Characteristics of tungsten layer deposited on graphite substrate by a low energy plasma focus device at different angular position

F.M. Aghamir*, A.R. Momen-Baghdadabad

Dept. of Physics, University of Tehran, Tehran 14399, Iran

A R T I C L E   I N F O

Keywords:
Tungsten coating
Graphite substrate
Plasma focus device
X-ray diffraction
Nanoindentation analysis

A B S T R A C T

Layers of tungsten were deposited on two types of graphite substrates at three different angular position by a low energy plasma focus device. First series of substrates included only raw graphite while carbon interlayers were used for the second type. Tungsten deposition process was carried out at 0°, 15°, and 30° angular location with respect to the device anode axis during 40 focus shots at optimum argon gas pressure. The characterization of the deposited tungsten coatings was verified by X-ray diffraction (XRD), scanning electron microscopy, energy-dispersive X-ray spectroscopy, Raman spectroscopy and Nanoindentation analyses. Tungsten-carbon structures such as WC₁₋ₓ, W₂C, WC, and W₂(C, O) were detected by XRD analysis. Compounds such as WC₁₋ₓ, W₂C and W₂(C, O) were identified on raw graphite substrate while WC₁₋ₓ, WC, W₂C were formed on the graphite substrates with carbon interlayer. For both types of samples positioned at 30 degrees with respect to device axis, the WC₁₋ₓ phase, which is a high temperature structure with high melting point, was detected more than other tungsten-carbon structures. The coating of carbon interlayer on substrates changes surface morphologies and leads to homogenous deposition of tungsten layer on the surface. The increase in angular position of substrates led to creation of flat and smooth surfaces. Raman spectroscopy shows the presence of WO₃ and amorphous carbon structures in both types of prepared samples. Nanoindentation analysis indicates that the hardness of samples increases after tungsten deposition process. The substrate angular position with respect to anode axis is an effective parameter in deposition process of tungsten layers.

1. Introduction

Carbon compounds such as graphite have been widely used due to their special features like high thermal shock resistance, light weight, high strength, and availability. Graphite can be employed as a radiator in plasma boundary for reduction of heat load on the target plates in fusion reactors [1]. However, high erosion rates of graphite at high temperature cannot be overlooked [1,2]. Tungsten with some notable features such as high melting point, good thermal properties, low sputtering and erosion rate is a perfect solution for protective coatings [1,3–6]. However, thermal expansion coefficient of tungsten can be a challenging factor leading to mismatch between coating layer and typical substrate at high temperature. Close thermal expansion coefficient of graphite and tungsten makes them an ideal combination for coating process [7]. Tungsten coating on graphite is an ideal choice for plasma-facing walls in fusion reactors. There are number of deposition methods for tungsten coating on graphite including chemical vapor deposition, physical vapor deposition, plasma spray, electro-deposition, and magnetron sputtering [8–12]. There is yet another deposition method using plasma focus device, which has special features such as high deposition rate, as well as, energetic deposition processes.

The plasma focus (PF) device is a simple apparatus with wide range of applications. The device is well known as a compact pulsed source of different kinds of emissions such as soft and hard X-rays [13,14], neutrons beams [15,16], relativistic electrons [17], and intense ion beams [18,19]. During the operation of PF device, a high voltage from capacitor bank is applied to the central electrode at the optimum gas pressure. As the result of an electrical breakdown along the insulator sleeve surface, a plasma current sheath is formed. The current sheath dynamic in the radial collapse phase leads to formation of a high density and high temperature plasma column to produce relativistic electron and intense ion beams. The intense ions emitted from hot and dense plasma have been used for material processing such as surface modification [20], ion implantation [21,22], and deposition of high temperature and hard coating as an outer layer for protection of typical substrate surface [23,24]. During the deposition process of tungsten coating on graphite substrates, collision of different energetic ions leads to generation of tungsten-carbon compounds. Some of the generated...
tungsten-carbon phases such as WC_{1-x}, which is a high temperature phase with high melting point (2785 °C) [25–27], are hardly produced by other deposition methods. The WC_{1-x} composite is important for use in high temperature applications, such as nuclear and general engineering sectors and in aerospace [25].

