Kinetic Investigation into the Formation of Titanium Nitride from Titanium Dioxide by Carbonitrization

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The production of titanium nitride by direct reaction of nitrogen and titanium oxide requires unrealistic conditions such as a high nitrogen partial pressure and quite low oxygen partial pressure. In contrast, titanium nitride can be prepared experimentally by carbonitrization with commercial grade nitrogen gas. However, because carbonitrization is a gas-solid reaction, a high reaction rate is not expected. I carried out a kinetic investigation into the carbonitrization reaction to clarify the titanium nitride formation mechanism. To achieve this, I used simultaneous thermal gravimetric and differential thermal analysis (TG-DTA). The ratio of carbonitrization to other reactions, such as the combustion of carbon, was determined using reaction enthalpies from a thermodynamic literature. Using kinetic analysis, the net carbonitrization reaction was found to comprise a series of consecutive reactions, and the order of the reaction was determined to be $n = 0.1$ to 0.5. That is, the reaction of titanium nitride formation is controlled by diffusion processes, as indicated by the dimension of $l^n$, and is dependent on the previous combustion process, the combustion of carbon.

1. Introduction:

Titanium nitride (TiN) is mechanically and chemically stable and has been applied to tools and machine components (such as automotive parts) to modify their surface properties. Usually, TiN surface layers are produced on titanium materials by a nitriding process using flowing pure nitrogen gas or ion nitridization. Moreover, the TiN layers have also been coated on non-titanium materials by physical vapor deposition (PVD) and ion nitridization. Recently, the applications of TiN have expanded beyond tools and machine components to high-performance materials such as electronics devices. TiN is effective material in metallurgical field to produce metallic titanium by thermal decomposition at low temperatures ($<3000$ K) compared to those required for typical titanium compounds, and we have previously demonstrated this kind of production process using metallic titanium.

Commonly, the produced TiN layers, except for those generated by deposition, are formed on the mother material, such as metallic titanium, by the nitriding reaction. Therefore, the metallic titanium is the starting material for TiN production. From an economic viewpoint, because the production of metallic titanium is a multistage process and requires much electricity, the use of titanium oxide as the starting material for TiN production is more economical than using metallic titanium. However, it is experimentally difficult to satisfy the thermodynamic conditions for the direct nitridization of titanium dioxide. Furthermore, the reaction requires a high nitrogen partial pressure and a quite low oxygen partial pressure, as indicated by thermodynamic data. On the other hand, carbonitrization has been already demonstrated by White et al., and the production of TiN has been experimentally performed at 1423 K. In our previous study, we also experimentally demonstrated the production of TiN from titanium dioxide by carbonitrization at 1910 K. In our experiment, the carbonitrization was performed using a commercial grade nitrogen gas, and the activity of carbon was controlled using a carbon crucible. However, because the carbonitrization process to produce TiN is preceded by a solid-gas reaction, the mass production of TiN in this way requires very long reaction times. In the present study, I have aimed to clarify the carbonitrization reaction mechanism to attain a reasonable reaction time for the mass production of TiN.

