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Chemical Vapor Deposition of Pyrolytic Carbon on SiC Fibers

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Abstract—We carried out thermodynamic analysis of reactions underlying the preparation of pyrolytic carbon from a number of carbon-containing compounds and experimentally determined the optimal temperature range for the deposition of thin (1–3 μm) pyrolytic carbon layers onto continuous silicon carbide fibers. The results indicate that, among the compounds studied, the highest deposition rate of pyrolytic carbon is ensured by the pyrolysis of toluene and *n*-heptane. The slowest deposition rate is observed in methane pyrolysis. Rate data are used to determine the apparent activation energies for the pyrolysis of C_7H_8, C_7H_{16}, $(CH_3)_2CO$, CCl_4, and CH_4.

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INTRODUCTION

Chemical vapor deposition (CVD) offers a number of advantages over other widespread processes for producing coatings (thermal evaporation, cathode sputtering, electron-beam evaporation, laser ablation, and others), in particular, simplified apparatus and high deposition rates. The key features of CVD were described in detail in many works (see, e.g., [1–3]). CVD is used to deposit both metals and nonmetals, in particular, carbides, nitrides, silicides, and pyrolytic carbon.

Continuous silicon carbide fibers grown by CVD are used as reinforcing agents in metal- and ceramic-matrix composites. SiC-fiber-reinforced composites can withstand temperatures as high as 1273 K and above. A serious impediment to many potential applications of SiC-fiber-reinforced metal-matrix composites is the chemical interaction between the fibers and matrix at elevated temperatures. One effective way to prevent (or reduce) fiber–matrix interaction is to protect reinforcing fibers with antidiffusion barrier layers from materials nonreactive with both the fibers and matrix. Commonly employed materials for such barrier layers include refractory metal carbides and nitrides and pyrolytic carbon [4–7].

Pyrolytic carbon barrier layers are substantially easier to produce than coatings from refractory metal carbides and nitrides. At the same time, pyrolytic carbon ensures sufficiently effective protection of silicon carbide fibers in metallic matrices. Moreover, pyrolytic carbon layers are capable of eliminating surface defects of fibers, thereby substantially enhancing their strength. In particular, Nutt and Wawner [8] reported that deposition of a pyrolytic carbon layer increased the strength of silicon carbide fibers by a factor of 2.

In depositing antidiffusion barrier layers, including those of pyrolytic carbon, one must taken into account that long-term anneals at temperatures above 1470 K and even short-term anneals above 1570–1670 K markedly reduce the strength of silicon carbide fibers. This is particularly true of *W*-SiC fibers [9, 10]. In connection with this, barrier layers must be deposited at lower temperatures.

The objective of this work was to carry out thermodynamic analysis of reactions underlying the preparation of pyrolytic carbon from a number of carbon-containing compounds (toluene, methane, carbon tetrachloride, acetone, and *n*-heptane) and to determine the optimal temperature range for the deposition of thin (1–3 μm) pyrolytic carbon layers onto continuous silicon carbide fibers.

THEORY

Thermodynamic analysis allows one to establish conditions favorable for gas-phase reactions. To this end, we evaluated the Gibbs energy of reactions of the type

$$C_xH_y \longrightarrow xC + yH \qquad (1)$$

in the temperature range 773–1773 K.

The Gibbs energy was calculated using well-known equations of chemical thermodynamics [11]:

$$\Delta G(T) = \Delta H(T) - T\Delta S(T), \quad (2)$$

$$\Delta H(T) = \Delta H^0(298\ \text{K}) + \int_{298}^{T} \Delta C_p dT, \quad (3)$$

$$\Delta S(T) = \Delta S^0(298\ \text{K}) + \int_{298}^{T} (\Delta C_p/T) dT, \quad (4)$$

$$\Delta G(T) = \Delta H^0(298\ \text{K}) - T\Delta S^0(298\ \text{K}) - \int_{298}^{T} (\Delta C_p/T) dT + \int_{298}^{T} \Delta C_p dT. \quad (5)$$

In calculations, we used Ulich’s second approximation: $\Delta C_p = \text{const}$.

After integration, Eq. (5) takes the form

$$\Delta G(T) = \Delta H^0(298\ \text{K}) - T\Delta S^0(298\ \text{K}) - \Delta C_p(298\ \text{K}) T M_0, \quad (6)$$

where

$$M_0 = \ln\frac{T}{298.2} - 1 + \frac{298.2}{T}. \quad (7)$$

The input thermodynamic data (enthalpies, entropies, and heat capacities) for the carbon-containing compounds of interest were taken from Karapet’yants [12].

The calculated Gibbs energies in the range 773–1773 K are presented in Fig. 1. As seen, *n*-heptane and toluene are best suited (have the lowest pyrolysis temperatures) and methane and carbon tetrachloride are least suited to carbon CVD.

