Influence of nitrides on synthesis of tantalum(V) oxynitride (TaON) by heat-treatment without flowing ammonia

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Ta(V) oxynitride (TaON) powders for new pigments were prepared by heat-treatment for mixed powders of Ta(V) oxide, nitrides and alkaline fluorides in nitrogen atmosphere without flowing ammonia. This synthetic method is an eco-friendly and cost-effective way suitable for an industrial scale production of the powder containing TaON with the color of 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 pigments, and to substitute pigments containing harmful elements. In this study, influence of nitrides as the agent for nitridation of tantalum oxide on the formation of TaON in the synthetic method was examined. It has become apparent that the formation of TaON was promoted by using silicon nitride (Si3N4) for nitridation of tantalum oxide.

Inorganic pigments serve the purpose of imparting color to various compounds. In comparison with organic pigments, inorganic pigments are generally better able to withstand the influence of sunlight and chemical exposure. 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.

Tantalum(V) oxynitride (TaON) is generally obtained as a yellowish powder by ammonolysis of tantalum oxide (Ta2O5) powder with ammonia containing a little moisture. TaON has the same structure as baddeleyite, monoclinic ZrO2. The ammonolysis of the tantalum-based oxide are generally very ammable. They make it difficult to promote mass production of the powders containing TaON are given in Table 1. The starting compositions for synthesis of the powders containing TaON are given in Table 1. The starting powders were mixed for 6h in ethanol using a Si3N4 planetary mill. After drying, the mixed powders were fired at 800–950°C for 3–6h in nitrogen atmosphere.

Table 1. Compositions of starting mixtures for TaON-containing powder synthesis (mass%)

| Sample | Ta2O5 | ZrO2 | Si3N4 | AlN | LiF | NaF | KF |
|--------|-------|------|-------|-----|-----|-----|----|
| 35     | 61.1  | —    | —     | —   | —   | —   | 10.5 |
| 35Z05  | 59.3  | 0.9  | —     | 29.0 | —   | —   | 10.8 |
| 35Z10  | 57.6  | 1.8  | 31.1  | —   | 1.7 | —   | 11.0 |
| 35Z20  | 53.6  | 3.7  | 31.1  | —   | —   | —   | 11.6 |
| 122    | 61.7  | —    | 32.6  | 1.6 | 4.1 | —   | —   |
| 122Z10 | 58.1  | 1.8  | 34.2  | 1.7 | 4.2 | —   | —   |
| 312    | 59.6  | —    | 31.5  | —   | —   | —   | 8.9 |

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Crystalline phases were identified by an X-ray diffractometer (XRD: Cu Kα, 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 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).

The chromaticity of powders and over-glaze colors are estimated using the chroma (C*

Figure 1 shows the X-ray diffraction (XRD) pattern of sample 35 prepared using AlN as the nitriding agent without m-ZrO₂ and heated at 800°C for 6 h. The strong peaks of TaON appeared with the weak peaks of NaTaO₃, Na₃Ta₂O₁₁, Na₂Ta₆Si₂O₁₅ and Si₃N₄ for the fired powders. In the case of using Si₃N₄ as the nitriding agent, the formation of TaON occurred even without m-ZrO₂ addition as seed crystals. The larger amount of TaON was formed in the samples used Si₃N₄ as the nitriding agent (122 and 122Z10) in comparison with the samples used AlN (35Z05, 35Z10 and 35Z20).

