

## THERMIONIC VACUUM ARC DEPOSITED Al-DOPED AMORPHOUS CARBON NANOCOMPOSITE COATINGS

C.P. LUNGU<sup>1</sup>, V. IONESCU<sup>2</sup>, M. OSIAC<sup>3</sup>, C. COTARLAN<sup>4</sup>, O. POMPILIAN<sup>1</sup>,  
A.M. LUNGU<sup>1</sup>, V. CIUPINA<sup>2</sup>

<sup>1</sup>*National Institute for Laser, Plasma and Radiation Physics,  
Magurele, 077125, Romania*

<sup>2</sup>*Department of Physics, Ovidius University, Constanta, 900527, Romania  
e-mail: ionescu.vio@gmail.com*

<sup>3</sup>*Faculty of Physics, University of Craiova, Craiova, 200585, Romania*

<sup>4</sup>*National Institute of Materials Physics, Bucharest-Magurele 077125, Romania*

Aluminum doped amorphous carbon nanocomposite films(a-C(Al)) have been deposited by thermionic vacuum arc(TVA) technique, which implies a new discharge type in pure metal vapor plasma. The surface morphology, crystalline structure, film composition and chemical bonding were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. The friction property of the a-C(Al) 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 0.28 for the friction coefficient.

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### 1. Introduction

Tetrahedral (diamond-like) amorphous carbon (ta-C) coatings are well known for their unique combination of properties, but they suffer from low thermal stability (above 350°C), adhesion and low toughness [1, 2]. Hou and Gao [3] reported that the ta-C coatings deposited by pulse laser deposition peels off as the coatings thickness exceeds 200 nm, due to the high residual stress acquired during deposition process.

Nanocomposite, metal-containing amorphous carbon films (a-C:Me) are the new generation of these carbon based coatings, providing tremendous potential to modify and tailor their properties expanding their applications in the fields of automotive industry, biomedical investigation microsystems (MEMS) and nanotechnology.

The incorporation of metals into hydrogen free a-C matrix is an effective way to reduce the residual stress, but hardness of the coatings suffers, being reduced with about 60%, in the case of a:C-Al coatings (with only 10%Al) deposited by a filtered cathode vacuum arc (FCVA) technique [4].

If the grain size of the metallic crystallites in the a-C matrix falls down to nanometer range, hardness will sharply increase, the operation of dislocations being hindered.

Generally, a-C:Me coatings showed inferior wear resistance though lower compressive stresses and better adhesion to substrates such as steels [5].

Tribological behavior of the a-C:Me films was extensively reported in the review by Klages and Memming [6]. The main points from this review are: low friction was observed for the coatings with the carbide forming metal present at low levels (0.13%).

In this paper we used a novel technique for the deposition of amorphous Carbon-Metal coatings, named thermo-ionic vacuum arc (TVA) [7], obtaining high sp<sup>3</sup> carbon bonding films with zero internal stress, continuous and smooth. The purpose of this study is the correlation of the morphological and structural features for the amorphous carbon coatings containing aluminum (such as crystallite grain size

and bonding types formed by C and Al) with the mechanical properties (the friction coefficient), modifying the Al atomic percent in the films.

## 2. Experimental

The deposition technique employed for the preparation of the C-Al coatings was based on the running of two electron beams emitted by two externally heated cathodes of W, which were bombarding simultaneously the two anodes

(a graphite rod and 99.99% purity metal flakes of Al placed in a TiB<sub>2</sub> crucible). The thermoelectrons accelerated by high anodic voltages generated the vaporization of the anode materials with a vapor pressure nearby anodes in the domain of 1-10 Pa. Applying high voltages (1-5 keV) between cathodes and anodes, bright plasmas were ignited in C and Al vapors. Neutrals and ionized atoms with the energy of 10-200 eV were directed toward substrates.

The pressure inside the vacuum chamber was under  $5 \cdot 10^{-5}$  torr. During deposition process, the substrates used (steel polished and BK7 optical glass disks with the diameter of 25mm) were heated at the constant temperature of 200°C.

