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Diamond deposition on thin cylindrical substrates

GORDANA S. RISTIĆ[1*#], ŽARKO D. BOGDANOV[1], MILAN S. TRTICA[1#] and ŠĆEPAN S. MILJANIĆ[1,2]

[1]*VINČA Institute of Nuclear Sciences, P.O. Box 522, 11001 Belgrade and* [2]*Faculty of Physical Chemistry, University of Belgrade, P.O. Box 137, 11001 Belgrade, Serbia*

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Abstract: Diamond coatings were deposited onto different cylindrical substrates (Cu, SiC, W and Mo) by the hot filament chemical vapor deposition (CVD) method. Continuous, adhered and well-faceted crystalline coatings of diamond were obtained on Cu-wire using a special pretreatment with a mixture of diamond and metal powders as well as carefully controlled deposition at lower power. Diamond deposition on SiC-fiber gave continuous and uniform coatings when only the filament power was properly selected. Uniform, homogeneous, euchedral diamond coatings on W- and Mo-wires, attained at a higher filament power, confirmed once more the convenience of refractory metals as substrates for diamond deposition by the CVD technique. Characterization of the obtained coatings was realized using scanning electron microscopy (SEM). The obtained results are compared with the literature data. Differences are discussed with regard to the chemical nature of the substrates as well as their thermophysical characteristics.

Keywords: diamond coating; CVD; cylindrical substrates; Cu; SiC; W; Mo.

INTRODUCTION

The ease with which diamond film can follow any substrate shape and simultaneously maintain the characteristics of the hardest precious solid make it an attractive engineering material. The chemical vapor deposition (CVD) technique enables the synthesis of a diamond coating on various 3-D objects made of different materials in a rather simple and inexpensive way. Among the various CVD techniques, the hot filament CVD method stands on first place for its versatility and scalability, as well as its low cost and ease of realization. The activating agent of this method – the hot filament itself – can be quickly and easily adjusted

* Corresponding author. E-mail: eristic@vinca.rs
# Serbian Chemical Society member.
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to a particular task by a proper choice of filament power and the manner of the filament-to-substrate mounting.

Different substrate materials in many different shapes are used in diamond CVD. The requirements for these come from various engineering and scientific areas. In technological applications generally, a strong adhesion between the substrate and the coating is required, as it determines the strength of a substrate–coating system. Sometimes, the substrate should provide only a mechanical support for the growing coating (*e.g.*, for self-standing structures). A cylindrical substrate shape, both in micro and macro dimensions, with either sharp or rounded edge is required in numerous applications, such as special burrs (dental, tool-drill), various probes (thermal, X-ray), cross-field amplifiers, flow nozzles, wire dies, fiber-components for reinforcing composites (metal, ceramic, polymer).

Diamond coatings deposited on thin cylindrical substrates made of different materials, copper, silicon carbide, tungsten, molybdenum are presented in this work. Cu is a soft metal, inert to deposition working conditions, commonly used in growing self-standing elements;[1–4] the latter ones of a cylindrical form, especially with a closed end, could be very useful as storage vials, sample vessels, special test tubes. SiC fiber is a high-tech product, characterized with high strength and high heat resistance as well as low thermal expansion and low electrical conductivity. Diamond-coated SiC fibers can be used for reinforcing different composite materials, *e.g.*, those which are concerned with rigidity, low density and high temperature conditions (up to 1200 °C).[5] The refractory metal W, a strong and hard material, when coated with diamond is used in many demanding technological applications, such as tools,[6] high-temperature probes,[7] and wear-resistant parts.[8] Mo, another refractory metal of lower density and better ductility, as well as lower price, can substitute W in some applications.[9]

