Effect of mineralizers on formation of tantalum(V) nitride (Ta₃N₅) with heat-treatment of tantalum(V) oxide-aluminum nitride mixtures without flowing ammonia

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Ta(V) nitride (Ta₃N₅) powders for non-toxic red pigments were prepared by heat-treatment of mixed powders of Ta(V) oxide, aluminum nitride and alkali fluorides in a nitrogen atmosphere without flowing ammonia. This synthetic method is environmentally friendly as compared with such conventional methods as ammonolysis with large amounts of flowing ammonia. In this study, the effect of mineralizers on formation of tantalum(V) nitride (Ta₃N₅) with heat-treatment of Ta₂O₅–AlN mixtures was examined. The results revealed that the formation of Ta₃N₅ was promoted by co-doping with potassium fluoride (KF) and lithium fluoride as mineralizers. Doping with KF led to improvement of the chroma of the powders by controlling the grain growth of Ta₃N₅ and developing the facets of the grains.

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Inorganic pigments are commonly used in many industrial fields. In comparison with organic pigments, inorganic pigments are generally better able to withstand the influence of sunlight and chemical exposure. Cadmium sulfoselenide pigments (CdSe₧₋ₓSₓ) have been widely used for various applications as vivid red pigments. However, the transition metals or heavy metals such as Cd, Se, Pb, Co and Sb are toxic. When the metal contents exceed a certain level, they pose a serious threat to the environment and human health. Therefore, the vivid inorganic pigments containing the toxic elements have been limited in many countries and strong demand has emerged for environmental-friendly alternatives.

Tantalum(V) nitride (Ta₃N₅) is generally obtained as a reddish powder by ammonolysis of tantalum oxide (Ta₂O₅) powder with ammonia.¹,² This powder has been considered as a replacement for such traditional toxic pigments as Cd compounds, because tantalum compounds are non-toxic. It has also been studied as a visible light-driven photocatalyst with good reduction and oxidation potentials.³ Ta₃N₅ is non-toxic, however, is generally produced by flowing large amounts of ammonia which is both toxic and flammable. Moreover, it is difficult to produce a large quantities of Ta₃N₅ powder, 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.⁴ This synthetic technique leads to safer preparation of Ta-based nitride and oxynitrides in a shorter time as compared with preparation by ammonolysis. It is a cost-effective way suitable for industrial-scale production of powders containing Ta(V)-based nitride or oxynitrides. We also revealed that the formation of TaON was promoted by using silicon nitride (Si₃N₄) as a substitute for AlN in the nitridation of the tantalum oxide.⁵ AlN was consequently used as a nitriding agent to promote the formation of Ta₃N₅ in this study. The effect of mineralizers on formation of tantalum(V) nitride (Ta₃N₅) by heat-treatment of Ta₂O₅–AlN mixtures in this synthetic method was examined. The formation of Ta₃N₅ was promoted by the addition of potassium fluoride (KF) as a mineralizer, and formation of TaON was simultaneously suppressed. Moreover, the formation of Ta₃N₅ was accelerated by co-doping with potassium fluoride (KF) and lithium fluoride (LiF).

Ta₂O₅ powder (TAO02PB, Kojundo Chemical Lab. Co., Ltd., Saitama, Japan) was used as the starting powder. AlN powder (E, Tokuyama Corp., Tokyo, Japan) was used as the nitriding agent. Potassium fluoride (KF) powder (KKH07XB, Kojundo Chemical Lab. Co., Ltd., Saitama, Japan), lithium fluoride (LiF) powder (Wako Pure Chemical Industries, Ltd., Osaka, Japan) and sodium fluoride (NaF) powder (Wako Pure Chemical Industries, Ltd., Osaka, Japan) were added as mineralizers to promote a reaction of Ta₂O₅ with AlN.

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The starting compositions for synthesis of the powders containing Ta₃N₅ are given in Table 1. Ta₂O₅, AlN and alkaline fluorides were mixed at 18.2, 60.5 and 21.3 mol %, respectively, for all samples. The starting powders were mixed for 6 h in ethanol using a Si₃N₄ planetary mill. After drying, the mixed powders were fired at 750 and 800°C for 3 h under a nitrogen flow.

