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Characterization of cascade arc assisted CVD diamond coating technology Part I. Plasma processing parameters

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Abstract

Cascade arc plasma-assisted CVD (CACVD) technology is based on an innovative reactor design which utilizes the properties of a lineararc plasma column. While operating in the same pressure range, from 0.1 Torr up to atmospheric pressure, the CACVD reactor overcomes the disadvantages of conventional Arc Torch CVD reactors by creating a homogeneous concentrated plasma column in a cylindrical or rectangular reaction chamber with a length of 1 m or more. Substrate holders are configured to act as a virtual liner confining the arc in a channel containing the substrates. In the CACVD reactor channel, an arc plasma is shaped by magnetic fields, creating a uniform plasma environment over extended lengths. It has been used to deposit polycrystalline diamond and related coatings on 3D substrates. In the cascade arc process, the temperature gradient and flow of energy are directed transversal to the hydrodynamic flow, which allows protection of the deposition area from direct impact with high-speed plasma flow. In high temperature CACVD processes, the temperature of substrates is determined by the balance between energy flow conveyed from the plasma column, radiative losses, and heat removal through cooling of the substrate holders and reactor wall. Precise control of the substrate temperature in high temperature CVD processes is critical for depositing polycrystalline diamond coatings. Composite powder variable conductance insulation (CPVCI) has been developed to control substrate temperature during deposition of polycrystalline diamond coatings in the CACVD reactor. Direct measurements of the substrate temperature vs. incoming energy flow from arc plasma allow estimation of the thermal balance of the substrates. The voltage-ampere characteristics as well as plasma transfer processes in an Ar-H₂-CH₄ cascade arc in relation to the thermal balance of substrates and deposition rate of polycrystalline diamond coatings are discussed.

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1. Introduction

Creation of nonequilibrium conditions for heat and mass transfer plays a key role in low pressure syntheses of thermodynamically metastable diamond and related materials. There are several well-known ways to provide such conditions in CVD reactors: hot filament CVD (HFCVD); combustion flame CVD (CFCVD); arc jet plasma-assisted CVD (AJCVD); laser-assisted CVD (LCVD); and RF or microwave plasma-assisted CVD (RF or MW CVD). In nonequilibrium environments, the concentration of reaction species can be much higher than allowed by thermodynamic

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equilibrium conditions. The two critical mechanisms responsible for providing the fluxes of reaction species impinging upon the substrate surface and thus affecting the productivity and quality of diamond coatings are: first, the generation of the reaction species in the source zone of the reactor (activated atomic hydrogen and hydrocarbon radicals in the case of diamond coatings); and second, the transport phenomena involved with the transfer of reaction species to the substrate surface [1,2]. In HFCVD reactors, the flow of thermodynamically nonequilibrium reaction species are generated by hot filament surface reactions and transferred to the substrates by diffusion through the small gap between filament and substrates. The concentration of atomic hydrogen can be further increased by superimposed DC glow discharge using a DC-biased hot filament [3,4].

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Nonequilibrium reaction media can also be generated in the vicinity of the substrate by selective optical excitation of reaction species with laser radiation (optical pumping) [4] or by collision excitation in plasma-assisted processes [5]. In nonequilibrium low-pressure glow discharge, RF, microwave, or magnetomicrowave (ECR) plasmas, the temperature of electrons can greatly exceed the temperature of heavy particles [6]. In this case, the oscillation and vibration modes of reaction molecules can be effectively excited by electron collisions while the gas temperature can remain relatively low. The dissociation rate of molecular species also exceeds equilibrium values. This results in the generation of atomic hydrogen and excited states of hydrocarbon radicals, which play an important role in the synthesis of diamond films [7,8]. Because the generating area is located in the vicinity of the substrate surfaces, diffusion transfer plays the most important role in supplying activated reaction species from the generating area to the substrates. In these processes, the coating zone is primarily determined by the characteristic size of the generating area, while the rate of deposition is ordinarily limited by molecular diffusion transfer of reaction particles and ranges from 1 to 10 µm/h. It is more difficult to reach high productivity and uniformity when coating shank-shaped (3dimensional) substrates (drill bits, dental burs) in processes based on molecular heat and mass transfer, while these processes are particularly compatible with the coating of flat substrates [30].

Conventional hydrodynamic transfer from a hot energy release zone toward the substrates to be coated also creates the flow of nonequilibrium reaction species. In this case, the generating area is located at a significant distance from the substrates. The excited reaction molecules are carried from the generating area by high-speed gas flow. This approach is utilized in the arc torch/combustion torch jet reactors.

DC arc jet reactors represent one of the currently available plasma-enhanced CVD methods to produce diamond coatings. Typically, a DC arc torch is assembled in a vacuum chamber in which the substrate part to be coated is placed in the line of sight of the plasma jet. Process gases are injected in the chamber at or near the torch nozzle, and substrate temperature is controlled by adjusting the flow of cooling water supplied to the substrate holder. This DC arc jet process yields very large deposition rates of continuous diamond films ranging from 10 to 1000 μ m/hr [9].

These reactors have severe limitations: (1) it is a lineof-sight type of process, it has limited capabilities to coat 3D parts, and it is not possible to stack a number of parts in the path of the arc jet; (2) as the arc jet plasma expands into a bell shape, it shows excessively large composition gradients and inhomogeneous thermal properties along its axis or any cross-section. As a result, considerable coating thickness variations are observed between the central and peripheral substrate regions. There are several ways to overcome these limitations. One solution is to increase the diameter of the arc jet by increasing the arc power. This solution is still limited to a diameter of deposition zone to about 25cm, even with several hundred kW of arc power [9]. Another way is to position the substrates to be coated along an arc column. This approach was implemented in a reactor design using low pressure, freestanding high current arc [10]. However, this approach is limited to low-pressures. When gas pressure increases, the arc discharge contracts to a narrow arc column of highly ionized plasma surrounded by a relatively low temperature and low ionized gas shield. In this mode, the freestanding arc is more prone to short circuits through the wall of the reactor and the substrate fixtures. This creates difficulties in providing uniform delivery of reaction species toward substrates to be coated.

The cascade arc plasma-assisted CVD (CACVD) reactor provides a cascade arc-assisted CVD coating deposition process in a DC or AC arc column generated in a rectangular or cylindrical reaction zone of virtually unlimited length [11]. The reactor also allows considerable flexibility in the positioning of substrates to be coated. This is accomplished by creating a homogeneous concentrated plasma column along the reaction channel, configuring the substrate holders to act as a liner confining the arc in the channel containing the substrates and manipulating the plasma column into contact with the substrates, using a combination of longitudinal and transverse magnetic fields.

In comparison with conventional DC arc jet reactors and freestanding arc reactors, the CACVD process offers a number of advantages while maintaining high deposition rates:

- it is not line-of-sight process and therefore a multitude of 3D parts can be stacked in the plasma column and be coated simultaneously and evenly on all sides;
- the plasma column is expected to show no axial chemical composition inhomogeneity or thermal gradients, therefore, the resulting coatings should not exhibit appreciable thickness variations;
- the operating pressure ranges from 1 mTorr up to atmospheric pressure;
- it can be easily scaled-up.

In this paper, we discuss an opportunity for the industrial production of superhard materials using CACVD technology.

