

## Carbon-copper amorphous composite coatings grown by thermionic vacuum arc method

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**Abstract.** Copper doped amorphous carbon composite films (a-C(Cu)) have been deposited by thermionic vacuum arc (TVA) technique, using two electron beams emitted by externally heated cathodes: applying high voltages (1-5kV) between cathodes and the two anodes (C, Cu), two bright plasma were ignited in C and Cu atoms. Chemical composition, morphology, microstructure and crystallographic properties of the films were studied by scanning electron microscopy (SEM), low-angle X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The friction property of the a-C(Cu) coatings sliding against sapphire ball in dry conditions at room temperature were investigated by an CSM ball-on-disk tribometer, revealing a minimum value of 0.19 for the friction coefficient.

**Keywords:** TVA, amorphous carbon, nanocomposite, XPS spectra

### 1. Introduction

DLC ( amorphous diamond-like carbon) coatings for tribological applications have extensively been investigated for the last 10 years. DLC coatings doped with metals or metal carbides have shown promising results due to a combination of high wear resistance and low friction (low adhesion to some engineering work materials) [1-3].

The metal-containing amorphous carbon (a-C:Me) or tetrahedral (diamond-like) amorphous carbon (ta-C:Me) films have been intensely studied, specially due to their applications as implantable microelectromechanical systems (MEMS) for *in-situ* diagnosis and/or treatment of medical conditions [4,5] and as RF MEMS switches [6].

These properties suggest the use of Me-DLC in wear-resistant and interfacial applications, as for example buffer layers.

Composite ceramic coatings, such carbon-metal coatings, consist in systems with two or more thermodynamically driven segregated components. The grain boundaries included in these two-phase materials introduce the lattice

distortions that increase hardness, which is especially higher for nanometer sized grains. In the case of polycrystalline solids, this hardening effect is expressed through the Hall-Petch relation:

$$\sigma_y = Kd^{-1/2} + \sigma_0 \quad (1)$$

where the enhancement of the yield stress  $\sigma_y$ , is connected to the grain size,  $d$ , by means of two constants,  $K$  and  $\sigma_0$ . According to this model, if the grain size of the metallic crystallites in the amorphous-carbon (a-C) matrix falls down to nanometer range, hardness will sharply increase. In fact, such defects act as obstacles for dislocation motion through the solid. If the embedded grains are nanoscaled, we can refer to this material as nanocomposite. Then, it is said that mechanical properties are improved by superlattice effects. Below 10 nm of grain size, dislocations do not exist any longer in nanocomposites, being then replaced by grain boundary sliding.

Co-sputtering and co-evaporation of metal whilst growing carbon films are the most popular methods to deposit these composite films. For example, Pt-DLC composite thin films were synthesized by a radio frequency (RF) sputtering deposition technique, and

improved electrical conductivity and reduced film stress were obtained by the addition of platinum [7]. Carbon–nickel nanocomposite thin films were prepared by direct current(dc) magnetron sputtering of Ni and C targets in argon at 0.25 Pa [8]. Copper/ hydrogenated amorphous carbon (Cu/a-C:H) composite films have also been obtained by a hybrid deposition technique combining the plasma-enhanced chemical vapor deposition of carbon with the sputter-deposition of copper in argon–acetylene gas mixtures [9].

Although high quality and rapid growth rates have been achieved, many of these methods require complex experimental setups and high substrate temperatures.

In this study we proposed a novel technique for the deposition of amorphous Carbon-Metal coatings, named thermo-ionic vacuum arc (TVA) [10], obtaining high  $sp^3$  carbon bonding films continuous and smooth. Taking into account that the TVA method uses pure graphite as evaporation source, contrarily to hydrogen containing precursors (for example, the CVD method that uses  $CH_4$  as carbon source), we obtained hydrogen-free carbon-metal composite films with randomly oriented nanocrystalline phase, having a minimal residual stress and increased adherence.