The crystalline phases present were identified using an X-ray diffractometer (XRD: Cu Kα, 40 kV, 200 mA, RINT-2550, Rigaku Denki Co., Ltd., Tokyo, Japan). Photographs of the Ta₃N₅ particles were obtained using a transmission electron microscope (TEM: JM2010, JEOL, Tokyo, Japan).

More than 100 particles of the samples were counted on TEM micrographs for the determination of the minor axis size and the major axis size of the columnar Ta₃N₅ particles. 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) and the color coordinates (H V/C) in the Munsell system. The chromaticity of the powders was estimated using the chroma (C*). The chroma (C*) can be formulated as $C^* = \sqrt{(a^*)^2 + (b^*)^2}$.

Figures 1(a)–1(c) show the X-ray diffraction (XRD) patterns of the samples heat-treated at 750 and 800°C for 3 h with the single addition of KF, LiF or NaF. Strong peaks of Ta₃N₅ appeared with the peaks of KTaO₃, K₆Ta₁₀.₈O₃₀ and AlN for the fired powder with the addition of KF [Fig. 1(a)]. There were no peaks of TaON in the XRD pattern. In the case of the addition of LiF [Fig. 1(b)], a large amount of Ta₃N₅ was also formed, but formation of TaON occurred simultaneously. A large quantity of TaON was formed with Ta₃N₅ when NaF was added [Fig. 1(c)]. Sodium tantalates were formed as byproducts in large quantities with the addition of NaF.

Figures 2(a) and 2(b) show the X-ray diffraction patterns of the samples co-doped with KF + LiF or KF + NaF and heat-treated at 750 and 800°C for 3 h. Formation of Ta₃N₅ was promoted by co-doping with KF + LiF, while the for-

| Table 1. Compositions of starting mixtures for Ta₃N₅-containing powders (mass %) |
|---------------------------------------------------------------|
| Ta₂O₅ | AlN | alkaline fluorides |
|---------------------------------|-----|-------------------|
| TN-K | 68.4 | 21.1 | 10.5(KF) |
| TN-L | 72.6 | 22.4 | 5.0(LiF) |
| TN-N | 70.4 | 21.7 | 7.8(NaF) |
| TN-KL | 70.4 | 21.7 | 5.5(KF) + 2.4(LiF) |
| TN-KN | 69.6 | 21.5 | 4.3(KF) + 4.7(NaF) |

Fig. 1. X-ray diffraction patterns of TN-K (a), TN-L (b) and TN-N (c) heat-treated at 750 and 800°C for 3 h.

Fig. 2. X-ray diffraction patterns of TN-KL (a) and TN-KN (b) and heat-treated at 750 and 800°C for 3 h.
formation of TaON was controlled [Fig. 2(a)]. Formation of byproducts was also suppressed by co-doping with KF + LiF. In the case of co-doping with KF + NaF, formation of TaON was adversely promoted [Fig. 2(b)].

Figures 3(a) and 3(b) show the resultant powders heat-treated at 750°C for 3 h and 800°C for 3 h. The L*a*b* and Munsell color coordinate data for the powders are summarized in Table 2. The powders doped with KF or KF + LiF had a strong reddish tinge and high chroma (C*), because they consisted mainly of Ta3N5 with a yellowish-red hue and did not include TaON, which has a dull yellowish hue. The other powders were dull yellowish-red (brown), possibly due to coexistence of Ta3N5 and TaON. The coexistence of TaON was responsible for the strong yellowish hue of the samples with NaF added [TN-N(800-3), TN-KN(800-3), in particular]. It is also considered that the difference in chroma among the samples depended on the crystallinity and particle size of the powders,6,7) TN-K (KF) and TN-L (LiF), which exhibit a large difference in chroma, were observed in TEM [Figs. 4(a)–4(d)]. The Ta3N5 particles have columnar shapes with preferential growth along the [100] direction, as shown in Fig. 4(e) [The structure of Ta3N5 is orthorhombic (a = 3.8862 Å, b = 10.2118 Å, c = 10.2624 Å) and consists of TaN6 octahedra, with a structure similar to that of anisolite (Ti3O5)].8) Figures 4(e) and 4(f) show the

![Diagram](image)