2. Background

In low-pressure diamond coating deposition processes controlled by diffusion transfer, the typical deposition rate ranges from 0.5 to about 3–µm/h [1–4,9,10,32]. Based on a diamond film density of 3.5 g/cm³, this corresponds to a flux of carbon atoms, which will ultimately form the film on the substrate, of $j_C \gtrsim 10^{15} - 10^{16}$ cm⁻² s⁻¹. Assuming the

conversion factor of carbon-containing species into the diamond film in an Ar-H₂-CH₄ plasma is $\gamma_{\rm D}$ of the total flux of carbon-containing species impinging upon the surface at elevated surface temperature, the required total flux of carbon-containing species in diamond coating deposition process, $j_{\rm CT}$, must exceed $j_{\rm CT} \gtrsim (1/\gamma_{\rm D})(10^{15} - 10^{16}) \text{ cm}^{-2} \text{ s}^{-1}$. The total flux of carbon-containing atomic particles may then be estimated as $j_{\rm CT} \alpha 1/4 C_{\rm CH} n v_{\rm p}$, where $n \sim 10^{17} {\rm cm}^{-3}$ is the gas density, $C_{\rm CH}$ is concentration of carbon containing species, and $v_p \sim 10^5$ cm/s is the mean velocity of atomic particles. For typical conditions in various low-pressure plasma-assisted CVD diamond coating deposition technologies using H₂/CH₄ mixture as reaction gas, the methane concentration is C_{CH4} ~1%. Thus, the flux of carbon containing species may be estimated as $j_{CT} \lesssim 2.5 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$, which gives an estimation of conversion factor in a range from $\gamma_D \sim 10^{-3}$ to 10^{-4} , in agreement with other investigations [7]. This estimation provides some idea about minimal mass transfer rates required for commercially viable diamond coating deposition process.

2.1. CACVD discharge functional zoning structure

The CACVD reactor operates in a wide pressure range from 1 mTorr, at the low-pressure end, up to atmospheric pressure. In a tubular CACVD reactor, a linear arc discharge is established along the axis of the long cylindrical chamber, stabilized by water-cooled reactor walls and a superimposed external longitudinal magnetic field. The cross-section of the reactor channel is shown schematically in Fig. PI-1a¹. The source zone, where the generation of active ionized reaction species occurs, is located in the arc column, where the plasma temperature, dissociation, and ionization rates are at a maximum due to electron collisions in the highly ionized area of the size of the current conducting transversal cross-section zone. In the low-pressure regime ($p \leq 1$ Torr), the arc column enlarges to the entire diameter of the reactor channel. In moderate to high pressures, the arc plasma contracts forming a narrow arc column. Referring to Fig. PI-1a, the simple model of a constricted discharge given in [34] can be considered. In this three-zone model, electron generation occurs in the internal high temperature conductive zone. Recombination becomes significant at the edge of the arc column [34]. This allows to estimate the diameter of the constricted discharge column or source zone as $r_c \sim D_a / \alpha_r n_e$, where $D_a = D_i (1 + T_e / T_g)$ is the ambipolar diffusion coefficient, $T_{\rm e}$ and $T_{\rm g}$ are electron and gas temperature, respectively, n_e is electron density, and α_r is the recombination constant. Assuming typical low-pressure arc plasma parameters $n_{\rm e} \sim 10^{12}$ cm⁻³, $\alpha_{\rm r} \sim 10^{-7}$ cm³/s, $D_{\rm a}$ ~300 cm²/s, one can estimate $r_{\rm c} \sim 1$ mm [18, 34]. A more accurate estimation can be obtained by considering the



Fig. PI-1. Schematic illustration of plasma distribution in transversal crosssection of CACVD reactor channel: (a)—axially symmetric mode; (b) magnetic steering mode.

current transfer cross-section as the electron generation zone in an arc discharge. The radius of this high temperature highly ionized zone, r_c , continues the cross-section in which almost all arc current is concentrated, i.e., may be estimated by the following relation:

$$I_{\rm a} = 2\pi E_{\rm a} \int_0^{r_{\rm c}} \sigma(r) r dr, \qquad (1)$$

where I_a and E_a are respectively current and electric field in arc column and $\sigma(r)$ is the electrical conductivity of the arc plasma, $(\Omega \cdot \text{cm})^{-1}$. In this section, plasma conductivity can be estimated by the Spitzer formula:

$$\sigma(r) = 1.53 \times 10^{-4} T_{\rm e}^{3/2} / \Lambda, \tag{2}$$

where Λ is the Coulomb logarithm of the arc plasma in the conductive zone [28]. For a rough estimation of the conductive zone radius, the plasma temperature can be taken as about 1 eV, and $\Lambda \approx 10$, i.e., provides an estimate for the radius of the current conductance zone on the order of 1 cm in a wide range of arc currents associated with the CACVD process (from 50 to 500 A).

¹ Figure numeration is as follows: Fig. PI-1a is Fig. 1a of Part 1.

From it, the specific power density in the conductive zone $P_{\rm c}$ can be estimated as:

$$P_{\rm c} = \frac{I_{\rm a} E_{\rm a}}{\pi r_{\rm c}^2} = \sigma_{\rm c} E_{\rm a}^2 \alpha T_{\rm e}^{3/2} E_{\rm a}^2, \tag{3}$$

where σ_c is the characteristic conductivity in the highly conductive zone where the electron temperature $T_c \sim 1$ eV. Considering the decreasing (low current) portion of a typical U-shape voltage–current characteristic of an arc discharge, one can guess that the electron temperature as well as the specific volume arc power in the arc column will increase when the arc current increases. In the high current portion of the U-shape volt–ampere characteristic, the electric field increases as the arc current increases. In this area, any further increase of the arc current does not contribute significantly to an increase in electron temperature in as much as most of the Ohmic heating in the high current arcs is dissipated by radiation loss [28].

In the moderate to atmospheric pressure range, the diffusion transfer zone can block the reaction species from reaching the substrates to be coated installed along the reactor channel wall. Externally generated transversal–rotational magnetic field can be used for shifting the arc channel toward the reactor wall and rotating it around the reactor axis as shown schematically in Fig. PI-1b. This works as a magnetic blender, steering the arc plasma over the deposition zone and increasing the delivery rate of ionized and activated reaction species toward substrate surfaces. The plasma generation rate in the arc column (source zone) is determined by electron collisions with other atomic particles. Transfer processes in the arc plasma are dependent upon pressure range and reactor channel diameter.

2.2. Low pressure range: free fall mode

In the low-pressure regime, ranging from 1 mTorr to \sim 1 Torr, the ions generated in the arc column fall freely to the reactor walls. In a low pressure, high current arc discharge, almost all the species ionize and dissociate to the atomic ion level due to direct electron collisions in the central area of the reactor channel. If the free path of the ions exceeds the radius of the reactor channel, $l_i > R_c$, recombination of ions will occur primarily by collisions with reactor walls and substrate surface. This condition allows the ion to move without collisions from the point where it was generated toward the wall of the reactor. This ionic translational motion is the result of the axially symmetric radial potential V(r) formed within the plasma by the distribution of charged particles. In this case, the source zone extends to the entire reactor channel cross-section, and most of the ions and other atomic particles generated by electron collisions reach the walls of the reactor. The physical model which describes this low-pressure arc discharge was first developed by Tonks and Langmuir

[12]. In this model, the electron density n_e is governed by the Boltzmann distribution:

$$n_{\rm e}(r) = n_0 \exp\left(\frac{eV(r)}{kT_{\rm e}}\right),\tag{4}$$

where k is the Boltzman constant. In this model, the ion current density conveyed by the plasma toward the reactor wall is given by the following expression:

$$j_{\rm i} = 0.382 en_0 \left(\frac{kT_{\rm e}}{M_{\rm i}}\right)^{1/2},$$
 (5)

where M_i is mass of an ion, and *e* is the electron charge [13]. The particle balance in this discharge is quite simple: the rate of ionization (by electron-atom collisions) is equal to the number of ions conveyed by the arc plasma towards the reactor wall. It can be estimated from Eq. (5) that the characteristic ion current density at the wall surface ranges from 1 to 10 $A \cdot cm^{-2}$ which corresponds to a total atomic ion flux of approximately 10^{19} – 10^{20} cm⁻²·s⁻¹. The concentration of carbon-containing species (methane) in the Ar-H₂-CH₄ plasma used in this diamond deposition process is approximately 0.1% of the total atomic particle flux. This gives an estimate for the total carbon flux toward the substrates to be coated in this low pressure arc discharge of $i_{\rm CT} \approx 10^{16} - 10^{17} \text{ cm}^{-2} \cdot \text{s}^{-1}$, which is at least two orders of magnitude lower than the flux required to achieve a typical deposition rate of diamond coatings of about 1µm/h However, the advantage of using low pressure arc plasma for processing diamond coatings is that atomic hydrogen reaches a maximum concentration in this regime [32,33].