EXPERIMENTAL

The deposition experiments were performed in a hot filament CVD reactor coupled to a vacuum apparatus equipped with a pump, a gas flowmeter and pressure gauges.[10] The activating filament was formed as a large-diameter coil and the substrates were mounted through the coil centre, in order to obtain homogeneous and uniform diamond coatings on the thin cylindrical substrates, as well as to avoid complexity and expensiveness of the experimental apparatus (*e.g.*, use of several filaments arranged symmetrically around the substrate, or the possibility of substrate rotation aside the filament). A disadvantage of the coaxial mounting, *i.e.*, impossibility of substrate temperature measurement, either by an optical pyrometer or by a thermocouple, was overcome by performing several preliminary deposition experiments, with purpose of which was to determine the optimal power of the activating filament. The tantalum filament (0.5 mm diameter) coil of 2–3 turns (8 mm diameter) was heated by an electric current from the ac mains through variable transformers. The filament power was controlled manually and kept constant at about 150 or 240 W, depending on the substrate type. It was also possible to modify the effects of the applied power by changing the position of the substrate.

Wire substrates with a typical length of 50 mm were coaxially mounted in a special cartridge/holder into the tantalum coil. By pulling the cartridge into/out of the holder, the substrate mounting could be adjusted. First, the copper wire (0.20 mm diameter) of electrolytic purity was manually abraded with emery paper (P 500) perpendicular to the length axis. As the deposition result was unsatisfactory, the other Cu substrates were manually abraded with a mixture of powders* (Mo:W:diamond = 20:50:30). The SiC fiber (SCS-6, Speciality Materials, Lowell, USA) with a diameter 0.142 mm was used as obtained without any pretreatment. Refractory metal wires (W, Mo) of several diameters were used in deposition experiments. The thicker ones (0.5 mm diameter) were manually abraded with emery paper (P 320), perpendicularly to the length axis. The thin Mo wire (0.1 mm diameter) and W wire (0.025 mm diameter) were not pretreated, but used as received.

Other experimental conditions were as follows: working gas mixture methane (0.5 %) in hydrogen, total gas pressure 30 mbar, gas flow rate 50 cm^3 min^{-1}, deposition duration 9 or 16 h. Before the deposition, the Ta filament was conditioned by heating in the mixture of methane (5 %) in hydrogen for about 45 min.

Characterization of the obtained diamond coatings was performed by scanning electron microscopy (Jeol JSM 35, accelerating voltage 25 kV)

RESULTS AND DISCUSSION

For the achievement of good quality diamond coatings, of all four investigated materials, Cu required the most attention and effort. Diamond deposition on Cu was a peculiar challenge in that copper does not react with the working atmosphere to form carbide (which would assist the growth and adhesion of a diamond coating) and because the thermal expansion coefficients of Cu and diamond are very different (which causes thermal stress in the coating, subsequent cracking and coating delamination upon cooling from deposition to room temperature). In diamond deposition experiments on the thin, cylindrical substrate, *i.e.*, on the Cu filament, another disadvantage of Cu became evident – the melting temperature of Cu, which is very close to the working temperature of diamond deposition. This inherent characteristic of Cu was not so noticeable in the experiments with planar, thick (2.5 mm) substrates mounted laterally with respect to the activating filament.[10] A small diameter (0.20 mm) of the substrate was chosen in the present experiments in order to achieve a thicker diamond coating, inside which bonding forces could equalize and possibly surpass the thermal stress after termination of the deposition.

An insufficient power of the activating tantalum filament, 125 W, gave negligible diamond nuclei on the thin non-diamond layer during 9 h deposition, whereas with a sufficient filament power of 150 W during 9 h deposition resulted in continuous coatings. The coatings obtained on two Cu substrates at the same filament power (150 W) for the same duration (9 h) but pretreated differently are shown in Figs. 1a–1d. The diamond fiber morphology with characteristic nodules, Fig. 1a, and a crack in the coating, Fig. 1b, are shown as distinctive represen-

* Particle sizes, diamond: 0.310 μm; Mo and W: 5 μm, predominantly.