Oxidation reactions of Si₃N₄ (1) and AlN (2) are characterized by the standard free energies \( \Delta G^\circ \) and \( \Delta G^\circ_2 \), respectively.

\[
1/3\text{Si}_3\text{N}_4(s) + \text{O}_2(g) \rightarrow \text{Si}_2\text{O}_3(s) + 2/3\text{N}_2(g) \quad (1)
\]

\[
4/3\text{AlN}(s) + 2\text{O}_2(g) \rightarrow 2/3\text{Al}_2\text{O}_3(s) + 2\text{N}_2(g) \quad (2)
\]

The values of \( \Delta G^\circ_1 \) (−579.7 kJ/mol) and \( \Delta G^\circ_2 \) (−612.3 kJ/mol) around the reaction temperature (1200 K) were obtained using JANAF tables. When the standard free energy of the oxidation reaction of TaON (3) is \( \Delta G^\circ_3 \), the reactions between Ta₂O₅ and the nitrides (Si₃N₄ and AlN) are characterized by the free energies, \( \Delta G^\circ_3 - \Delta G^\circ_1 \) (4) and \( \Delta G^\circ_3 - \Delta G^\circ_2 \) (5). The value of \( \Delta G^\circ_3 \) is unknown, because the standard Gibbs’s energy of formation for TaON is not found in JANAF tables and other literatures.

\[
4/3\text{TaON}(s) + \text{O}_2(g) \rightarrow 2/3\text{Ta}_2\text{O}_3(s) + 2/3\text{N}_2(g) \quad (3)
\]

\[
1/3\text{Si}_3\text{N}_4(s) + 2/3\text{Ta}_2\text{O}_3(s) \rightarrow 4/3\text{TaON}(s) + \text{SiO}_2(s) \quad (4)
\]

\[
4/3\text{AlN}(s) + 2/3\text{Ta}_2\text{O}_3(s)
\rightarrow 4/3\text{TaON}(s) + 2/3\text{Al}_2\text{O}_3(s) + 2/3\text{N}_2(g) \quad (5)
\]

The nitriding ability of AlN for Ta₂O₅ is higher than that of Si₃N₄, because the value of \( \Delta G^\circ_2 - \Delta G^\circ_3 \) is lower than that of \( \Delta G^\circ_3 - \Delta G^\circ_2 \). Si₃N₄ seems to be suitable for the nitriding agent of the formation of TaON, because the nitriding ability of Si₃N₄ for Ta₂O₅ is moderately low as compared to that of AlN.

However, the chromaticity of 122 (\( L^*a^*b^* = 71.0/−3.0/19.0 \)) and 122Z10 (\( L^*a^*b^* = 68.6/−4.0/17.1, C^* = 17.6 \)) heated at 950°C for 3 h were lower than that of 35Z05 prepared using AlN as the nitriding agent (\( L^*a^*b^* = 71.6/10.0/36.5 \)).

Figure 3 shows the XRD patterns of 122Z10 and 122 samples prepared using Si₃N₄ as the nitriding agent with and without m-ZrO₂ and heat-treated at 950°C for 3 h. The strong peaks of TaON appeared with the peak weak peaks of NaTaO₃, Na₂Ta₂O₁₁, Na₂Ta₆Si₂O₁₅ and Si₃N₄ for the fired powders. In the case of using Si₃N₄ as the nitriding agent, the formation of TaON occurred even without m-ZrO₂ addition as seed crystals. The larger amount of TaON was formed in the samples used Si₃N₄ as the nitriding agent (122 and 122Z10) in comparison with the samples used AlN (35Z05, 35Z10 and 35Z20).

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 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).

The chromaticity of powders and over-glaze colors are estimated using the chroma (C*

Figure 1 shows the X-ray diffraction (XRD) pattern of sample 35 prepared using AlN as the nitriding agent without m-ZrO₂ and heat-treated at 800°C for 6 h. The strong peaks of Ta₂N₅ appeared with the peaks of KTaO₃, K₃Ta₂O₅ and AlN for the fired powder. There were no peaks of TaON in the XRD pattern. The resultant powder of 35Z05 heat-treated at 800°C for 3 h had a bright yellowish hue (\( L^*a^*b^* = 71.6/10.0/36.5 \)).