2. Approximation of the enthalpy using TG-DTA measurements

The carbonitrization reaction was investigated in situ by a thermal gravimetric and differential thermal analysis (TG-DTA, NETZSCH-Gerätebau, STA-449 F3 with a rhodium furnace and thermogravimetric sensor) under flowing nitrogen. Figure 1(a) shows a schematic diagram of a typical DTA that has two sensors (thermocouples) for the reference and the measured samples, which are located in furnaces.
During the measurement, when reactions occur in the measured sample, the thermal behavior can be seen as a difference in the electric motive force (EMF) between the two sensors. Figure 1(b) shows a schematic diagram of a typical TG where one sensor is used for the measured sample in the furnace. In the present study, because carbonitization requires a large mass-volume of the sample, as shown by our previous research\textsuperscript{12}, the TG measurements were made using a device with a large sample holder. The applied equipment has another sensor located close to the sample in the furnace, as shown in Fig. 1(b), and the difference in the temperature between the sample and furnace can be measured in calculated DTA (c-DTA\textsuperscript{®}) mode. Although in c-DTA\textsuperscript{®} mode only the different temperatures between the sample and furnace are measured, the enthalpy change of the reacting sample can be determined as shown in Fig. 2, which shows the melting behavior of nickel. The measurement temperature was corrected from the intersection (onset) point of the melting temperatures of several metals (indium, zinc, and silver) as a linear function using literature references\textsuperscript{16}. Next, the sensor sensitivity was corrected by using the enthalpies of melting of the metals. Here, Fig. 3(a) shows the heat flow (temperature difference) of a typical DSC, and Fig. 3(a) shows a typical DTA plotted against temperature difference as a function of a time. In the case of the DSC trace shown in Fig. 3(a), the heat flow curve takes the form of a peak at a certain time (or temperature as a function of time) because the generated heat from the reacted sample is immediately released to the heat server to equilibrate the temperature between the reference and sample. On the other hand, in the case of DTA, as shown in Fig. 3(b), the heat flow curve is not sharp like that of DSC because there is no route for heat exchange, and the generated heat is not released theoretically. Admittedly, the sensors are in contact with the thermocouple surrounding the furnace, so some heat is released, as shown by the real curve in Fig. 3(b). However, the released heat is quite small in the DSC measurement. Therefore, the DTA curve can be theoretically interpreted as an ideal curve, as shown in Fig. 3(b).

That is, although the DSC curve indicates the magnitude of the enthalpy changes estimated from the peak shape per reaction time ($\Delta H/\Delta t$) to that of limited heat change per unit time ($dH/dt$) using the cumulative curve estimation. In fact, the function ($dH/dt$) is corrected by a proportionality factor $\lambda dT/dx$). From this relationship, in the case of small differences in temperatures accompanied by a small heat change measured by DTA having thermally long pathway, $x$, the heat release can be quite small or neglected. Therefore, the DTA curve is interpreted as a cumulative curve. However, for a rapid reaction, such as the melting of a pure material, because the enthalpy change at the time is large, the heat releasing behavior is significant, as shown in Fig. 2, and the difference between the DSC and DTA curves is small. For a continuous reaction with a small enthalpy change, (such as the combustion of carbon or a titanium oxidation whose reaction rate varies with several factors, such as a temperature, activity, and partial pressure), because the heat release is small at all times, the DTA curve can be interpreted as an ideal curve, as in Fig. 3(b). The temperature dependence of the sensor sensitivity has been investigated\textsuperscript{16,17} and is known to be a linear function that depends on the thermal conductivity of the measurement system, furnace, and other factors. Therefore, we experimentally investigated the temperature dependence of the sensor sensitivity for the equipment using the enthalpies of melting of metals and the cumulative curve assumption. Here, although the thermal analysis curve is known to be constituted and effected by some factors\textsuperscript{18,19}, the closely corrections for the curve is not performed in the present study by the mentioned reason. Figure 4 shows the temperature dependence of a ratio of reproducibility (traceabilities) of the melting enthalpies of the metals. The ratio of reproducibility is defined as the ratio of the enthalpy changes estimated from the peak shape per reaction time ($H_{area}/I$) to that of limited heat change per unit time ($dH/dt$) using the cumulative curve estimation. In fact, the function ($dH/dt$) is corrected by a proportionality factor $\lambda dT/dx$.

Fig. 2 Differential temperature analysis curve for the melting of nickel measured using the large sample pan type DTA.

![Fig. 2](image-url)

Fig. 3 Schematic diagrams of theoretical differential thermal analysis curves of (a) conventional differential scanning calorimetry (DSC) and (b) conventional DTA.
constituted by linear approximations for the enthalpy and temperature changes per certain time. The ratio of reproducibility is showed within 80 to 90%, and the 10 to 20% loss in the reproducibility is due to heat release and cumulative error by the linear approximations.