2.3. Moderate pressure range: diffusion transfer mode

In large channel diameters, ranging from 3-50 cm, with pressure ranging from a few Torr to atmospheric pressure, the arc discharge contracts and forms a relatively narrow, highly conductive ionized arc column. This highly ionized zone is separated from the reactor wall by a relatively low conductive, less ionized zone where ion recombination has taken place by collisions between ions, electrons, and neutral atomic particles. The reaction species propagate through this zone by diffusion. In the CACVD diamond coating deposition process, plasma forms from an argon/ hydrogen/methane mixture. In the plasma column, molecular components (hydrogen and methane) will dissociate, and ions will be generated by electron collisions with atoms and molecules. These particles will propagate towards the wall of the reactor by diffusion through the lower ionization shield surrounding the arc column. The ion concentration will decrease by recombination with electrons, while molecular species concentration will increase by recombination due to atomic particle collisions. Finally, the heterogeneous recombination of atomic particles will occur on the wall of the reactor and on the substrate surfaces. The flux of any neutral particles conveyed by the arc plasma column through the less ionized intermediate zone towards the reactor wall is determined predominantly by temperature and concentration gradients. This diffusion flux occurs in the same way in the CACVD process as in the other well known CVD processes: HFCVD, MWCVD, which are different mostly by the nature of the generation of reaction species. The diffusion flux can be determined by the following relationship [4]:

$$j_m = -\left(c^2/\rho\right) M_m M_{Ar} D_m \left[-x_m + k_{\rm T} \nabla ln T_{\rm g}\right], \tag{6}$$

where x_m is the mole fraction of species m, c is the total molar concentration, ρ is the plasma density, M_m is the molecular weight of m, T_g is the gas temperature, k_T is the thermal diffusion ratio, D_m is the molecular diffusion coefficient of the given species in Ar (assuming that partial concentrations of H₂ and CH₄ are much less than that of Ar). In the case of the diamond CVD coating process, both terms in Eq. (6) are of similar order of magnitude [4]. Thus, on the basis of Eq. (6), one can estimate the diffusion flux of neutral species toward the reactor walls in a CACVD process by the following:

$$j_{Tm} = -(c^2/\rho)M_m M_{Ar} D_m k_{\rm T} [P_{\rm s}/\lambda_{\rm p} T_{\rm g}], \qquad (7)$$

where λ_p is the thermal conductivity of plasma, T_g is temperature of atomic particles in plasma, and P_s is the transversal thermal flux density conveyed by plasma toward the substrate surface (in W/cm²). In the case of a cylindrical CACVD reactor, P_s can be determined by the following expression, assuming at least local thermal equilibrium between ions, atoms, and molecules in a low temperature zone:

$$P_{\rm s} = \lambda_{\rm p} \nabla T_{\rm g} \alpha (I_{\rm a} \times E_{\rm a}) / \pi D_{\rm c}, \tag{8}$$

where $D_{\rm c}$ is the diameter of the reactor channel.

These formulae show that the flow of neutral reaction species conveyed from the high temperature zone in the arc plasma column towards the substrate surfaces is proportional to the thermal flux generated by the arc plasma column in the direction of the reactor wall.

When gas pressure increases, the role of volume recombination of ions by ion–electron collisions and molecular recombination processes also increase. In the collision- and diffusion-dominated case, the axially symmetric plasma flow in the cylindrical CACVD reactor operating in the moderate pressure range can be governed by a mass balance equation. Neglecting the diffusion along the axis of the reactor channel, this gives:

$$v_z \partial n_e / \partial z = Z n_e - \alpha_r n_e^2 - A j_i, \qquad (9)$$

where v_z is the axial velocity of the plasma flow, $Z=Z(n_e,T_e)$ is the ionization rate per electron, and j_i is diffusion flux of charged particles [13,14]. In a highly ionized, nonisothermal plasma, the temperature gradient follows the flow of charged particles. In this case, the flux of charged particles, j_i , is:

$$j_{\rm i} = -D_{\rm a} \bigtriangledown n_{\rm e}, \tag{10}$$

For a plasma in local thermodynamic equilibrium with a relatively low plasma temperature, it is possible to estimate the electron concentration on the basis of the Saha formula:

$$n_{\rm e}\alpha \exp(-E_{\rm ion}/2kT_{\rm e}),\tag{11}$$

where E_{ion} is the ionization potential of an atomic particle. Substituting this value of n_e for j_i gives:

$$j_{i}\alpha - D_{a}n_{e}(-E_{ion}/T_{e}^{2}) \nabla T_{e}\alpha - D_{a}(E_{ion}/T_{e}^{2})$$

$$\exp(-E_{ion}/2kT_{e}) \nabla T_{e}$$
(12)

Substitution for the gradient of the electron temperature owed to transversal (side) energy flow P_s from Eq. (8) provides the following estimate for the flux of ionized reaction species conveyed by plasma toward substrates located near the reactor wall:

$$j_{\rm i} \alpha D_{\rm a} \left(E_{\rm ion} / T_{\rm e}^2 \right) \exp(-E_{\rm ion} / 2kT_{\rm e}) P_{\rm s} / \lambda_{\rm p}$$
⁽¹³⁾

Thermal conductivity, λ_{p} , includes all thermal transfer processes: thermal transfer due to electrons and neutral components, thermal transfer due to atomic ionizationrecombination, and molecular dissociation-recombination processes. This expression shows that, in highly ionized arc plasmas, diffusion flow of ionized particles follows the temperature gradient, and hence, it is proportional to the transverse energy flow, P_s , similar to the diffusion flow of neutral particles (Eq. (7)). However, in the case of ion diffusion, the diffusion flux is also a strong function of electron temperature. Therefore, at least in the vicinity of the highly ionized conductive zone, the ion diffusion flow increases rapidly when electron temperature increases resulting in an increase of concentration of ionized species in the source zone. It can be seen from Eq. (3) that the electron temperature in the arc column increases with an increase in the specific power density in the conductive zone, P_c. However, it was found that, in a thermalized DC arc discharge plasma, both $P_{\rm c}$ and $T_{\rm e}$ increase slowly when the arc current increases [28]. Therefore, other ways of increasing the electron temperature in an arc discharge based on nonequilibrium approaches are important for further improvement of the effectiveness of the CACVD process. For instance, electron temperature increase may be achieved by superimposing microwave oscillations which contribute to the heating of the electron component of the plasma environment [11]. An example of such a process is the experimental study of a vortex-stabilized UHF discharge in a microwave resonator. In these experiments, the electron temperature exceeds the temperature of heavy particles (gas temperature) by several orders of magnitude due to microwave electromagnetic heating of the electron component, leaving the gas particles at a relatively low temperature [35].