In the present manuscript, the deposition of tungsten coating on graphite substrates with and without carbon interlayers at different angular position with respect to the tungsten anode tip axis has been investigated. The choice of carbon interlayers stems from proximity of thermal conductivity parameters of carbon and tungsten coating. The experiments were performed at room temperature using a 4.9 kJ plasma focus device operated with argon filling gas. The tungsten layer thin films were examined to determine the generated phases of tungsten-carbon and mechanical properties by x-ray diffractometer and nanoindentation measurement. Raman spectroscopy is used to detect bond structures of tungsten thin film. Scanning electron microscopy (SEM) is used to investigate the surface morphology and film thickness. Coupled with SEM, energy-dispersive X-ray spectroscopy (EDX) was utilized to determine atomic and weight percentage of various elements of the deposited coating. The outline of the article is as follows: The experimental setup is described in Sec. II. The diagnostic methods along with analysis and discussion on experimental results are given in Secs. III. Conclusions are drawn in Sec. IV.

2. Experimental setup

The deposition of tungsten coating on graphite substrates were carried out on a 4.9 kJ low energy Mather-type PF device. The PF system was operated on an 11 μF capacitor bank that was charged at 15 kV (1.2 kJ) and was filled at optimum gas pressure of 20 Pa to obtain the strong focus. The schematic of the experimental setup showing the vacuum chamber, anode-cathode electrodes, the metallic holder and the shutter along with the spark gap is given in Fig. 1. The central anode electrode of PF device was a flat-end, 13.6 cm long and 2 cm in diameter copper cylinder. Six copper rods, each 12 cm long and 0.9 cm in diameter were symmetrically placed around the central anode electrode. The cathode electrodes were screwed down to a copper base plate. The anode was separated from cathode baseplate by a pyrex in- ter electrode. The cathode metal holder and shutter were designed by solidworks computer program for the deposition process. A pure tungsten tip was inserted on the anode electrode.

A typical substrate holder was designed and constructed such that it could hold samples at three different angular positions. A removable shutter was located between the anode and substrates. The holder axis was along the central electrode and was located 7 cm away from the anode tip. The entire anode-cathode holder assembly was placed inside a stainless steel chamber. The vacuum chamber was evacuated up to 4 Pa by a rotary mechanical pump before the introduction of pure argon gas (99.999%). The pure graphite substrates were cut in small sizes (10 mm x 10 mm x 4 mm). The surfaces of graphite substrates were ground down on 600,1000,2000 and 3000 grit SiC papers prior to deposition. The polished substrates were cleaned in ethanol ultrasonic bath for 10 min each. Two series of samples were prepared for tungsten deposition process. The first series of graphite substrates were then mounted on the holder steps at 0.15 and 30 degrees with respect to the tungsten anode axis. For second series of substrates, a typical carbon structure with high level of defects was considered as the interlayer. In order to fabricate the interlayer, the anode tip of the PF device was replaced by a graphite insert and the substrate was positioned at 75° deposition angle with respect to the axis. The SEM and Raman analyses of the interlayer and substrate are shown in Figs. 3 and 4. The thin films were deposited during the period of the repetition of 40 shots at 7 cm from the anode top.

To record the transient voltages, a high voltage probe (Tektronix P6015A) was connected at the bottom of the anode electrode. A Pearson current monitor (Model 4418) was used to measure the transient discharge current signal. A typical high voltage signal along with discharge current is shown in (Fig. 2).

The surface morphology and thickness of the coating layers are investigated by field emission scanning electron microscope (FE-SEM-TeScan-Mira III-Czech Republic) along with EDX (Oxford 80-XMAX-England). The operating voltage of captured SEM images was 15 kV and the elemental mapping analysis was performed by Oxford Instruments EDX system at 15 kV. The Raman spectrum of the samples were recorded using Takram. P50COR10 spectrometer operating at 532 nm of Nd:YAG laser system with 6 cm\(^{-1}\) resolution. X-ray diffraction (XRD) patterns of the deposited coating layers were recorded by a Philips (PW 1710) diffractometer, exposing the samples to Cu-Kα radiation in range of 10–80° with a step size of 0.05° per second. Mechanical properties of deposited coating layers are investigated by a nanoindentation measurement (TriboScope system, Hysitron Inc. USA), equipped with a cube corner type indenter tip, for hardness and elastic modulus determination. The results of SEM, EDX, XRD, Raman spectroscopy, and nanoindentation analysis are presented in the following section.