3. Experimental Details

Titanium dioxide powder (Anatase, reagent grade, Wako Pure Chemical Industries, Ltd.) was used as the starting material. The powder of roughly 1500 mg in weight was inserted into a carbon crucible of 16 mm in outside diameter, 12 mm in inside diameter, 40 mm in length and roughly 6400 mg in weight. The prepared sample was heated to 1923 K at various heating rates (from 0.04 to 0.3 K/s, i.e., 2.5 to 20 K/min) using a simultaneous thermal analysis system. A thermogravimetric type pin sensor with an S-type thermocouple was used. The carbon crucible of the sample was placed on an alumina slip-on plate of 17 mm in diameter. Temperature and sensitivity calibrations were carried out using the melting behavior of metals (In (only for temperature calibration), Zn, Ag, and Ni) in an alumina crucible. The furnace was filled with a commercial grade nitrogen gas (G2 grade, <0.3 ppmO2) that flowed at a rate of 0.17 to 1.5 mL/s (10 to 90 mL/min) from the top of the furnace, while gas was added from bottom of the furnace at 0.17 mL/s (10 mL/min) to protect the balance mechanism of the equipment. The nitrogen gas flow from the top of the furnace was guided by an alumina tube of 1 mm in an inner diameter and 2 mm in an outer diameter to the carbon crucible to react the sample directly. The carbon crucible was weighed before and after the experiment, and the carbon crucible was re-used in the next experiment.

4. Results

4.1 Surface morphologies of the products

Figure 5(a) to (h) show the surface morphologies produced by the carbonitization from the titanium dioxide at various heating rates and nitrogen gas flow rates. In particular, Fig. 5(c) shows a yellow surface, indicating the formation of the product, and we have previously investigated this yellow material to be titanium nitride by X-ray diffractomet-

![Graph](image)

**Fig. 4** Temperature dependence of the reproducibility of the cumulative heat change for the common heat change (estimated by the peak area) using the large sample pan type DTA.

![Images](image)

**Fig. 5** Surface morphologies of the products after carbonitization at various heating and gas flow rates.
Table 1 lists ratios of weight changes for the various heating rates and gas flow rates. Here, the "crucible/total" ratio indicates a reactivity of solid carbon for all samples, and the "TiO$_2$/crucible" ratio indicates the reactivity of the main sample (i.e., titanium dioxide) for the combustion of carbon determined from the weight changes. By comparison, although the carbon combustion in the case of 5 K/min is the most intense, the reacted titanium dioxide for the combusted carbon is not significant than under other conditions. The ratio of "loss/initial state of TiO$_2$" also indicates the reactivity of the titanium dioxide. Although the ratio of produced titanium dioxide is the highest in the case of 5 K/min, that of 10 mL/min also shows higher reactivity and a higher ratio of the reacted titanium dioxide to combusted carbon. This means that, although the case of 20 mL/min (gas flow rate) indicates a higher reaction rate than in the other cases, the 10 mL/min (gas flow rate) can be regarded as a more environmentally friendly condition.

### 4.2 Separation of the complex reactions

Complex reactions occur in the reaction cell (carbon crucible) such as the reduction of titanium dioxide, nitridization of reduced titanium, and oxidation of carbon. The enthalpies and weight changes, $\Delta H$ and $\Delta w$, during the nitridization and oxidation of titanium (as differences of left-hand and right-hand sides of the reactions) have been investigated previously$^{[14]}$, as shown in eqs. (1), (2).

$$\text{Ti} + \frac{1}{2}\text{N}_2(g) = \text{TiN},$$

$$\Delta H = -336 \text{ kJ/mol (exothermic), } \Delta w = +14 \text{ g/mol}$$

$$\text{Ti} + \text{O}_2(g) = \text{TiO}_2,$$

$$\Delta H = -939 \text{ kJ/mol (exothermic), } \Delta w = +32 \text{ g/mol}$$

$\Delta H$ is the enthalpy change of the reactions, and $\Delta w$ is the weight change before and after the reaction, respectively. Similarly, the enthalpies and weight changes for the oxidation of carbon have been investigated previously$^{[14]}$, as shown in eqs. (3) to (5).

