Controlling the synthesis of TaC nanopowders by injecting liquid precursor into RF induction plasma

Takamasa Ishigakia,*, Seung-Min Oha,b, Ji-Guang Lia, Dong-Wha Parkb

aAdvanced Materials Laboratory, National Institute for Materials Science, Namiki 1-1, Tsukuba-shi, Ibaraki 305-0044, Japan
bDepartment of Chemical Engineering, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, Korea

Received 30 September 2004; revised 16 November 2004; accepted 17 November 2004
Available online 28 January 2005

Abstract
Thermal plasma processing has been used to synthesize nano-size powders through the condensation of reactant species from a vapor phase. Further development of this synthesis method will require the careful selection of an appropriate precursor and precise control of products species and their particle sizes. Direct introduction of liquid mist into thermal plasma gives us a wider choice of precursors than does vapor-phase precursor injection and lets us inject the precursors in larger amounts. In the present work, nano-size tantalum carbide powder was prepared from a liquid precursor, tantalum ethoxide Ta(OC₂H₅)₅, by using r.f. thermal plasma. The liquid precursor was atomized to generate micron-sized mist droplets, and the mist was introduced into plasma. This atomized precursor evaporated quickly in the high-temperature plasma flame, and nanoparticles were formed as temperature decreased. The process was controlled by changing the hydrogen addition, process pressure, carrier gas flow rate for mist injection, and quenching condition. Adding hydrogen improved the powder quality by removing solid carbon, but excess hydrogen suppressed the formation of tantalum carbide. The quenching conditions gave significant effects on the reduction of particles size by two thirds and yielded average particle sizes as small as 8 nm.

Keywords: Tantalum carbide; Nanopowder; Induction thermal plasma; Liquid precursor; Hydrogen addition

1. Introduction
Tantalum carbide (TaC) is a promising material due to its hardness (≈3000 kg/mm²) [1], its high melting point (≈4000 °C) [1], its resistance to chemical attack and thermal shock [1,2], its superconductivity [2], and its catalytic activity [3]. It is used to make cemented-carbide cutting tools [4,5], as a hard coating on metal to increase the corrosion and wear resistance [6], and to make low-electron- emissivity parts, crucibles for molten metals, and high-temperature heating elements [7]. It is also expected to be used as a catalyst for ammonia decomposition and hydrogen dissociation [3,8]. TaC is conventionally prepared by using graphite or amorphous carbon in a carburization reaction with tantalum or tantalum oxide [1,2,4,9,10], this process is usually carried out at temperatures so high (about 1700 °C) [2] that the sub-carbide Ta₂C is also formed [9]. Problems with residual oxygen and exaggerated particle growth have also been encountered in the carburization of tantalum oxide [4]. Although the self-propagating, high-temperature synthesis (SHS) process used for the carburization reaction was improved recently, the co-formation of Ta₂C still made it hard to obtain a pure TaC powder [10,11]. The reaction temperature needed to form TaC was reduced, improving impurity control, by instead pyrolyzing a polymeric precursor derived from tantalum alkoxide. The mechanical properties of the carbide made this way are severely reduced at higher temperatures [12], however, and the final product contains excessive amounts of free carbon because the precursor polymer is insoluble in common solvents [13].

We have therefore developed a thermal plasma process for the preparation of TaC nanopowder. Thermal plasma processing technology—some characteristics of which are a high temperature, a high energy density, and a very short processing time (of the order of 10 ms)—has attracted
considerable attention because of its great potential for production of nano-sized powder. Various types of precursors can be rapidly vaporized in thermal plasma region, and this vaporization is followed first by homogeneous nucleation from the vapor phase and then by grain growth. Grain growth can be suppressed, resulting in the formation of nano-sized powders, by removing the reactant from the plasma region rapidly [14–16]. A wide range of nanopowders have recently been prepared by using a thermal plasma process [17–20], but there are few reports of the production of TaC nanopowder [21].