Deposition rate  $r_d$  and film thickness  $d$  were measured and controlled *in situ* using a FTM7 quartz microbalance. The intensities of the heating currents of the cathode filaments were between 40 and 50 A. The intensity of the TVA current and voltage for C vapor discharge was  $I_{disc} = 1.2-1.4$  A and  $U_{disc} = 700 - 950$  V, respectively. In the case of the discharge in Al vapor, those value were  $I_{desc} = 0.6-0.7$ A and  $U_{desc} = 800-900$ V.

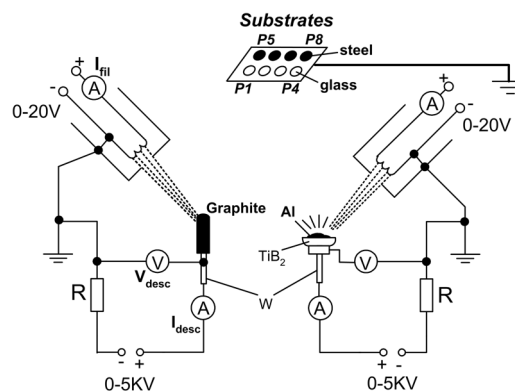


Fig.1. Experimental set-up for C-Al composite coatings deposition

The first layer deposited on substrates was a Al layer (with the thickness of 300nm), followed by the C-Al composite layer, having a thickness of 2  $\mu$ m. The friction coefficient measurements were performed using a CSM ball-on-disk tribometer consisting of rotating disks (our samples) sliding on stationary Safire balls (6 mm in diameter) at a sliding speed of 0.1m/s in dry conditions at room temperature (22°C) and relative humidity of air. Normal load of 1 N and sliding radius of 10mm were chosen in this analysis.

The morphological analysis were performed using a Philips model ESEM XL 30 TMP scanning electron microscope operated at 30 kV.

The crystalline structure of the coatings were investigated using the Shimadzu model 600 powder diffractometer operating with Cu K $\alpha$  radiation (45 kV, 40 mA) and diffracted beam monochromator, based on a step scan mode with the step of  $2\theta = 0.02^\circ$  and 0.5 s per step.

The X-ray photoelectron spectroscopy technique was used in this paper 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 discussion

In the XRD pattern shown in Fig.2, the diffractions at  $2\theta = 38.55^\circ$ ,  $44.75^\circ$ ,  $65.14^\circ$  and  $78.36^\circ$  can be assigned to (111), (200), (220) and (311) planes of Al cubic close-packed phase, results that confirm the existence of Ag 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 [8]:

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

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 FWHM (full width at half-maximum) and  $\theta$  is the Bragg's angle.

The calculated grain size of Al crystallites lies in the range of 19 -21 nm in the a-C matrix.

S. Zhang et al.[9] reported from XRD analysis an amorphous nature of the a-C(Al) coatings deposited by a magnetron sputtering technique, with 19 at.% Al in the films.

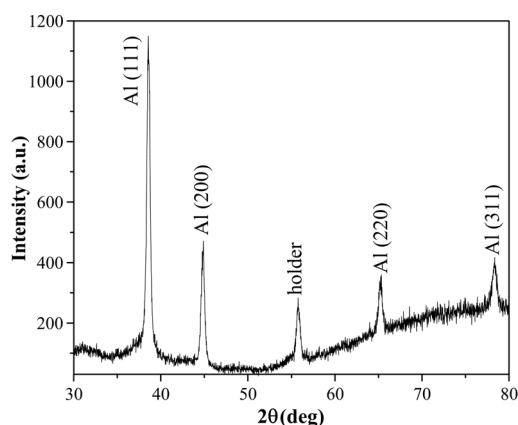


Fig.2. Typical X-ray diffraction pattern of C-Al nanocomposite film

The composition of the C-Al 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  $\text{Ar}^+$  ion sputtering, Al atomic concentration increased from 43.3 % to 56.7 %.