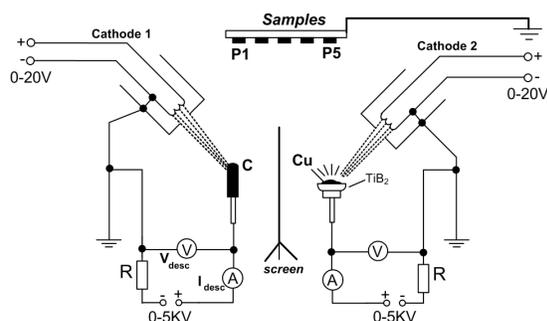
The purpose of this study is the correlation of the morphological and structural features for the copper-doped amorphous carbon coatings (such as crystallite grain size, and bonding types formed by C and Cu) with the mechanical properties (the friction coefficient), modifying the Cu atomic percent in the films.

## 2. Experimental

The thermo-ionic vacuum arc deposition method is based on the usage of two electron beams emitted by two externally heated cathodes of W, with the diameters of 1mm. The graphite anode (a rod of 10 mm in diameter and 150 mm in length) and the copper anode (consisting in high purity metal flakes of Cu placed in a  $TiB_2$  crucible) were bombarded simultaneously by the high anodic voltage accelerated electronic beams.

Two bright plasmas in vapors of pure carbon and metallic atoms, respectively, were formed in the high vacuum chamber, after applying high voltages (1-5KV) between cathodes and anodes. In this way, the atomic beams and ionic beams (formed by plasma ionization of C and Cu atoms) were coming freely or accelerated in the field between anodes and substrates: steel polished disks (25 mm in diameter and 3 mm in thickness) and BK7 optical glass disks with the same diameter and 1 mm in thickness. During deposition process, the substrates were heated at the constant temperature of 200°C. The sample substrates were settled in appropriate sample holder and situated on an imaginary line, parallel with the carbon and copper evaporators, each sample being placed at different distances relative to each of the evaporators. In this way in a single running deposition, were produced coatings with different relative carbon-copper concentrations, in order to emphasize the role of copper inclusion in a carbon matrix.

Deposition rate  $r_d$  and film thickness  $d$  were measured and controlled *in situ* using an Edwards FTM7 quartz microbalance. The intensity of the heating currents of the cathode filaments were about 40-50 A. The intensity of the TVA current and voltage for C vapor discharge was  $I_{desc} = 1.0-1.3$  A and  $U_{desc} = 300 - 500$  V, respectively. In the case of the discharge in Cu vapor, those values were  $I_{desc} = 0.5-0.9$ A and  $U_{desc} = 900-1100$ V. The first layer deposited on substrates was a Cu layer (with the thickness of 300 nm), followed by the carbon-copper composite layer, having a thickness of 2  $\mu$ m.



**Fig.1.** Experimental set-up for C-Cu composite coatings deposition

The friction coefficient and wear resistance measurements were performed using a CSM ball-on-

disk tribometer consisting of rotating disks (our samples) sliding on stationary sapphire balls (6 mm in diameter) at a sliding speed of 0.1 m/s in dry conditions at room temperature and at the normal load of 1N.

SEM investigation was carried out using a Philips model XL-30 ESEM TMP scanning electron microscope operated at 30 kV.

The XRD patterns were obtained using an Shimadzu model 600 powder diffractometer operating with Cu K $\alpha$  radiation (45 kV, 40 mA) and a diffracted beam monochromator, based on a step scan mode with the step of 0.02° 2 $\theta$  and 0.5 s per step.

The low-angle X-ray diffraction analysis were performed to establish the presence of the crystalline phases in the coatings and to calculate the average crystalline size of the particles, using Sherrer's formula.

The X-ray photoelectron spectroscopy technique was used in this research to investigate the bonding states and the atomic concentration of the elements in the surface chemistry of the material analysed in "as received" state and after Ar<sup>+</sup> ion sputtering for 10 minutes. The XPS measurements were recorded with a VG ESCA 3 MK II spectrometer system equipped with a monochromated Al K $\alpha$  X-ray source.