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2.4. Plasma composition

Control of the gas phase composition is essential in optimizing CVD diamond coating process characteristics [31]. Assuming local thermodynamic equilibrium in the cascade arc discharge, which is more probable at higher pressures, the concentrations of atomic particles can be estimated. Fig. PI-2 shows the concentrations of individual species in Ar-H₂-CH₄ gas mixture over a wide range of temperatures and pressures calculated by the thermodynamic equilibrium software "ASTRA" [15,16]. A typical gas composition was chosen for the CACVD diamond coating deposition process: 20% of hydrogen to argon ratio and $\sim 0.6\%$ of methane to hydrogen ratio. It can be seen that, in the low temperature range, the solid carbon deposition area is well defined between 600 and 2500 K (Fig. PI-2c). The ionization rate decreases when the pressure increases. Nevertheless, the concentration of all atomic species and electrons, including atomic hydrogen as well as dissociated

carbon containing species, increase with increasing pressure. In temperatures of about 1 eV and gas pressure ranging from 1 to 40 Torr (associated with the conductive zone of arc discharge at moderate gas pressures), the process gas is highly ionized and the arc plasma region consists of almost fully dissociated species (Fig. PI-2a,b).

Using these values for reactors with channel diameters ranging from 3 to 5 cm and taking the coefficient of ambipolar diffusion $D_a \approx 300 \text{ cm}^2/\text{s}$, one can estimate the diffusion flux of ionized plasma species toward the reactor walls as $j_i \sim 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$. This flux is at least two orders of magnitude lower than in Tonks–Langmuir mode. This estimate demonstrates that, in the arc discharge at elevated pressure, the excited neutral particles become the primary contributor to the impingement rate responsible for the formation of diamond films. It was shown that in MWCVD diamond deposition process, using 1.4% CH4/H2 as a reaction gas, the rate of deposition increases from 0.3 to 3 μ m/hr as pressure increases from 27.5 to 250 Torr. This was attributed to growth of the



Fig. PI-2. Concentration of various reaction species in $Ar/H_2/CH_4$ plasma having typical composition for diamond coating deposition process (Ar/20% H_2 ; $H_2/$ 0.6% CH₄): (a)—reaction species concentrations vs. temperature at high temperature range; (b)—reaction species concentrations vs. pressure at high temperature range; (c)—reaction species concentrations vs. temperature at low temperature range.



Fig. PI-2 (continued).

concentrations of hydrocarbon radicals, in particular CH, in MW discharge plasma [36].

It can be noted that, in nonequilibrium plasmas, the population of excited states of atoms and molecules can substantially exceed that of thermodynamic equilibrium. In this case, the rotational and vibrational temperatures of excited molecules and radicals can exceed the translational temperature (gas temperature) in molecular gas plasma [29,37–41]. It was found that, in an Ar–H₂ nonequilibrium arc plasma, the concentration of excited hydrogen atoms can be attributed to the dissociative recombination of the ArH⁺molecular ions, provided that the concentration of excited hydrogen atoms can equilibrium value by orders of magnitude [29,38].

2.5. Influence of magnetic fields

The effectiveness of the CACVD process can be improved further by using external longitudinal and transversal-rotational magnetic fields. In the low to moderate pressure range, an external longitudinal magnetic field can provide a significant increase in the dissociation rate of molecular reaction species and excitation of atoms and molecules by increasing the frequency of collisions between electrons and atomic particles. It also inhibits the transversal diffusion flux of charged particles resulting in an increase in electron concentration [13,14]. Increase of the concentration of excited states can be seen as an increase in the intensity of atomic and molecular emission lines due to superimposed longitudinal magnetic fields [29]. This effect does not significantly contribute to the increase of specific volume power, $P_{\rm c}$, and the electron temperature, $T_{\rm e}$, in the arc discharge. An increase of the intensity of the longitudinal magnetic field in arc discharge at moderate to atmospheric pressure also results in the generation of plasma oscillations due to magnetohydrodynamic instabilities. These instabilities appear as a change of the arc column geometry from a direct cylinder to a helical shape and/or an oscillation of the diameter of the arc column. This can induce a magnetohydrodynamic turbulence in the plasma flow, while the subcritical hydrodynamic Reynolds number $Re \ll Re_{cr}$ still corresponds to laminar flow conditions. Other plasma oscillations and instabilities can be responsible for creating turbulence in arc plasma flow. One example of such effect is provided by ion acoustic waves. This type of plasma wave can be created in high current arcs at pressures as low as 0.1 Torr, resulting in the generation of high-energy ion fluxes [17].

Transversal–rotational magnetic fields rotate the plasma column and simultaneously shift the conductive zone toward the reactor channel wall, as shown schematically in Fig. PI-1b. This provides intensive steering of plasma components over the reaction zone and increase of concentrations of ionized and activated atomic particles in the vicinity of the reactor wall. This allows for further enlargement of the diameter of the reactor channel without a significant decrease in the concentration of excited states and dissociated reaction species in close proximity to the reactor wall. There are also other ways for perturbation of the position of arc column in a reactor channel by influence of external magnetic fields. For instance, there is a possibility of dynamic magnetic steering of the arc column by imposing of impulse transversal or longitudinal magnetic field created by separate magnetic coils positioned downstream to the reactor channel. In any case, magnetic steering is able to provide space dependent oscillations of the concentration of plasma components over reaction zone, inducing the artificial turbulence state of the plasma environment.

Plasma turbulence, whether created by intrinsic plasma instabilities or by external magnetic fields, results in an increase of the plasma diffusion transfer rates. This can be taken into account by introducing the effective plasma diffusion flux. Considering diffusion in the radial direction, the following form can be written for the general case when $Re>Re_{cr}$ at high pressure, high axial velocity plasma flow:

$$j_{\text{itotal}} = j_{\text{ia}} + \langle u_{b}' \eta \rangle_{\text{MHD}} + \langle u_{b}' \eta \rangle_{\text{HD}}, \qquad (14)$$

where j_{ia} is the ambipolar diffusion flux, u'_p is the pulsating component of plasma velocity, and n'_i is the pulsating component of ion concentration [18,19].

In the case of magnetic steering using a transversalrotational magnetic field, the highly ionized conductive zone may be considered as a dynamic ionizer and activator of reaction media. To reach the maximum effectiveness of ionization and activation of reaction species in the vicinity of the reactor wall, it is important that the deactivating time, τ_d , for certain reaction species critical for the deposition process will exceed the period of rotation of the transversal-rotational magnetic field. Losses of ionized particles in the arc plasma are due to diffusion towards the reactor wall followed by surface and volume recombination. The deactivating time of hydrogen ions near the reactor wall due to diffusion losses is approximately: $\tau_{\rm D} \approx 4 r_{\rm c}^2 / D_{\rm H^+}$, where $D_{\rm H^+}$ is the ambipolar diffusion coefficient of hydrogen ions in argon. For an orderof magnitude estimation, D_{H^+} calculated at a pressure of 20 Torr and a near-the-wall temperature of 2000 K, using normalized mobility of H⁺ in Ar of $K_0=5.75 \text{ cm}^2 \cdot (\text{Vs})^-$ [20], gives $D \approx 570 \text{ cm}^2/\text{s}$. Taking the radius of the source zone (plasma generating area) in the arc column to be: $r_{\rm c} \sim 1$ cm, one can estimate $\tau_D \lesssim 7 \cdot 10^{-3}$ s. Deactivating time due to volume recombination can be estimated as:

 $\tau_{\rm R} \approx 1/\alpha_{\rm r} n_e;$

where $\alpha_r \sim 10^{-7} \text{ cm}^3/\text{s}$ is the dissociative recombination coefficient [18]. For an order-of-magnitude estimation, we can take $n_e \approx 10^{10} \text{ cm}^{-3}$ as the average electron density in the reaction zone, resulting in $\tau_R \sim 10^{-3}$ s. Deactivating time due to diffusion losses of neutral excited reaction species can be expressed in the same way as for diffusion losses of ions: $\tau_N \approx 4r_e^2/D_N$. The diffusion coefficient of CH₄ in hydrogen at similar processing conditions (temperature ~2000 K, pressure 20 Torr) was estimated in [4] as $D_{CH4} \sim 326 \text{ cm}^2/\text{s}$ resulting in $\tau_{CH4} \sim 0.01 \text{ s}$.

