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CHARACTERIZATION OF TERNARY C-Si-Al NANOCOMPOSITE THIN FILMS OBTAINED BY TVA METHOD

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Thin film depositions on certain substrates can improve or diminish the physical-chemical behavior of the coated material. For the present work there were used three basic elements: C, Si and Al as coating materials on glass, silicon and OLC45 steel substrates. The purpose of the research is to obtain an optimum combination for properties' improvement, as hardness, adherence and low friction. Nevertheless, such special characteristics can be found likely in a composite material. Ternary C-Si-Al samples of 1 micron thickness were successfully obtained for the first time using Thermionic Vacuum Arc (TVA) deposition method. Depth profile measurements confirmed both the thickness of the obtained layer and the high roughness of the layers deposited on OLC 45 steel substrate. The granular structure of the films was pointed out by SEM, AFM and TEM measurements. XPS measurements highlighted the formation of aluminum and silicon oxides due to the layer exposure to the residual gas existent in the deposition chamber. The friction coefficient of the coatings was two or three times lower in comparison with the one of the uncoated substrates. Film hardness was found to be high with values between 3600 and 5000N/mm^2 (~3.6-5.0 GPa), depending on the penetration depth.

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1. Introduction

Thin film depositions on certain substrates can completely change the physical-chemical characteristics of the coated material, adding specific advantages. For mechanic devices parts with relative motion during their operating time it is desired to reduce the friction between metallic or nonmetallic surfaces. The small variation of the friction coefficient both along the contact surface and during the operation process was attained. High resistance to temperatures in the range -200^{0}C to 450^{0}C or even on enlarged domains, high resistance to dust, to destructive action of active chemicals like acids, bases and the possibility to work with removed lubricants for at least limited periods in emergency cases are obtained and the results were confirmed by specific analyses.[1, 2] Another aim attained by using these composite materials was to enlarge the operating life of the devices and to ensure their protection against the corrosive action of water and vapors. The improvement of decorative parts appearance was also attained. This type of deposition can reduce the surface' wearing caused by the contact corrosion, gripping, etc. and also helps avoiding the stick-slips. Another positive result was that the creaking between relatively moving parts was completely removed.

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The obtained new coating part as a result of deposition process has a great resistance against the pressures on its surfaces. From the economic point of view, the reduced cost of the parts production is very important because the quantity of the coating materials is insignificant while the main part of the device can be made of a raw material with small fabrication cost.

All these characteristics offer the possibility to use these depositions to coat the automotive parts, springs, arbors, gears, cranked axles, centre pins, bearings etc. These specific coatings must present certain characteristics like flexibility and resistance to abrasion, very good adherence to substrate, compatibility with the substrate both physically and chemically with no destructive attack of the substrate, lack of friction electric charge generation in order to avoid sparks and explosions in organic chemical vapors [3]. Another important aspect excellently accomplished was the long life time of the deposited materials. This innovative characteristic can be obtained by depositions of structures containing materials able to ensure at the same time a high resistance – a certain capacity to resist to high pressures, to cavitations and on the other hand to present a certain consistency soft enough to allow compatibility with the substrate, to follow its form and to be adherent to it. Thus, the deposited material on the substrate must be both hard and soft. This innovative property can be obtained only by special materials' mixing, ones to ensure the hardness and ones to ensure the softness.

This type of coatings can be performed both as sandwich layers of different parameters and thicknesses and as mixed layers with certain convenient concentrations of the components [4,5]. For this second type of deposition, the soft material particles must be distributed as uniform as possible into a matrix of sufficiently hard material. It can also be used a composite granular structure formed from a layer of deposited material and a layer of mixed material. Usually the thickness of the deposited layer must be in the range of tens of microns able to blur the substrate inequalities and also to be able to include the particles of bigger or smaller dimensions as the impurities brought by the lubrication oil.

The materials recommended for these depositions are: aluminum, which combined with carbon, ensures the improvement of lubrication characteristic in order to diminish the friction coefficient and ***silicon***, which distributed into aluminum as fine particles, ensures a higher hardness of the substrate [6]. High hardness can be also obtained with copper, nickel etc. Silicon also contributes to an enhanced gripping resistance by its contact surface polishing action. Hence appears the need for fine silicon particles existing in the mix. The third desired material is ***carbon*** that ensures both high lubrication of the composite layer and high resistance against chemical and corrosive environment attack.