EXPERIMENTAL

To establish the optimal temperature range for pyrolytic carbon deposition, we used the experimental setup schematized in Fig. 2.

Pyrolytic carbon was deposited by the following procedure: After saturation with carbon-containing vapor in a glass bubbler thermostated at 290 K, the argon carrier gas was introduced into the deposition chamber (*4*). The silicon carbide fiber in the chamber was heated by an electric current flowing through mercury contacts (*2*). The fiber temperature was measured by an OMP-054 optical micropyrometer. The residence time of the fiber in the reactor was 20, 40, 60, 80, or 100 s.

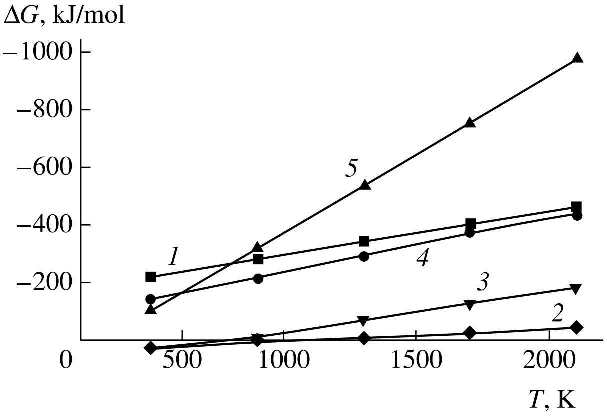

Fig. 1. Gibbs energy as a function of temperature for pyrolysis of (*1*) C_7H_8, (*2*) CH_4, (*3*) CCl_4, (*4*) $(CH_3)_2CO$, and (*5*) C_7H_{16}.

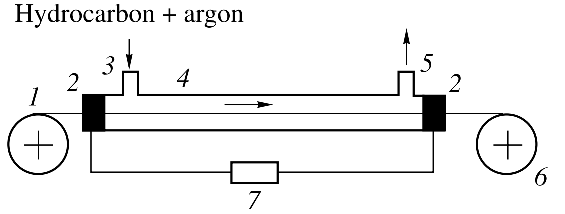

Fig. 2. Experimental setup for pyrolytic carbon deposition: (*1*) SiC fiber feed spool, (*2*) mercury contacts, (*3*) inlet tube, (*4*) deposition chamber, (*5*) outlet tube, (*6*) C/SiC fiber takeup spool, (*7*) power supply.

The carbon resulting from the pyrolysis of the carbon-containing compound deposited on the immobile silicon carbide fiber. The thickness and quality of pyrolytic carbon layers grown using different temperature–time combinations were determined with an MIM-8 optical microscope.

RESULTS AND DISCUSSION

Our results indicate that the optimal temperature range for pyrolytic carbon deposition from the carbon-containing compounds in question is 1473–1573 K. The coatings grown at lower temperatures were too thin (<0.1 μm). Higher temperature deposition reduced the strength of the silicon carbide fibers, preventing them from being used as reinforcing agents of composites.

The thicknesses of pyrolytic carbon layers grown at 1473 and 1573 K and different deposition times are listed in Table 1. As seen, the highest deposition rate of pyrolytic carbon is ensured by the pyrolysis of toluene and *n*-heptane, and the slowest deposition rate is observed for the pyrolysis of methane and carbon tetrachloride. The pyrolytic carbon deposits grown from tol-

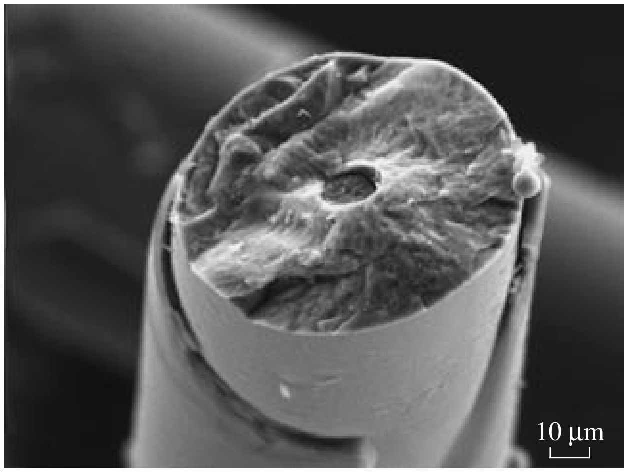

Fig. 3. Cross-sectional fracture surface of a silicon carbide fiber coated with pyrolytic carbon.

