Chemical Vapor Deposition of Tantalum Carbide from TaCl_5 - C_3H_6 -Ar- H_2 System

Daejong Kim^{*,†}, Sang Min Jeong^{***}, Soon Gil Yoon^{**}, Chang Hyun Woo^{***}, Joung Il Kim^{***},
Hyun-Geun Lee^{*}, Ji Yeon Park^{*}, and Weon-Ju Kim^{*}

^{*}Nuclear Materials Development Division, Korea Atomic Energy Research Institute, Daejeon 34057, Korea

^{**}Department of Materials Engineering, Chungnam National University, Daejeon 34134, Korea

^{***}Research and Development Division, Tokai Carbon Korea, Anseong 17602, Korea

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ABSTRACT

Tantalum carbide, which is one of the ultra-high temperature ceramics, was deposited on graphite by low pressure chemical vapor deposition from a TaCl_5 - C_3H_6 -Ar- H_2 mixture. To maintain a constant $\text{TaCl}_5/\text{C}_3\text{H}_6$ ratio during the deposition process, TaCl_5 powders were continuously fed into the sublimation chamber using a screw-driven feeder. Sublimation behavior of TaCl_5 powder was measured by thermogravimetric analysis. TaC coatings have various phases such as $\text{Ta}+\alpha\text{-Ta}_2\text{C}$, $\alpha\text{-Ta}_2\text{C}+\text{TaC}_{1-x}$, and TaC_{1-x} depending on the powder feeding methods, the $\text{C}_3\text{H}_6/\text{TaCl}_5$ ratio, and the deposition temperatures. Near-stoichiometric TaC was obtained by optimizing the deposition parameters. Phase compositions were analyzed by XRD, XPS, and Raman analysis.

Key words: Tantalum carbide, Chemical vapor deposition, Chloride process, UHTC

1. Introduction

Ultra-high temperature ceramics (UHTCs) are used as structural materials or coating materials in extreme environmental conditions such as ultra-high temperatures and corrosion because they have high melting points, high mechanical strength in an ultra-high temperature environment, abrasion resistance, and environmental resistance.¹⁾ Tantalum carbide (TaC) is a kind of UHTCs and it is one of Group V transition metal carbides. It has melting points of 3300°C or higher degrees, and in the case of $\text{TaC}_{-0.89}$, which is TaC with a deficit of carbon, the melting point may reach about 4000°C in.²⁾ It exhibits high stability to the melting point without any phase changes, high hardness, high strength, and excellent thermal shock resistance, so it can be applied to the condition where thermomechanical loading is applied, wear-resistant structural parts, and components for thermal heat protection in the form of a composite material or coating material. Recently, due to its properties such as resistance to chemical attack, excellent compatibility with a heat-resistant metal, and very low gas permeability as well as high melting points, it is being considered for a coating material for the support portion of sapphire growth crucibles or for SiC epi susceptors.³⁾

TaC can be formed by methods such as hot isotatic pressing(HIP),^{4,5)} hot pressing(HP),⁶⁾ the molten salt method,⁷⁾

spark plasma sintering (SPS),⁸⁾ plasma spraying,⁹⁾ laser ablation deposition,¹⁰⁾ sputtering,¹¹⁾ and chemical vapor deposition (CVD).¹²⁻¹⁶⁾ When TaC is deposited using the CVD process, techniques such as metal-organic CVD (MOCVD),¹²⁾ hot-filament CVD,^{13,14)} and hot-wall CVD¹⁵⁻¹⁷⁾ are used depending on source materials and heating methods.

In order to use it as the coating material for a semiconductor susceptor or for a crucible for the single crystal growth for light emitting diode (LED) application, the impurity concentration of TaC coating layers is required to be very low. Thus, CVD method is suitable for this purpose, and hot-wall CVD is favorable for uniform deposition of TaC onto large components. Therefore, in this study, TaC was deposited by the hot-wall CVD method using TaCl_5 as the source material, and parameter studies and optimization were carried out in order to obtain excellent TaC coating layers.