2. Experiment

C-Si-Al ternary depositions using thermionic vacuum arc (TVA) method

TVA deposition method [7,8] is recommended for ternary layers depositions with above described specific characteristics [9,10]. The deposition process takes place in high vacuum in the presence of ions generated from the depositing materials, with the possibility to continuously change the position of the part to be deposited in order to obtain the needed coating conformity. Thus, simultaneous ternary depositions were performed from the plasmas ignited in both **c**arbon and silicon atoms and from thermal evaporated aluminum atoms coming from the third crucible. The difference in design for the aluminum set-up was the fact that instead of bombarding with the electron gun the material, we were bombarding the crucible. This way Al is only heated and not forced to ignited TVA plasma. The reason for doing this is the control of the deposition rate. Aluminum has a very high deposition rate when plasma is being ignited. One positive aspect offered by this deposition technique consists in using punctual evaporation sources which allow for a large variety of elemental concentration of the materials simultaneously deposited [11], the samples being mounted at different distances to the sources. The lack of any gaseous inclusion inside the deposition layer due to extremely high vacuum conditions is another advantage offered by TVA deposition method.[12,13] All these aspects are essential for high quality depositions.

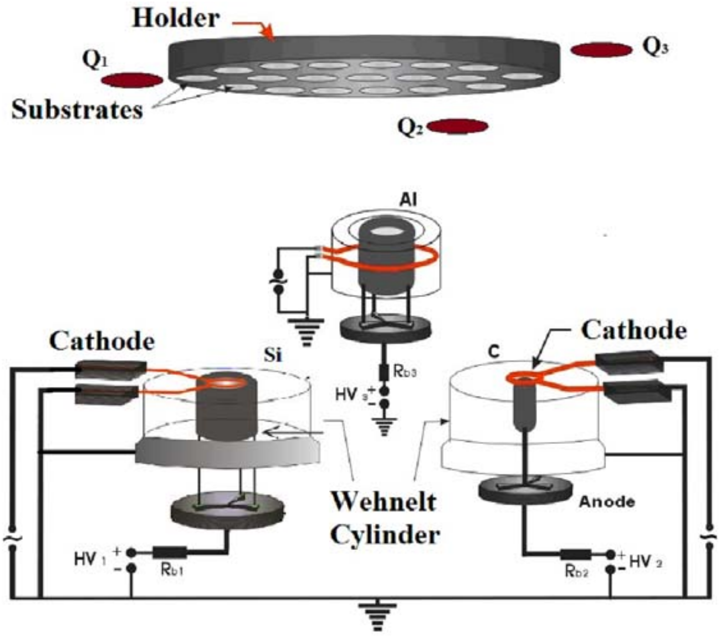


Fig. 1. Experimental set-up used for ternary depositions by TVA method

C-Si-Al ternary composite films were deposited using three TVA guns. Glass, silicon and OLC45 substrates were used. The film thickness and deposition rate was monitored for each of the three interest elements during the deposition process using three Q-pod micro-quartz balances (Q1, Q2, and Q3). The final thickness of the deposited layer was given by summarization of corresponding thickness for each element (Fig. 1). Deposition parameters used for each deposition are presented in the Table 1.

Table 1. Deposition parameters for the three deposited materials

	C	**Si**	**Al**
U_a (kV)	2.36	2.9	1.9
I_a (A)	1.22	0.45	0.1
I_f (A)	38.1	34.8	30.5
Deposition Rate (Å/s)	0.9	1.09	2.6
Total amount deposited (nm)	370	300	330

3. Results and discussion

3.1 Structural and morphological analysis for the deposited films

The layer thickness and film roughness were measured using a DEKTAK depth profiler. Depth profile measurements confirmed the 1 micron film thickness and high roughness due to substrate (Fig. 2).