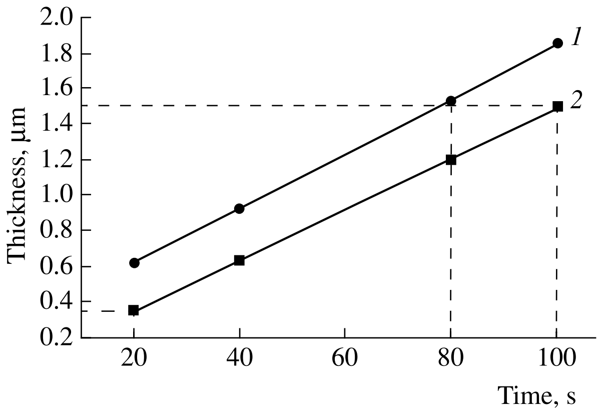

Fig. 4. Thickness as a function of deposition time for pyrolytic carbon layers grown from acetone at (*1*) 1573 and (*2*) 1473 K.

uene and *n*-heptane had smooth surfaces and consisted of fine grains. Figure 3 shows a fracture surface of a silicon carbide fiber coated with pyrolytic carbon at 1573 K using toluene.

The temperature effect on the pyrolysis rate can be represented by the Arrhenius equation [13]

$$K = Ae^{-E_a/(RT)}, \tag{8}$$

where K is the reaction rate constant; A is the preexponential factor, proportional to the number of molecular collisions; and E_a is the apparent activation energy.

Activation energy is a key parameter for elucidating the reaction mechanism: only E_a allows one to ascertain whether a particular reaction is plausible.

Knowing the reaction rate constant K at several temperatures, one can evaluate the apparent activation energy by the equation [14]

$$E_a = \frac{4.58\log(K_{T_2}/K_{T_1})}{\frac{1}{T_1} - \frac{1}{T_2}}. \tag{9}$$

To calculate a reaction rate constant, one must know the form of the rate equation. It is, therefore, preferable to determine the apparent activation energy from the temperature dependence of the rate of some process (e.g., deposition rate), rather than from that of the rate constant of the process. This approach to determining E_a as a function of temperature was described by Emanuel’ and Knore [15] and Emyashev [16] for static experimental conditions.

According to Emanuel’ and Knore [15], to evaluate the apparent activation energy it is sufficient to determine the time it takes for the deposit to rich a predetermined thickness at different temperatures,

$$E_a = \frac{4.575T_2T_1}{T_2 - T_1}\log\frac{1/\tau_{T_2}}{1/\tau_{T_1}}, \tag{10}$$

where τ_{T_2} is the deposition time at temperature T_2, and τ_{T_1} is the deposition time at temperature T_1.

Table 1. Thicknesses of pyrolytic carbon layers grown from carbon-containing compounds at 1473 and 1573 K and different deposition times

Compound	Δd, μm									
	1473 K					1573 K				
	20 s	40 s	60 s	80 s	100 s	20 s	40 s	60 s	80 s	100 s
C_7H_8	1.18	2.20	2.40	3.42	4.10	1.22	2.24	3.02	3.75	5.00
CH_4	0.22	0.28	0.31	0.35	0.41	0.39	0.41	0.42	0.45	0.48
CCl_4	0.28	0.41	0.45	0.60	0.75	0.50	0.60	0.75	0.90	1.10
$(CH_3)_2CO$	0.40	0.68	0.98	1.26	1.50	0.65	1.10	1.25	1.65	1.95
C_7H_{16}	0.42	1.41	1.84	2.48	3.45	0.80	1.65	2.40	3.00	3.75

Table 2. Apparent activation energies of pyrolysis reactions

Reaction	E_a, kJ/mol
$C_7H_{16} \longrightarrow 7C + 8H_2$	36
$C_7H_8 \longrightarrow 7C + 4H_2$	72
$(CH_3)_2CO \longrightarrow 3C + 2H_2 + H_2O$	78
$CCl_4 \longrightarrow C + 2Cl_2$	171
$CH_4 \longrightarrow C + 2H_2$	398

In this work, we calculated the apparent activation energy by Eq. (10). The values of τ_{T_2} and τ_{T_1} were determined from the layer thicknesses measured as a function of deposition time at 1473 and 1573 K. Figure 4 displays such data for acetone.

The apparent activation energies evaluated in this manner for all of the carbon-containing compounds studied here are listed in Table 2. The highest values of E_a were obtained for the pyrolysis of methane and carbon tetrachloride, and the lowest values were obtained for the pyrolysis of *n*-heptane and toluene, which correlates with the rate data for these compounds.

CONCLUSIONS

We carried out thermodynamic analysis of reactions underlying the preparation of pyrolytic carbon from carbon-containing compounds in a broad temperature range, 500–2000 K. The results indicate that *n*-heptane and toluene are best suited (have the lowest pyrolysis temperatures) and methane and carbon tetrachloride are least suited to carbon CVD.

Kinetic studies of pyrolytic carbon deposition on silicon carbide fibers using carbon-containing compounds demonstrate that the highest deposition rate of pyrolytic carbon is ensured by the pyrolysis of toluene. The slowest deposition rate is observed for methane pyrolysis.

The apparent activation energies for the pyrolysis of C_7H_8, C_7H_{16}, $(CH_3)_2CO$, CCl_4, and CH_4 are determined.

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