**Fig. 3.** Photographs of Ta3N5-containing powders heat-treated at 750°C for 3 h (a) and 800°C for 3 h (b).

**Fig. 4.** TEM images of Ta3N5 grains and Ta3N5 grain size distribution of TN-K(800-3) (a, c, e) and TN-L(800-3) (b, d, f).

|                  | L*   | a*   | b*   | C*   | Munsell  |
|------------------|------|------|------|------|-----------|
|                  |      |      |      |      | H         | V    | C     |
| TN-K(750-3)      | 59.9 | 39.8 | 33.7 | 52.2 | 9.0R      | 6.0  | 10.3  |
| TN-KL(750-3)     | 54.2 | 36.8 | 28.3 | 46.5 | 8.4R      | 5.4  | 9.2   |
| TN-KN(750-3)     | 55.1 | 32.0 | 26.1 | 41.2 | 9.0R      | 5.4  | 8.1   |
| TN-L(750-3)      | 49.6 | 19.8 | 18.2 | 26.9 | 0.8YR     | 4.9  | 5.0   |
| TN-N(750-3)      | 58.4 | 25.3 | 25.2 | 35.7 | 0.9YR     | 5.8  | 6.8   |
| TN-K(800-3)      | 55.3 | 38.0 | 29.7 | 48.2 | 8.5R      | 5.5  | 9.6   |
| TN-KL(800-3)     | 51.0 | 33.6 | 24.5 | 41.6 | 8.1R      | 5.0  | 8.3   |
| TN-KN(800-3)     | 55.0 | 14.0 | 17.3 | 22.2 | 3.2YR     | 5.4  | 4.0   |
| TN-L(800-3)      | 48.2 | 19.0 | 15.1 | 24.3 | 9.6R      | 4.7  | 4.6   |
| TN-N(800-3)      | 52.9 | 15.8 | 16.8 | 23.0 | 2.0YR     | 5.2  | 4.3   |
Ta\textsubscript{3}N\textsubscript{5} grain size distributions of TN-K(800-3) (e) and TN-L(800-3) (f). The average size of the Ta\textsubscript{3}N\textsubscript{5} grains in TN-K doped with KF and in TN-L doped with LiF are represented by minor axis sizes of 35 ± 16 nm (TN-K) and 69 ± 23 nm (TN-L), and major axis sizes of 122 ± 56 nm (TN-K) and 188 ± 79 nm (TN-L), respectively. The Ta\textsubscript{3}N\textsubscript{5} grains in TN-K commonly displayed discernible crystal edges and facets as shown in Fig. 4(c) as compared with the grains in TN-L doped with LiF shown in Figs. 4(b) and 4(d). The small particle sizes and well-developed facets of the Ta\textsubscript{3}N\textsubscript{5} grains as shown in Figs. 4(a) and 4(c) contributed to the high chroma of TN-K powders and TN-KL powders doped with K.

Powders containing Ta\textsubscript{3}N\textsubscript{5} were synthesized by firing Ta\textsubscript{2}O\textsubscript{5}–AlN mixtures doped with alkali fluorides in N\textsubscript{2} without flowing ammonia. The effect of mineralizers on formation of tantalum(V) nitride (Ta\textsubscript{3}N\textsubscript{5}) by heat-treatment of Ta\textsubscript{2}O\textsubscript{5}–AlN mixtures was examined. It was revealed that formation of Ta\textsubscript{3}N\textsubscript{5} was promoted by co-doping potassium fluoride (KF) and lithium fluoride (LiF) as mineralizers. Furthermore, doping with KF led to the improvement of the chroma of the powders by controlling the grain growth of Ta\textsubscript{3}N\textsubscript{5} and developing the facets of the grains.

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. Hara, G. Hitoki, T. Tanaka, J. N. Kondo, H. Kobayashi and K. Domen, Catal. Today, 78, 555–560 (2003).
4) M. Ohashi and T. Sugiyama, J. Ceram. Soc. Jpn., 121, 397–400 (2013).
5) M. Ohashi, K. Kusumoto, T. Sugiyama and K. Kato, J. Ceram. Soc. Jpn., 124, 959–962 (2016).
6) Y. I. Kim, Ceram. Int., 40, 5275–5281 (2014).
7) S. Nobuoka, Shikizai Kyokaishi, 55, 758–765 (1982).
8) J. Strahle, Z. Anorg. Allg. Chem., 402, 47–57 (1973).