O$_7$ mixture with La/(Sr + La) ratio of 0.5 was synthesized by firing at 1350°C for 4 h after mixing the powders (SrCO$_3$, La$_2$O$_3$ and Ta$_2$O$_5$) at the molar ratio of Sr/La:Ta = 0.5:0.5:1.0. The LaTaO$_4$–Sr$_2$Ta$_2$O$_7$ precursor was milled by a Si$_3$N$_4$ planetary ball mill for 0, 24 and 72 h. The AlN powder (F, Tokuyama Corp., Tokyo, Japan) was used as an agent for nitridation. The potassium fluoride (KF) powder (KKH07XB, Kojundo Chemical Lab. Co., Ltd., Saitama, Japan) was added as a mineralizer to promote a reaction of LaTaO$_4$–Sr$_2$Ta$_2$O$_7$ precursor with AIN.

The starting composition for synthesis of the pigments containing Ta-based oxynitride is given in Table 1. The LaTaO$_4$–Sr$_2$Ta$_2$O$_7$ precursors milled for different times were mixed with AIN and KF for 6 h in ethanol using the Si$_3$N$_4$ planetary mill. After drying, the mixed powders were fired at 800–900°C for 3 h in nitrogen atmosphere.

Crystalline phases present were identified by an X-ray diffractometer (XRD: Cu $K\alpha$, 40 kV, 200 mA, RINT-2550, Rigaku Denki Co., Ltd., Tokyo, Japan).

The color characteristics were measured in the wavelength range from 400 to 700 nm (10 nm pitch) using a spectrophotometer (CM–700d: Konica Minolta Sensing Inc., Osaka, Japan) with a diffusing reflectance attachment (10° observer, DUV standard). The color characteristics were measured twice and the average results were used. In this study, the color characteristics were measured in the L*a*b* color space and the chroma ($C^\ast$) was used as a parameter of color contrast. The chroma was calculated from the equation $C^\ast=\sqrt{L^\ast a^\ast+b^\ast}$, where $L^\ast$, $a^\ast$ and $b^\ast$ are the L* (luminance), a* (red–green component) and b* (yellow–blue component) values, respectively.

Table 1. Compositions of starting mixtures for Sr$_{1-x}$La$_x$TaO$_{2+x}$N$_{1+x}$ ($x = 0.5$) containing pigments

| Sample/mass % | LaTaO$_4$–Sr$_2$Ta$_2$O$_7$ | AIN | KF  |
|---------------|---------------------------|-----|-----|
| X50           | 57.2 [La/(Sr + La) = 0.5] | 31.2| 11.6|
illuminant D65 and observer 10°. They were estimated in terms of L*a*b* color coordinates (L* = brightness axis, maximum values: 100 = white, 0 = black; a* = green–red axis, negative direction = green, positive direction = red; b* = blue–yellow axis, negative direction = blue, positive direction = yellow).

Photographs of the pigment particles were obtained using a scanning electron microscope (FE-SEM; S-4300, HITACHI, Tokyo, Japan). The particle size was measured on the SEM photographs. More than 100 particles of each sample were analyzed on the SEM photographs for the determination of the particle size.

3. Results and discussion

The formation of Sr1-xLa2TaO7-Ni+4, perovskites (solid solutions of the perovskites SrTaO2Ni and LaTaON2) was observed in the sample [X50 (Table 1)] fired above 800°C. Figure 1 shows the X-ray diffraction patterns of X50 powder prepared using the LaTaO4–Sr2Ta2O7 precursors milled for 0, 24 and 72 h. The strong peaks of Sr1-xLa2TaO7-Ni+4 perovskite (x = 0.5) appeared with the weak peaks of AlN, Sr2Ta2O7 and La0.33TaO3 for the powder fired at 900°C for 3 h. Within different milling times for the oxide precursor, there was no change in the peak positions and peak broadening.

Figure 2 shows the pigments containing Sr1-xLa2TaO7-Ni+4 (x = 0.5) synthesized from oxide precursors milled for different times. The chromaticity of the pigments was enhanced with increasing the milling time for the oxide precursor. The a* value decreased temporarily when the milling time increased from 0 to 24 h, and increased when the milling time increased from 24 to 72 h. The chroma (C*) can be formulated as C* = [(a*)² + (b*)²]¹/². The chroma of the oxynitride pigments increased exceedingly with increasing the milling time for the oxide precursor (Fig. 4).

The particle morphology of LaTaO4–Sr2Ta2O7 precursors milled for 0, 24 and 72 h and the oxynitrides prepared from oxide precursors milled for 0, 24 and 72 h was examined directly by FE-SEM and selected images are presented in Fig. 5. The non-milled oxide precursor (a) had a plate-like shape and the size distribution was homogeneous. The oxide precursors decreased in size, and exhibited the irregular shape and faceted surface morphology by milling (b, c). The size distribution of the oxide precursors also became quite inhomogeneous by milling. The oxynitride particles commonly displayed discernible cube edges and faces, reflecting the crystal habit of the primitive perovskite block (d, e, f). It indicates high crystallinity of the oxynitrides. As the milling time for the oxide precursor increased from 0 to 72 h, the cube-shaped particles showed a great decrease in the particle size from 512 to 81 nm. The decrease in particle size affects the light scattering coefficient of pigment particles and the optimum particle size provides the maximum scattering coefficient. This resulted in the increase in the chroma of the oxynitride pigments with increasing the milling time for the oxide precursor.

The oxynitride pigments prepared from the oxide precursors milled for 0, 24 and 72 h were mixed with a borosilicate frit at the weight ratio of 1:9, and applied on glazed ceramic plates (porcelain plates with a transparent lime glaze) at 800°C (Fig. 6).
The color of the over-glazed oxynitride pigments became light with the increase in the milling time for the oxide precursor. Figure 7 shows the color coordinates ($a^*$, $b^*$) for the over-glazed pigments containing $\text{Sr}^{1,1}_{x}\text{La}_{x}\text{TaO}_{2+x}\text{N}_{1+x}$ ($x = 0.5$) synthesized from oxide precursors milled for 0, 24 and 72 h. The $a^*$ and $b^*$ values decreased greatly when the milling time increased from 0 to 24 h. The chroma of the over-glazed oxynitride pigments decreased exceedingly with increasing the milling time for the oxide precursor from 0 to 24 h (Fig. 8). This is because the small oxynitride particles tend to be more soluble in the borosilicate frit and more oxidized in the condition of the heat-treatment at 800°C in air. However, the $L^*$, $b^*$ and $C^*$ values increased by over-glazing, as compared with those of pigment powders. This is because more light gets into the particle of the pigment, when the refractive index of the binder (the borosilicate glass) is near to that of the pigment. As the result, the more light of some wavelengths was absorbed selectively, and the more light of the remaining wavelength was reflected. It led to the increase of the $L^*$, $b^*$ and $C^*$ values.

4. Conclusions

The pigments containing tantalum(V)-based oxynitrides have been synthesized by firing in $\text{N}_2$ without flowing ammonia. This simple synthetic technique is more suitable to the production of the Ta-based oxynitride pigments on a large scale than the conventional ammonolysis method. The planetary ball millings for the oxide precursors decreased the particle size of Ta(V)-based oxynitride ($\text{Sr}^{1,1}_{x}\text{La}_{x}\text{TaO}_{2+x}\text{N}_{1+x}$) and improved the chroma ($C^*$) of the pigments. However, the smaller oxynitride particles with brighter color were apt to be soluble and oxidized in the borosilicate frit in the case of the application to over-glaze color.

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