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Chapter 5

DLC Thin Films and Carbon Nanocomposite Growth by Thermionic Vacuum Arc (TVA) Technology

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/63367

Abstract

The aim of this chapter is to report the results on synthesis **DLC thin films and carbon nanocomposites by** the versatile **nanofabrication method based on plasma** entitled **thermionic vacuum Arc (TVA)**. TVA technology is based on the localized ignition of the arc plasma in vacuum conditions. Among thin film coating methods by vacuum deposition techniques with high purity, low roughness, and good adhesion on the substrates, **TVA is one of the major suitable methods to become a powerful coating technology**. Two or three different TVA discharges can be ignited simultaneously in the same chamber for multi-material processing using TVA and separate power supplies. These TVA discharges are localized and do not interfere with each other. Simultaneous two or three TVA discharges were already used for the production of alloy/composite of various materials. This is due to the high versatility concerning the configuration of experimental arrangements, taking into account the number of electron guns, symmetry of the electrodes, relative position of the anode versus cathode, and also the huge opportunity to combine the materials to be deposited: bi- and multi-layers, nanocomposites, or alloys in order to have specific applications. This chapter presents the comparative results concerning the surface-free energy information processing, the reflective index, the hardness, and the morphology to provide a coherent description of the diamond-like carbon films and carbon nanocomposites synthesized by thermionic vacuum arc (TVA) and related configurations where Me = Ag, Al, Cu, Ni, and Ti**: binary composites (C-Me, C-Si) and ternary composites (C+Si+Me)**. The results include reports on the distribution in size, surface, geometry, and dispersion of the nanosized constituents, tailoring and understanding the role of interfaces between structurally or chemically dissimilar phases on bulk properties, as well as the study of physical properties of nanocomposites (structural, chemical, mechanical, tribological). The results presented

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here could have a great impact on the development of advanced materials and many manufacturing industries, as well as expanding the technologically important field of interface science where the control of the film-substrate interface would be critical.

Keywords: DLC, nanocomposites, carbon, thermionic vacuum arc, nanofabrication

1. Introduction

Diamond-like carbon (DLC) is an important form of amorphous carbon consisting of a mixture of both sp^2 and sp^3 coordinated carbon. It is also known that hydrogenated carbon films show a wide range of properties concerned with hardness (3000–5000 kg mm^{-2}), chemical inertness, thermal conductivity, wear resistance (1.6×10^{-9} mm^3/mN), low friction coefficients (0.1–0.2), electrical resistivity, optical transparency from ultraviolet to infrared, and tunable band gap by manipulating sp^2 and sp^3 bonding ratio [1–6].

Unfortunately, the widespread use of DLC thin films has been limited by poor adhesion of these films to substrates, because of large compressive stresses induced in the films during the deposition process. It has been reported that the residual stresses in these films arise from a change in the local chemical bonding and changes in bonding angle and bonding length, caused by the ions penetrating into the film surface during processing [3, 7, 8].

The study of multiphase nanocomposite material involves that at least one of the constituent phases has one dimension less than 100 nm. The nanocomposite films are sought due to their multifunctionality, the opportunity of designing unique combinations of properties, difficult to achieve otherwise with traditional materials. The challenges in reaching this promise are tremendous especially in the case of **carbon-based nanocomposites** [9–11].

Thin film depositions on specific substrates can totally alter the physical-chemical properties of the coated material, adding certain advantages. During the operation time of mechanical devices with moving parts, it is desirable to reduce 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 imperviousness to temperatures in the range −200 to 450°C or even on broader domains, high resistance to dust particles and to corrosive action of active chemicals such as acids, bases, and the possibility to work without lubricants for a limited period of time in emergency cases are some of the properties of the obtained coatings. These results were confirmed by specific analyses [12, 13]. One of the goals accomplished with the use of these composite materials was to protect the devices against the damaging action of water and vapors thus increasing their operating lifetime. Also, an enhancement in the appearance of decorative parts was observed. Ternary deposition of these materials can reduce the surface wearing caused by the contact erosion, gripping, etc. and also helps avoiding the stick-slips. Also, the creaking between relatively moving parts was completely removed.

Due to the deposition process, the obtained coated part has a great resistance to applied pressure. From an economic point of view, the part production cost is reduced significantly

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due to the fact that the main body can be made of a bulk material with small fabrication cost on which an insignificant quantity of composite layers is deposited. These depositions can be used to enhance the characteristics of mechanical parts such as automotive parts, springs, arbors, gears, cranked axles, central pins, bearings, etc. These specific coatings must have certain characteristics such as 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 [14]. An important aspect was related to the high wear resistance of the deposited materials. Materials used for the deposition must have the characteristics mentioned above and also present a certain consistency soft enough to allow compatibility with the substrate, to follow its form, and be adherent to it. Thus, the deposited materials used for this study must be both hard and soft.

In this chapter, results on synthesis of **DLC thin films and carbon nanocomposites by** the versatile **nanofabrication method based on plasma** entitled **thermionic vacuum arc (TVA) are reported**.