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

C-Al Samples	C (at%)	Al (at%)
P 1	72.3	27.7
P 2	72	28
P2_sputtered	43.3	56.7
P 3	68.6	31.4
P 4	68.1	31.9
P5	68	32

After the Gaussian deconvolution of  $C1s$  spectral line for P2 sample (fig.3.), we obtained four peaks at binding energies of 282.5eV, 285eV, 286.9eV and 288.9eV. The smallest peak (D) at 282.5eV indicated the presence of some C-Al bonding type compound in the sample; the peak A at 285eV revealed C-C bonds, 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.

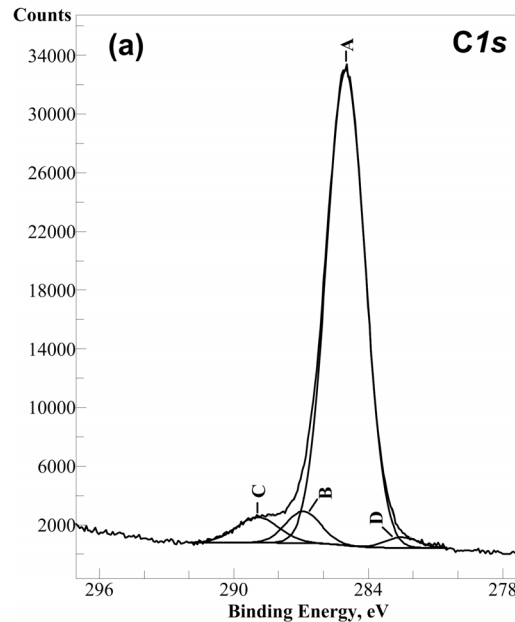


Fig.3.  $C1s$  XPS spectra for "as received" P2 sample of CAI composite film; A:285 eV, B:286.9 eV, C:288.9 eV, D: 282.5 eV.

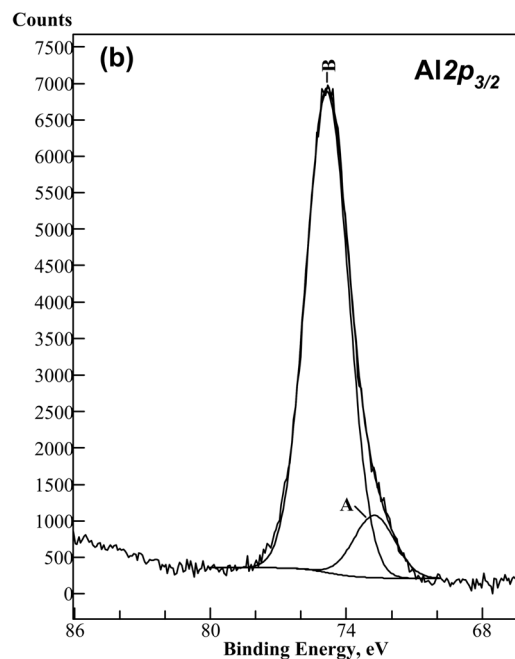


Fig.4.  $Al2p$  XPS spectra for "as received" P2 sample of CAI composite film; A: 72.7 eV, B: 74.8 eV.

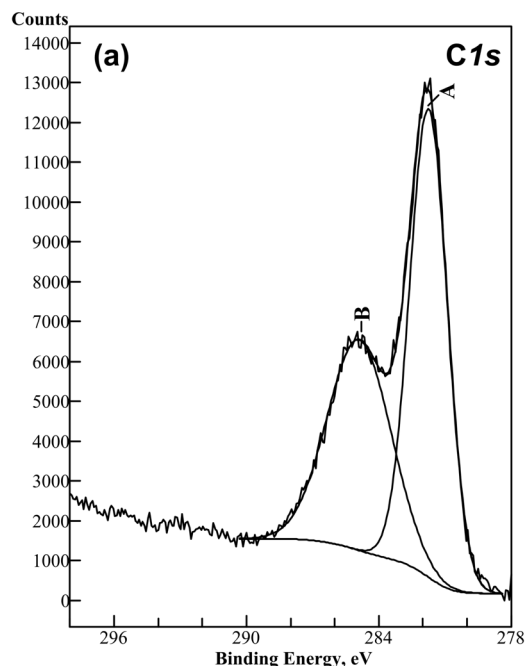


Fig.5. C1s XPS spectra for P2 sample of CAI composite film, after  $\text{Ar}^+$  ionic sputtering; A: 281.8 eV, B: 284.9 eV.