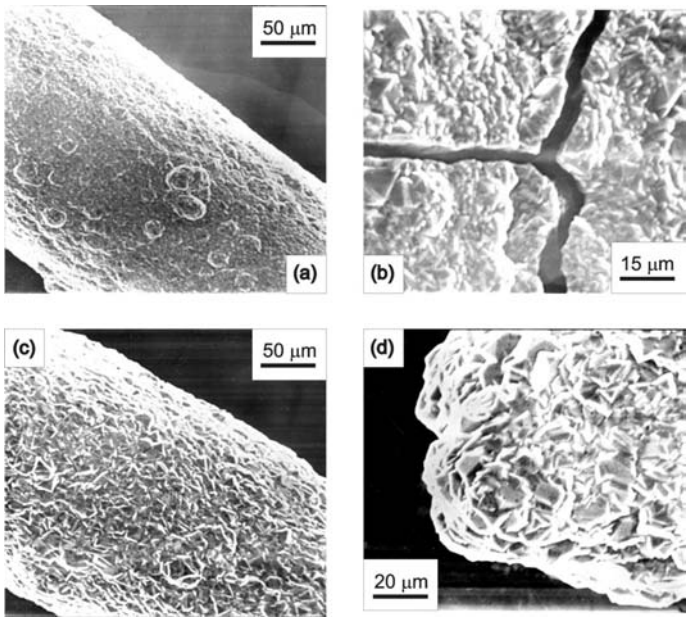

Fig. 1. Diamond fiber with a Cu core: diamond nodular morphology on an abraded substrate (a); crack in the coating grown on the abraded, unseeded substrate(b); diamond morphology on the abraded and seeded substrate (c); detail of the nodular end of the fiber shown in Fig. 1c (d).

sentatives of deposition on a Cu substrate abraded only with emery paper. This nodular morphology was previously observed in diamond coatings obtained by the hfCVD method on a thin Cu wire (50 μm) manually abraded,[1] with the addition of diamond grit (1–3 μm).[2–4] The samples obtained after abrading with a mixture of powders (Mo, W and diamond) are presented in Figs. 1c and 1d; the characteristic nodular morphology, composed of faceted diamond crystallites in Fig. 1c, and a detail of the fiber nodular end in Fig. 1d. Such a pretreatment procedure was aimed at improving the deposition of diamond on Cu. Rapid formation of the carbide layer and the extremely high diamond nucleation density on molybdenum,[11] as well as our positive experience,[10] were the reasons for choosing Mo as a component in the seeding mixture. Including W in the seeding mixture could positively affect the adhesion of the diamond deposit, as tungsten carbide has the lowest thermal expansion coefficient of all refractory metal carbides.[12] Diamond crystallites constitute an important component (sometimes the only one) of seeding powders, as they meet all the requirements (topochemical, geometrical) for diamond nucleation and growth. A gradual increase of the power to 150 W until a 9-h deposition period resulted in the diamond coatings seen in Figs. 1c and 1d: the particles of the seeding mixture helped the diamond crystallite habit of the coating to be restored, although nodules in the layer seemed to be unavoidable. One of the possible causes of this nodular morphology might be

the active participation of the Cu substrate in the diamond coating deposition, due to the similarity of the temperatures of Cu melting and diamond deposition. Hence, in such an experimental set-up, deposition onto a shorter substrate or pulling the substrate out of the active helix by some 1–2 mm is suggested, as the hottest temperature zone is just at the centre of the tantalum helix.

A similar pretreatment procedure of a flat Cu substrate, *i.e.*, abrading/seeding with diamond powder, annealing, melting the surface, and successive diamond film growth by the hfCVD method,[13] corroborated the necessity of providing the Cu surface with reactive germs, and the importance of the careful control of the activating filament power. The micro-sized diamond used for manual abrasion of the substrate surface, as well as a powder mixture of micro-sized refractory metal (Ti) and nano-sized diamond used for ultrasonication, enhanced very well the nucleation density and diamond film growth, respectively.[14]