This estimation demonstrates that a transversal-rotational magnetic field even with relatively low rotation frequency $f_{\rm B} \gtrsim 60$ Hz can provide significant improvement of ionization and activation of the reaction environment near the reactor wall area for tubular CACVD reactors.

3. Experimental

3.1. CACVD Reactor Design

The CACVD reactor comprises a long, tubular or rectangular channel with upstream and downstream electrode ports, as shown schematically in Fig. PI-3. Carrier and reactive gases are input at two axial locations, and a long DC arc column is established between the electrodes confined by a number of coils which control both transverse-rotational and longitudinal magnetic fields [11]. The electrical resistivity along the reactor walls is made to exceed the resistivity of the arc column by using a sectional channel design, with each section insulated from the next to prevent breakdown between sections and a short circuit of the arc discharge [28]. The width of a single metal reactor section l_s can be determined by the following condition:

$$E_{\rm a} \times 1_{\rm s} \ll V_{\rm cat} + V_{\rm an},\tag{15}$$

where E_a is electric field in the arc column, V_{cat} and V_{an} are cathode and anode voltage drops, respectively. For enhancing arc stability and ease in reigniting the arc discharge, a stabilizing zone is created using the carrier gas (argon) between the cathode and an auxiliary anode prior to the reactive gases injection inlet. The stabilizing zone also allows for formation of a vortex in the rotating plasma column before the reaction species are introduced. A mixing zone is located downstream from the stabilizing zone and prior to the reaction zone where the substrates to be coated are located.

Magnetic fields are employed to guide the plasma column within the reaction zone. Longitudinal coils positioned uniformly about the reactor tube in the region of the reaction zone create an axial magnetic field. increasing plasma activity and focusing the plasma column into a relatively narrow stream. Additional coils positioned adjacent to the reaction zone create a transverse magnetic field that controls the radial positioning of the plasma column within the reaction zone and directs the plasma toward the substrates. A phase-shifted AC electric current is applied through the transverse coils to create a rotating magnetic field in the reaction zone. In operation, a high current DC power supply creates a voltage between the cathode and the anode, and the rotating magnetic field directs the plasma column into contact with the substrate holders, arranged around the periphery of the reaction zone. The direction of the rotating magnetic field as well as the direction of vortex rotation in the gas can be alternated during the process, providing further equalization of the plasma distribution parameters.

Two 1-m length cylindrical CACVD reactors were used in this work: Reactor No. 1 (3-cm diameter channel), and



Fig. PI-3. Schematic longitudinal cross-section view of CACVD reactor

Reactor No. 2 (4-cm diameter channel). Both reactors were equipped with high current hollow cathodes and tubular water-cooled copper anodes with axially symmetrical magnetic coils for rotating anodic arc spots. Both reactors worked in an $Ar-H_2-CH_4$ gas mixture environment ranging in pressure from 0.1 up to 100 Torr. Reactor No. 2 was also equipped with a 13.56 MHz, 5 kW ENI RF generator, which imposed microwave power over the regular DC arc discharge.

3.2. Substrate installation

In the sectional reactor channel, the substrates to be coated can be installed either at the walls of reactor sections, as shown in Fig. PI-4b, or suspended in the reactor channel on a high temperature insulated cable (Fig. PI-4a) [10]. In each case, the substrate holders act as a "hot liner", confining the arc within the channel created either within annular substrate holders or between the axially suspended substrate holder blocks and the inner wall of the tube, which is water cooled to act as a cool liner. The substrate holders are separated by insulators or narrow dielectric gaps which prevents short circuiting of the arc across the conductive substrates or across the conductive surface of a film being deposited on dielectric walls. In the case presented in Fig. PI-4b, the substrates to be coated (drill bits or cutting inserts) are installed in water-cooled sections of the reactor. Each section is separated from the adjacent sections by insulative spacers. In this design, separate sections are made of anodized aluminum, providing sufficient electrical



Fig. PI-4. Substrate holder arrangements: (a)—insulated substrate holder blocks suspended by silica cable along the reactor channel axes; (b)—substrate holders installed in wall-through positions along the reactor walls.

insulation between adjacent reactor sections. Each section is also hermetically sealed with Viton o-rings from the neighboring sections, creating a cascade of insulated reactor channel levels with a common water-cooled passage. A photograph of a single reactor section with six substrate holders installed through the section wall is shown in Fig. PI-5.

A single substrate holder assembly and its cross-section at the substrate stem level are illustrated in Fig. PI-6. Two types of such substrate holders were designed. One can hold a square carbide insert as a substrate to be coated (Fig. PI-6a). Another can hold 12 metal rod substrates 2-mm diameter×20-mm long (Fig. PI-6b), which are used in the manufacturing of CVD diamond dental burs. The substrate temperature during operation is controlled by using a composite powder variable conductance insulation (CPVCI)



Fig. PI-5. Photograph of a single section of the reactor channel with six wall-through substrate holders.

material placed between the insert and the substrate mount. The thermal contact resistance of the CPVCI is inversely proportional to the temperature, decreasing as temperature increases to remove heat from the substrate. A thin stainless steel tube supports the substrate mount and also serves to control heat transfer [23]. Up to 1000 metal rod substrates (2-mm diameter×20-mm length), or 90 carbide inserts (12×12 mm), could be installed in the substrate holders in Reactor No. 2.

3.3. Process diagnostics

Substrate temperature as well as temperature distribution in different components of the substrate holders inserted in the wall of the reactor's sections was measured by means of a type K thermocouple. The accuracy of chromel-alumel thermocouple measurement was $\pm 2\%$. For the direct measurement of substrate heating due to the plasma, the design of the substrate holder shown in Fig. PI-6b was modified to allow a thermocouple tip to be immersed in the reactor channel at different distances from the reactor axes. In other instances, direct temperature measurements were made via direct contact of the thermocouple with various substrate holder components. An optical pyrometer with disappearing filament was also used for estimation of the substrate temperature for both the substrates inserted through the holes in the reactor wall (Fig. PI-4b) or suspended along the reactor axis (Fig. PI-4a). For this purpose, optical view ports with quartz optical windows were installed in selected reactor sections opposite to substrate holders. Optical windows were also used for observation of the plasma radiation associated with oscillations of the plasma discharge. In this case, photo diodes connected to an oscilloscope were used to collect optical signals from the arc plasma column. Static and dynamic



Fig. PI-6. Substrate installation: (a)—substrate holder assembly for flat square substrates; (b)—substrate holder assembly for metal rod substrates. Numbered components are: substrate carrying assembly (30), substrate holder base (32), housing (34), o-ring (35), substrate mount (36), substrate (40), CPVCI material (38), insert (40), substrate mount (36) to provide adequate thermal control via adjustment of thermal contact resistance between the insert and substrate mount. In the case of shank-shaped substrates such as metal rods, the substrate mount can be filled by CPVCI material (38) that serve as a substrate carrier and thermal control media. The CPVCI material is pressurised by mount plug (46). A thin stainless steel tubing (55), which supports substrate mount (36) also serves as a means to further transfer heat energy to the various heat sink stages [23].

electric parameters of the reactor were collected by measurement of the reactor sections potentials.