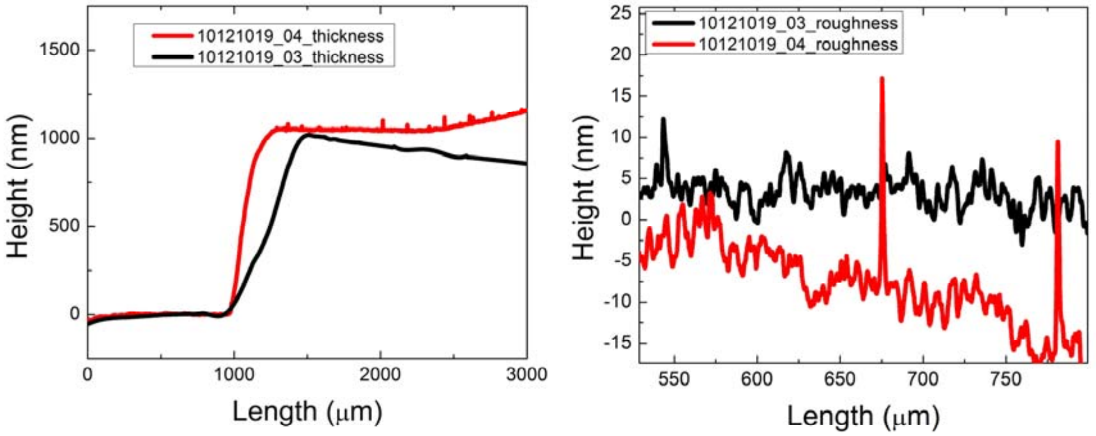


Fig. 2. Thickness and roughness measurements on OLC45 substrates

SEM and EDS measurements were performed to observe surface morphology and atomic relative concentration distribution of the three elements inside the film. The granular nano composition is present as seen in the SEM image. (Fig. 3). Although EDS analysis does not offer data on depth profile because it integrates the signal of the strained electrons, it can offer accurate data on composition. The relative concentrations of the three measured elements using EDS analysis were identified in the range 58 at% C, 9 at% Al and 30% Si; as it was expected, an increased C concentration was obtained in the films due to the chosen deposition parameters. The oxygen concentration in the films was 2%. This contamination with oxygen was attributed to the post deposition exposure of samples. However, EDS is not e reliable method for determining the C-Si-Al relative concentrations, the high silicon concentration could be also attributed to the substrate.

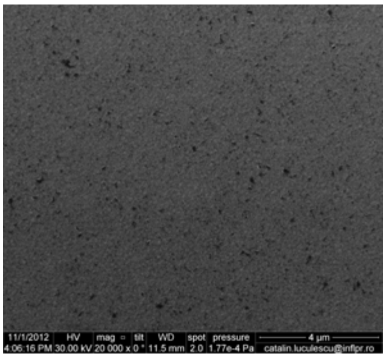


Fig. 3. SEM image of the C-Si-Al film deposited on silicon substrate

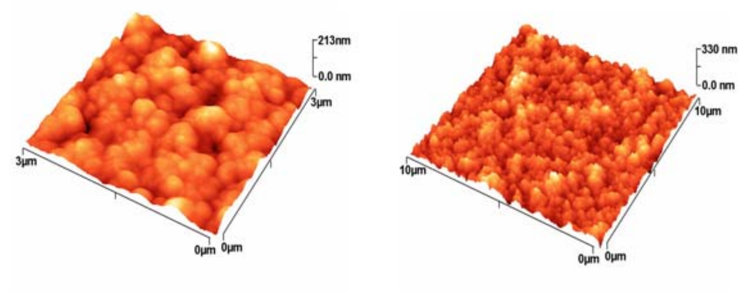
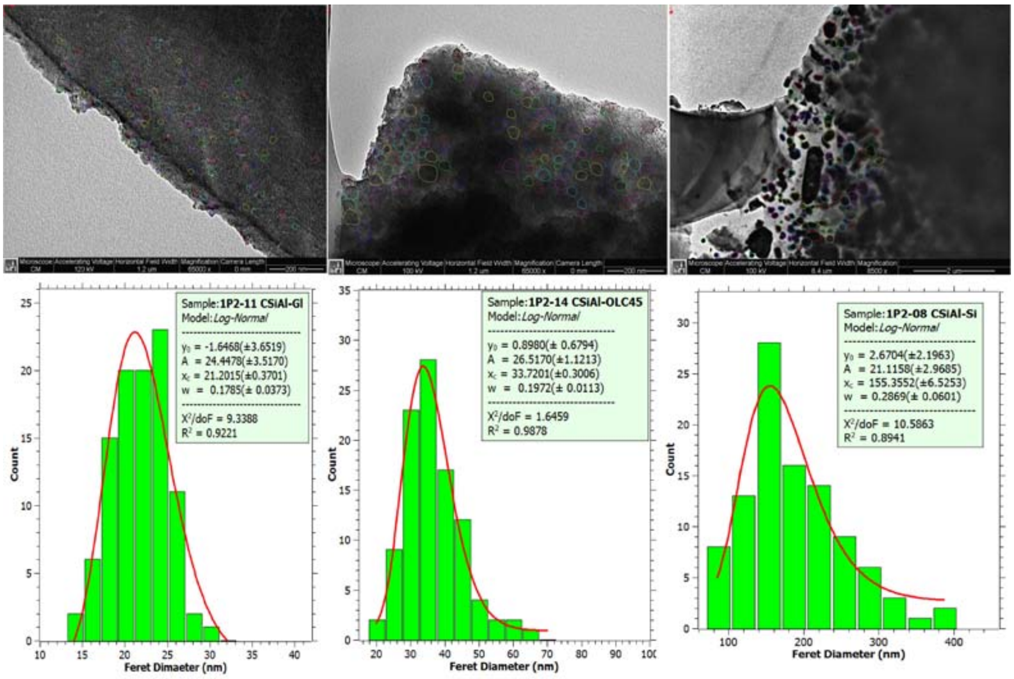