### 3. Results and Discussions

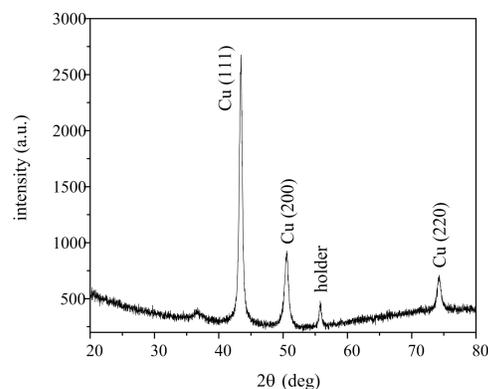
In the XRD pattern shown in Fig.2, the diffractions at 2 $\theta$  = 43.47°, 50.33°, 74.27° can be assigned to (111), (200) and (220) planes of Cu cubic close-packed phase, results that confirm the existence of Cu nanocrystalline phases in the films. We can see also that the peak intensities and full width at half maximum (FWHM) at all the orientations are almost the same, indicating uniform grain size and random orientation.

Ignoring the microstraining effect (which affects the XRD peak width), as a first-order approximation, the average crystalline size can be estimated by the Debye – Scherrer formula :

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where  $K$  is a constant ( $K = 0.91$ ),  $D$  is the mean crystalline dimension normal to diffracting

planes,  $\lambda$  is the X-ray wavelength ( $\lambda = 0.15406$  nm in our case),  $\beta$  in radian is the peak width at half-maximum height, and  $\theta$  is the Bragg's angle. The calculated grain size of Cu lie in the range of 12 -16 nm in the a-C matrix.



**Fig.2.** X-ray diffraction pattern of C-Cu composite film

The composition of the C-Cu films deposited on glass substrates, resulting from XPS quantitative analysis, was tabulated in Table 1. It can be seen in this table that for P2\_sputtered sample, after 10 minutes of Ar<sup>+</sup> ion sputtering, Cu atomic concentration increased from 25.9 % to 46.4%.

**Table 1.** Composition of the C-Al films resulting from XPS quantitative analysis

C-Cu Samples	C (at%)	Cu (at%)
P 1	77.8	22.2
P 2	74.1	25.9
P2_sputtered	53.6	46.4
P 3	71.2	28.8
P 4	70.9	29.1
P5	55.7	44.3

After the Gaussian deconvolution of C1s spectral line for P2 sample (Fig.3.), we obtained three peaks at binding energies of 285 eV, 287.2 eV, 289.3 eV.

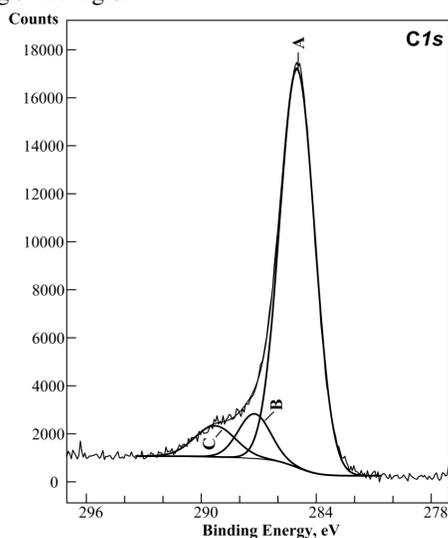
The peak A at 285 eV revealed C-C bonds with high  $sp^3$  hybridisation, and the last two peaks (B and C) could be attributed to some C-O-C and O-C=O contamination formed on the coatings surface.

In the Cu2p<sub>3/2</sub> deconvoluted spectra from Fig.4, the peak A at 931.9 eV indicated the existence of Cu<sup>0</sup> oxidation state, and the peak B at 934.2 eV showed the presence of Cu<sup>2+</sup> oxidation state in stoichiometric CuO,

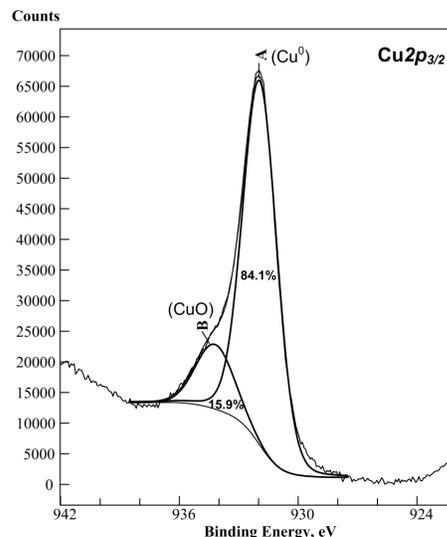
which suggests that only copper without carbon chemical bonding has been incorporated into the a:C matrix. Here, the contribution of  $\text{Cu}2p_{3/2}$  from copper profile was 84.1%, and from  $\text{CuO}$  15.9%.