Diamond coatings on the SiC fiber grown at a filament power of 150 W after deposition for 16 h are shown in Figs. 2a–2d. A top-view of the diamond-coated fiber is shown in Fig. 2a. The characteristic morphology can be seen in Fig. 2b. A native fracture of the same sample, presenting an about 20 μm thick diamond coating, is given in Fig. 2c. A detailed view of the fracture is presented in Fig. 2d. Diamond deposition on the SiC fiber developed well with an activating filament power up to 150 W. The SiC fiber[15] (diameter 142 μm) consists of a car-

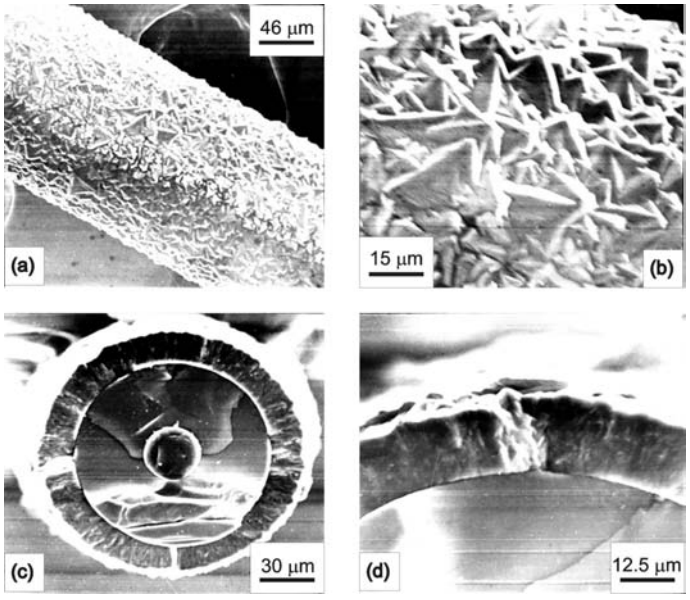

Fig. 2. Diamond fiber with a SiC core: top view of the diamond coated SiC fiber (a); detail of the morphology (b); native fracture showing an about 20 μm thick diamond coating (c); detail of the native fracture of the same sample (d).

bon core (33 μm) coated with β-SiC and a thin (about 3 μm) pyrocarbon overcoat. During the deposition experiment, the pyrocarbon layer was etched by atomic hydrogen and deposition of diamond occurred readily on the bare silicon carbide. No cracks or gaps can be seen in micrographs, evidencing diamond coating on the SiC fiber, Figs. 2a–2d. Adhesion of the diamond coating–SiC fiber system is very good because thermal expansion coefficients of diamond and SiC are quite similar.[12] Diamond-coated SiC fibers incorporated into a metal matrix composite (Ti–6Al–4V) should transfer their stiffness to the composite and enable weight savings compared to the existing reinforcement fibers.[5]

Diamond deposition on W and Mo wire substrates was performed with a filament activating power of about 240 W. The micrographs of diamond-coated W substrates of different diameters, obtained during 9 h deposition are presented in Figs. 3a–3d. Continuous and uniform coatings composed of euchedral crystallites obtained on the thick (0.5 mm) and thin (0.025 mm) wire substrates can be seen in Figs. 3a and 3c. During the course of the deposition, a common chemical compound with carbon from the working atmosphere, *i.e.*, carbide was formed, which is very favorable for diamond nucleation and growth. Due to the rather low difference in the thermal expansion coefficients of tungsten carbide and diamond,[12] the thermal stress was low, which also contributes to a good coating–substrate adhesion. In order to gain an inside view of the diamond fiber