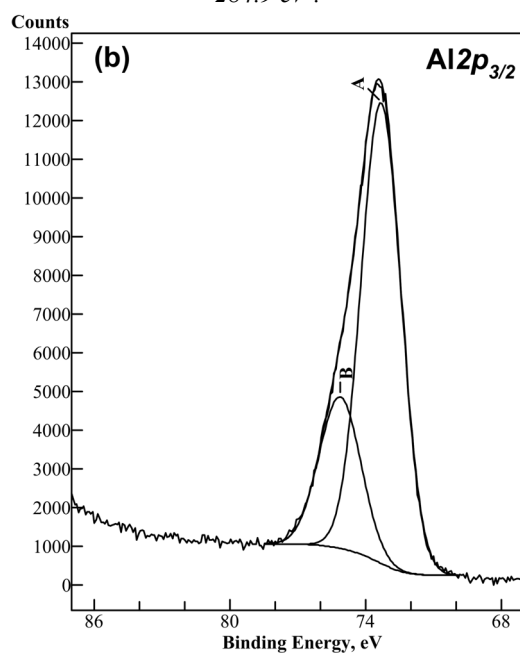


Fig.6. Al2p XPS spectra for P2 sample of CAI composite film, after  $\text{Ar}^+$  ionic corrosion; A: 73.3 eV, B: 75.1 eV.

In the  $\text{Al}2p_{3/2}$  deconvoluted spectrum from fig.4, the peak A at 72.7eV indicated the existence of  $\text{Al}^0$  oxidation state, and the peak B at 74.8eV showed the presence of  $\text{Al}^{3+}$  oxidation state in stoichiometric  $\text{Al}_2\text{O}_3$ .

From the fig.5, we seen that the C1s spectral line peak B showing C-Al chemical bonding was shifted towards lower binding energies with 0.7eV, being much more pronounced as intensity. In the fig.6, we observed that the binding energy of  $\text{Al}2p_{3/2}$  peak A indicating  $\text{Al}^0$  chemical state is slightly shifted with

0.6eV above the reference position (72.7eV), after  $\text{Ar}^+$  ionic bombardment; an increasing of the  $\text{Al}2p_{3/2}$  /  $\text{C}1s$  spectral intensity ratio was also observed.

Almost identical  $\text{C}1s$  and  $\text{Al}2p$  spectral lines for the other four "as received" samples of CAI composite coatings were registered, just a very small variation of the spectral intensity between different samples being observed.

Zhang P. et al.[10] showed from XPS measurements that the carbide phase was not present in FCVA deposited a-C:Al nanocomposite carbon films .

I. R. Videnović et al.[11] reported also an pronounced negative shift of  $\text{C}1s$  spectral lines and an positive shift towards higher binding energies of  $\text{Ag } 3d_{5/2}$  spectral lines in their studies of  $\text{Ar}^+$  ionic treated silver containing amorphous hydrogenated carbon coatings.

The explanation of those XPS spectral lines modifications after  $\text{Ar}^+$  ionic bombardment of the samples is based on the fact that it was accomplished an preferential sputtering, a-C layers being removed more faster then Al clusters, and in this way the surface has been enriched in Al[12]. The concentration at the surface will be governed by interplay between preferential sputtering and radiation enhanced diffusion/segregation processes.

From the morphological SEM image presented in fig.7, uniform crystalline structures (of about  $0.5\div 2\mu\text{m}$  in diameter) can be seen on the surface of the C-Al composite film with the lowest Al at.% concentration.

In the film morphology of C-Al composite coatings with the highest Al at.% concentration, shown in fig.8, the submicron crystalline formations at the surface were more pronounced from the point of view of their height.

In Fig. 9 it can be observed that the minimum value of friction coefficient  $\mu$  (0.28) was measured for the sample P1, with the lowest atomic concentration of Al: 27.7% .

The high value of friction coefficient (for the samples P4 and P5) can be related to high roughness. The small increasing and dropping of the friction coefficients during the sliding distance for each of the samples analyzed can be explained by the variation of the area of contact between the pin and the film.