The Romanian original method, **thermionic vacuum arc (TVA)**, has been studied and successfully used for the synthesis of a large range of metals, oxides, and carbon, as attested by published papers, patents, and internationally funded projects. There is a great potential for this method to become a **powerful thin film technology** for a large range of applications. Nanometer-scaled thin film deposition such as metals, alloys, DLC, and refractory metals such as W, Mo, Ta, Nb, Re, and B and also nanocomposites: binary **C+Me**, as well as ternary composites **C+Me$_1$+Me$_2$**with low roughness, good smoothness, and low friction coefficient, could be synthesized in different TVA electrode configurations.

2. Basic principle of TVA method and experimental setup

The plasma arc discharge is obtained by the bombardment of electrons emitted by the filament from inside of a Wehnelt cylinder directed toward the anode. The material to be deposited from the crucible is heated until evaporation by those accelerated electrons. An increasing positive DC high voltage is applied on the anode, and consequently, the ions of the materials appear by fast electron neutral collisions. The degree of ionization increases due to the accelerated electrons that continuously vaporize the anode material and due to the collision with neutrals, at a certain value of the voltage, a bright plasma is ignited.

The experimental setup for TVA method allows the simultaneous deposition of different materials, providing the possibility of obtaining multi-component thin films in a special two-electron gun configuration (**Figure 1**) or three-electron gun configuration (**Figure 2**). The electron guns are symmetrically arranged with respect to the holder mounted at an optimum distance on the central axis. The electric arc is ignited between the cathode and the anode material carbon or metal continuously evaporated by the electrons accelerated at high voltage and incident of the anode. The anode temperature of each element was adjusted in order to have comparable evaporation rates.

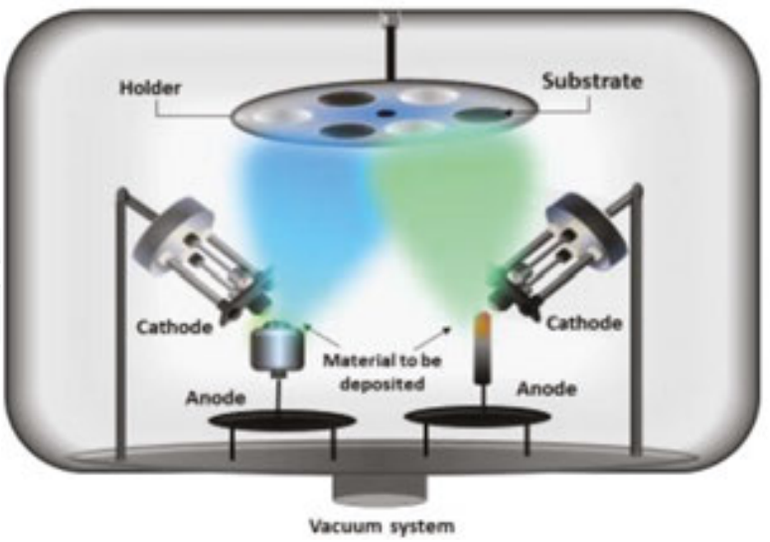


Figure 1. Experimental setup for binary films.

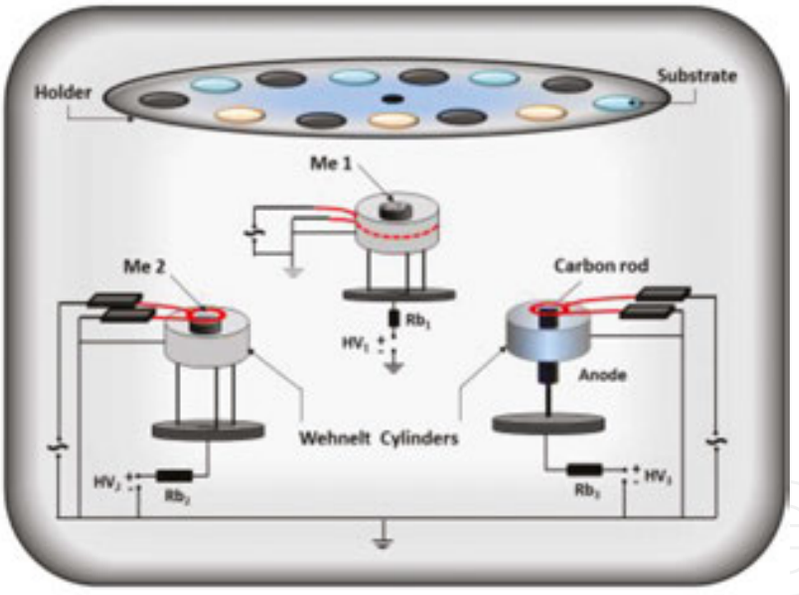


Figure 2. Experimental setup for ternary films.

The originality of the TVA method consists in the fact that the energy introduced into the system for ignition of the plasma is supplied simultaneously by an electron gun and a high-voltage source. The creation of the vapors is obtained by the electron bombardment of the anode material (e.g., carbon or metal) with electrons emitted by the filament and accelerated between the electrodes. The thin film is growing under the bombardment of incident energetic ions, besides the neutral atoms of the material to be deposited from the anode. Taking also into account the discharge performed in vacuum conditions, one of the great advantages of this

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method consists of its high degree of purity. Another advantage is related to the direct proportionality between the energy of ions and the cathode fall. The cathode is at ground potential so, with respect to the wall of vacuum vessel, the plasma potential is equal to the cathode fall. Therefore, for characteristic anode currents of 1 A, a potential difference equal to the cathode fall will accelerate the ions toward the walls of the vacuum vessel up to energy of 500 eV.