Fig.. 4. AFM 3D images and roughness values for Ra and RMS for surfaces of 3 x 3 μm and 10 x 10 μm respectively.

From the AFM measurements performed on the C-Si-Al thin film structures on silicon substrates (Fig. 4) it was obtained the information regarding the value of the roughness of the deposited layer which was found to be in the range of 22 to 34 nm. The performed AFM measurements on the silicon substrates samples confirm the granular structure of the obtained thin film, being in conformity with SEM analysis results.

TEM analysis was performed using a CM120ST microscope with an acceleration voltage of 100kV. The samples were prepared using the scratch method, consisting of several stages. Firstly, the film surface was scratched with a diamond knife. Then a rake was used to add an alcohol drop on a grid covered with form-var solution. The grid was put on the scratched area. After a few seconds the grid was lifted up and placed on a filter paper for an hour in order to allow for alcohol evaporation.



a) Glass substrate **b) OLC45 substrate** **c) Silicon substrate**

Fig. 5. TEM images (up) with particles selection for statistic determination and grain size distribution (down) of the deposited films on different substrates.

For the areas presented in figure 5 there were diffraction figures obtained for each type of samples. These figures were fitted with radial distribution functions and so the peaks were obtained using ELD modulus for the polycrystalline materials implemented in CRISP2 application [14]. As a result of this processing, the samples deposited on glass and OLC45 substrates showed amorphous structure while those deposited on silicon showed also crystalline components[15].

Using the values obtained after deciding the crystallites, the histogram is performed for Feret like diameters. The fitting function is log-normal distribution due to skewness value = 0.89, indicating a normal distribution bended towards right and kurtosis = 0.79 respectively, showing a sharp distribution in comparison with the normal one. As it can be seen in Table 2, the crystallites dimension depends on the nature of the substrate.

Table 2: Mean crystallites' dimensions of C-Si-Al films depending on the substrate

Substrate type	Crystallites Shape	Medium diameter (nm)	Errors
Glass	Almost spherical	21.20	±0.81
OLC45 Steel	Almost spherical	33.72	±0.30
Silicon	Almost spherical	155.35	±6.52

X-Ray Photoelectron Spectroscopy (XPS) analysis was carried out on PHI Quantera SXM equipment, with a base pressure in the analysis chamber of 10^{-9} Torr. The X-ray source was Al K_{α} radiation (1486.6eV, monochromatized) and the overall energy resolution is estimated at 0.65 eV by the full width at half maximum (FWHM) of the $Au4f_{7/2}$ line. In order to take into account the charging effect on the measured Binding Energies (BEs) the spectra were calibrated using the C1s line (BE = 284.8 eV, C-C (CH)n bonding) of the adsorbed hydrocarbon on the sample surface. A dual beam neutralizing procedure (e^- and Ar^+ ion beams) has been used to compensate the charging effect in insulating samples [16]. After running survey XPS spectra, the high resolution photoelectron spectra of the most prominent XPS transitions (C 1s, O 1s, Al2p and Si2p) were recorded (fig. 6).