2. Experimental Procedures

TaC was deposited using TaCl_5 - C_3H_6 -Ar- H_2 . The low pressure chemical vapor deposition device used for TaC deposition is shown in Fig. 1. Deposition experiments were carried out placing a high purity graphite disc plate with the diameter of 50 mm and thickness of 1 mm on an inclined graphite plate with an inclination of 7°. The source material was high purity TaCl_5 powder (> 99.99%, STREM CHEMICALS, INC). In order to maintain a uniform partial pressure of TaCl_5 during the deposition process, a constant amount of the powder was continuously fed into the sublimator using a screw-driven powder feeder. In order to evaluate the characteristics of TaCl_5 powder feeding, the supply amount of the

[†]Corresponding author : Daejong Kim

E-mail : dkim@kaeri.re.kr

Tel : +82-42-868-4559 Fax : +82-42-868-8549

Fig. 1. Schematic of LPCVD system for TaC coating.

powder according to the rotational speed of the feeder screw and the amount of the powder fed into the sublimation chamber according to time were measured using a scale in real time, and the optimal feeding rate of powder was determined on the basis of the results. After 90g of TaCl_5 was filled into a cylinder for TaC deposition, the vacuum state was maintained long enough to remove the internal air, and then the powder was fed into the sublimation chamber evenly for 30 minutes at the rotation speed of the screw feeder of 3.9 rpm.

In addition, thermogravimetric analysis (TGA) was carried out to conduct evaluation of the sublimation behavior of the powder, and mass changes were measured by getting high purity helium, a kind of inert gas, to flow in at the flow rate of 50 sccm. After it was transformed into a gaseous state at 180°C , which is the sublimation temperature of crystallized TaCl_5 , through TGA analysis, TaCl_5 gas was made to flow into the reactor using Ar as a carrier gas at the flow rate of 800 sccm.

C_3H_6 was used as the source gas of carbon. By changing the amount of C_3H_6 while maintaining a constant supply amount of TaCl_5 , the ratio of Ta/C was adjusted. TaC deposition was performed at 1100°C and 1300°C . Deposition pressure was kept constant at 6.7 kPa using a throttle valve, and diluent gas H_2 was made to flow in so that the total flow rate could be 3000 sccm. The conditions of TaC deposition are summarized in Table 1.

The equilibrium compositions in H_2 - C_3H_6 - TaCl_5 system were calculated using the HSC chemistry ver. 6.0. The changes in equilibrium compositions with the amount of diluent gas H_2 were estimated under the conditions of TaCl_5 : C_3H_6 = 3 : 1, 1300°C , and 0.1 bar.

3. Results and Discussions

3.1. Sublimation and Feed Behavior of TaCl_5 Powder

When carbides are deposited using solid powder materials, the amount of sublimated powder should be supplied at a constant partial pressure to obtain coating layers having a uniform phase. Therefore, when sublimation occurs after feeding all powder before deposition, the adjustment of sublimation temperatures and pressure of the sublimation chamber is an important factor. However, as deposition proceeds, the stoichiometry of coating layers depending on deposition time can be changed if the sublimation of the powder does not proceed constantly due to problems such as consumption or agglomeration of the powder.¹⁸⁾ In order to solve this problem, a powder feeding system which is a type of screw feeder was used in order to induce sublimation supplying a constant amount of powder during deposition. Fig. 2 shows the supply amount of the powder as a function of the rotational speed of the screw of the powder feeder and elapsed time. At the beginning of powder feeding, powder is not fed until it reaches the sublimation chamber. It increases in proportion to the rotation speed of the screw. Subsequently, it can be seen that a constant amount of the powder is fed constantly without fluctuation depending on time, and linearity is maintained even though the rotational speed of the screw is changed. The feeding rate of the powder is found to change linearly as the rotation speed of the screw increases, and thus, the amount of the fed powder during any deposition time can be determined and it is precisely adjustable.