3. DLC thin films

DLC of varying sp^3/sp^2 ratio was obtained by changing the deposition conditions. The sp^3 phase is responsible for the high mechanical properties and the sp^2 phase for the electron conductance properties of DLC films [15, 16]. It was found that in order to tune amorphous carbon to have a specific sp^3 fraction, the following parameters of the TVA technology are essential: filament current (I_f), arc current (I), applied voltage (V), and the distance to the substrate (d). The influence of these plasma parameters on the preferential formation of sp^3 sites was analyzed.

In the case of carbon, the previous work proved that thermionic vacuum arc method can be used to produce smooth DLC films with relatively low growth stress and high nanohardness with a controlled final percentage of sp^3 content, between 20–67%—depending on plasma parameters. It was found that the sp^3:sp^2 ratio is higher at higher applied voltage, when the plasma potential and consequently the carbon ion energy are higher [17].

The extension of thermionic vacuum arc technology to coatings using gases or evaporable liquids as in the case of gaseous thermionic vacuum arc (GTVA) instead of solid materials is of great interest especially for DLC growth. While in the TVA method the anode is solid—a carbon rod—being suitable for practically any solid material, the GTVA method enables the growth of ultrathin and ultrapure DLC coatings using CH_4 as gas precursor in vacuum conditions [18].

Although the principle is the same, there are main operational differences between the two forms of TVA technology (electrodes configuration, breakdown voltage, specific parameters), not pointed out in this chapter. Both type of discharges offer the following advantages for thin carbon layer depositions: high rate of evaporation up to 100 nm/min; no buffer gas is necessary; very low thermal energy transfer and very stable discharge conditions. The prepared thin film layers are smooth, compact, and of very fine structures; no cathode impurities can be found in deposited thin films; low mechanical stress of the deposited layer; and very good adherence.

The deposition of a-C/DLC films have a rather high residual compressive stress which depends on the deposition method. The limit for practical application of a-C/DLC film high stress is caused by the weakening of film bonding to the substrate; thus, when reaching some critical thickness, the stress can result in the delamination of film from the substrate [19, 20].

For this reason, the initial steps have been undertaken in this direction in order to optimize the structure of carbon-metal composite films and the interaction with other materials.

4. Binary composites deposited by TVA technology

It is well known that one way to alter the grain size of the material in a controlled way is by using the co-deposition of two materials. Practically, there is no limit for TVA deposition to combine two elements in order to obtain binary composites. A plenty of mixture based on carbon has been synthesized during the last years by the TVA method [21–24]. We will focus on the best combination for anticorrosion and wear resistance properties: C-Ag, C-Al, C-Cu, C-Ni, and C-Si.

As a soft and ductile element, **Cu**, as well as **Ag**, embedded into the amorphous carbon matrix, may improve tribological properties such as lowering brittleness rates. C-Cu films are considered as high-technology materials due to their unique characteristics that have made them of particular interest in a wide variety of applications.

The excellent properties of the Ag-incorporated carbon films can be related to the following: first, due to the face-centered cubic structured, Ag nanoparticle has a significantly smaller elastic modulus than carbon, which can absorb compressive stress from the carbon matrix [25, 26]. Meanwhile, the formation of bonds between the nanocrystallites and the matrix can be diminished due to an increase in toughness of composite film [27–29].

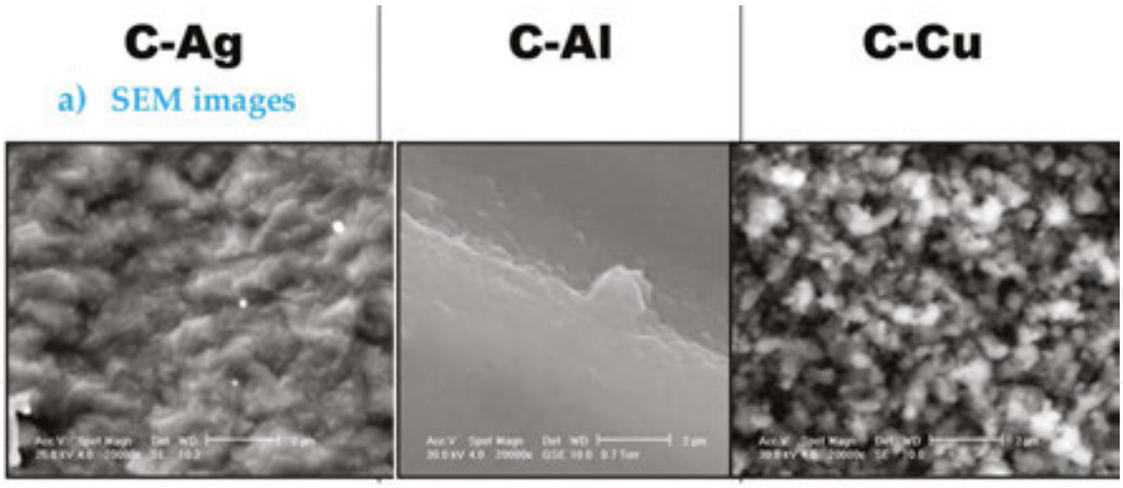
Also, the C-Ag thin films present a high interest thanks to the prospect of various applications such as catalysts, optical filters, and photographic processes for biology and medicine [30, 31]. The incorporation of silver into carbon films offers the possibility to provide coatings that are hemocompatible and antibacterial [32–35].

