TRIBOLOGICAL PROPERTIES OF CARBON-TUNGSTEN NANOCOMPOSITES SYNTHETIZED BY THERMIONIC VACUUM ARC (TVA) METHOD

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Abstract. This paper is focused on the characterization of the C-W films with different concentration of W by Thermionic Vacuum Arc technology. The microhardness of C–W films as well as the roughness decrease with W concentration. The values of the coefficient of frictions were found lower than the uncoated substrates.

Key words: Thermionic Vacuum Arc (TVA), C-W nanocomposites, AFM.

1. INTRODUCTION

The field of nanocomposites involves the study of multiphase material where at least one of the constituent phases has one dimension less than 100 nm. The promise of nanocomposites lies in their multifunctionality, the possibility of designing unique combinations of properties unachievable with traditional materials. The challenges in reaching this promise are tremendous especially in the case of carbon based nanocomposites [1-3]. They include control over the distribution in size and dispersion of the nanosize constituents, tailoring and understanding the role of interfaces between structurally or chemically dissimilar phases on bulk properties. Large scale and controlled processing of many nanomaterials has yet to be achieved.

The continuous development of technology is based on new materials with improved properties used in highly performing devices [4, 5]. Size, surface, geometry, and crystal phase of nanostructures are important parameters for controlling their properties. The study of physical properties of nanocomposites (structural, chemical, mechanical, tribological) is one of the most prosperous and rich branches of materials science today [6-8].
In view of this, nanocomposites of C coating with very thin buffer layers metal like W become a major area of interest, particularly for tribological applications [9-13]. An important amount of work is presently dedicated to studying synthesis of high quality carbon tungsten films using different methods [14-19]. The main drawbacks of the used methods are the related difficulties due to the high melting point of these materials which implies a difficult control of the deposition processes.

Among them, thin film deposition process by Thermionic Vacuum Arc (TVA) might become one of the most suitable technologies to produce nanocomposites of the materials with high melting points. Moreover, the TVA method allows the deposition in high or ultrahigh vacuum conditions, without the presence of any additional gas, ensuring high purity of the thin film [20, 23].

In this way it is possible to prepare two different component films such as: carbon and silver, rhenium and chromium, copper and iron, copper and cobalt, copper and nickel, copper and silver, copper and nickel-iron alloy, silver and cobalt, etc. [24-31].

The aim of this paper is to report a novel development of the Thermionic Vacuum Arc (TVA) technology in a special two electron gun configuration: the influence of tungsten composition in carbon-tungsten nanostructures for tribological applications.

2. EXPERIMENTAL SET-UP

The Thermionic Vacuum Arc (TVA) method uses an electron beam emitted by an externally heated cathode accelerated by a high anodic voltage. The electron beam can evaporate the anode materials as neutral pure particles and facilitate their deposition on the substrate when the electron energy and current intensity are not too high. By increasing up to a certain value the anode potential, the evaporation rate rises enough to allow a bright discharge to be ignited in the evaporated pure material. The discharge is hereby maintained even when the current is as low as a few hundreds mA [32].

When the dimensions of the vacuum chamber are large enough and some electrical improvements could be provided, one can ignite two TVA discharges in two different metal vapours and can be obtained combining well structured films with very interesting properties.

Thermionic Vacuum Arc (TVA) method allows the simultaneous deposition of different materials, providing the possibility of obtaining multi-component thin films [33, 34]. The experimental set-up in a special two electron guns configuration is presented in Fig. 1.
Two separate electron beams emitted by two externally heated cathodes (grounded tungsten filaments) accelerated by two high anodic voltages were directed toward graphite and tungsten anodes. The anodes are symmetrically arranged with respect to the central line. First, the applied current to the cathode filament will ensure the thermoelectronic emission on the anode. Next, the DC high voltages (1–5 kV) will provide a steady state density of the species. At a certain value of the high voltage two bright discharges appear.

![Fig. 1 – Electrodes set-up for simultaneous deposition of two materials on the same sample.](image)

The anode temperature of each element was adjusted in order to have comparable evaporation rates. The role of the panel is to avoid the interaction between plasmas. The substrates were located at various distances between the two independently ignited discharges in the vacuum chamber. The deposition was made on iron discs and silicon wafers in different positions from the anodes.