$$\text{C} + 2\text{O}_2(g) = 2\text{CO}_2(g),$$

$$\Delta H = -396 \text{ kJ/mol (exothermic), } \Delta w = -12 \text{ g/mol}$$

$$2\text{C} + \text{O}_2(g) = 2\text{CO}(g),$$

$$\Delta H = -230 \text{ kJ/mol (exothermic), } \Delta w = -24 \text{ g/mol}$$

$$\text{C} + 2\text{CO}_2(g) = 2\text{CO}(g),$$

$$\Delta H = +166 \text{ kJ/mol (endothermic), } \Delta w = -12 \text{ g/mol}$$

The enthalpies and weight changes of the carbonitization in various reaction patterns can be expressed as follows from the previous relationships.

$$2\text{TiO}_2 + \text{N}_2(g) + 2\text{C} = 2\text{TiN} + 2\text{CO}_2(g)$$

$$\Delta H = +415 \text{ kJ/mol (endothermic), } \Delta w = -60 \text{ g/mol}$$

$$2\text{TiO}_2 + 2\text{N}_2(g) + 4\text{C} = 2\text{TiN} + 4\text{CO}(g)$$

$$\Delta H = +746 \text{ kJ/mol (endothermic), } \Delta w = -36 \text{ g/mol}$$

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<thead>
<tr>
<th>Heating rate/K-min$^{-1}$</th>
<th>crucible/total</th>
<th>TiO$_2$/crucible</th>
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Table 1: Weight ratios before and after the experiments at various heating rates and gas flow rates.
2TiO₂ + N₂(g) + 4CO(g) = 2TiN + 4CO₂(g)

\[ \Delta H = +83 \text{ kJ/mol (endothermic)} \]

\[ \Delta w = -84 \text{ g/mol} \] (8)

The enthalpies and weight changes of the reactions are connected by the following relationships.

\[ \Delta w = x + y \] (9)

\[ \Delta H = Ax + By \] (10)

Here, \( x \) and \( y \) are weight changes of the carbonitrization expressed by eqs. (6) to (8) and the oxidation of carbon represented by eqs. (3) to (5). Then, the weight change, \( \Delta w \), is represented by the summation shown by eq. (9). On the other hand, \( A \) and \( B \) are proportionality factors for the enthalpy changes of the carbonitrization and the oxidation of carbon, respectively. Then, the enthalpy change, \( \Delta H \), is expressed by a summation of the multiplied factors shown by eq. (10). Figures 7(a) and (b) show the enthalpy and weight changes per unit time for the reactions at 5 K/min and 10 mL/min investigated from the TG-DTA curves, respectively. Figure 7(c) shows weight changes for the carbonitrization reaction (6) and the formation of carbon dioxide (3) using eq. (9), (10) per unit time. Figure 7(d) shows the cumulative weight changes for the total sample and carbon crucible, estimated using the relationship in Fig. 7(c). Figures 8(a) to (h) show the cumulative weight changes for the whole sample and the carbon crucible at the various conditions. The inserted values near the cumulative curves in the figures are the weight change ratios of combusted carbon in the carbon crucible and the reacted sample to the total sample weight before and after the experiment. Here, the plausibility of the assumed carbonitrization and combustion reactions could be confirmed from the differences in the inserted balance ratio of weight loss. When the weight losses match well, as shown in Fig. 8, the assumed reactions are consistent with the actual reactions. From our investigation, the carbonitrization estimated by the reaction (6) is plausible in many cases, and the combustion of carbon estimated from the carbon dioxide formation reaction (3) is also plausible. In Figs. 8(c) and (h), although two kinds of carbonitrization (6), (7) are shown in the figures, the carbonitrization estimated by reaction (7) is more plausible than that of reaction (6) from the comparison as minor cases in the present study. The difference in the estimated reactions is only difference of the produced carbon oxides (carbon dioxide or carbon monoxide). However, the produced carbon monoxide is influenced to the reactivity, as expressed by reaction (8). Therefore, the high reactivity is performed in the case of 5 K/min and 20 mL/min by the formation of carbon monoxide. However, the influence of this reaction seems to be limited in the present study, because relationships (9), (10) are not satisfied by reaction (8).