We used tantalum ethoxide as the precursor because the precursor in the thermal plasma should be completely vaporized in a very short residence time. The evaporation of raw materials can be improved by injecting them into the plasma flame as a mist, and hydrogen species derived from the alkoxide promote heat transfer to particles and thus increase the particle temperature. As there is not an appropriate Ta compound with a vapor pressure high enough, mist injection in thermal plasma has a big advantage when we want to prepare nanoparticles by condensation from a vapor phase. We demonstrated the simple preparation of tantalum carbide nanopowder from alkoxide precursor. The composition and morphology of synthesized powder was controlled by adjusting the hydrogen addition, process pressure, carrier gas flow, and quench condition. In this report, we emphasize the importance of the cooling condition in controlling the nucleation and growth condition and the resultant particle size.

2. Experimental

2.1. Preparation of TaC nanopowder

The experimental apparatus we used for preparing TaC nanopowder is shown in Fig. 1. A mist of tantalum ethoxide [Ta(OC2H5)5] (> 99.9%, Showa Denko K.K., Tokyo, Japan) was generated by using Ar gas with an atomization probe (Model SA-635, TENKA Plasma Systems, Sherbrooke, QC, Canada) and was injected at the center of the plasma torch (Model PL-50, TENKA Plasma Systems, Sherbrooke, QC, Canada). Because tantalum ethoxide is quite sensitive to moist air and is easily hydrolyzed, it was stored in a glove box filled with argon and transferred to the atomization probe by using a peristaltic pump that was also set in a glove box. The atomized precursor was rapidly dissociated in the plasma plume, and gaseous products were condensed by rapidly cooling the plasma flow in the reactor chamber. A typically 40-kW plasma was generated using a 2-MHz power supply (Nihon Koshuha Co. Ltd, Yokohama, Kanagakwa, Japan). Additive hydrogen was mixed to the sheath Ar gas, and the quenching rate was increased by radially injecting Ar or He at the bottom of plasma torch through eight 1.0-mm holes perpendicular to the torch axis [22–24]. The evacuated gas stream containing product powder was passed through a filter assembly. Typical experimental conditions are listed in Table 1. After the plasma powder synthesis, an Ar-0.5 vol% O2 gas mixture was flown for 1 h to prevent the serious oxidation of very reactive nanoparticles. Then the synthesized powders were collected in air at the reactor wall and filter.

2.2. Analytical methods

An X-ray diffractometer (Cu Kα radiation)(RINT 2000, Rigaku, Akishima, Tokyo, Japan) was used to analyze the phase composition. The phase composition was determined by using pre-determined mixtures of Ta, TaC, and Ta2O5 and comparing the (111) peak area of TaC with the (110) peak area of Ta and the (001) peak area of Ta2O5. Particle morphology was observed by using a transmission electron microscope (Model JEM-2000EX, JEOL, Akishima, Tokyo, Japan) and a scanning electron microscope (Model JSM-6340F, JEOL, Akishima, Tokyo, Japan). The particle size in synthesized powder was determined by measuring the dimensions of about 500 particles on SEM photos, and the amount of carbon was measured by using a carbon analyzer (Model EMIA-511, Horiba, Kyoto, Japan).

| Plasma power | 40 kW |
| RF frequency | 2 MHz |
| Reactor pressure | 400, 500, 600, 750 Torr |
| Plasma gas | Ar: 30 L/min |
| Sheath gas | Ar: 80 L/min + H2: 10, 15 L/min |
| Carrier gas | Ar: 3.0–6.8 L/min, CO2: 0.2 L/min |
| Precursor feed rate | 4.6–8.9 g/min |
| Tail quench gas | Ar-20 L/min, He-20 L/min |
3. Results and discussion

