Synthesis of tantalum(V)-based nitride and oxynitrides on aluminum nitride particles and its application to over glaze color

Masayoshi OHASHI¹ and Toyohiko SUGIYAMA

National Institute of Advanced Industrial Science and Technology (AIST), 2266–98 Shimoshidami, Moriyama-ku, Nagoya 463–8560, Japan

Ta(V)-based nitride and oxynitrides have been prepared by solution-precipitation process in a liquid phase formed on the surface of aluminum nitride particles during heat-treatment in nitrogen atmosphere. This eco-friendly and cost-effective process is suitable for an industrial scale production of the pigments containing Ta(V)-based nitride or oxynitrides, compared to the conventional method such as ammonolysis of tantalum oxide with flowing large amounts of ammonia. The pigment synthesized by this method was mixed with a borosilicate frit to prepare an over glaze color. The color applied on glazed ceramic plates showed the brilliant color of yellowish red-yellow with high chroma values. They have a potential to be employed as non-toxic ceramic pigments, and to substitute pigments containing harmful elements.

Key-words : Tantalum nitride, Oxynitride, Ceramic pigment, Aluminum nitride, Non-toxic

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1. Introduction

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

Tantalum nitride (Ta3N5) and oxynitride (TaON) are generally obtained as reddish and yellowish powders by ammonolysis of tantalum oxide (Ta2O5) powder with ammonia.¹,²) The reddish and yellowish powders have been considered promising replacements that could eliminate toxic metals (e.g. Cd and Se from cadmium-based pigments) emissions to the environment, because tantalum compounds are non-toxic. It is also reported that they can be tuned from yellow to deep red by chemical composition adjustments.³)

While Ta3N5 and the oxynitrides are surely non-toxic, it is problem that the ordinary production process of Ta3N5 and the oxynitrides needs large amounts of toxic and flammable ammonia flow. In addition, the ammonolysis of Ta2O5 is very sluggish. They make it difficult to promote mass production of the (ox)nitride pigments.

N-We have synthesized tantalum nitride and oxynitrides using aluminum nitride (AIN) as nitrogen source for nitridation of Ta2O5 and Sr-La-Ta oxides without flowing ammonia. This synthetic technique leads to a safer preparation of Ta-based nitride and oxynitrides in a shorter time as compared to the preparation by ammonolysis. It seems to be an eco-friendly and cost-effective way suitable for an industrial scale production of the pigments containing Ta(V)-based nitride or oxynitrides.

Note

¹ Corresponding author: M. Ohashi; E-mail: masa-ohashi@aist.go.jp

2. Experimental

The Ta2O5 powder (TAO02PB, Kojundo Chemical Lab. Co., Ltd., Saitama, Japan) was used as a starting powder. 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 Ta2O5 with AlN. The La2O3 powder (LA001PB, Kojundo Chemical Lab. Co., Ltd., Saitama, Japan) and the SrCO3 powder (Yoneyama Chemical Industries Ltd., Osaka, Japan) were used for the synthesis of LaTaO7-SrTa2O7 mixtures which were precursors of Sr1-xLa-xTaO2-N1+x. The LaTaO7-SrTa2O7 mixtures with La/(Sr + La) ratios of 0.2, 0.5 and 0.8 were synthesized by firing at 1350°C for 6 h after mixing the three kinds of powders (SrCO3, La2O3 and Ta2O3) at the molar ratios of Sr/La:Ta = 0.8:0.2:1.0, 0.5:0.5:1.0 and 0.2:0.8:1.0.