5. Discussion

From the carbonitrization process, we separated the combustion of carbon, as shown in Fig. 8. The curves for the formation of titanium nitride contain unique inflection points. In these cases, complex reactions are expected. Moreover, because the carbonitrization reaction forming the titanium nitride is influenced by the combustion of carbon, it is reasonable to consider that the carbonitrization is a composite reaction. From the shapes of reaction curves having inflection points, it is reasonable to consider that the carbonitrization occurs via consecutive reactions. A typical consecutive reaction can be expressed by eq. (11).

\[ A \xrightarrow{k_1} B \xrightarrow{k_2} C \] (11)

Here, \( C \) is the reactivity of the final product (titanium nitride) and is determined from the weight loss of carbon and total sample from the reaction curves. On the other hand, \( B \) can be regarded as a previous reaction necessary for carbonitrization. Because the estimated carbonitrization process (6) requires direct contact of the carbon with the titanium dioxide, we can conveniently assume an adsorption reaction of carbon on the titanium dioxide, following eq. (12).
Here, the equation shows the transport of carbon from the surface on the graphite crucible to the titanium dioxide, and it is independent on the weight and enthalpy change (Δw = 0, ΔH = 0). Moreover, the applied high purity nitrogen gas in the present study includes a low concentrate oxygen, whose partial pressure reaches 10^{-4} to 10^{-5}, and the oxygen expressed in the eq. (12) came from the oxygen contained in the atmosphere gas of the commercial grade nitrogen gas as one of impurity elements. B is conveniently interpreted as the carbon adsorbed on the titanium dioxide. When the formation of titanium nitride can be regarded as an irreversible reaction under a suitable atmosphere control, the reaction rate constant, k, is treated as \( k_3 \gg k_4 \). Equation (11) can be expressed as eq. (13)

\[
\frac{dC_A}{dt} = -kC_A^n \tag{14}
\]

When the order of reaction, \( n \) (\( n \neq 1 \)), is determined, \( C_A \) can also be expressed by eq. (15). Here, the rate constant of the reaction, \( k \), is assumed to be an Arrhenius type factor comprising a frequency factor (as the square root of temperature) and the activation energy.

\[
C_A^{-n+1} = (-n+1)k_1t + C_{A_0}^{-n+1} \tag{15}
\]

The \( C_B \) can also be expressed by eq. (16).

\[
\frac{dC_B}{dt} = k_1C_A^n - (k_2 + k_3)C_B^{n-1} \tag{16}
\]

Here, \( C_A \) and \( C_B \) are obtained, and \( C_C \) can be obtained from eq. (17).

\[
C_C = 1 - C_A - C_B \tag{17}
\]