4. Results and discussion

4.1. Electrical characteristics of the CACVD process

4.1.1. Static characteristics

The voltage–current characteristics of the cascade arc discharge in reactors No.1 and 2 were investigated in a pressure range from 0.5 up to 50 Torr for various Ar/H₂ gas compositions in arc currents ranging from 12 to 250 A with and without external magnetic fields. As expected, addition of hydrogen has a dramatic effect on the arc voltage. Fig. PI-7 shows the voltage–current characteristics of the cascade arc discharge in an argon and argon–hydrogen mixture near the lower end of the pressure range. The U-like volt–ampere characteristic in argon has a minimum at $I \approx 150$ A at a pressure of about 0.5 Torr. The arc voltage increases significantly as the hydrogen concentration increases. This

results from a high degree of contracting of the arc column in hydrogen arc discharge due to high molecular thermal conductivity of hydrogen plasma [28]. At lower pressure ranges, the arc voltage increases more than 50% when hydrogen partial pressure becomes equal to that of argon. It continues to grow with the increase of hydrogen partial pressure. The arc voltage exceeds 2 V/cm (more than two times greater than in argon arc) at gas pressures of about 2 Torr in Reactor No. 1 (channel diameter, 30 mm).

Volt–ampere characteristics of arc discharge in argon/ 20% hydrogen gas mixture in Reactor No. 2 are shown in Fig. PI-8. In arc current ranging from 30 to 70 A, voltage decreases when current increases. A significant increase of arc voltage was also found with an increase of gas pressure. This corresponds to a side energy flux, P_s , according to Eq. (8). Both arc voltage and side energy flux increase when gas pressure increases. An increase of both arc voltage and side energy flux with increased hydrogen concentration in an argon/hydrogen arc discharge is shown in Fig. PI-9 for Reactor No. 2. This tendency was also demonstrated through an investigation of a freestanding argon/hydrogen



Fig. PI-7. Electrical characteristics of low pressure high current Ar/H₂ arc discharge in Reactor No. 1.

arc discharge at atmospheric pressure [21]. A comparison of the charts presented in Figs. PI-7 and PI-9 reveals that argon as a buffer gas contributes very little to the arc power when the hydrogen concentration exceeds about 10%. This can be attributed to the fact that hydrogen has an ionization potential more than 2 eV lower than that of argon (13.595 vs. 15.755 eV). This explains the predominant hydrogen contribution to the total ion concentration in the Ar/H_2 arc.

The influence of magnetic fields on arc characteristics was investigated by comparison of volt–ampere characteristics of cascade arc discharge in superimposed longitudinal and transversal-rotating magnetic fields. The magnitude of the longitudinal magnetic field was varied in the range 0– 100 Gs, while rotating magnetic field was held at a level of about 50 Gs near the axis of the reactor channel. No significant influence of magnetic fields on static voltage– current characteristics was found in the investigated range of discharge parameters.

Fig. PI-10 shows the arc voltage vs. hydrogen to argon flow ratio in an argon/hydrogen/methane gas mixture used in the processing of polycrystalline diamond coatings in Reactor No. 1. The arc current was slightly different in these processes, ranging from 22 to 26 A. This difference relates to no more than a 10% change in the magnitude of the arc voltage. An increase of hydrogen concentration in excess of 10% does not show significant impact on arc voltage. In this discharge, the arc voltage increases with an increase of gas pressure and decreases with an increase of arc current similar to arcs in pure argon and hydrogen. The absolute value of arc voltage appears to be about the same as for pure hydrogen, having the same pressure as the hydrogen partial pressure in the gas mixture. The methane component in the $Ar/H_2/CH_4$ mixture had concentrations less than 1% of hydrogen and did not contribute appreciably to the arc voltage and side energy flow.

4.1.2. Arc plasma oscillations and instabilities

Oscillograms of the electrical potential of the reactor sections indicate different oscillations of the plasma potential. This shows that an increase in hydrogen to argon ratio in the gas environment can create an oscillation of section voltage. In as much as each reactor section operates



Fig. PI-8. Volt-ampere characteristics and transversal energy flux in Ar/20% H₂ discharge in Reactor No. 2. Arrows show to which ordinate (left or right) these groups of data belong.



Fig. PI-9. Electrical characteristics of arc discharge in Reactor No. 2 vs. hydrogen-to-argon ratio.

as a collecting electrostatic probe, the oscillations of its potential correspond to oscillations in the plasma potential. In parallel, the oscillations of the plasma radiation were indicated by recording optical signals from the optodiod focused on the center of the reactor channel at varying distances from the cathode. In the low pressure range (P < 7Torr), a wide spectrum of plasma oscillations were observed with relatively low amplitude, less than 10% of the arc electric field in the same location. It was found that, in the pressure range ($P \sim 1$ Torr), ion acoustic oscillations have a significant influence on discharge characteristics [17]. When gas pressure exceeds 3-5 Torr, the low amplitude oscillations disappear, and the discharge enters a calm mode. In the pressure range $P \ge 7$ Torr, an increase in hydrogen to argon ratio in the gas environment can also create oscillations of section voltage. In this case, the amplitude of the oscillations is much higher, about 3-5 V, which is comparable with the magnitude of the arc electric field. An

increase in the amplitude of these oscillations usually precedes arc interruption. In this situation, the increase of arc current has a stabilizing effect on arc discharge instabilities. Fig. PI-11 shows an approximate estimation of the boundary of the arc stability area under control of arc current vs. hydrogen to argon ratio and gas pressure. When arc interruption occurs, the arc is automatically reignited by high voltage impulse ignition as shown in Fig. PI-3b. When the arc current is less than a certain critical value required for stabilizing the arc discharge, the cascade ignition can cause transfer from a continuous arc discharge to a periodic impulse discharge mode with repetition frequency ranging from 10 to 100 Hz. An increase of arc current retains the arc discharge in continuous operating mode. Changing the regime of plasma oscillations with an increase of gas pressure can be explained by the increasing influence of the reactor wall and the stabilizing effect of the gas vortex at the higher gas pressure range. A further increase in gas pressure,



Fig. PI-10. Electrical characteristics of arc discharge in Ar/H₂/CH₄ gas mixture observed for various diamond coating deposition runs.



Fig. PI-11. Cascade arc stability diagram.

especially in molecular gases (when the arc column contracts to a smaller diameter), creates large-scale magnetohydrodynamic instabilities and gas turbulence, which have a predominant influence on arc oscillations. The lower modes of magnetohydrodynamic instabilities in moderate to high pressures can be identified by periodic contracting of arc column and its helical winding shape transformation. This contributes to the increase of arc voltage by increasing the length of the arc column per unit length of the reactor.