Another element **Al** is remarkable for its low density and for its ability to resist corrosion being less affected by environmental factors such as air and water and consequently being suitable for coating application in open air.

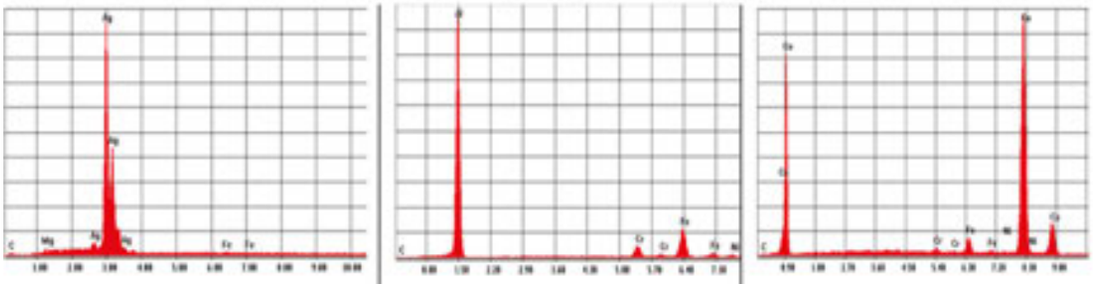
The morphology (a), composition (b), and scanning electron microscopy (SEM) images after the tribological tests are as shown in **Figure 3** for all these binary composites synthesized by the TVA method.

In the same context, due to the high resistance to corrosion of **Ni**, it was found that C-Ni coatings on stainless steel were very effective in improving the wear resistance. Surface morphology analyzed using an AFM (Atomic Force Microscope) in tapping mode also shows a significant roughness of the coating. **Figure 4a** shows a typical image of the of a C-Ni sample (Ni concentration of about 40%), and the RMS - Root Mean Square roughness is of about 500 nm. In this case, C-Ni coating seems to have followed the substrate morphology creating a rough surface. However, for friction parameters this is actually beneficial for the retention of the lubricating liquid in the running-in phase or after long time nonoperating mode of the engine shaft.

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b) EDX spectra and the relative elemental composition



Element	Wt %
C	2.1
Mg	1.39
Ag	95.8
Fe	0.71
Total	100

Element	Wt %
C	2
Al	74.04
Cr	5.35
Fe	17.14
Ni	1.48
Total	100

Element	Wt %
C	3.34
Cr	0.86
Fe	2.98
Ni	0.91
Cu	91.92
Total	100

c) SEM images after the friction test

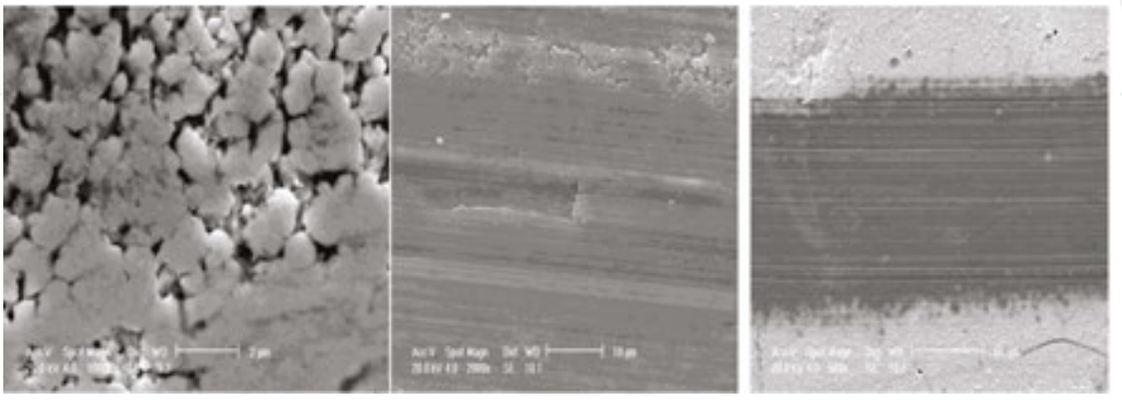


Figure 3. Topographical images and compositional results for **C-Ag, C-Al**, and **C-Cu** films.