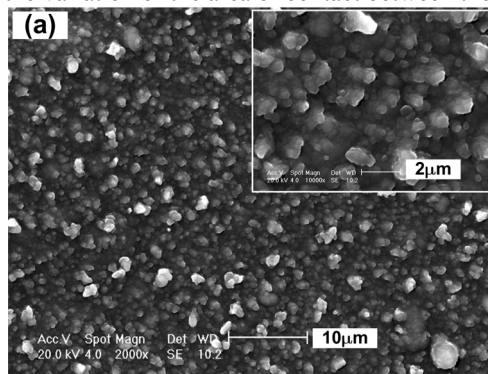


Fig. 7. SEM image of the P1 C-Al composite sample.

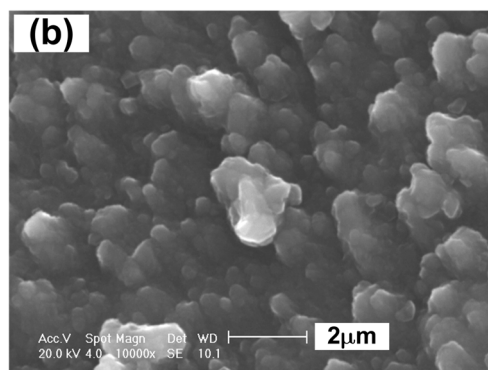


Fig. 8. SEM image of the P5 C-Al composite sample.

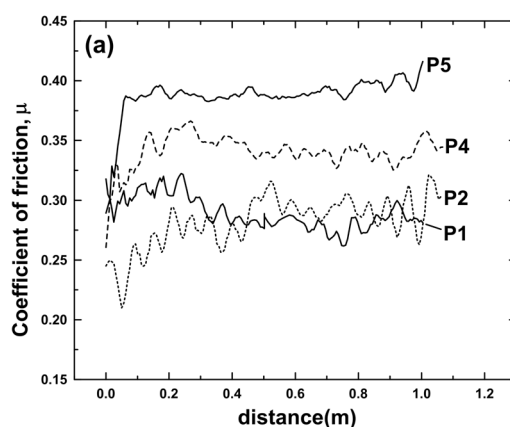


Fig. 9. The variation of the friction coefficient with sliding distance for the nanocomposite samples of C-Al.

E. Liu et al.[13] noted that the friction coefficient of the FCVA deposited ta-C:Al films had a value of about 0.25, their tests being performed with an ball-on-disk tribometer in ambient air (RH 50%) and at room temperature (22°C).

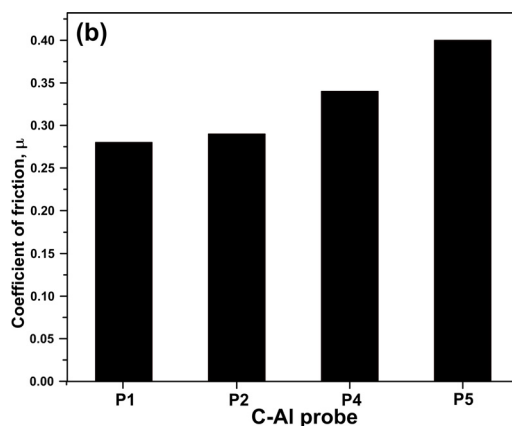


Fig.10. Comparative representation of the medium friction coefficient for each of the analyzed samples.

#### 4. Conclusions

The TVA method for the deposition of thick (2 $\mu$ m) amorphous carbon-aluminum composite coatings has proved to be a very good technique.

The existence of the cubic crystalline phases of Al in the a-C matrix was relieved from an XRD diffraction pattern; the mean grain size of the crystallites was estimated at about 19-21 nm.

XPS measurements indicated the presence of Al<sup>0</sup> and Al<sup>3+</sup> oxidation states in the samples and the shifts of the C1s and Al 2p<sub>3/2</sub> spectral line peaks after ionic sputtering in the argon plasma.

The tribological analysis showed a minimum value of the friction coefficient (0.28) for the sample with lowest atomic concentration of Al (27.7%) studied.

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