Equation (16) is a function of \( C_A \) and \( C_B \) and can be solved numerically using Euler’s law. Figures 9(a) to (h) compare the temperature dependence of the kinetically estimated curves of titanium nitride formation plotted from eq. (16), (17) and the separated weight loss of the same reaction determined from the enthalpy and weight changes (9), (10) at various experimental conditions. Here, Fig. 9(e) is a blank, and 1551 Kinetic Investigation into the Formation of Titanium Nitride from Titanium Dioxide by Carbonitization.
because the phenomena of initiation reaction was missed by technical problem, as shown in Fig. 8 (e). Both curves for the formation of the titanium nitride are in good agreement. The assumed orders of reaction, activation energies, and frequency factors from the kinetic investigation are listed in Table 2. Here, the equilibrating concentration in the table will be explained later. From the kinetic investigation, the determined order of reaction of the previous reaction, which is assumed to be the transportation of carbon to the surface of titanium dioxide, is 1, and the determined factor indicates a type of reaction control. Moreover, the order of reaction of the main reaction, which is assumed to be the carbonitration reaction producing titanium nitride, was determined to range from 0.1 to 0.5, which indicates diffusion control. In particular, the determined range of 0.1 to 0.5 is interpreted as corresponding to grain boundary diffusion. Here, because the adsorption is interpreted as a surface reaction on the graphite crucible and titanium dioxide, the determined dimension order of reaction of 1 is plausible. On the other hand, the carbonitization to produce the titanium nitride occurs on the surface of titanium dioxide. For the reaction to progress, the produced titanium nitride and an unreacted titanium dioxide on the surface must be replaced by diffusion; thus, the determined dimension, <$\leq 1$, seems to be plausible. Here, the relationship between the activation energies was determined to be $E_1 < E_2$ and $E_1 < E_3$ for the rate constants $k_1$, $k_2$, and $k_3$. This indicates that the adsorption of carbon on the titanium dioxide surface, as indicated by $E_1$, occurs more readily than the re-adsorption of carbon on the graphite surface and carbonitration to produce titanium nitride. Moreover, because the rate of titanium nitride production depends on the diffusion rate of the produced titanium nitride and the unreacted titanium oxide, the relationship is reasonable. For the frequency factors, although it is expected that the factors relate to the gas flow and heating rates, the dependence is not clear from the experiments in the present study. On the other hand, because the frequency factors are independent of the gas flow rate, the rate-determining step of the reaction is not the delivery of nitrogen gas within the experimental conditions. Finally, the equilibrating concentrations were conveniently determined to range from 0.1 to 0.2 (10 to 20%). Although it is expected that the production of titanium nitride reaches completion after long reaction times, the produced titanium nitride is within 6%, as listed in Table 2, for the range from 10 to 20% in range of the present study. It is reasonable to consider that the range from 10 to 20% is a limitation of the reaction expressed by the eq. (13). This means that the estimated reaction pass way expressed by the eq. (13) is not enough to completion of the titanium nitride formation, and next pro-
cess, whose reaction controls all of the reactions, after the reaction "C" is hidden in the range of present study. Thus, although the production of titanium nitride controlled by the reaction "C" and the next reaction of "C" depends on the counter-diffusion processes of the produced titanium nitride and unreacted titanium oxide, the difference of the diffusion process is dependent on the length or a boundary layer of the diffusion path. Detail of the diffusion processes to completion of titanium nitride formation will be investigated in next research. Consequently, the application of finely powdered titanium dioxide could be effective in decreasing the length of the diffusion path, and the use of a mixture made of carbon and titanium dioxide could also be effective in increasing the reaction area for the practical mass production of titanium nitride.

6. Conclusions

I experimentally investigated the mechanism of titanium nitride production by carbonitization using simultaneous thermogravimetric and differential thermal analysis. Titanium nitride was produced from titanium dioxide by carbonitization under a flowing nitrogen atmosphere at various heating and gas flow rates. The most valuable condition to produce titanium nitride was 5 K/min for the heating rate and 20 mL/min for the gas flow rate in the present condi-

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Table 2 Kinetic factors assumed for the consecutive reaction at various heating rates and gas flow rates.
tions. The carbonitrization reaction producing titanium nitride was accompanied by the combustion of carbon, and the net carbonitrization from the single TG and DTA curves was determined from the differences in the enthalpies and weight changes of the reactions. The estimated reactions were matched well to the weighed weight changes before and after the experiments. The net carbonitrization reaction was also kinetically investigated. The reaction curves for net carbonitrization showed several inflection points and thus, the reaction was modeled as a series of consecutive reaction, i.e., a multistep reaction process. The determined dimensions for the order of reactions were 1 and 0.1 to 0.5 for the precursor reaction, which is interpreted as the adsorption of carbon, and main carbonitrization reaction, respectively, and these reaction orders correspond to reaction control and diffusion control, respectively. Moreover, from the comparison of activation energies of the reactions, because that of the carbonitrization was higher than those of the other reactions, the rate of titanium nitride production was determined to be the rate determining step.

REFERENCES

16) DIN 51007: Thermal analysis; differential thermal analysis; principles, standard by Deutsches Institut Fur Normung E.V. (German National Standard), 06/01/1994.