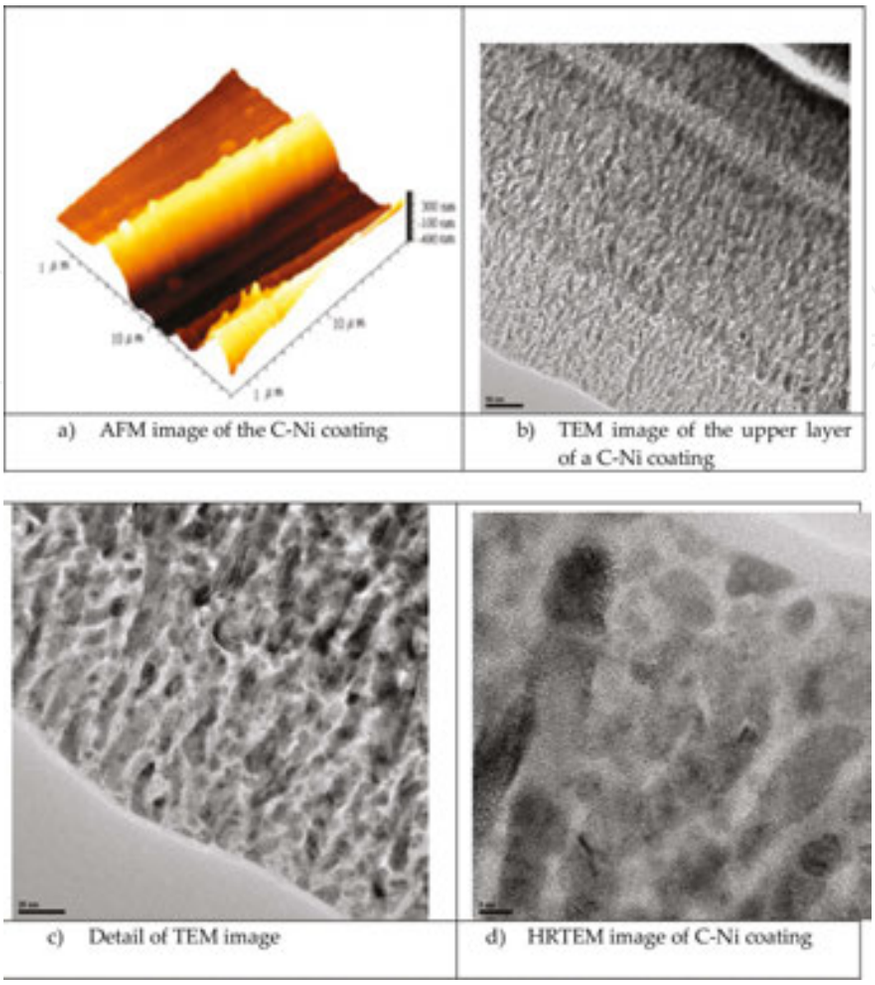


Figure 4. AFM and TEM images of C-Ni coating.

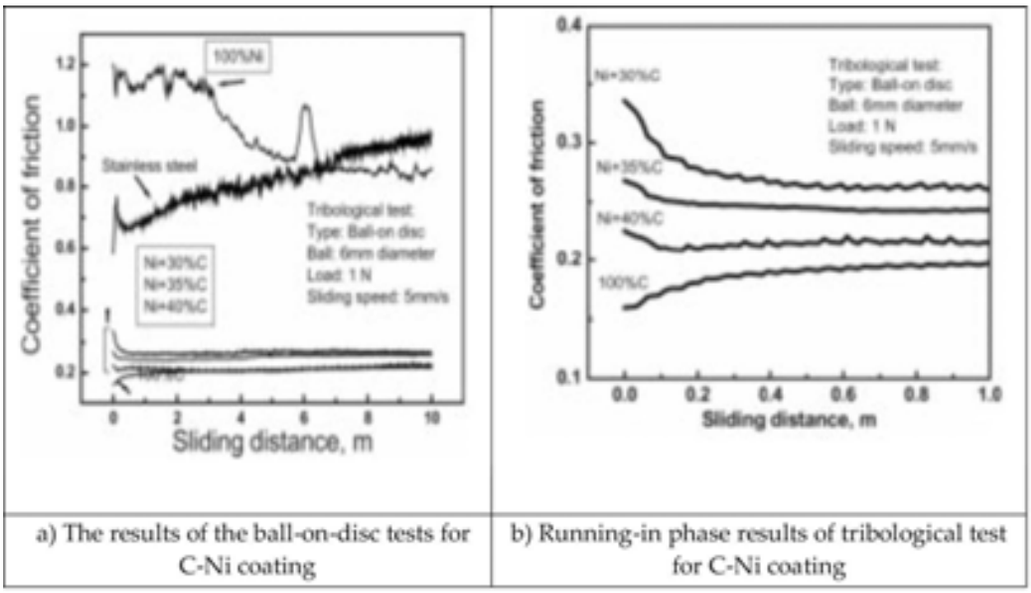
Figure 4b and **c** shows the images from the transmission electron microscopy (TEM) investigations of the C-Ni coatings. The structure of the upper layer presents tubular features with about 10 nm width and 50–100 nm length. These appear together with small grains with a lateral size of about 5 nm.

The high-resolution transmission electron microscopy (HRTEM) image of the grains in the upper layer is presented in **Figure 4d**. One could see the crystalline structure in most of the grains, while the surrounding matrix is amorphous.