3. Results and discussion

3.1. XRD analysis

The typical XRD pattern of tungsten coating layers deposited on graphite substrates, with and without interlayer, at different angular position in the range of 10–80° are shown in Fig. 5. The XRD patterns clarify some critical crystalline phases of tungsten-carbon (tungsten carbide) structures such as W_{2}C in hexagonal and orthorhombic forms,WC_{1-x} in cubic form as a high temperature phase, WC in hexagonal, and W_{2}(C,O) in cubic form. The latter indicates that tungsten oxycarbide compound is generated on the graphite surface during deposition process while WC formed only on substrates with interlayer [28–30]. Presence of tungsten carbide phases can be attributed to energetic tungsten ions ablated from anode tip to interact with graphite surface. The pure tungsten crystal peaks for the coated layer were detected at 40.5° and 71° along with (110) and (211) crystal planes. Furthermore, the tungsten carbide phases of W_{2}C at 35.8°, 62.5° and 75° with crystal planes (002), (110), and (112) [28,31], WC_{1-x} at 37°, 43.2°, 62.5°, and 75° with crystal planes (111), (200), (220), and (311) [28–31], WC at 35.4° with crystal plane (100) [32], and W_{2}(C, O) at 36.5°, 42.5°, 62°, and 74.5° with crystal planes (111), (200), (220), and (311) [29,33] are detected.

According to Fig. 5, as angular position varies from 0° to 30° the intensity of W and W_{2}C peaks decreases to lower values. However, the WC_{1-x} structure follows an opposite trend as the angular position increases. The presence of the highest WC_{1-x} content at 30° angular position suggests that greater number of energetic tungsten ions are generated at 30° with respect to central axis of anode. The XRD patterns indicate that tungsten carbide replaces tungsten oxycarbide once carbon interlayer is deposited on graphite substrate. This phenomenon is best explained by inspection of Fig. 6 which displays the deposition process during one shot in PF device. Fig. 6 shows that graphite is formed by accumulation of graphene clusters. On the surface of raw graphite substrates, some bonds contain oxygen such as C–OH and C–O. Oxygen can occupy the vacancies of π states of graphene and contaminate graphite substrates. During deposition process by PF, two sets of ions interact with substrate samples. Argon gas ions with higher energies (≥ 0.8 MeV) collide with samples surface and create dangling bonds of oxygen and carbon on graphite [34]. Argon ions can also penetrate inside clusters and create defects. After a delay of few microseconds, tungsten ions with lower energies arrive at samples surface and interact with defects, as well as, many dangling bonds produced by earlier interaction of argon ions. Tungsten ions can now make different bonds with carbon and oxygen such as tungsten carbide and tungsten oxycarbide. The XRD patterns show no sign of tungsten oxycarbide
when carbon interlayer is used. This is due to participation of oxygen dangling bonds during deposition process and tungsten contributing to formation of other structures such as WC_{1-X} phase. The carbon interlayer can remove, cover or bury oxygen contamination at graphite interface. Furthermore, Raman analysis shows the formation of two new bonds in carbon interlayer; C=C bonds of aromatic network around 1490 cm\(^{-1}\) and sp\(^3\) states around 1250 cm\(^{-1}\). These two new bonds could be the reason behind production of WC structure which is visible in XRD analysis. All of these issues affect the growth mechanism and change surface morphology after application of carbon interlayer. For substrates with interlayer, when the angular position is shifted from 0 to 30°, formation of W\(_2\)C structure is gradually reduced and diminishes at 30° completely. However, WC_{1-X} follows an opposite trend and its maximum amount at 30° is noticeable. The XRD patterns can be used to compute the average crystallite size of each phase by Scherrer’s equation:

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

Where \(\beta = \text{FWHM} \times \frac{2}{\pi}\), \(k\) is Scherrer constant, \(\lambda\) is the X-ray wavelength, and \(\theta\) is the diffraction angle \([35–37]\). The estimated average crystallite size of various phases such as W, WC, WC_{1-X}, W\(_2\)C and W\(_2\)(C, O) are listed in Table 1. According to the tabulated values, for samples without interlayer, when angular position shifts to higher angle, the average crystallite size of tungsten carbide phases increases. However, for those with interlayer, the average crystallite size of samples remain constant.

### 3.2. SEM and EDX analyses

The surface morphology of tungsten coating layers at different angular position for samples without interlayer, as well as, those with carbon interlayer are shown in Figs. 7 and 8, respectively. Appearance of tungsten islands in different sizes on graphite surface is noticeable in Fig. 7. The surface roughness shown in Fig. 7a is due to the large size tungsten island distribution. According to surface morphology, as the sample angular position increases the tungsten island sizes decrease from 6 to 1 \(\mu\)m, leading to smoother surface. Therefore, changing the angular position of samples can improve the surface morphology.
creating a smooth and rather flat coating layer with uniform distribution of tungsten atoms on graphite surface. Fig. 8 illustrates surface morphology of tungsten coating on carbon interlayer. According to the Figure, application of interlayer leads to creation of a more homogeneous surface which is due to the overlap of tungsten islands boundaries. This phenomenon can be attributed to the absence of tungsten oxycarbide and increasing presence of WC1-x structure.