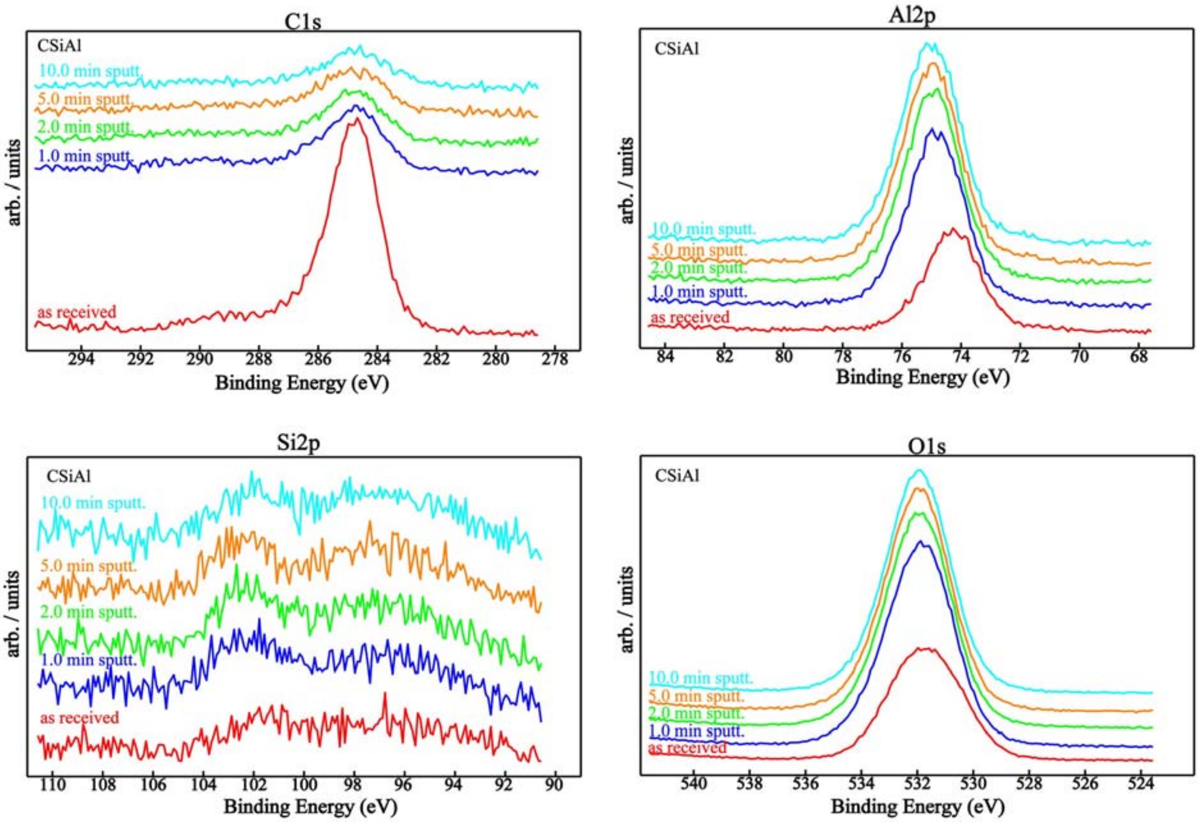


Fig. 6. XPS lines corresponding to C1s, Al2p, Si2p and O1s lines for the samples deposited on silicon substrate.

It is appropriate to note here that all the calculations were performed assuming that the samples were homogeneous within the XPS detected volume. We have to emphasize that the errors in our quantitative analysis (relative concentrations) were estimated in the range of ± 10%, while the accuracy for Binding Energies (BEs) assignments was ± 0.2 eV [17]. Sampling depth is estimated according to the corresponding sputter rates, as : 1 min sputtering ~ 12 nm depth; 2 min sputtering ~ 14 nm; 5 min sputtering ~ 20 nm; 10 min sputtering ~30 nm depth.

We can notice the presence of the hydrocarbon layer on the top of the surface which is progressively decreasing and stabilizes (up to ~7%) after Ar ion etching, showing that its presence is not only on the surface as a contaminant, but also it is incorporated into the sample's matrix. A chemical shift (~0.6 eV) occurs between the Al2p XPS spectrum in the "as received" state and in the sub-surface region of the sample. This can be explained due to OH groups adsorbed on the outermost layer of the surface.

The sampling depth is estimated to ~ 30 nm under Ar ion etching conditions: 1keV, scan (3 mm x 3 mm) and 10 min sputtering time. A tiny amount of silicon (~0.5%) can be detected on the surface and in the sub-surface region as O-Si-O bounds (see deconvoluted spectra in Fig. 7). Indeed, even at these very low concentrations, the Si chemistry investigation is still possible and reliable.

