Improvement of chroma of tantalum(V) nitride pigment by low-temperature oxidation treatment

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Tantalum(V) nitride (Ta3N5) pigment have attracted considerable attention as an alternative candidate for the colors of the cadmium base. The improvement of chroma of the pigment is necessary to raise the charm as the color. In this study, the Ta3N5 pigment was prepared by heat-treatment for mixed powders of Ta(V) oxide, aluminum nitride and potassium fluoride in nitrogen gas which kept supplied during the synthesis until it got cooled to room temperature. The pigment prepared in such completely inert atmosphere had slightly dull color. However, the chroma of the pigment was largely improved by a subsequent low-temperature oxidation treatment.

Key-words : Tantalum nitride, Ta3N5, Pigment, Non-toxic, Oxidation, Chroma

Inorganic pigments are commonly used in many industrial fields. The inorganic pigments are available at low cost in respect to organic pigments. Especially in the glass and ceramic industries, there is no alternative to the inorganic pigments for coloring.

The non-toxic tantalum(V) nitride (Ta3N5) pigments have attracted considerable attention as an alternative candidate for the colors of the toxic cadmium base (CdSe1−xSx). Ta3N5 is generally obtained as a reddish powder by ammonolysis of tantalum oxide (Ta2O5) powder with ammonia gas.1,2) However, it is difficult to produce a large amount of the Ta3N5 powder by ammonolysis, because the reaction rate of ammonia gas and the tantalum-based oxide is generally very low.

We have synthesized tantalum nitride and oxynitrides using aluminum nitride (AlN) as the agent for nitridation of Ta-based oxides without flowing ammonia.3,4) This synthetic technique leads to a safer preparation of the Ta-based nitride and oxynitrides in a shorter time as compared to the ammonolysis. It is a cost-effective way suitable for an industrial scale production of the powders containing Ta(V)-based nitride or oxynitrides. At present, the improvement of chroma of the Ta3N5 pigments is necessary in particular to raise the charm as the color. Effect of subsequent oxidation process after the synthesis in nitrogen atmosphere on chroma of the Ta3N5 pigments was investigated in this study.

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(C*) can be formulated as $C^* = [(a^*)^2 + (b^*)^2]^{1/2}$. The hue angle (h) could be calculated as $h = \tan^{-1}(b^*/a^*)$.

The Ta$_3$N$_5$ pigment (A) was synthesized by firing the mixed powder of Ta$_2$O$_5$ and AlN with KF at 780°C for 3 h in nitrogen gas which kept supplied during the synthesis until it got cooled to room temperature. It was confirmed that the pigment (A) was composed of Ta$_3$N$_5$, K$_6$Ta$_{10.8}$O$_{30}$ and a small amount of AlN residue by XRD as shown in Fig. 1. Figure 2(a) shows the powder (A) fired at 780°C for 3 h in nitrogen atmosphere and the powder (B) prepared by oxidizing the powder (A) at 320°C for 10 min in air. The coexisting phases of K$_6$Ta$_{10.8}$O$_{30}$ and AlN are colorless and does not absorb light in the visible region, because the band gap of K$_6$Ta$_{10.8}$O$_{30}$ and AlN are 3.635$^9$ and 6.03 eV$^9$, respectively. The reddish color of the powders is ascribed to Ta$_3$N$_5$. The powder (B) had the brighter color than the powder (A). Figure 2(b) shows the diffuse reflectance spectra of the powder (A) and (B). The reflectance in a long wavelength range of the visible light increased by the oxidation treatment. Moreover, the spectrum of the powder (B) featured the steeper absorption edge than that of the powder (A). The XRD pattern did not changed before and after the subsequent heat-treatment even by oxidation at 500°C for 10 min in air.

Figure 3 shows the change in chroma of the powder by oxidizing at 250–500°C for 10 min in air. The chroma started to increase from 250°C and reached the maximum at 320°C. It decreased gradually when oxidized at higher temperatures. It became apparent that short oxidation processing around 300°C was effective to improve chroma of the powder.

Figure 4 shows the change in hue angle (h) of the powder by oxidizing at 250–500°C for 10 min in air. The hue angle changed to lower values by the oxidation in the temperature range of 280–430°C. In other words, the powder changed in a more reddish color by the oxidation of 280–430°C. This resulted from the increase in reflectance in a long wavelength range of visible light as shown in Fig. 2(b).