Fig. 9 shows EDX elemental mapping analysis along with EDX spectra from cross-sectional SEM images for samples prepared without interlayer. EDX elemental mapping analysis reveals that tungsten islands mostly cover tungsten carbide layer. This indicates that the produced coating is not a composite of tungsten and tungsten carbide structure. Tungsten atoms form crystalline tungsten islands on a typical tungsten carbide layer. The deposition process in PF device is such that tungsten atoms interact with dangling bonds to form tungsten carbide structure. After repetition of few shots, produced tungsten carbide layer acts as a barrier and does not allow crossing of tungsten atoms. After number of shots, saturation in formation of tungsten carbide takes place and secondary tungsten atoms form crystalline tungsten islands on tungsten carbide layer. Therefore, the exact measurement of tungsten coating layers thickness at each deposition angle is complicated. The estimated depth of tungsten island on tungsten carbide layer of graphite samples mounted at angular positions 0°, 15° and 30° were 1900, 1100, and 600 nm, respectively. The reduction of thickness at larger angular position is due to lower amount of ion flux. According to EDX spectra,
the amount of atomic and weight percentage of tungsten decrease as the deposition angle increases. This can be attributed to lower amount of ion flux at higher angular positions.

### 3.3. Raman spectroscopy

Raman spectra of prepared tungsten coating for samples without and with interlayer are illustrated in Figs. 10 and 11. The Raman spectra show two series of overlap peaks. The first set is related to crystalline WO$_3$ structures which are located around 716 and 807 cm$^{-1}$. The second series is attributed to defect ratio in graphene cluster positioned around 1350 and 1590 cm$^{-1}$ which is assigned by D and G peaks [38,39]. The absence of crystalline WO$_3$ in XRD patterns suggests that the amount of this typical structure is too little. Furthermore, formation of WO$_3$ stems from remaining tungsten vacancies on the surface of tungsten islands after the deposition process is completed. At this stage, samples are exposed to air and oxygen atoms join tungsten dangling bonds. Close inspection of Raman spectra intensities of WO$_3$ and the D and G peaks points to formation of crystalline WO$_3$ thin shell positioned at the outer part of tungsten coatings. Before tungsten
deposition process, for graphite samples without interlayer, the \( I_D/I_G \) value was around 0.22. However, after deposition, due to deeper penetration of argon ions versus tungsten, a layer of defected graphene cluster (amorphous carbon) was formed between tungsten carbide layer and graphite substrate, in which the \( I_D/I_G \) ratio can be estimated between 0.47 < \( I_D/I_G \) < 0.69. The schematic of tungsten coating on graphite substrates is shown in Fig. 12. The Raman spectrum of carbon interlayer indicates that \( I_D/I_G \) ratio of interlayer is around 0.59. Since \( I_D/I_G \) ratio after deposition process is located in the range of 0.42 < \( I_D/I_G \) < 0.63, it appears that during ion bombardment the interlayer is more stable than graphite. The Raman analysis confirms that an amorphous carbon film is shaped in both samples either with or without interlayer. The \( I_D/I_G \) ratios of both sets of prepared samples show the same distinct trend when angular position increases and the largest value of \( I_D/I_G \) ratio is observed at 30° angular position. The highest number of defects at 30° angular position suggests that ions colliding on samples at this deposition angle have highest value of energies. Furthermore, the ratio of peak intensity at 716 and 807 cm\(^{-1} \) (\( I_{716}/I_{807} \)) was verified and compared to \( I_D/I_G \) values. For tungsten coating on graphite without interlayer, when the substrate angular position increases, the \( I_D/I_G \) values follow the same trend as \( I_{716}/I_{807} \). However, for the coating on carbon interlayer the \( I_D/I_G \) ratios follow an opposite

Fig. 9. EDX elemental mapping analysis from cross-section of samples deposited at a) 0°, b) 15° and c) 30° angular position without interlayer.
trend compared to $I_{116}/I_{807}$ ratio.