Regarding **the frictional properties** of the coatings, the tests were performed using a ball-on-disc tribometer provided by CSM INSTRUMENTS, in ambient atmosphere (~50% humidity and ~23°C). Using a dead weight, a load of 1 N was applied. Carbon-based binary composites were covering 25 mm diameter stainless steel discs, and the counterpart was a 6-mm ball-bearing steel. The track radii were 3 and 4 mm, respectively, and the sliding speed was about 5 mm/s. A total of approximately 10 m of sliding was performed in about 30 min. Recorded friction coefficient (on a PC) was studied using OM (Optical Microscope). As shown in **Figure**

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5, the coefficient of friction of the prepared films drastically decreased about three to five times compared to those of the initial substrate (stainless steel) or with pure Ni coatings.



a) The results of the ball-on-disc tests for C-Ni coating

b) Running-in phase results of tribological test for C-Ni coating

Figure 5. Frictional behavior of C-Ni coatings.

Due to the ion bombardment in the TVA technique, compact C-Ni films with no columnar structure were formed on stainless still surface, while irregular and hemisphere-type protuberance C-Cu films were obtained on the same substrate surfaces. In principle, the surface roughness could be further optimized by adjusting the deposition parameters (such as the intensity of the filament heating current, the introduced electrical power and the anode-cathode distance, and the distance between the anodes and the substrate). Measured coefficients of friction of the C-Me (for Me concentration in the range of 30–40%) by using a CSM pin-on-disc tribometer in dry sliding overlays were found to be reduced by a factor of 3 to 5, compared with that of the stainless steel used as substrate or covered with a pure metal [36].

5. Ternary composites deposited by TVA technology

Using the thermionic vacuum arc deposition method, ternary thin film structures with improved physical properties for industrial applications were obtained for the first time. Properties such as resistance to abrasion, good adherence, high hardness, low friction, and a strong compatibility with the coated material were observed. In order to obtain these characteristics, a mixture of C, Al, and Si was deposited on different substrate glass, silicon, and OLC45. **Carbon** was used in this mixture for its high lubrication of the composite layer and high resistance against chemical and corrosive environment attack. In combination with **aluminum**, it ensured the lubrication and a low-friction coefficient value of the thin film.

On the contrary, **silicon** is a very attractive material: **tough, with low friction, second only to diamond in wear resistance**. For this reason, C-Si has excellent properties such as high strength and hardness, thermal and chemical stability, oxidation resistance, high melting point, high erosion resistance, etc. All of these properties make CSi a perfect material for high power, high temperature electronic devices as well as cutting and abrasion applications. Silicon carbide is composed of tetrahedral carbon and silicon atoms with strong bonds in the crystal lattice [37].

The deposition took place under high vacuum conditions. During this phase, the parts were rotated in order to assure a uniform coating. Both carbon and silicon were deposited using the TVA method [38] by igniting a plasma in their pure vapors. The third material aluminum was deposited using a thermal evaporation setup. This setup allows for a smoother control of the deposition rate than in the case of the TVA setup for this material. One of the advantages offered by TVA technique consists in using punctual evaporation sources which allow for a large variety of elemental concentration for ternary depositions by positioning the samples in respect with the sources [39]. The lack of any gaseous inclusion inside the deposition layer due to extremely high vacuum conditions is another advantage offered by TVA deposition method [40]. All these aspects mentioned above are essential for obtaining high-quality depositions.