The broadening of diffraction profiles in XRD measurements depends on instrumental factors and the characteristics of crystalline materials. The characteristics of crystalline materials affecting the broadening are chiefly crystallite size and internal strain. If the instrumental factors causing the broadening can be excluded, the breadth ($\beta$) of an XRD peak profile is generally expressed as follows:

$$\beta = \beta_c + \beta_s.$$ 

In the limiting case of pure crystallite size broadening, the breadth ($\beta_c$) is related to the effective crystallite size $\bar{c}$, the X-ray wavelength $\lambda$ and the Bragg angle $\theta$ by the equation:

$$\beta_c = \lambda / \bar{c} \cos \theta.$$
For pure strain broadening, the breadth ($b_s$) is related to the effective strain ($\eta$) and the Bragg angle ($\theta$) by the equation:\(^{11)}

$$b_s = \eta \tan \theta.$$

The breadths of the diffraction peak profiles of Ta$_3$N$_5$ in this study are proportional to the strain in/on Ta$_3$N$_5$ grains, because the grain size of Ta$_3$N$_5$ (the crystallite size of the Ta$_3$N$_5$ grains) does not probably change before/after the oxidation at such low temperatures around 300°C. The breadths ($b_s$) of X-ray diffraction peaks (020) and (110) before (A) and after the oxidation (B) were calculated as the integral widths using the integral intensities of the diffraction peak profiles as summarized in Table 1. The integral widths ($b_s$) got narrow by the low-temperature oxidation at 320°C. The reduction in the integral widths probably reflect the relaxation of the distortion of the Ta$_3$N$_5$ crystals prepared in nitrogen atmosphere by annealing with slight surface oxidation at 320°C. The increase of reflectance in a long wavelength range of visible light and the change to the steeper absorption edge of the reflectance spectrum might result from the relaxation of the strain in/on the Ta$_3$N$_5$ grains by annealing with the low-temperature oxidation. The large difference in oxygen content of Ta$_3$N$_5$ grains in the powder (A) and (B) was not observed in the EDS analysis [oxygen content in Ta$_3$N$_5$; (A) 9.5 ± 1.3, (B) 10.7 ± 2.3 at %]. However, atmospheric oxygen is more likely to have an influence on the improvement of the chroma, because the improvement of chroma was not observed when similar subsequent heat-treatment was conducted in nitrogen atmosphere. Moreover, the difference in grain size and morphology before and after the subsequent heat-treatment was not recognized at all in TEM observation. As a result of EDS analysis in TEM, fluorine was included in K$_8$Ta$_{10.8}$O$_{30}$ (1–2 at% F) partially and not in Ta$_3$N$_5$. The other F-containing phases could not be found in the EDS analysis.

The Ta$_3$N$_5$ pigment prepared in the completely inert (nitrogen) atmosphere had slightly dull color. However, the chroma of the pigment was largely improved by a subsequent low-temperature oxidation treatment. The improvement was more likely to be brought by the relaxation of the strain in/on the Ta$_3$N$_5$ grains with the treatment.

### Table 1. Integral widths of X-ray diffraction peaks (020) and (110) of Ta$_3$N$_5$ before (A) and after the low-temperature oxidation at 320°C (B)

|       | $b_s$ (020) | $b_s$ (110) |
|-------|------------|------------|
| A     | 9.13       | 6.16       |
| B     | 8.53       | 6.07       |

### References

1. G. Brauer, J. R. Weidlein and J. Strahle, *Z. Anorg. Allg. Chem.*, 348, 298–308 (1966).
2. H. P. Letschert and W. Voigt, *Japanese Patent*, P2000-247614A (2000).
3. M. Ohashi and T. Sugiyama, *J. Ceram. Soc. Jpn.*, 121, 397–400 (2013).
4. M. Ohashi, K. Kusumoto and K. Kato, *J. Ceram. Soc. Jpn.*, 126, 959–962 (2018).
5. G. Zhang, W. Jiang and S. Yu, *Mater. Res. Bull.*, 45, 1741–1747 (2010).
6. Q. Guo and A. Yoshida, *Jpn. J. Appl. Phys.*, 33, 2453–2456 (1994).
7. L. Alexander, *J. Appl. Phys.*, 21, 126–136 (1950).
8. L. Alexander, *J. Appl. Phys.*, 25, 155–161 (1954).
9. W. H. Hall, *P. Phys. Soc. Lond. A*, 62, 741–743 (1949).
10. F. W. Jones, *Proc. R. Soc. Lon. Ser.-A*, 166, 16–43 (1938).
11. A. R. Stokes and A. J. C. Wilson, *P. Phys. Soc.*, 56, 174–181 (1944).