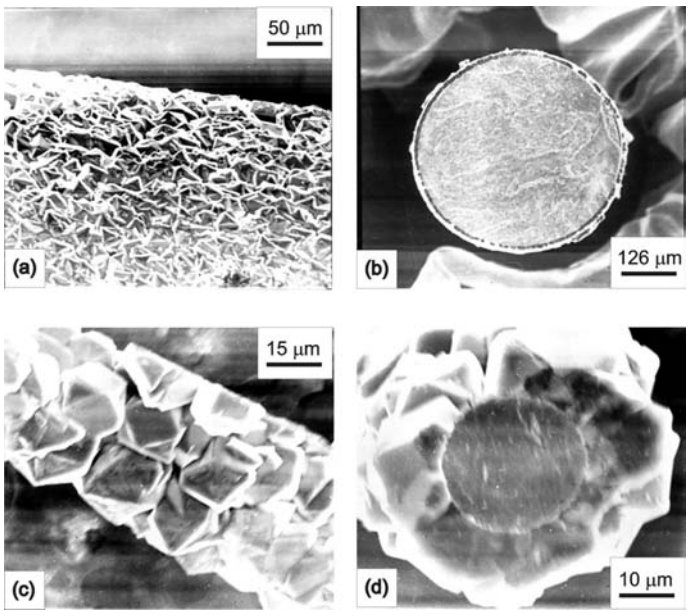

Fig. 3. Diamond fiber with a W core: morphology of the continuous and homogeneous coating on the thick (0.5 mm) W core (a); cross section of the same sample (b); top view of the thin W-cored (0.025 mm) diamond fiber (c); native fracture of the same sample (d).

structure, transversal sections were made. Both cross sections of the thick W-cored diamond fiber, in Fig. 3b, and the native fracture of the thin W-cored diamond fiber, in Fig. 3d, appear neat without cracking and chipping, thus proving the usability of tungsten in various technological applications: thermocouple probe,[7] flow controller micronozzle,[8] X-ray microdosimeter,[16] *etc*.

Diamond coatings on the Mo wire substrates of diameters 0.5 mm and 0.1 mm, grown during 9 h deposition, are given in Figs. 4a–4d. The morphology of the continuous coating on the 0.5 mm diameter Mo wire is presented in Fig. 4a, and the cross section of the same sample can be seen in Fig. 4b. The top view of the coating deposited on the 0.1 mm diameter Mo substrate is shown in Fig. 4c. The native fracture of the same sample, seen in Fig. 4d, displays a stratified appearance: the diamond layer (at the top), an interlayer (carbide) and the initial material, molybdenum, in the fiber core. A coating fragment next to the fiber fracture indicates the condition of the fiber, *i.e.*, the existence of stress in the shown specimen. As was previously observed,[10] diamond deposition on Mo can be realized without any surface pretreatment, *i.e.*, without the introduction or removal of existing defects, without seeding or application of some physical/ /chemical agent. The coatings obtained on the cylindrical substrates are counterparts of the ones obtained on planar substrates in terms of morphology, structure and characteristics. The coatings are continuous and homogeneous, Figs. 4a and

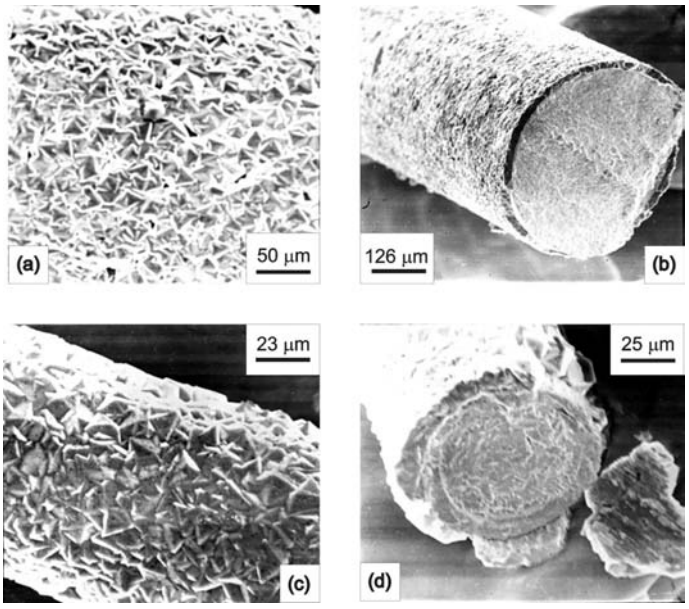

Fig. 4. Diamond fiber with a Mo core: morphology on the thick (0.5 mm) wire substrate (a); cross section of the same sample (b); top view of the coating deposited on the thin (0.1 mm) wire substrate (c); native fracture of the same sample showing a stratified fiber structure (d).