The starting compositions for syntheses of the pigments containing Ta-based nitride or oxynitrides are given in Table 1. The starting compositions for syntheses of the pigments containing Ta-based nitride or oxynitrides are given in Table 1.

| Sample/mass % | Ta2O5 | LaTaO7-SrTa2O7 | ZrO2 | AlN | KF |
|---------------|-------|----------------|------|-----|----|
| 27p           | 68.3  | —              | —    | 21.1| 10.6|
| 35Z05         | 59.4  | —              | 0.9  | 28.9| 10.8|
| X80           | —     | 57.5 [La/(Sr + La) = 0.8] | —    | 31.0| 11.5|
| X50           | —     | 57.2 [La/(Sr + La) = 0.5] | —    | 31.2| 11.6|
| X20           | —     | 56.9 [La/(Sr + La) = 0.2] | —    | 31.4| 11.7|

Table 1. Compositions of starting mixtures for Ta nitride and oxynitride-containing pigments

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for 3 h in nitrogen atmosphere. The resultant powder (35Z05)
the cross section of the resultant powder (35Z05)
scanning transmission electron microscopy (STEM) mode for
method.

bonded slices and prepared by the conventional ion milling
the resultant powder, the disk specimen were cut out from the
Ti slices, and bonded together. For cross-sectional TEM study of
at 800°C for 3 h) were dispersed in epoxy resins, put between two
EDS elemental mapping was carried out to visualize the ele-
mental distribution in the cross section of the resultant powder
(35Z05) fired at 800°C for 3 h in nitrogen atmosphere. The resultant powder (35Z05 fired
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Ti slices, and bonded together. For cross-sectional TEM study of the resultant powder, the disk specimen were cut out from the bonded slices and prepared by the conventional ion milling method.

3. Results and discussion

3.1 Ta3N5

Figure 1 shows the XRD patterns of 27p heated at 700–900°C
for 6 h. Crystalline phases present in 27p heat-treated at 700–
900°C for 6 h with an addition of KF are summarized in Table 2. The L* a*
b* color coordinate data of the powders are also summarized in Table 2. The L* a*
b* values decreased with increasing firing temperature. The highest a* value and the highest chroma ([(a*)2+(b*)2]1/2) was obtained for the sample fired at 750°C. An over-glaze color was prepared by mixing the powder of 27p fired at 750°C with a borosilicate frit at the weight ratio of 1:4. The color was applied on a glazed ceramic plate and
fired at 600°C in air [Fig. 2 (27p)]. The over-glazed color showed a vivid yellowish red after firing. The L* a*
b* values and the Munsell HV/C values were 51.3/45.4/53.6 and 1.2YR 5.1/12.7, respectively. The a* and b* values of the over glazed color were much higher than those of the original powder of 27p fired at 750°C.

3.2 TaON

The formation of TaON was observed with K-tantalates in 35Z05 after firing above 750°C by XRD. The formation of Ta3N5 was observed in the experiment of ZrO2 free composition, as same as observed in 27p. However, TaON was formed in 35Z05 by the addition of a small amount of monoclinic ZrO2 (m-ZrO2). The m-ZrO2 acted as seed crystals for the formation of TaON in 35Z05, because TaON has a monoclinic structure similar to m-ZrO2 (baddeleyite). The resultant powder of 35Z05 heat-treated at 800°C for 3 h had a bright yellowish hue. A small amount of Ta3N5 appeared together with TaON in 35Z05 fired at 850°C for 3 h. The charge reduction of Ta(V) occurred in 35Z05 firing at 900°C, and Ta3N5 was formed. TaON was not observed in 35Z05 fired at 800–900°C in the case of no addition of KF.

EDS elemental mapping was carried out to visualize the elementaldistribution in the cross section of the resultant powder (35Z05) fired at 800°C for 3 h in nitrogen atmosphere. Figure 3 shows EDS maps of Al, Ta, K and Ta+K with a STEM image. The analysis of the cross section of the 35Z05 resultant powder revealed the presence of a thin layer including large amounts of Ta and K on the surface of a spherical AlN particle. This result implies the reaction and precipitation of TaON and K-tantalates in a liquid on AlN particles during firing. Figure 4 shows the schemes regarding the formation of TaON on AlN particles. A liquid phase was first made from the starting powders (KF, Ta2O5 etc.) on AlN particles. Ta2O5 and AlN subsequently dissolved into the liquid phase as cations and anions, and TaON and K-
tantalates precipitated on the AlN particles as observed in Fig. 3. Monoclinic ZrO$_2$ (m-ZrO$_2$) mainly acted as a seed for the formation of TaON. Ta$_3$N$_5$ in 27p seemed to be formed on AlN particles without m-ZrO$_2$ in the similar process. It can therefore be presume that the Ta(V)-based nitride and oxynitride are synthesized via the solution-precipitation process in the liquid phase formed on the surface of AlN particles in this synthetic method.