4.2. Thermal management of substrates in CACVD diamond coating process

4.2.1. Thermal control by radiation cooling

Thermal transfer properties of substrates in CACVD process with different thermal management schemes were studied in a wide variety of process parameters. First, the freestanding substrates, immersed in the plasma environment were investigated. A substrate holder provided high accuracy measurement of plasma heating at different distances of substrate surfaces from the reactor channel wall by a built-in precision thermocouple (Fig. PI-6c). All these measurements were done in Reactor No. 2 with an arc current of 64 A, arc voltage of 200 V, and side power flux of 12 W/cm². It was observed that the temperature of the substrates heated by plasma and cooling by radiation have a similar dynamic of heating as shown in Fig. PI-12. In the case of the thermocouple junction ball tip, we can neglect the conduction cooling in comparison with radiation cooling when the temperature of the tip reaches high temperature area. In this case, the temperature of the thermocouple tip is governed by the following equation [22]:

$$\rho_{\rm TC} c_{\rm p} V_{\rm TC} \frac{\mathrm{d}T_{TC}}{\mathrm{d}t} = Q(x) - \sigma A_{\rm TC} T_{\rm TC}^4, \tag{16}$$

where $\rho_{\rm TC}$, $c_{\rm p}$, $V_{\rm TC}$, and $A_{\rm TC}$ are the density, specific heat capacity, volume, and surface area of the thermocouples, respectively. $Q(x)=q(x)A_{\rm TC}$ is the thermal flux conveyed by surrounding plasma toward the thermocouple tip, which is immersed in the plasma at a distance x from the wall of the reactor, and $\sigma=5.67\times10^{-12}$ W/cm² K⁴ is the Stefan– Boltzmann constant (we assume that surface of the thermocouple tip has emissivity $\varepsilon \approx 1$). We can rewrite this equation in the following form:

$$\frac{\mathrm{d}f_{\mathrm{T}}}{\mathrm{d}\tau} = 1 - f_{\mathrm{T}}^4,\tag{17}$$

where $f_{\rm T}=(\sigma/q)^{1/4}T_{\rm TC}$, and $\tau=[(\sigma/q)^{1/4}(qA_{\rm TC}/V_{\rm TC}\rho_{\rm TC}c_{\rm p})]t$. The universal function $f_{\rm T}$ is also shown in Fig. PI-12. Using the universal function $f_{\rm T}(\tau)$, the temperature $T_{\rm s}$ of the substrates immersed in the arc plasma and cooling by radiation can only be described by the following formula:

$$T_{\rm s} = (q/\sigma)^{1/4} f_{\rm T}(\tau).$$
 (18)

After the dynamic heating stage, the substrate temperature stabilizes at a magnitude determined by the balance



Fig. PI-12. Heating dynamic measured by built-in thermocouple (Fig. PI-4c) with junction ball extended in plasma at different distances from the substrate holder mount. It is compared with normalized temperature calculated using Eq. (17).

between thermal flux conveyed by surrounding plasma environment and radiation cooling:

$$T_{\rm s} = \left(q/\sigma\right)^{1/4},\tag{19}$$

The temperature of a carbide insert suspended near the axis of the reactor channel on a silica cable in Reactor No. 1 is shown in Fig. PI-13. Rotating the silica cable rotated the substrate within the reactor channel. Rotational magnetic field provided additional equalization of the plasma energy flow directed toward the substrate surface. In this case, the substrate temperature measured by optical pyrometer, increases rapidly when arc current increases. The amount of heat conveyed by the plasma toward the insert was calculated using Eq. (8), based on the assumption that there is only one heat sink mechanism: radiative cooling. The substrate temperature exceeds 1000 °C at an arc current as low as 20 A with increased hydrogen concentration. Fig. PI-13 also shows the temperature of the thermocouple junction ball immersed in the plasma at different distances from the reactor channel wall in Reactor No. 2. For this experiment, 11 stainless steel rods 1.6-mm diameter×19-mm long were installed in the substrate holder mount together with the thermocouple. The substrate mount was filled with pure BN powder as a substrate support media. Typical process parameters for the deposition of diamond coatings in Reactor No. 2 were used: arc current 65 A, arc voltage 200 V, hydrogen to argon ratio 20%. The corresponding thermal flux conveyed by plasma was calculated using Eq. (8). It can be seen that substrate temperature and corresponding incoming thermal flux increase with the depth of immersion inside the reactor channel. The substrate temperature also increases with an increase of gas pressure. The gas pressure has a greater effect on the substrate temperature when the substrate is immersed deeper inside the reactor channel. When substrate is installed near the reactor wall.

the measured thermal flux is in good agreement with the side energy flux generated by the arc discharge.

The same approach was used for assessment of the uniformity of heat distribution over the CACVD reactorcoating zone. However, instead of measuring the temperature of a freestanding thermocouple junction ball, the thermocouple was attached to the mount plug (46) of substrate holder shown in Fig. PI-6b. The substrate mount was filled with BN powder, stabilizing thermal transfer through the mount, and supporting 12 stainless steel rods installed in the mount slots. The temperature distributions among substrate holder plugs, all having even positions in relation to the reactor axis, are shown in Fig. PI-14. It can be seen that temperature nonuniformity does not exceed $\pm 5\%$. The area of the reactor zone where temperature diversity reaches a maximum is located next to the stabilizing zone near the cathode. This can be explained by nonestablished plasma composition in this area of the reactor.

4.2.2. Thermal control by conduction cooling

Achieving higher deposition rates by increasing the hydrogen to argon ratio, and at the same time, securing a stable operation mode for the arc discharge requires higher arc currents at higher power consumption per unit length of the reactor channel. This results in an increase of heat transfer toward the substrates, suspended in the plasma arc column which have only one heat sink mechanism: radiation cooling. In this case, the area of parameters which allows control of the substrate temperature for deposition of diamond coating in the reactor (with a relatively narrow channel) is quite limited. This situation improves little by installation of the substrates (carbide inserts) at the reactor wall, using the substrate holder shown in Fig. PI-4b. The high contact thermal resistance between substrate (carbide insert) and substrate holder mount prevents using the heat sink capability of the substrate holder. A new approach,



Fig. PI-13. Temperature of the thermocouple junction ball (Fig. PI-4c) extended at different distances into the plasma and corresponding transversal energy flux.



Fig. PI-14. Substrate mount plug temperature variation vs. position of substrate holders in the reaction zone and arc voltage distribution along the reactor channel in Reactor No. 2.

based on using composite powder thermal transfer media with variable conductance insulation properties, was developed for the thermal management of the substrates in high temperature vapor deposition processes [23].

It has been found that a two-phase mixture, composed of a relatively low melting point alloy or metal and a particulate ceramic material, will function as an autoregulating heat transfer system. In as much as the thermal conductivity of gases is very low, generally about three orders of magnitude lower than solids, the effective thermal conductivity of a solid powder is determined primarily by the thermal properties of the bulk powder material that forms a skeleton-like structure and the effective contact area between neighboring particles [24-26]. Thermal radiation makes a significant contribution to thermal transfer properties of ceramic powders at high temperatures [27]. In the case of two-component metal-ceramic powder mixtures, applying pressure to the powder can increase the effective contact area. It increases dramatically when the metal component is melted but shrinks to the initial value when the temperature decreases and the metal component solidifies, providing that the ceramic component is nonwettable by the metallic component. This affects the value of the effective thermal conductivity of the two-component mixture: increasing it significantly when the temperature exceeds the melting point of the metal component and decreasing it significantly when the temperature of the mixture drops below the melting point of the metal component. Thus, the mixture of nonwettable metalceramic powder provides a variable thermal conductivity property at a certain temperature range, which can be used as a composite powder variable conductance insulation (CPVCI) medium [23]. Thermal expansion of metals and ceramic particles differ as much as 5 to 10 times in the high temperature regime. For example, the thermal expansion of aluminum alloys in 600–1000 °C is about $\alpha_m \sim 25 \times 10^{-6}$ K⁻¹, while for BN or graphite, it is only $\alpha_c \sim 1-2 \times 10^{-6}$ K⁻¹. When the temperature of a metal-ceramic powder mixture drops below the liquidus point of the metal component,

large thermal expansion differences result in splitting the ceramic particles from the metal phase. This well-known thermal–mechanical noncompatibility of metal–ceramic composition creates difficulties for sintering cermet materials by powder metallurgy techniques.