The weight changes depending on the temperatures of TaCl_5 powder were measured using TGA and the results are presented in Fig. 3. TaCl_5 powder reacts very rapidly with

Table 1. Chemical Vapor Deposition Conditions for TaC Deposition

	Deposition Temperature ($^\circ\text{C}$)	Pressure (kPa)	C_3H_6 (sccm)	Ar-C (sccm)	H_2 -D (sccm)	Total flow (sccm)	Feeder speed (rpm)
TaC-007	1300	50	10	800	2190	3000	3.9
TaC-008	1300	50	10	800	2190	3000	3.9
TaC-010	1300	50	20	800	2180	3000	3.9
TaC-012	1100	50	20	800	2180	3000	3.9
TaC-014	1300	50	30	800	2170	3000	3.9

Fig. 2. TaCl_5 powder feeding behavior; (a) weight changes of the TaCl_5 powder as a function of elapsed time and (b) the feeding rate as a function of rotation speed of the screw.

Fig. 3. TGA curve for the TaCl_5 powder in He.

moisture at room temperature. Although the TGA experiment was conducted in a He environment, the powder was exposed to the air while the sample was prepared and while the powder was fed into the TGA holder, which may have resulted in the adsorption of H_2O . For this reason, the decrease in mass was observed because of the desorption of water during the initial temperature increase. The decrease

Fig. 4. Thermodynamic stable phases in $\text{TaCl}_5\text{-C}_3\text{H}_6\text{-Ar-H}_2$.

in mass due to the sublimation of TaCl_5 powder used in the experiment is believed to start at about 150°C . A very high sublimation speed is observed in the vicinity of 180°C .

3.2. Deposition Behavior of Ta-C

The chemical vapor reactions at a high temperature of TaCl_5 and C_3H_6 proceeds in the following steps.¹⁹⁾

TaC compounds are produced by the reaction of Ta and C formed as a result of the decomposition of C_3H_6 and TaCl_5 at a high temperature. If there is an excessive amount of Ta , then Ta_6C_5 , Ta_4C_3 , Ta_2C , etc. may be formed, and if there is a more amount of Ta , the formation of metallic Ta is promoted. At this time, H_2 is generated as a result of decomposition of C_3H_6 , and participates in the decomposition reaction of TaCl_5 . Although C_3H_6 has a high production rate of reactive carbon concentration by pyrolysis at a temperature between 1100°C and 1300°C ,²⁰⁾ the amount of H_2 generated by decomposition of C_3H_6 is not sufficient to decompose TaCl_5 considering the experimental conditions, as shown in the Fig. 4. Therefore, in this study, the degradation of TaCl_5 was allowed to occur sufficiently regardless of the changes in the amount of C_3H_6 by using H_2 as diluent gas. Under the conditions of $\text{TaCl}_5\text{:C}_3\text{H}_6 = 3 : 1$, 1300°C , and 0.1 bar, the degradation of TaCl_x gas was found to increase as H_2 increased, and TaCl_x gas was decomposed almost completely in H_2 of about 1.5 kmol, demonstrating a high efficiency of TaC .

Figure 5 shows the change in the microstructure of TaC coating layers depending on the powder feeding method. When sublimation is induced by feeding all the powder into the sublimation chamber at the same time before the deposition experiment, TaCl_5 vapor pressure in the sublimation chamber is maintained in the saturated state at an early stage of deposition. However, the vapor pressure may be

Figure 7 shows the changes in the microstructure of coating layers according to the deposition temperature and change of $C_3H_6/TaCl_5$ ratio. As shown in Fig. 7 (a) and (b), if it is deposited for 30 minutes, the thickness of the coating layer increases from about 11 μm to 65 μm as the deposition temperature increases from 1100°C to 1300°C. In addition, the $\alpha-Ta_2C+\zeta-Ta_4C_3$ phase formed at 1300°C was transformed into $Ta+\alpha-Ta_3C$ at 1100°C as shown in Fig. 8(a).

Fig. 7. Microstructure of Ta-C coating layers; (a) TaC-012, (b) TaC-010 and (c) TaC-014.

Fig. 8. XRD patterns of Ta-C phases showing the influence of (a) the deposition temperature and (b) the $\text{C}_3\text{H}_6/\text{TaCl}_5$ ratio on phase compositions.