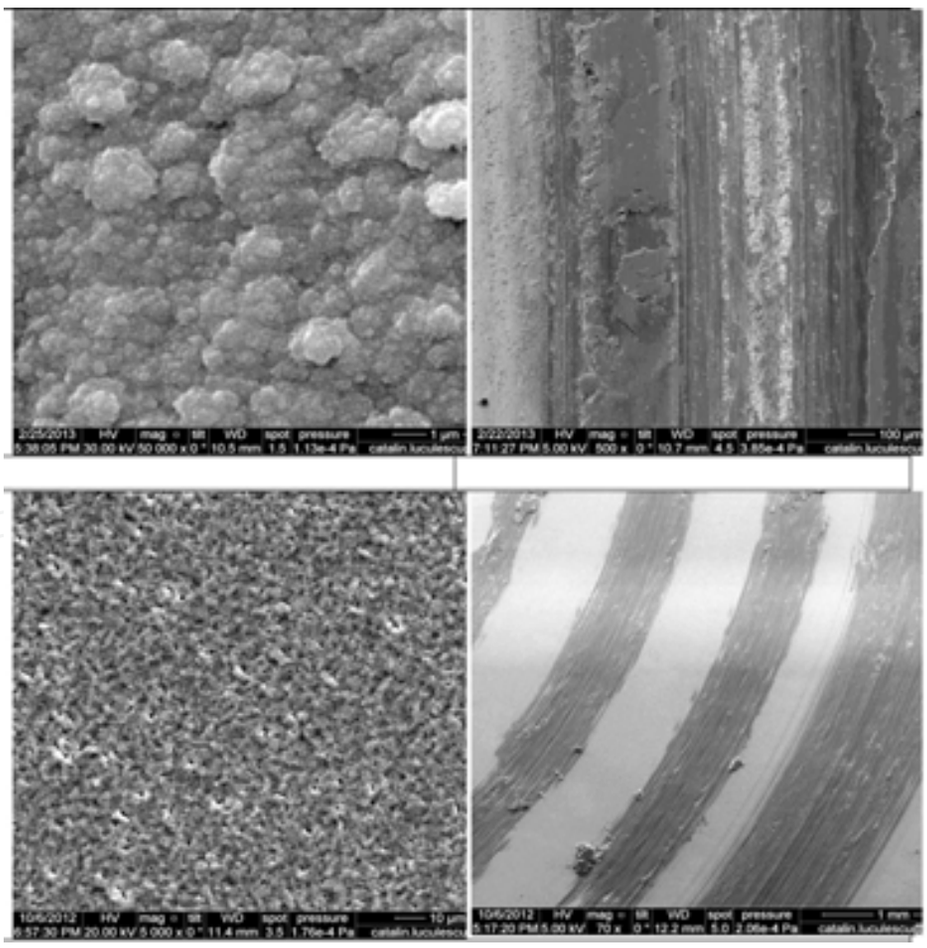


Figure 6. SEM image of the C-Si-Al film deposited on silicon (left) substrate and wear image (right).

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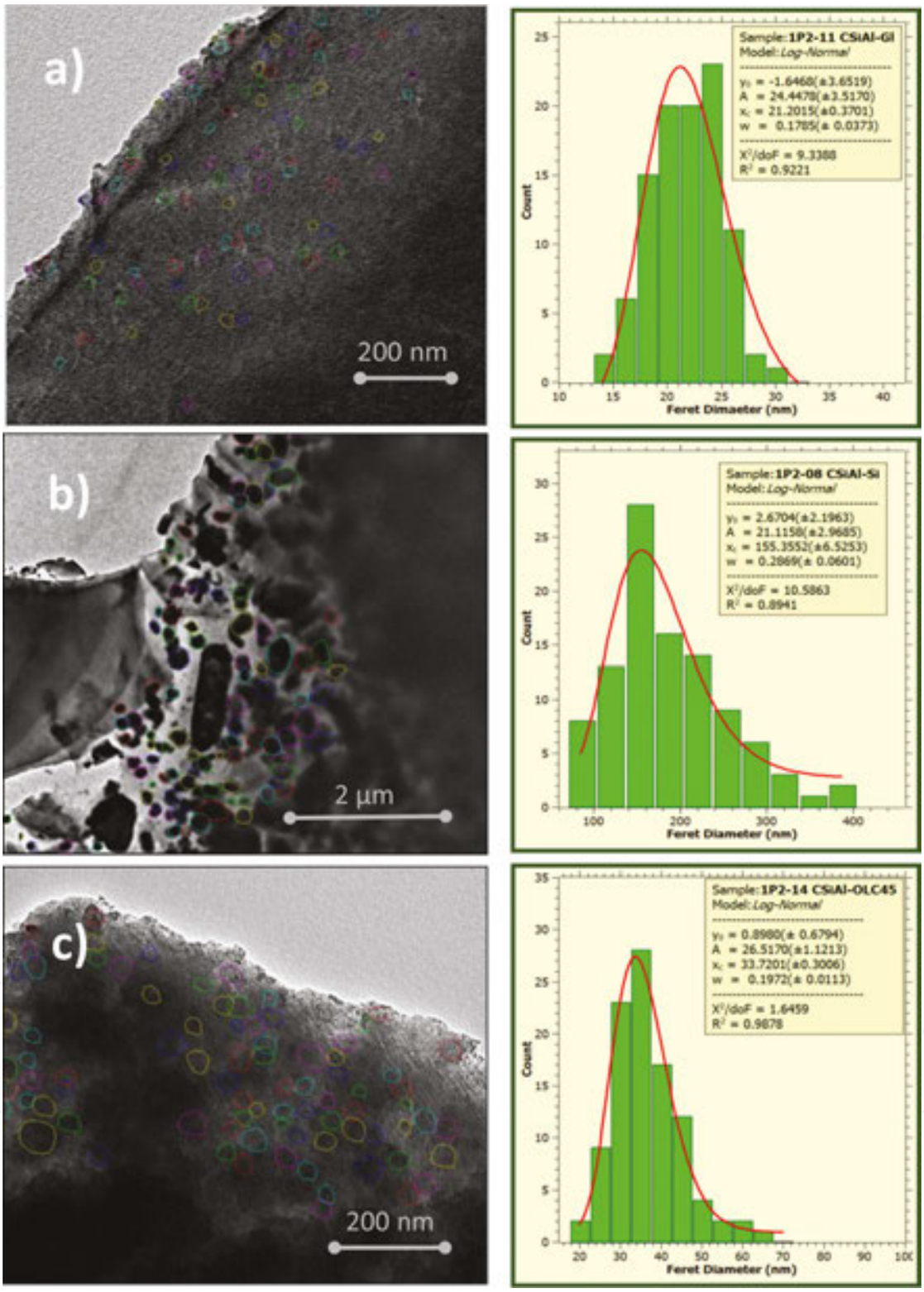


Figure 7. TEM images (left) with particles selection for statistic determination and grain size distribution (right) of the deposited films on different substrates.