### 3. RESULTS AND DISCUSSIONS

The deposition rates and consequently the relative concentrations of C and W in the prepared films were determined by the discharge parameters (V, I) and geometrical parameters (anode-cathode distance, anode-substrate distance), as it is presented in Table 1.
Table 1

Working parameters for C-W composites

<table>
<thead>
<tr>
<th>Materials</th>
<th>Deposition conditions</th>
<th>Deposition rate (nm/s)</th>
<th>Anode-filament distance (mm)</th>
<th>Anode-sample distance (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>$I_e = 100$ A, $U_{arc}$ (V) 1900</td>
<td>0.4</td>
<td>4</td>
<td>240</td>
</tr>
<tr>
<td>W</td>
<td>$I_e = 58$ A, $U_{arc}$ (V) 2000</td>
<td>0.3</td>
<td>3</td>
<td>280</td>
</tr>
</tbody>
</table>

The working pressure during the deposition process was about $1.9 \times 10^{-3}$–$9.9 \times 10^{-4}$ Pa. The evaporation rate was stabilized and controlled with an accuracy of 10%. Thickness measurements were performed in situ using a FTM 7 thickness monitor.

The thickness of the C-W nanocomposites obtained by Thermionic Vacuum Arc (TVA) method was approximately 2 µm C/W ± 50 nm. The samples have been kept in the deposition chamber for a longer time, under high vacuum, in order to cool down the system temperature, after the power supplies were switched off.

The surface topography of the C-W thin films was investigated by Atomic Force Microscopy performed by XE-70 Park Systems’ AFM in air operating in tapping mode.

Fig. 2 – AFM images of the C-W thin films (C/Si: 0% W, C-W/Si -1: 5% W, C-W /Si – 2: 10% W, C-W /Si – 3: 15% W, C-W /Si – 4: 20% W).
Fig. 2 summarizes the correlation between the film surface properties with the composition of the film. As it can be noticed, the roughness of films with 15% W embedded in C matrix is significantly lower than in case of 5% W added in.

Tribological properties in dry sliding were evaluated using a CSM ball-on-disc tribometer. The tribometer counterpart was a 6-mm sapphire ball. Mechanical mixing and transfer play important roles in determining the sliding behaviour of these composite coatings. The tests were performed in an ambient atmosphere (50% humidity and 23°C temperature). A 1 N and 5 N normal loads were applied using deadweight, the track radii were 6 and 8 mm in a sliding speed of 10 mm/s. During the tests, the friction coefficient was recorded on a PC.

Fig. 3 – Tribological behavior of the C-W films.

Fig. 3 shows the frictional behaviour of the C-W films deposited on iron substrates by TVA method. The values of the coefficients of friction of the prepared films were in the range of 0.15-0.35, which means three to four times lower than the uncoated substrates.

The microhardness of the deposited films was measured for 15 s at a load of 98 mN using a metallographic Karl Zeiss microscope (Epityp 2) equipped with a Hanemann microhardness tester.

The results of the micro-hardness measurements are summarized in Fig. 4, where the average values of more than 3 measurements are plotted with error bars. It is to be noted here that the layers with 40% W concentration have lower hardness than that with the 10% W concentration. This behaviour is quite unexpected because W is known to have higher hardness than C. A possible explanation could be the formation of a significant porous structure by the addition of W as though its
growth mechanism has not been known yet. This porous structure is the main cause for the film softening. Nevertheless, the influence of the substrate should not be neglected.

![Graph showing micro-Vickers microhardness obtained on the C-W deposited films, at different percentages of W in C matrix (Load: 98mN).](image)

The brittleness of the film (a) with low content of W is high, as can be deduced from the cracks formed around the indentation imprints. The softening that was observed in the overlays (b - d) is considered to be very beneficial for the improvement of conformability and embeddability of the plain bearing overlays.

### 4. CONCLUSIONS

C-W nanocomposites have been successfully prepared using a special TVA two guns configuration. In this way, Thermionic Vacuum Arc (TVA) method offers convincing advantages for emerging technological applications and providing the possibility of obtaining multi-component thin films. Hydrogen free nanostructured carbon-tungsten films have been performed with valuable properties as low friction and high wear resistance in dry sliding.

The carbon - tungsten films were identified as a nanocrystals complex (5 nm average diameter) surrounded by amorphous structures with a strong graphitization tendency, leading to creation of adherent and wear resistant films. The friction coefficients (0.15–0.35) of the C-W coatings was decreased more than 3–5 times in comparison with the uncoated substrates. Raman spectra showed separate D and G peaks, higher in case of 15 % of tungsten in carbon matrix.

This decreasing behavior was also noticed for the hardness’s value at higher percentages of W in C – W films. This unexpected behaviour might be explained
by the porous structure, as revealed by AFM images. However, a high percentage of tungsten in the carbon film is suitable for plain bearing overlays in the tribological application.

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