4c. In the native fracture of the thin fiber sample, Fig. 4d, the course of the deposition process can be easily seen: first the formation of a carbide layer and then subsequently diamond growth. Strong bonding forces between the substrate and the grown carbide layer as well as ones within the polycrystalline diamond layer can be assumed, since no gaps were visible. On the contrary, a gap between the layers of carbide and diamond could be discerned. The compact coating splinter observed when fracturing the sample, Fig. 4d, indicates the existence of the thermal stress in the coating and evidences a sporadic detachment of the coating from the substrate. It is possible to obtain a stress-free cylindrical diamond coating grown on Mo by making it thick compared to the substrate and then to make it free-standing, *i.e.*, to remove the substrate (by dissolution in hot acids). Subsequently, it can be brazed onto another part for further application.[9]

CONCLUSIONS

Diamond coatings on thin cylindrical substrates, required in numerous specific applications, were achieved on several different materials. It is found that the substrates exert a considerable influence on the deposited coatings. Chemical reactivity of the substrate material is the main prerequisite to begin diamond deposition without any surface pretreatment. In cases when the substrate material (W, Mo) reacts with the working deposition atmosphere, a common chemical compound, carbide, is formed, that enables a gradual, continuous transition from one crystal lattice to the other. Good adhesion and durability of the substrate––coating interface exist whenever strong chemical bonds are formed, which can prevail over debonding forces. In the case when the substrate material (Cu) does not react with the working atmosphere, bonding between the substrate and the coating was weak and, consequently, adhesion was poor.

The thermophysical characteristics of the substrate material are very important as diamond deposition occurs at high temperatures. The thermal expansion coefficients of the substrate (*i.e.*, of its grown carbide) and the coating should be as similar as possible in order to minimize the thermal stress that occurs upon cooling from working to room temperature. Thus, in the series of examined materials, the thermal stress decreases in the order Cu, Mo, SiC and W.

In deposition on the thin copper wire, low power deposition as well as the special pretreatment of the substrate surface, reactive seeds added to the surface, proved it is possible to obtain continuous, adhered and well faceted diamond coating on a chemically inert substrate.

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ИЗВОД

ДЕПОЗИЦИЈА ДИЈАМАНТА НА ТАНКИМ ЦИЛИНДРИЧНИМ СУПСТРАТИМА

ГОРДАНА С. РИСТИЋ[1], ЖАРКО Д. БОГДАНОВ[1], МИЛАН С. ТРТИЦА[1] и ШЋЕПАН С. МИЉАНИЋ[1,2]

[1]ВИНЧА Институт за нуклеарне науке, п.пр. 522, 11001 Београд и [2]Факултет за физичку хемију, Универзитет у Београду, п.пр. 137, 11001 Београд

Дијамантске превлаке депоноване су методом усијаног влакна ХДП на различитим цилиндричним супстратима (Cu, SiC, W и Mo). Добијене су непрекидне, приањајуће и лепо фасетиране дијамантске превлаке на Cu- жици, коришћењем специјалне предобраде смешом прахова рефракторних метала и дијаманта, уз брижљиву контролу депозиције при мањој снази, тј. нижем степену усијања влакна. Депозиција дијаманта на SiC влакну дала је непрекидне и уједначене превлаке већ само погодним избором снаге активирајућег влакна. Уједначене, равномерне и еухедралне дијамантске превлаке на W и на Mo жици, добијене при већој снази усијаног влакна, потврдиле су погодност рефракторних метала као супстрата за депозицију дијаманта ХДП техником. Карактеризација добијених превлака урађена је скенирајућом електронском микроскопијом (SEM). Добијени резултати су упоређени са подацима из литературе. Разлике су продискутоване с обзиром на хемијску природу супстрата и његове термофизичке карактеристике.

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