Deposition Kinetics of CVD-Silicon Carbonitride Coatings
A. Varliamov, S. Afanas’Eva

To cite this version:

HAL Id: jpa-00253851
https://hal.archives-ouvertes.fr/jpa-00253851
Submitted on 1 Jan 1995

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Deposition Kinetics of CVD-Silicon Carbonitride Coatings

A.G. Varlamov and S.V. Afanas'eva

Institute for Structural Macrokinetics RAS, Chernogolovka, 142432 Moscow Region, Russia

Abstract

In the present work some conformities of atmospheric CVD-process with silicon carbonitride layers synthesis as an example are discussed. It is proposed the chemisorption - kinetic mechanism of the coatings heterogeneous synthesis. The possibility of this mechanism existence is conditioned by the limited adsorptive capacity of the growing surface and by defining the surface processes as the leading (limiting) stage of the CVD-synthesis. The effect of "the chemisorptive surface memory" is discovered. The idea of it is as follows: after a sharp changing of CVD-synthesis temperature the surface keeps the information about the blocked centers number at its previous state.

Introduction

Earlier the investigation of ceramic coatings CVD-synthesis was carried out because of the necessity to have semiconductive and dielectric layers for electronics [1]. It was showed, that layers with required quality and uniformity of properties were able to obtain at low pressure (10^{-2} - 1 torr) of the starting mixture reagents (LPCVD) [2-3]. LPCVD- ceramic coatings synthesis is characterized by:

a) Linear growth of the layer thickness depending on time (the rate of the layer thickness growth is constant).

b) The layer thickness growth exponentially depends on temperature (the CVD-synthesis limiting stage is a heterogeneous chemical reaction).

c) The growth rate (1 - 10^2 nm/h) and thickness (1 - 10^2 nm) are small.

Recently depositing of coatings, that modify the surface properties of the vital parts of engines and devices is very important. The thickness of the coatings must be 10^3 - 10^5 nm. It demands essential increasing of the deposition rate of ceramic coatings. It may be achieved by increasing starting mixture reagents pressure in comparison with LPCVD. In this case there are a lot of effects, that do have not any explanation in literature [6].

In the present work some conformities of atmospheric CVD-process with silicon carbonitride layers synthesis as an example are discussed.
Experimental results and discussion

All experiments were fulfilled on a quartz plant with a thermostatic unflowing reactor as the major element. 0.1 mm diameter tungsten filament-substrate was put into the reactor and heated by electric current. Graduating the substrate surface temperature was carried out by the thermophysical method [8] with the registration of surface thermoradiation [9]. The gas mixture consisted of tetramethylsilane (TMS), hydrazine (H) and molecular hydrogen. The total pressure of the gas mixture was 700 torr, the partial pressure of the TMS and H - 20 and 8 torr. As a result of the heterogeneous chemical reaction the layers of monophase amorphous silicon carbonitride were deposited on the hot substrate surface [10].

Fig. 1 shows the kinetic curves of the layer thickness isothermal growth in the temperatures: 1 - 1458 K, 2 - 1538 K, 3 - 1593 K, 4 - 1658 K, 5 - 1718 K.

\[ \frac{d\delta}{dt} = V_0 + (V_0 - V_{\infty}) \exp(-\alpha t) \]  

(1)

\( V_0 \) is the layer growth rate at the initial time \( t \to 0 \);

\( V_{\infty} \) is the layer growth rate at the stationary (linear) stage;

\( \alpha \) is the characteristic time of the change towards the stationary regime.

To explain the experimental data the following physical model is used. In the base of it is the special (active) surface centers existence idea [11], and defining the surface processes as the leading (limiting) stage [12] of the CVD-synthesis. The active surface centers are considered energetically uniform and the number of them is constant within the surface unit. Let the starting gas mixture reagents \( C_g \) and \( D_g \) interact in the gas phase and form intermediate products \( P_{P_g} \), \( P_{P_g} \) diffuse towards the heated surface and chemisorb on its active centers.
As a result of the heterogeneous chemical reaction the chemisorbed on the active centers intermediate particles PP transform into final products of the two sorts: K - particles, that complete the surface, forming condensed product and reproducing the active centers; M - particles, that, being in a chemisorbed condition, block the surface active centers. The life time of the blocking particle M is longer than the characteristic time of the heterogeneous chemical reaction of the K-condensed product formation. The M - blocking particle can diffuse over the growing surface occupying one or another active center and desorb from the surface, deblocking it. The initial surface is formed by K - particles.

The rate of the condensed phase mass growth on a unit surface is proportional to the rate $W$ of the chemical reaction of the condensed product formation on an active center and to the unit surface active centers number $N$,

$$\frac{l}{S} \frac{dm}{dt} \propto WN$$  \hspace{1cm} (2)

where $S$ is growing surface.

At the initial time ($t \rightarrow 0$) there are not any blocking particles. The unblocked centers number of the growing surface is the biggest. The rate of the condensed product mass growth is the maximum. In the process of the heterogeneous chemical reaction, together with the K- condensed product synthesis accumulating the blocking particles M on the growing surface and blocking the active centers take place. This causes the condensed product mass growth rate decreasing. In the course of time dynamically adsorption - desorption equilibrium of the blocking particles M, corresponding to the unblocked active centers constant number is settled on the growing surface. It causes linear (constant rate) growth of the condensed product mass at the later stage of the process.