3.1. Effect of H₂ addition and H₂/Ta(OC₂H₅)₅ ratio on the reaction products

Chemical equilibrium composition, calculated by mini-
imization of the Gibbs’ free energy [25], was used to predict
effective process parameters for preparing TaC nanopowder
from Ta(OC₂H₅)₅. The equilibrium compositions calculated
for Ta(OC₂H₅)₅ decomposition and for the Ta(OC₂H₅)/H₂
system are shown in Fig. 2. Atomized precursor readily
dissociated in the thermal plasma plume and recombined to
form various products depending on additive gas and the
particle temperature, which depended on the process
parameters. We can see in Fig. 2(a), that solid-state TaC
could be produced over the wide temperature range from
1300 to 4400 K, and Ta₂O₅ at temperatures below 1300 K.
Carbon appeared as gaseous species, CO(g), CO₂(g), C(g),
C₂(g), Cₓ(g), CH(g), CH₂(g), C₂H(g), C₂H₂(g), and C₃H(g),
at temperatures over 3000 K, and below 3000 K these
species were solidified to carbon. The effect of added
hydrogen—50 mol H₂ per mol Ta(OC₂H₅)₅—is shown in
Fig. 2(b). Additive hydrogen caused the formation of
CₓHᵧ(g) compounds and rapidly decreased the carbon
content at temperatures over 2700 K and the TaC content
at temperatures over 3700 K. Gaseous Ta species were also
increased at temperatures over 4000 K because of the
decomposition of TaC by excess hydrogen. As shown in
Fig. 2(b), in the temperature range from 2700 to 3800 K the
only solid-state material was TaC. The calculation results
indicated that the adding of hydrogen would improve the
powder quality by removing carbon but that excessive
hydrogen would increase the Ta species content.

The grown nanopowder accumulated on the reactor wall
and filter. Because 60–70% of the powder was collected at the
reactor wall, all following references to powder in this paper
will actually be to powders collected at the reactor wall.

Increasing the molar ratio of H₂ to Ta(OC₂H₅)₅ increased
the TaC content by removing solid carbon. Thus, the TaC
content reached its maximum value, 97.4%, in run no. 6

---

**Table 2**

| No | Pressure (Torr) | Sheath gas (H₂) [L/min] | Ta(OC₂H₅)₅ Carrier [L/min] | Tail gas [L/min] | TaC | Ta | Ta₂O₅ | Collected at the reactor wall | Collected at the filter |
|----|----------------|-------------------------|---------------------------|-----------------|-----|----|-------|------------------|-----------------|
| 1  | 400            | 15                      | 6.2                       | 31              | 94.4| 1.0| 4.5   | 86.8            | 4.5             |
| 2  | 400            | 10                      | 6.0                       | 33              | 95.5| 0.7| 4.2   | 93.7            | 0.7             |
| 3  | 500            | 10                      | 6.0                       | 23              | 95.6| 0.0| 4.4   | 94.7            | 0.0             |
| 4  | 500            | 10                      | 5.9                       | 23              | 96.2| 0.0| 3.8   | 94.7            | 0.0             |
| 5  | 500            | 10                      | 6.1                       | 25              | 96.1| 0.0| 3.9   | 92.4            | 0.0             |
| 6  | 500            | 10                      | 6.2                       | 25              | 97.4| 0.0| 2.6   | 95.7            | 0.0             |
| 7  | 500            | 10                      | 6.0                       | 26              | 96.4| 0.0| 3.6   | 92.2            | 0.0             |
| 8  | 500            | 10                      | 6.3                       | 28              | 96.6| 0.4| 3.3   | 94.0            | 0.8             |
| 9  | 500            | 10                      | 6.0                       | 29 Ar-20        | 96.2| 0.0| 4.1   | 92.7            | 1.0             |
| 10 | 500            | 10                      | 5.7+CO₂-0.2               | 28              | 90.4| 0.0| 9.6   | 91.7            | 0.5             |
| 11 | 500            | 10                      | 3.0                       | 29              | 95.7| 0.3| 4.0   | 93.7            | 0.5             |
| 12 | 500            | 10                      | 3.6                       | 37              | 96.6| 0.9| 2.5   | 93.1            | 1.4             |
| 13 | 600            | 15                      | 6.8                       | 59              | 94.8| 2.6| 2.7   | 88.7            | 5.4             |
| 14 | 600            | 10                      | 6.5                       | 27              | 95.3| 0.0| 4.7   | 94.1            | 0.0             |
| 15 | 750            | 10                      | 5.6                       | 39              | 90.9| 0.5| 8.6   | 84.1            | 0.7             |