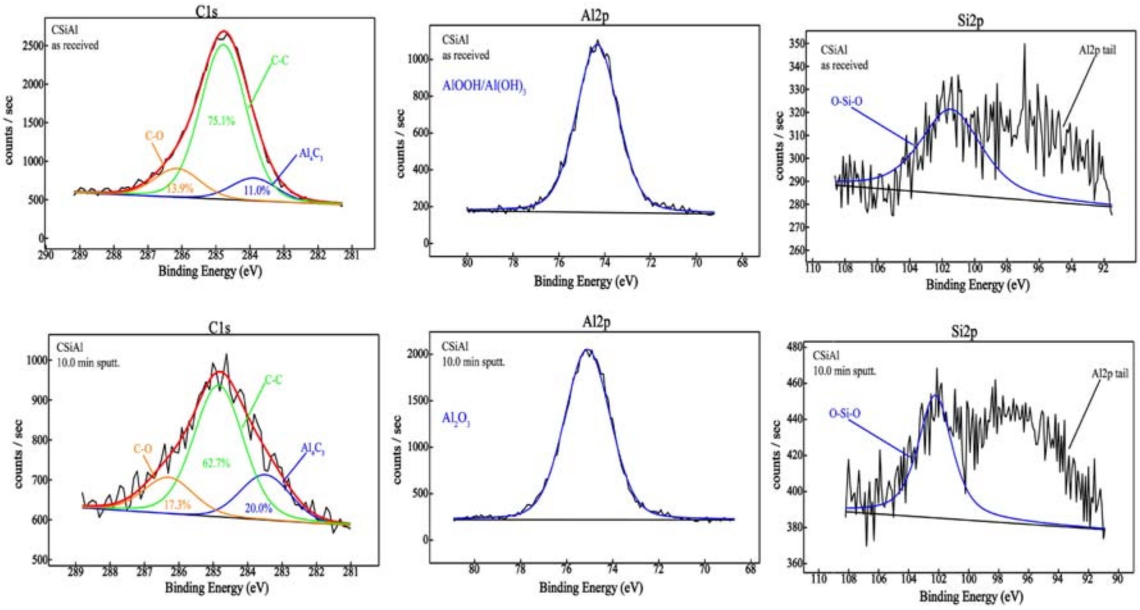


Fig. 7. Deconvoluted XPS lines corresponding to C1s, Al2p, Si2p and O1s lines "as received" and after 10 min Ar$^+$ sputtering on silicon substrate

The carbon chemistry [18] shows a different behavior after 10 min Ar etching (~30nm), displaying a new contribution due to the presence of Al and C at high temperature.

Thus, aluminum carbide occurs by direct reaction of aluminum and carbon:

$$4\,\mathrm{Al} + 3\,\mathrm{C} \rightarrow \mathrm{Al_4C_3} \tag{1}$$

By reaction with surface adsorbed water the formation of hydroxide could occur:

$$\mathrm{Al_4C_3} + 12\,\mathrm{H_2O} \rightarrow 4\,\mathrm{Al(OH)_3} + 3\,\mathrm{CH_4} \tag{2}$$

The Al_4C_3 feature is increasing with depth up to 20% (after 10 min Ar etching on Si substrate).

After deconvolution procedure of the Al2p spectrum we can assign the chemical species $AlOOH/Al(OH)_3$ existence on the top surface. A tendency of decreasing in the C content associated with the corresponding rise in the Al content can be noticed for higher sputtering time (10 min).

XPS depth measurements for C-Si-Al deposited layers on OLC-45 substrates were performed after 10 and 15 min Ar ion sputtering 1 keV (3X3). The deconvoluted spectra are presented in Figs 7 and 8. Thus, after 15 min etching (~40nm) the atomic relative composition of the three elements was found out: C=49.27%; Al=39.8 %; Si=10.91%.

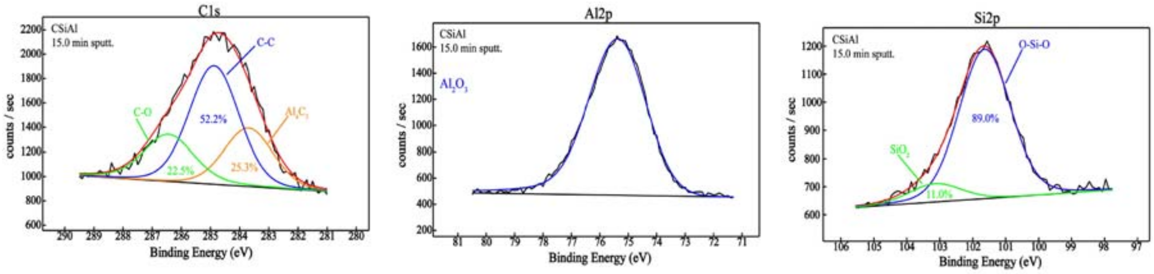


Fig. 8. The C1s, Al2p and Si2p XPS deconvoluted spectra of the C-Si-Al sample on OLC-45 substrates after 15 min sputtering.