To explain the above-said let us consider the 1-st order reversive reaction of the surface active center A changing into the blocked state B with the direct and back reactions constants $k_1$ and $k_2$.

\[
\begin{array}{c}
A \xrightarrow{k_1} B \\
\xleftarrow{k_2}
\end{array}
\]

The kinetic equation of the unblocked centers number changing is:

$$\frac{dN}{dt} = -k_1 N + k_2 \left( N_{\text{max}} - N \right)$$  \hspace{1cm} (3)

At $t = 0$ $N = N_{\text{max}}$  \hspace{1cm} (4)

$k_1/k_2 = K$ - is the adsorption-desorption equilibrium constant of the blocking particles on the active centers. The (3-4) system solution is:

$$N = N_{\text{max}} + K N_{\text{max}} \frac{1}{1 + K} \exp \left[ -\left( k_1 + k_2 \right) t \right]$$  \hspace{1cm} (5)

Substituting (5) for (2) , we obtain the kinetic expression of the condensed product growth rate on the unit surface (6), which is similar to the experimental expression (1)

$$\frac{l}{S} \frac{dm}{dt} \propto \left[ \frac{WN_{\text{max}} + K WN_{\text{max}}}{1 + K} \right] \exp \left[ -\left( k_1 + k_2 \right) t \right]$$  \hspace{1cm} (6)
Comparing expressions (1) and (6) we see, that the initial \( V_0 \) and stationary \( V_\infty \) rates of the layer growth are connected by the correlation (7)

\[
\frac{V_0}{V_\infty} = 1 + K
\]  

(7)

where

\[
V_0 \propto W N_{\text{max}}
\]  

(8)

The \( a \)-coefficient connected with the rate of changing into the stationary regime is determined by the sum of the adsorption and desorption constants:

\[
a = k_1 + k_2
\]  

(9)

The model can be called the chemisorption - kinetic mechanism of the coatings heterogeneous synthesis. The possibility of this mechanism existence is conditioned by the limited adsorptive capacity of the growing surface [11] and by defining the surface processes as the leading (limiting) stage [12] of the CVD- synthesis.

![Figure 2: Leap-like decreasing of the substrate surface temperature.](image)

In the frameworks of the chemisorption- kinetic mechanism a lot of consequences exist, that may be tested experimentally. In particular, at the CVD- process stationary stage each temperature must be in correspondence with the surface blocked centers constant number. The synthesis temperature increasing together with the heterogeneous chemical reaction rate \( W \) must lead to the blocked centers number increasing. A leap-like decreasing of the CVD- synthesis temperature is supposed to result in "freezing" (increasing the life time) of the blocking particles on the active center of the growing surface. The number of the blocked centers after a considerable decreasing of the temperature will be the same as before the temperature leap. Consequently, the layer growth rate after the sharp decreasing of the temperature is to be lower than the stationary growth rate under the isothermal conditions at that (lower) temperature. The confirmation of the coatings heterogeneous synthesis adsorption- kinetic mechanism correctness is the kinetic experiments results, obtained under the conditions of the leap-like heating. The idea of the below discussed experiment is (fig. 2): 1718 K heated substrate was isothermally kept in a
reactive medium during 30 sec. Then the substrate temperature was decreased in a leap-like way to 1458 K and the synthesis proceeded for 400 sec. The duration of the leap-like decreasing of the synthesis temperature itself was 0.05-0.1 sec, which couldn't influence the kinetic measurements results.

The kinetic of the layer growth under the leap-like heating conditions are shown in Fig. 3. 1 and 2 -lines here are the kinetic curves of the layer growth under the isothermal conditions at 1458 K and 1718 K. As shown in Fig. 3, after treating the substrate at 1718 K for a short time (30 sec) and leap-like decreasing of the synthesis temperature to 1458 K 0 C the layer growth is linear and the growth rate is 5.85 times lower than under the isothermal heating conditions at the same temperature. The phenomenon was named the effect of "the chemisorptive surface memory". It may be explain by after a sharp changing of CVD- synthesis temperature the surface keeps the information about the blocked centers number at its previous state. In case of the subsequent leap-like increasing of the substrate temperature to 1718 K 0 C the layer growth continues with the momentary rate which the process had at the moment of the previous temperature changing.

![Figure 3: The kinetics of the layer growth under the leap-like heating conditions (3-line). 1 and 2 -lines here are kinetic curves of the layer growth under the isothermal conditions at 1458 K 0 and 1718 K 0 C.](image)

Thus, the starting reagents pressure increasing in the CVD- process leads to the coatings growth rate increasing. The heterogeneous chemical reaction of the condensed product formation is no more a limiting stage of the process (in contrast to LPCVD) because its rate becomes similar to the chemisorption-desorption processes rates. The interdependence of the heterogeneous chemical reaction and chemisorption is caused by limited chemisorptive capacity of the growing surface (a limited number of the surface active centers). The decreasing of the coatings growth rate is conditioned by the accumulation of particles, blocking the active centers, and the decreasing of the unblocked centers number. In the course of time a dynamically chemisorption - desorption equilibrium which is characterized by a constant number of the unblocked centers, is established, which causes linear growth of coatings. The effect of "the chemisorptive surface memory" is discovered. The idea of it is as follows: after a sharp changing of CVD- synthesis temperature the surface keeps the information about the blocked centers number at its previous state.
References