H/T: molar ratio of H₂ to Ta(OC₂H₅)₅.
(Table 2). Excessive hydrogen, however, enhanced the dissociation of TaC and the formation of Ta phase. From this experiment, the optimal molar ratio of excess hydrogen to Ta(OC₂H₅)₅ should be ≈ 25. The content of Ta phase was rapidly increased in runs no. 1 and 13 by the higher flow rate of additive hydrogen. These results indicate that additive hydrogen can improve particle heating by increasing heat transfer [26] and promote the dissociation of TaC by forming hydrocarbons.

3.2. Influence of plasma velocity on the particle size and constituent

Atomized precursor rapidly dissociated in the high-temperature region of plasma flame and recombined as the temperature decreased. Variation of plasma-generating pressure causes changes in plasma velocity and heat transfer [26]. Especially, the increased plasma velocity caused by the decrease of pressure gave rise to the change of particle size and reactant composition.

The particle size changed with the change of process pressure. SEM images of the powder confirmed that particle size increased with increasing pressure (Fig. 3). The growth of particles follows their nucleation from the vapor phase, and the longer flight times at the higher pressures give more time for crystal growth. The particle formation is initiated by the nucleation from a vapor phase, and the nucleation is followed by the in-flight particle growth. Thus, the increased plasma velocity results in the increase in cooling rate of plasma, and suppressed the particle size. The other interesting future in size distributions for the various pressures in Fig. 4 is that the decrease of pressure gave the narrowing of size distribution, as the plasma flow at the lower pressure is more strongly confined than that at the higher pressure.

Fig. 5 shows that the X-ray diffraction from TaC becomes narrow with the increase of process pressure from 400 to 750 Torr. The narrowing corresponds to the particle size increase shown in Fig. 3. Though the stoichiometric carbon content in TaC is 6.2 wt%, carbon content decreased when the process pressure was increased (Fig. 5). At 400 Torr the total carbon content was more than the stoichiometric content, while at 750 Torr the carbon content was substoichiometric (Fig. 6). The excessive carbon content should be attributed to free carbon formed through rapid quenching at low pressure. The carbon deficiency at high pressure, in contrast, could be due to lower conversion of carbon-containing species to TaC because the lower plasma velocity at the higher pressure reduced the cooling rate and promoted the formation of Ta₂O₅. As shown in Fig. 7, at 750 Torr well-faceted cubic TaC powder was synthesized because of the particle growth, while the Ta₂O₅ content was increased.

The flow of reactant species can also be controlled by the change of carrier gas flow rate, in this case the flow rate of mist-generation gas. When the flow rate of carrier gas was decreased, the X-ray diffraction of Ta₂O₅ phase increased.

![Fig. 3. TaC nano-size powders synthesized under various pressures.](image-url)
Because of restrictions due to the structure of the mist-generation probe, it was hard to remove the Ta$_2$O$_5$ phase by increasing the flow rate of the mist-generation gas. Trying to cool the plasma more rapidly, we added carbon dioxide, which has a large dissociation energy, to the mist-generation gas [27]. As shown in Fig. 7(c), however, adding even a small amount of CO$_2$ significantly decreased the TaC content and enhanced the formation of Ta$_2$O$_5$.