**3.4. Mechanical properties**

Fig. 13 shows nanoindentation load-displacement curves of tungsten coating layer at different angular position on two types of samples. Three important parameters the peak indentation load, the indenter displacement at the peak load, and the contact stiffness are of interest. The elastic modulus and hardness are generally calculated by Oliver and Pharr method [40]. The reduced elastic modulus $E_r$ of each tungsten coating layer at different angular position on two types of samples. Three important parameters the peak indentation load, the indenter displacement at the peak load, and the contact stiffness are of interest. The elastic modulus and hardness are generally calculated by Oliver and Pharr method [40]. The reduced elastic modulus $E_r$ of each tungsten coating layer at different angular position on two types of samples. Three important parameters the peak indentation load, the indenter displacement at the peak load, and the contact stiffness are of interest. The elastic modulus and hardness are generally calculated by Oliver and Pharr method [40]. The reduced elastic modulus $E_r$ of each
coated layer is defined as:

\[
E_i = \frac{S \sqrt{\pi}}{2 \rho_i \sqrt{A_i}}
\] (2)

where \( \beta \) is the constant of the indenter geometry, \( A_i \) is the contact area of the indenter, and \( S \) is the contact stiffness. Eq. (2) can be re-casted into:

\[
1 \frac{E_i}{E} = 1 - \frac{v^2}{E} + 1 - \frac{v^2}{E_i}
\] (3)

here, \( E \), \( v \), \( E_i \), and \( v \) are the elastic modulus and Poisson's ratio of the indenter and coated layer, respectively. The elastic modulus, \( E_i \) and Poisson's ratio, \( v_i \) of the indenter are 1140 GPa and 0.07, respectively. However, due to presence of many tungsten carbide phases with different percentages and multi-layers in the deposited tungsten coatings, computation of elastic modulus of each phase in the coated layer is not possible.

Plots of computed hardness versus substrate angular position are shown in Fig. 14. As the Figure shows the hardness decreases when the position angle of substrate rises. This can be attributed to different factors such as the thickness of coating, surface morphology and prec of different carbide contents in each layer. It should be noted that the hardness of deposited coating is critically dependent upon the material used as substrate [31]. For graphite substrate, the hardness is around 300 MPa. After the deposition of tungsten layer on raw graphite substrate, the hardness increases to 3.73 GPa at 30° substrate angular position. The largest hardness is experienced at 0° substrate angular position which was 7.33 GPa. For coating samples with interlayer, the computed hardness values are comparable with those without interlayer. The hardness of tungsten coating deposited on carbon interlayer at 0° angular position was 12 GPa which shows an improvement of 5 GPa in hardness over coatings on raw graphite. The difference can be ascribed to presence of WC and absence of W2C (O) structures; otherwise, the conformation of both types of deposited samples either with or without interlayer is the same. When angular position shifts to higher values, the hardness for both types of samples (with and without interlayer) decreases. According to SEM cross sectional images, the increase in hardness can be linked to higher layer thickness, tungsten content, and percentage of tungsten element shown in EDX analysis. The increase in tungsten content of thin films changes the amount of generated carbides leading to hardness variation.

4. Conclusion

Tungsten coating layers were deposited on graphite substrates at three different angular positions by a low energy plasma focus device. A typical carbon structure was utilized as an interlayer for verification of growth mechanism and characterization of tungsten coating on graphite. Investigation of XRD patterns of the deposited layers revealed that high energetic tungsten ion beam irradiated from plasma column generates tungsten-carbon structures during the deposition process. The study shows that using carbon interlayer affects carbide phases after tungsten deposition process, which in turn changes surface morphology leading to more homogenous coating on samples. In addition, a smoother and faster surfaces of deposited tungsten coating are formed on graphite as the substrate deposition angle increases. EDX elemental mapping analysis along with EDX spectra from cross-sectional SEM images shows that tungsten coating includes multi layers, as well as, tungsten islands on tungsten carbide film. Presence of amorphous carbon is due to deeper penetration of intense argon ions compared to tungsten. Close inspection of XRD and Raman results points to a very thin crystalline tungsten oxide shell on tungsten islands. Nano-indentation test performed on each sample exposed the mechanical properties of samples at different angular position. The test indicates that the hardness of the deposited surface increases significantly after tungsten deposition process. The presence of tungsten-carbon phases leads to strong adhesion of the deposited tungsten coating to graphite substrate. Furthermore, depending upon the substrate angular position, the hardness varies from 3.73 to 7.33 GPa and 3.70 to 12 GPa for samples without and with interlayer, respectively. Therefore, deposition of tungsten coating on graphite substrate by plasma focus device has the potential of producing surfaces with various hardness.

References


Zhypargul Abdullaeva, Emil Omurzak, Chihiro Iwamoto, Hiroki Okudera, Michio Koinuma, Shintaro Takebe, Saadat Sulaimankulova, Tsutomu Mashimo, High temperature stable WC1−x@C and TiC@C core–shell nanoparticles by pulsed plasma in liquid, RSC Adv. 3 (2) (2013) 513–519.


JCPDS Data Cards, No. 20-1315 and No. 25-1047, both for W2C and W2(C,O) phase is listed in card No. 22-0959, International Center of Diffraction Data, Newtown, PA, 1988.