If topmost metallic clusters are covered with a layer of a-C, it should be possible, in principle, to "uncover" them by  $\text{Ar}^+$  ion bombardment with sufficient energy, process based on the fact that it was accomplished a preferential sputtering, a-C layers being removed more faster than Cu clusters, and in this way the surface has been enriched in Cu [11]. The presence of a relatively low amount of oxidized copper (15.9%) at the surface represents the strongest argument of the coverage of surface Cu clusters with a thick layer of a-C.

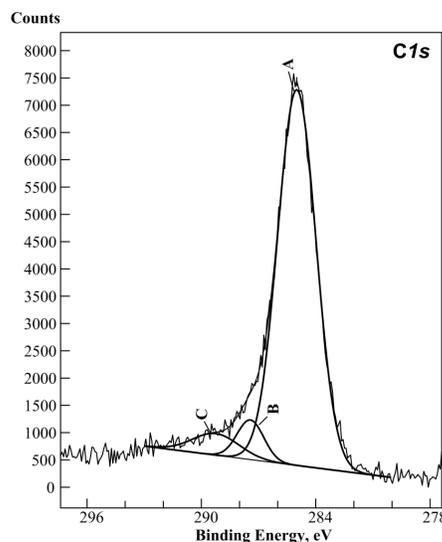
From the XPS measurements onto  $\text{Ar}^+$  ionic treated C-Cu coatings, one should observe the increase of the metallic spectral intensity with respect to the C 1s, as the cover a-C layer gets thinner. In our studies, we registered an increasing of the  $\text{Cu}2p_{3/2}/\text{C}1s$  spectral intensity ratio from 4 to 30 before, and after  $\text{Ar}^+$  ionic bombardment, respectively, as we see from the fig.5 and fig.6.



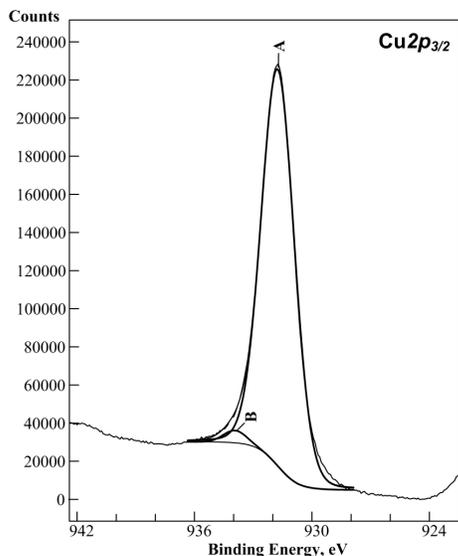
**Fig.3.** C1s XPS spectra for "as received" P2 sample of C-Cu composite film after deconvolution; A: 285 eV , B: 287.2 eV , C: 289.3 eV .



**Fig.4.**  $\text{Cu}2p_{3/2}$  XPS spectra for "as received" P2 sample of C-Cu composite film, after deconvolution; A: 931.9 eV , B: 934.2 eV .



**Fig.5.** C1s XPS spectra for P2 sample of C-Cu composite film, after  $\text{Ar}^+$  ionic sputtering; A: 285 eV , B: 287.4 eV , C: 289.2 eV .

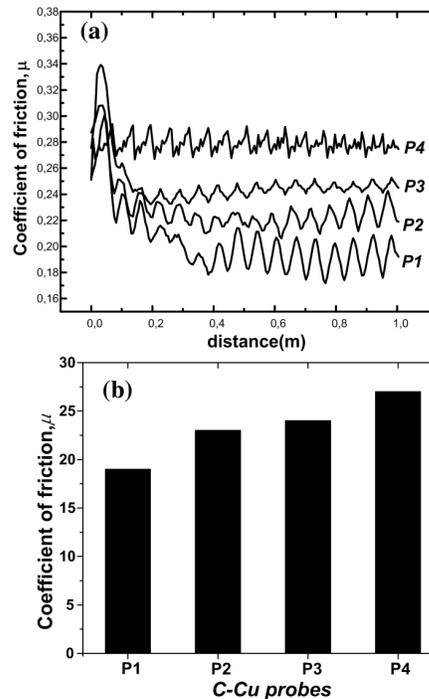


**Fig.6.**  $\text{Cu}2p_{3/2}$  XPS spectra for P2 sample of C-Cu composite film, after  $\text{Ar}^+$  ionic treatment; A: 931.7 eV, B: 933.9 eV.