![Size distributions of TaC nano-size powders synthesized under various pressures.](image)

![X-ray diffractions of the powders synthesized under various pressures.](image)

![Carbon content in the powders synthesized under various conditions.](image)
3.3. Injection of tail quenching gas

From the same reason discussed in the preceding section, the particle seize decreases with the increase of the plasma cooling rate by injecting quenching gas into tail flame. This technique can be used to decrease the temperature locally in the injected region and control the chemical reactions there [24]. According to the report of Soucy et al. [24], injecting Ar at 20 L/min should have an adequate cooling effect. As shown in Fig. 9, however, the particles synthesized with the tail injection of Ar were not smaller than particles synthesized when it was not injected. The broadening of size distribution shown in Fig. 10 indicates the turbulence of flow induced by the Ar gas radial injection. When He, which has a thermal conductivity higher than that of Ar, was injected as the tail quenching gas, the TaC particles synthesized were much smaller than the size of those synthesized when no tail quenching gas was injected.

![Fig. 7. TEM image of plasma-synthesized TaC nano-size particles.](image)

![Fig. 8. X-ray diffractions of the powders synthesized under different carrier gas flow. (a) Ar-3 L/min, (b) Ar-6 L/min, (c) Ar-5.7 + CO2-0.2 L/min.](image)

![Fig. 9. TaC nano-size particles synthesized with and without tail injection gases (pressure, 500 Torr).](image)
4. Conclusions

Nano-sized tantalum carbide was easily prepared from atomized tantalum ethoxide by using r.f. induction plasma. Additive hydrogen improved the powder quality by forming hydrocarbons and thereby removing carbon from the reaction mixture. The optimum molar ratio of $\text{H}_2$ to $\text{Ta(OC}_2\text{H}_5)_5$ was determined to be about 25, which yielded a powder that was 97.4 wt% $\text{TaC}$. Increasing the plasma cooling rate was expected to reduce both particle size and $\text{Ta}_2\text{O}_5$ content, and the average size of the synthesized $\text{TaC}$ nanoparticles decreased from 12.3 to 7.8 nm when He was injected at the plasma tail.

References

[1] E.K. Storms, The Refractory Carbides, Academic Press, New York, 1967, pp. 82–94.
[2] J.Y. Chan, S.M. Kauzlarich, Rare-earth halides as fluxes for the synthesis of tantalum and niobium carbide, Chem. Mater. 9 (1997) 531–534.
[3] J.B. Claridge, A.P.E. York, A.J. Brungs, M.L.H. Green, Study of the temperature-programmed reaction synthesis of early transition metal carbide and nitride catalyst materials from oxide precursors, Chem. Mater. 12 (2000) 132–142.
[4] N.A. Hassine, J.G.P. Binner, T.E. Cross, Synthesis of refractory-metal carbide powders via microwave carbothermal reduction, Int. J. Refract. Met. Hard Mater. 13 (1995) 353–358.
[5] G.E. Spriggs, A history of fine-grained hard metal, Int. J. Refract. Met. Hard Mater. 13 (1995) 241–255.
[6] A. Rubinshtein, R. Shneek, A. Kanon, J. Hayon, S. Nathan, A. Raveh, Surface treatment of tantalum to improve its corrosion resistance, Mater. Sci. Eng. A 302 (2001) 128–134.
[7] T.Y. Kosolova, Carbide: Properties, Production, and Applications, Plenum Press, New York, 1971, p. 298.
[8] D.M. Li, R. Hernberg, T. Mantyla, Catalytic dissociation of hydrogen on a tantalum carbide filament in the HFCVD of diamond, Diamond Relat. Mater. 7 (1998) 1709–1713.
[9] P.M. Amaral, J.C. Fernandes, L.G. Rosa, D. Martinez, J. Rodriguez, N. Shohojo, Carbide formation of Va-group metals (V, Nb and Ta) in a solar furnace, Int. J. Refract. Met. Hard Mater. 18 (2000) 47–53.
[10] T. Kim, M.S. Wooldridge, Catalytically assisted self-propagating high-temperature synthesis of tantalum carbide powders, J. Am. Ceram. Soc. 84 (2001) 976–982.
[11] O.A. Graeve, Z.A. Munir, Electric field enhanced synthesis of nanostructured tantalum carbide, J. Mater. Res. 17 (2002) 609–613.
[12] S. Yajima, T. Iwai, T. Yamamura, K. Okamura, Y. Hasegawa, Synthesis of a polytitanacarbosilane and its conversion into inorganic compounds, J. Mater. Sci. 16 (1981) 1349–1355.
[13] H. Preiss, D. Schultze, E. Schierhorn, Preparation of NbC, TaC and Mo:C fibres and films from polymeric precursors, J. Mater. Sci. 33 (1998) 4687–4696.
[14] T. Ishigaki, Y. Moriyoshi, T. Watanabe, A. Kanzawa, Thermal plasma treatment of titanium carbide powders: Part II. In-flight formation of carbon-site vacancies and subsequent nitridation in titanium carbide powders during induction plasma treatment, J. Mater. Res. 11 (1996) 2811–2824.
[15] T. Ishigaki, Y.-L. Li, E. Kataoka, Phase formation and microstructure of titanium oxides and composites produced by thermal plasma oxidation of titanium carbide, J. Am. Ceram. Soc. 86 (2003) 1456–1463.
[16] Y.-L. Li, T. Ishigaki, Controlled one-step synthesis of nanocrystalline anatase and rutile TiO$_2$ through thermal plasma oxidation of titanium carbide, J. Phys. Chem. B 108 (2004) 15536–15542.