From XPS analysis it can be concluded that at the surface both silicon and aluminum elements occurs in oxidized states. Relative concentration XPS depth profile shows that the surface contamination effect is suddenly attenuated due to Ar ion etching. Thus, after 1 min Ar sputtering (~ 12nm penetrating depth) the atomic relative concentrations of the three elements were, as follows: C = 33.62%, Al = 64.62% and Si = 1.76 % (Fig. 9).

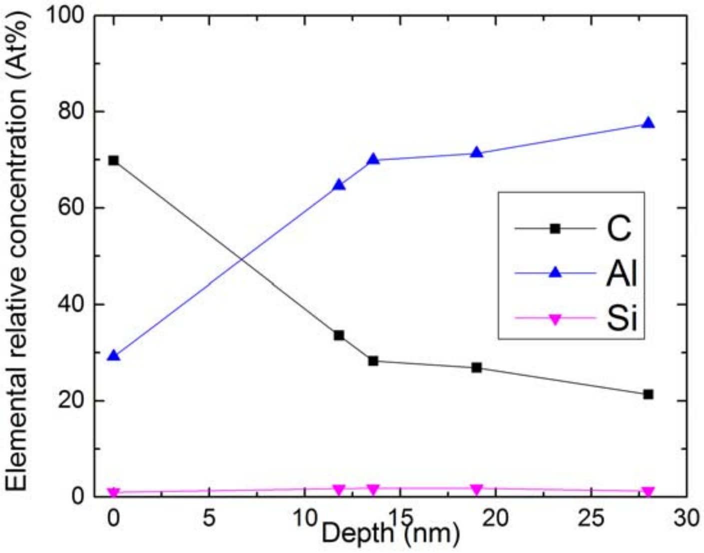


Fig. 9. Depth profiles of elemental relative concentrations from XPS analysis

One can notice a suddenly increase of the Si relative concentration by about one order of magnitude as compared to the sample using Si substrate. The same tendency of increasing of the relative concentration reveals also C from 26.7% after 10 min sputtering to 30.7 % after 15 min sputtering. This behavior is opposite related to the previous sample deposited on Si substrate. Under the same etching conditions the content of Al carbide (Al_4C_3) was larger for the layer deposited on OLC-45 substrate (24.3%) compared to 20.0% for the layer deposited on Si substrate.

3.2 Friction coefficient – dry friction measurement and wear rate

For tribologic characteristics determination, systematic measurements were performed using a ball-on-disc tribometer made by CSM Switzerland, with normal force of 1N, 3N and 5 N respectively, a stainless steel ball with a diameter of 6 mm, a dry sliding distance of 100 m, and linear speed of 20cm/s (fig. 10).

For C-Si-Al composite films, the friction coefficient exhibited values 2-3 times lower than that for the uncoated substrates. An increasing tendency of the friction coefficient with the increase of the applied force was noticed. At 3 N, film friction coefficient value becomes equal with the value as for the substrate. Over this value of the applied force, the film friction coefficient continues to increase.

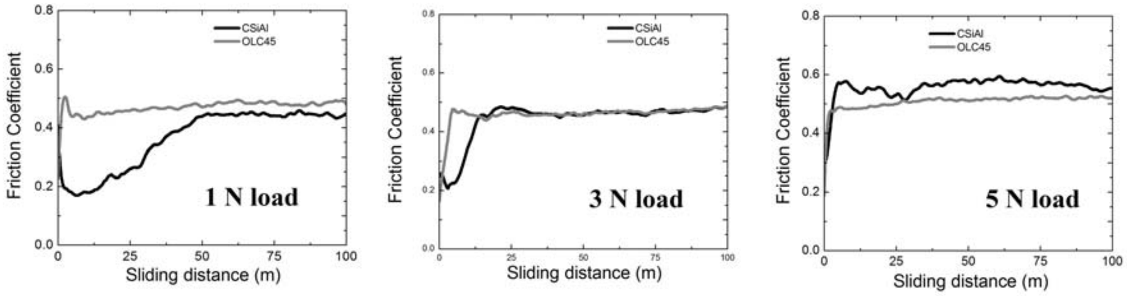


Fig. 10. Comparative view of the friction coefficient of substrate (OLC45) and of CSiAl film deposited on the substrate at different loading forces.

On the basis of depth profile measurements performed on the wearing traces (Fig. 11), the wear rate was estimated for 3 and 5 N loading forces respectively. For 1 N force, the rate could not be calculated due to high roughness of the substrate. The wear rate was 1.23E-05 mm^3/Nm for a force of 3N while for 5 N is higher: 6.16E-05 mm^3/Nm. These values indicate a good behavior of the deposited layers under working conditions.