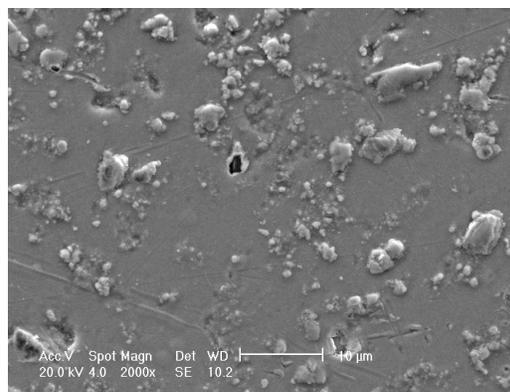
In Fig.7 can be observed that the minimum value of friction coefficient  $\mu$  (0.28) was measured for the probe P1, with the lowest atomic percentage of copper: 27.7%. The high value of friction coefficient (for the probe P3 and P4) can be related to high roughness.

SEM image of the wear track of the P4 probe (with high at% of Cu) showed in fig. 9(a) displayed cracks and a total exfoliation of the film after the tribological test, typical of the wear of hard and brittle films with weak adhesion on the substrate surface.

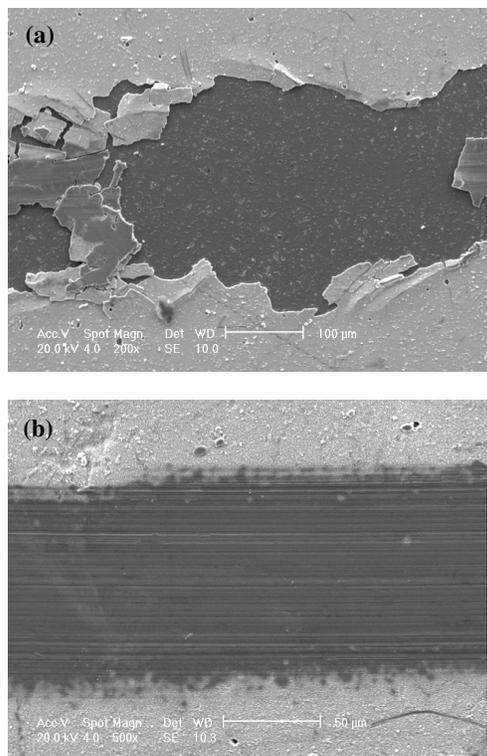
Microscopical wear track image of the P1 sample (with the lowest at% of Cu) from fig. 9(b) presented some very fine and uniform scratches on the film surface, the wear track exhibiting a smoother surface; this smooth surface, the reduced friction coefficient (the lowest value of 0.19) and increased wear resistance for this investigated P1 sample may result from the change of shear stress during friction as the C content in the film increased.



**Fig. 7.** The variation of the friction coefficient with sliding distance for the composite samples of C-Cu (a) and comparative representation of the medium friction coefficient for each of the analyzed probes (b).



**Fig.8.** Typical SEM image of P1 C-Cu composite sample



**Fig.9.** SEM images of wear tracks for C-Cu coatings: (a)-P4 probe and (b)-P1 probe

#### 4. Conclusions

The copper-containing amorphous carbon films with the thickness of 2 μm were successfully deposited onto steel and glass substrates using the TVA method.

The existence of the cubic crystalline phases of Cu in the a-C matrix was relieved from an XRD diffraction pattern; the mean grain size of the crystallites was estimated at about 12-16 nm.

The tribological measurements indicated a minimum value of the friction coefficient (0.19) for the probe with lowest atomic percentage of Cu studied.

Quantitative XPS investigations showed an increasing of the  $Cu2p_{3/2}/C1s$  spectral intensity ratio after ionic argon etching. Cu2p XPS spectra suggested the oxidation states of Cu ( $Cu^0$  and

$Cu^{2+}$ ) in the C-Cu probes, no carbide phase of copper being observed in this analysis.

#### 5. References

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