The composite powder mixture consisting of BN with different concentration of Tin powder was used as CPVCI media to control the substrate temperature in the CACVD diamond coating deposition process. In the case of flat substrates such as carbide inserts, the substrate holder shown in Fig. PI-6a was used. The layer of CPVCI (38) was placed between the backside of the insert (40) and substrate mount (36) (all numeration follow Fig. PI-6a). For coating shank-shaped substrates, the substrate holder shown in Fig. PI-6b was used. The substrate mount (36), where 12 metal rod substrates were installed, was filled with CPVCI and pressurized by plug (46). Both of these substrate holders have three stages of heat sink. Consider the substrate holder assembly shown in Fig. PI-6a. In this case, the first (high temperature) stage of heat sink arrangement is between the substrate and the substrate mount. The thermal resistivity of this stage is determined by contact thermal resistivity between insert (40) and substrate mount (36) now under control of the CPVCI thermal transfer layer (38). The second (intermediate temperature) stage is created by a thin wall stainless steel tube (55). This stage must hold a certain level of temperature of the substrate mount at the high temperature end to develop a thermal pedestal while having an ambient temperature provided by contact with the watercooled reactor wall at the low temperature end. Supposing the temperature of the substrate (carbide insert) is $T_{\rm S}$ and temperature of the substrate mount is $T_{\rm M}$, we can obtain the thermal resistances of each of these stages: $R_1 \approx (T_{\rm S})^{-1}$ $T_{\rm M}/q$, where conductive thermal flux $q_{\rm c}=q_{\rm p}-\varepsilon\sigma T^4$. $q_{\rm p}$ is the thermal flux conveyed from the plasma toward the substrate surface. The thermal resistance of the intermediate stage of the heat sink arrangement $R_2 \approx (T_{\rm M} - T_{\rm W})/$ $q_{\rm c}$, where $T_{\rm w}$ is temperature of the reactor wall. For an

order-of-magnitude estimation, we can take $q_c \approx 10 \text{ W/} \text{ cm}^2$, $T_S \approx 800$ °C, and $T_W=50$ °C, which are typical parameters for the diamond coating deposition process in the CACVD reactor. Taking into account that the thermal transfer mixture allows a temperature difference between the substrate and the substrate mount of less than 100 °C, we can estimate the thermal resistivity, $R_2 \approx 60 \text{ cm}^2$ °C/W, which is due primarily to the thin wall stainless steel tube (55).

A comparative study of thermal control of the substrates in the CACVD diamond coating deposition process was conducted on carbide inserts and stainless steel rods as substrates (Fig. PI-15). Carbide inserts were installed in Reactor No. 1 in the substrate holders shown in Fig. PI-6a with a layer of BN/TiN ceramic powder mixture (38) positioned between the insert (40) and the substrate mount (36). A thermocouple was placed along the axis of the substrate holder through the hole in the substrate holder mount (36) to be in direct contact with the backside of the carbide insert. The process parameters were typical for the diamond coating deposition process in Reactor No. 1: argon flowrate 2 slm, hydrogen to argon flowrate ratio 15%, arc current 24 A. When the thermal transfer powder layer consisted of only pure BN powder, the temperature of the insert increased to the level when the WC/6% Co alloy began melting. Addition of 20 wt.% of Tin powder to the CPVCI layer stabilised the temperature near 800 °C. A slight decrease of substrate temperature during the first couple of minutes of the process may be explained by the stabilising effect of the temperature field in the body of the substrate holder. An increase in Tin concentration three times to 60 wt.% resulted in a decrease of the substrate temperature. Fig. PI-15a shows the temperature of carbide inserts stabilised by CPVCI during the beginning stage of the typical diamond coating deposition process in Reactor No. 1. The side power flow was constant during the process.



Fig. PI-15. Temperature dynamic of the substrate carbide inserts subjected to diamond coating deposition process in CACVD reactor: (a)—temperature of carbide insert substrate vs. concentration of Tin in BN/Tin thermal regulating mixture; (b)—temperature of carbides in various diamond coating deposition runs.

Fig. PI-15b shows the temperature dynamic of the carbide insert stabilised by CPVCI thermal control interlayer during the entire diamond coating deposition process. It can be seen that the substrate temperature continues to decrease during almost the entire process time, which can be attributed to a change of the surface emissivity of the substrate by deposition of a diamond coating.

Results of temperature measurements of the stainless steel rod substrates are shown in Fig. PI-16. In this case, the substrate holder shown in Fig. PI-6b held 12 stainless steel rod substrates. The substrate holder was installed in Reactor No. 2. The thermocouple tip was brazed to the back butt-end of one of the rods. The substrate mount was filled with CPVCI thermal control powder mixture and pressurised by the plug (46). The process parameters were set to typical values for the diamond coating deposition process in this reactor: arc current 65 A, arc voltage 200 V, pressure 20 Torr, hydrogen to argon ratio 20%, side energy flow about 12 W/cm². It can be seen that, with an empty substrate mount, the temperature of the steel rod is less than with a mount filled with BN powder. This can be explained by the thermal insulation capabilities of pressurised BN powder. With addition of Tin to BN, the temperature of the back butt-end of the substrate rod can be controlled in a range between 450 and 550 °C. Taking into account the strong nonlinear temperature dependence of stainless steel in the range between 500 and 800 °C, it can be shown that it is possible to provide precise control of the steel rod temperature at the high temperature range from 600 to 800 °C by managing temperature at its low temperature butt-end in the range between 450 and 550 °C.

4.3. CACVD reactor scale-up

Using side power flux P_s and specific volume power P_c at similar magnitudes, it is possible to enlarge the diameter of the reaction chamber without compromising the power

and mass transfer conditions required for deposition of coatings. For example, an increase of the diameter of reactor channel to 20 cm will require increase of the arc current to the level of 500 to 1000 A, assuming that electric field within this large diameter channel does not exceeds 1-2 V/cm in the pressure range of 10-100 Torr and hydrogen to argon ratio about 20%. Still, there are certain limitations due to recombination and other collision-related processes resulting in a decrease in concentrations of reaction species when the distance between the source zone in the arc column and substrates located near the reactor wall increases. Application of transversal magnetic fields in the CACVD reactor directs the source zone into close proximity with the substrate surface. This allows achieving similar impingement rates for reactors with larger channel diameters which demonstrates scalability of the CACVD process.

5. Conclusions

It is shown that the cascade arc-assisted CVD process is capable in providing intensive heat and mass transfer conditions in a highly ionized plasma required for deposition of polycrystalline diamond films. Different embodiments of the CACVD reactor can accommodate various substrate geometries for industrial-scale production. The CACVD reactor can operate in a wide pressure range from 0.1 Torr up to atmospheric pressure. The transversal energy flow as well as the specific energy density were found to be critical parameters determining the temperature of the substrates in this diamond coating deposition process. When these parameters are maintained at similar magnitudes, the CACVD reactor diameter can be enlarged to over 20 cm to accommodate larger substrate geometries and to achieve higher production volume.

Using composite powder variable conductance insulation as a means for thermal management of substrates in



Fig. PI-16. Temperature of stainless steel rod substrates vs. Tin-to-BN ratio in CPVCI thermal regulating mixture: Reactor No. 2, arc current 60 A, transversal energy flux 12 W/cm², Ar/20% H₂ plasma.

CACVD process allows for precise temperature control of substrates with different shapes, which is required for deposition of high quality polycrystalline diamond coatings.

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