[17] A. Raveh, A. Danon, J. Hayon, A. Rubinshtein, R. Shneck, J.E. Klemberg-Sapieha, L. Martinu, Characterization of carburized tantalum layers prepared in inductive rf plasma, Thin Solid Films 392 (2001) 56–64.

[18] S.M. Oh, D.W. Park, Production of ultrafine titanium dioxide by dc plasma jet, Thin Solid Films 386 (2001) 233–238.

[19] N. Rao, S. Girshick, J. Heberlein, P. McMurry, S. Jones, D. Hansen, B. Michel, Nanoparticle formation using a plasma expansion process, Plasma Chem. Plasma Process. 15 (1995) 581–603.

[20] P. Buchner, H. Schubert, J. Uhlenbusch, M. Weiss, Diagnostics of an rf plasma flash evaporation process using the monochromatic imaging technique, Plasma Chem. Plasma Process. 21 (2001) 1–21.

[21] A. Fukunaga, S. Chu, M.E. McHenry, Synthesis, structure, and superconducting properties of tantalum carbide nanorods and nanoparticles, J. Mater. Res. 13 (1998) 2465–2471.

[22] X. Fan, T. Ishigaki, Y. Suetsugu, J. Tanaka, Y. Sato, In-flight nitridation of molybdenum disilicide powders by an induction plasma, J. Am. Ceram. Soc. 81 (1998) 2517–2526.

[23] X. Fan, T. Ishigaki, Parametric study on nitridation and carbonization of MoSi$_2$ powders in an induction plasma, Plasma Chem. Plasma Process. 18 (1998) 487–507.

[24] G. Soucy, M. Rahmane, X. Fan, T. Ishigaki, Heat and mass transfer during in-flight nitridation of molybdenum disilicide in an induction plasma reactor, Mater. Sci. Eng. A 300 (2001) 226–234.

[25] G. Eriksson, ChemSage Version 4.1, GTT-Technologies mbH, Herzogengerath, Germany, 1998.

[26] M.I. Boulos, P. Fauchais, E. Pfender, Thermal Plasma: Fundamentals and Applications, vol. 1, Plenum Press, New York, 1994.

[27] Y. Tanaka, T. Sakuta, Investigation on plasma-quenching efficiency of various gases using the inductively coupled thermal plasma technique: effect of various gas injection on Ar thermal plasma ICP, J. Phys. D: Appl. Phys. 35 (2002) 2149–2158.