Fig. 9. (a) XPS and (b) Raman spectra of TaC_{1-x} (TaC-T014).

However, phase changes depending on the change of temperature do not occur at a temperature below about 1450°C , as seen in the phase diagram of Fig. 6(b). Therefore, these phase changes may be attributed to the fact that as the temperature was lowered, the high-temperature thermal decomposition rate of C_3H_6 decreased to a greater extent than that of TaCl_5 . As a result, the surplus Ta generated by the decomposition of TaCl_5 was unable to react with C, and was deposited with the $\alpha\text{-Ta}_2\text{C}$.

Deposition was performed varying the ratio of C_3H_6 and TaCl_5 in order to find the optimum deposition conditions at 1300°C . When the amount of C_3H_6 was changed maintaining a constant amount of TaCl_5 , variation in the thickness of coating layers was hardly observed. On the other hand, when the ratio of $\text{C}_3\text{H}_6/\text{TaCl}_5$ was low (Fig. 5(b)), $\text{Ta}+\alpha\text{-Ta}_2\text{C}$ was formed and it was observed to have a smooth surface.

In addition, even when a bending stress was applied to coating layers, they were not broken but plastic deformation occurred readily. This means that the ratio of Ta was considerably high. However, the phase was found to change into $\alpha\text{-Ta}_2\text{C}+\zeta\text{-Ta}_4\text{C}_3$ and TaC_{1-x} as the ratio of $\text{C}_3\text{H}_6/\text{TaCl}_5$ was increased. When it changed into the combination of Ta_2C and TaC, the surface had a dome top structure and the fracture surface had a columnar structure.

Figure 9 shows the results of the XPS and Raman analysis of TaC coating layers having an TaC_{1-x} single phase. TaC was found to have four major XPS peaks. They were the peaks corresponding to TaC and Ta_xO_y , and these results may indicate that a very small amount of air entered the CVD system and the peaks of oxides were observed together.²¹⁾ Among the analyzed peaks, the peaks of Ta $4f_{5/2}$ and Ta $4f_{7/2}$ corresponding to TaC were found to have the binding energy of

approximately 25.3 eV and 23.5 eV, respectively and they nearly coincided with TaC peaks with the stoichiometric ratio.²¹⁾ In addition, when Raman analysis was conducted on a cross-section of TaC coating layers in the thickness direction, the results showed that the peaks of acoustic branches, A1 (110 cm⁻¹) and A2 (166 cm⁻¹) and the peaks of optical branches, O1 (606 cm⁻¹) and O2 (652 cm⁻¹), which are caused by the carbon deficit, were hardly detected. Thus, the amount of carbon deficit is considered to be very low.²²⁾ Moreover, the disorder-induced peak (1350 cm⁻¹) and graphite peak (1580 cm⁻¹), which are caused by C when TaC + C phase is formed, are not observed either. Therefore, it was concluded that when TaC coating layers were formed using the low-temperature chemical vapor deposition (LPCVD) method, single phase with excellent stoichiometry was formed.

4. Conclusions

By using the low pressure chemical vapor deposition (LPCVD) method in TaCl₅-H₂-Ar-C₃H₆ system, TaC was deposited on graphite. If deposition is achieved by sublimation using a chloride-based powder, changes in the sublimation amount depending on the deposition time are likely to occur. Therefore, in order to obtain TaC with a uniform phase by maintaining a constant partial pressure of TaCl₅ during deposition, TaCl₅ powder was fed into the sublimation chamber using a screw-driven powder feeder. The changes in the feeding time of TaCl₅ powder and in the rotational speed of the feeder were evaluated to have extremely high linearity. The application of a screw feeder resulted in an approximately twofold increase in the deposition rate and improvement of phase homogeneity. As the deposition temperature was increased, the deposition rate of TaC dramatically increased, and it was transformed into Ta-C phase, which contains more Ta. By optimizing the ratio of C₃H₆/TaCl₅ at 1300°C, it was possible to obtain near-stoichiometric TaC, and the measurement results showed that phase homogeneity was excellent in the direction of the thickness of TaC coating layers.

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