Figure 3 shows the XRD patterns of 35Z05, 35Z10 and 35Z20 prepared using AlN as the nitriding agent with and without m-ZrO₂ and heat-treated at 800°C for 6 h. The strong peaks of TaON were shifted to lower angles with larger amounts of m-ZrO₂ addition. The resultant powder of 35Z20 heat-treated at 800°C for 3 h had a bright yellowish hue (\( L^*a^*b^* = 71.6/10.0/36.5 \)).
(122Z10) and the powders oxidized at 700–900°C. Numbers in parenthesis indicate $L^*$ (brightness). The $b^*$ value increased as the oxidation temperature increased from 700 to 850°C, and decreased conversely by the further increase of the oxidation temperature to 900°C. There was no significant change in the $a^*$ value. The change in XRD pattern by oxidation of 122Z10 synthesized by the heat-treatment at 950°C for 3 h are given in Fig. 6. The intensity of TaON peaks was gradually weakened by a rise in oxidation temperature from 800 to 900°C and oxidation products (Li$_{1.60}$Ta$_{2.04}$O$_{18}$ and Ta$_2$O$_5$) appeared above 800°C. The decrease in the $b^*$ value by the increase of the oxidation temperature from 850 to 900°C is attributed to the oxidation of TaON. The greenish hue of the non-oxidized powder seems to be due to an impurity Nb(O$_{1-x}$N$_{y}$) with black color. The black color interferes with that of TaON to give the observed greenish hue of the TaON + Nb(O$_{1-x}$N$_{y}$) mixture. The increase in the $b^*$ value with increasing the oxidation temperature from 700 to 850°C (the change in color of the powder from dull greenish yellow to bright yellow) resulted from the oxidation of the black Nb(O$_{1-x}$N$_{y}$) to the white Nb$_2$O$_5$.

The XRD pattern of sample 312 prepared using Si$_3$N$_4$ and KF without m-ZrO$_2$ and heat-treated at 950°C for 3 h was presented in Fig. 7. The formation of TaON was also confirmed in the 312 synthesized using KF as with the 122 synthesized using LiF and NaF.

The TaON powders [35Z05, 122Z10 and 122Z10(800OX) (122Z10 oxidized at 800°C)] were mixed with a borosilicate frit at the weight ratio of 1:9, and applied on glazed ceramic plates at 800°C (Fig. 8). The $L^*$,$a^*$,$b^*$ and $C^*$ values of the over-glazed 35Z05 pigment (a) were 82.7/−8.9/40.1 and 41.1, respectively. The color of the over-glazed 35Z05 (a) was bright greenish yellow. The $L^*$,$a^*$,$b^*$ and $C^*$ values of the over-glazed 122Z10 (b)
prepared using Si₃N₄ as the nitriding agent were 64.2/−5.3/24.3 and 24.9, respectively. The color of the over-glazed 122Z10 (b) was duller than that of the over-glazed 35Z05 (a) prepared using AlN as the nitriding agent. The plate over-glazed using 122Z10 and oxidized at 800°C is shown in Fig. 8(c). The \( L^*a^*b^* \) values of the over-glazed 122Z10(800OX) (c) were 74.9/−7.2/31.5 and 32.3, respectively. The chromaticity of the over-glazed 122Z10 was improved by oxidation for the powder containing TaON.

The powders containing TaON were synthesized by firing in \( N_2 \) without flowing ammonia. This simple synthetic technique is more suitable to the production of the powders containing TaON on a large scale than the conventional ammonolysis method. When aluminum nitride was used as the nitriding agent in the synthesis, the formation of TaON occurred with the addition of m-ZrO₂ as a seed crystal, but the formation of Ta₃N₅ occurred without the addition. The large amount of TaON was formed even without the addition of m-ZrO₂ when silicon nitride was used as the nitriding agent. It has become apparent that the formation of TaON was promoted by using silicon nitride (Si₃N₄) for nitridation of tantalum oxide in comparison with the case of using aluminum nitride.

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