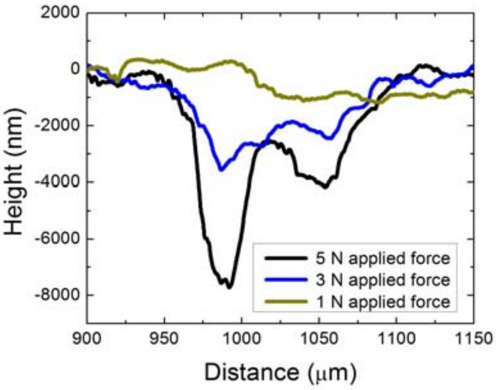


Fig. 11 Depth profile of the wearing traces after the ball-on-disc tests

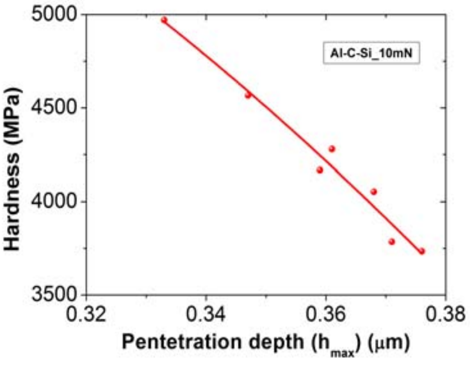


Fig.12 Micro hardness measurements at 10mN load

Hardness measurements:

Nano-indentation measurements were performed to determine film hardness. Figure 12 (right) shows the values obtained as a result of the seventh measurements performed on C-Si-Al using a 10N force at different depths (Fig. 12 left). Thus, film hardness is very high with values between 3600 and 5000N/mm^2 (~3.6-5.0 GPa).

4. Conclusions

Ternary thin film structures with improved physical properties such as flexibility and resistance to abrasion, good adherence, high hardness, low friction and a strong compatibility with the coated material were obtained for the first time using the innovative Thermionic Vacuum Arc deposition method. In order to obtain these characteristics of the thin film, a mixture of C, Al and Si was deposited on different substrates. Carbon was used in this mixture for its' high lubrication of the composite layer, high resistance against chemical and corrosive environment attack. The combination with aluminum ensured the lubrication and a low friction coefficient value of the thin film. The mixture was completed by fine silicon particles distributed into the aluminum matrix which ensured a higher hardness of the structure. These characteristics enhance the coated parts with special features like higher resistance to wearing and gripping, better inclusion of the rest particles inside, excellent conformity of the layer with the geometry of the coated parts. The thickness of the ternary structure was of about 1 micron.

Using EDS measurements accurate data on the relative concentrations of the deposited structure were obtained. As it was expected C at.% concentration was found higher up to 50%, 9% for Al and 30% for Si relative concentration. The low value of 2% for the oxygen content found in the samples proved once again the Thermionic Vacuum Arc efficiency in obtaining pure thin films without any unwanted impurities.

SEM analysis pointed out the high quality of the ternary surface, without major defects. The roughness values determined by the AFM analysis were in the range of 22-34 nm, confirming along with SEM measurement the nanometric granular structure of the obtained thin film.

TEM analysis confirmed an amorphous like structure for the samples coated on glass and OLC45 substrates and a crystalline structure for the samples coated on silicon, certifying the role of the substrate structure on the deposition atomic arrangement.

XPS analysis proved the presence of the hydrocarbon layer on the top of the surface progressively decreasing and stabilizes (up to ~7%) after Ar ion etching on the layer deposited on Si substrate. The content of carbon is higher and exhibits a significant increase for oxidized silicon on the layer deposited on OLC-45 substrate. The carbon chemistry displays a new contribution (Al_4C_3) due to the presence of Al and C at high temperature. It can be concluded that XPS measurements highlighted the presence of oxidized states and chemical species on the surface for both silicon and aluminum as well as the elemental relative concentrations on the outermost layer of the surface.

From the tribologic analysis, the friction coefficient of the ternary structure showed a two to three times decrease of this parameter compared with the uncoated substrates with a slight increasing tendency in the range of 0.17 to 0.58 with the increasing loading force. The calculated wear rate was in the range 1.23x10^{-5} and 6.16 x10^{-5} mm^3/Nm. The hardness of the ternary structure was high, being obtained by nano-identation analysis in the range 3600 to 5000 N/mm^2, decreasing with the depth measurement increase.

Materials characteristics presented in this article enhance the mechanical parts with special features like higher resistance to wearing and gripping, better inclusion of the particles inside the prepared layers, excellent conformity of the layer with the geometry of the coated parts.

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