The color of the resultant powder (35Z05) was greenish yellow due to occurrence of TaON. The 35Z05 fired at 800°C for 3 h was mixed with a borosilicate frit at the weight ratio of 1:4 to prepare an over glazed color. The color was applied on a glazed ceramic plate and fired at 750°C in air (Fig. 2 (35Z05)). The L* a* b* values and the Munsell HV/C values of the over-glazed 35Z05 were 80.5/−7.4/42.8 and 0.2GY 8/5.7, respectively.

3.3 Sr$_{1−x}$La$_x$TaO$_{2−x}$N$_{1+x}$ perovskites was observed in Xseries samples (X20, X50 and X80) fired above 800°C. It tended to start at a lower temperature in the sample with smaller $x$ value (e.g. X20). The oxynitride perovskites with bright yellowish colors were obtained by firing at 900°C for 3 h.

The X series samples fired at 900°C for 3 h was applied on a glazed ceramic plates in a similar manner as above (35Z05). The color coordination values of the X series pigments applied on glazed ceramic plates in L* a* b* and Munsell systems are summarized at Table 3. The L* value decreased and the a* value increased with increasing the $x$ value. Over-glazed X series samples had brilliant colors, varying from reddish yellow to yellow, depending on the $x$ value (cf. Fig. 2).

Figure 5 shows the reflectance spectra of the over-glazed color prepared from X series pigments as well as those prepared from 27p (Ta$_3$N$_5$) and 35Z05 (TaON). The edges of the reflectance spectra were shifted to shorter wavelengths with decreasing $x$ values. It corresponds to the color variation from reddish yellow to yellow. The spectrum of 27p featured the steep edge. It resulted in the higher Munsell chroma value, 12.7 of 27p. Color in the range from yellow to

| Firing conditions | Main phase | L*  | a*  | b*  | Munsell (HV/C) |
|-------------------|------------|-----|-----|-----|----------------|
| 27p 750°C-6 h     | Ta$_3$N$_5$| 51.3| 45.4| 53.6| 1.2YR 5.1/12.7 |
| 35Z05 800°C-3 h   | TaON       | 80.5| 7.4 | 42.8| 0.2GY 8/5.7    |
| X80 900°C-3 h     | Sr$_{1−x}$La$_x$TaO$_{2−x}$N$_{1+x}$ ($x = 0.8$) | 62.4| 55.9| 9.1YR 6.3/9.9  |
| X50 900°C-3 h     | Sr$_{1−x}$La$_x$TaO$_{2−x}$N$_{1+x}$ ($x = 0.5$) | 67.8| 65.4| 9.8YR 6.8/10.7 |
| X20 900°C-3 h     | Sr$_{1−x}$La$_x$TaO$_{2−x}$N$_{1+x}$ ($x = 0.2$) | 75.5| 63.9| 4.3Y 7.6/9.2   |

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yellowish red can be easily arranged only by the adjustment of the starting compositions and firing condition in N$_2$ atmosphere in this synthetic technique.

4. Conclusions

The pigments containing tantalum(V)-based nitride or oxy-nitrides have been synthesized by firing in N$_2$ atmosphere instead of ammonia flowing. This simple synthetic technique is suitable to the production of the Ta-based (oxy) nitride pigments on a large scale compared to the conventional ammonolysis method. The pigments synthesized by this method showed the brilliant color of yellowish red to yellow. They are useful for ceramic applications, replacing ceramic pigments containing toxic-metals.

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