SEM and EDS measurements were performed to observe the surface morphology and atomic relative concentration distribution of the three elements inside the film. The SEM image revealed the granular nanocomposition of the film (**Figure 6**). In spite of the fact that EDS (Energy Dispersive Spectroscopy) investigation does not offer information on depth profile since it incorporates the signal of the strained electrons, it can offer exact information on structure. The relative concentrations of the film components determined by EDS investigation were estimated at 58% C, 9% Al, and 30% Si. The increased C content in the film was obtained due to the chosen deposition parameters. The oxygen concentration was estimated to be 2%. This contamination was attributed to the post-deposition exposure of the samples to atmospheric air. We can argue that EDS is not a reliable method for determining silicon content of the C-Si-Al films due to the fact that the high silicon concentration could be attributed to the substrate.

TEM images (**Figure 7**) were fitted with radial distribution functions, and so the peaks were obtained Using log-normal function for the polycrystalline materials. Using the values obtained at some selected crystallites, the histogram is performed for Feret-like diameters.

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.

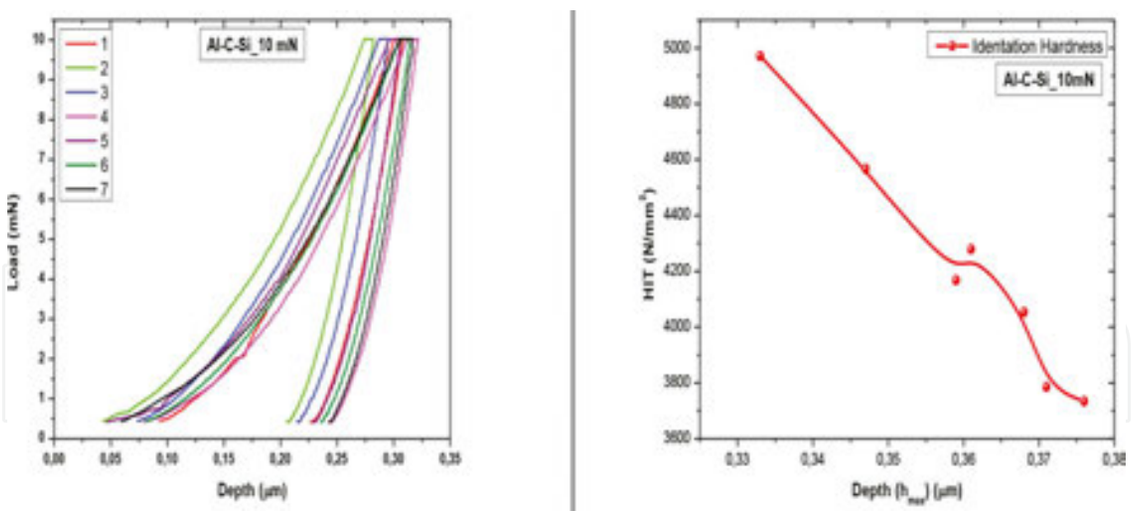


Figure 8. Micro hardness measurements at 10 mN load.

The film hardness was determined by nanoindentation measurements. **Figure 8** (right) shows the result of seven measurements performed on C-Si-Al using a 10-mN force at different depths [**Figure 8** (left)]. Thus, film hardness is very high with values between 3600 and 5000 N/mm^2 (~3.6–5.0 GPa).

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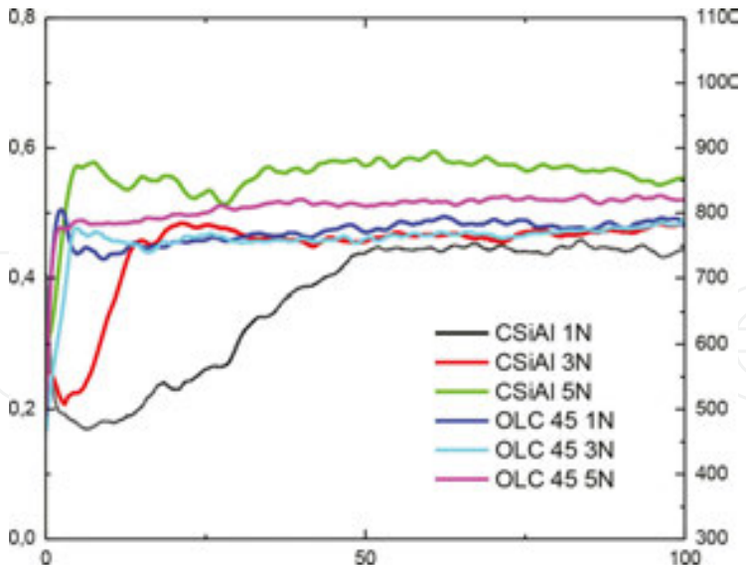


Figure 9. Comparative view of the friction coefficient of substrate (OLC45) and of CSiAl film deposited on the substrate at different loading forces.

For tribological characterization, 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 (**Figure 9**). For C-Si-Al composite films, the friction coefficient exhibited values 2–3 times lower than that of the uncoated substrates. An increasing tendency of the friction coefficient with the increase of the applied force was noticed. At 3 N, the film friction coefficient becomes equal with the value for the substrate. Over this value of applied force, film friction coefficient continues to increase.

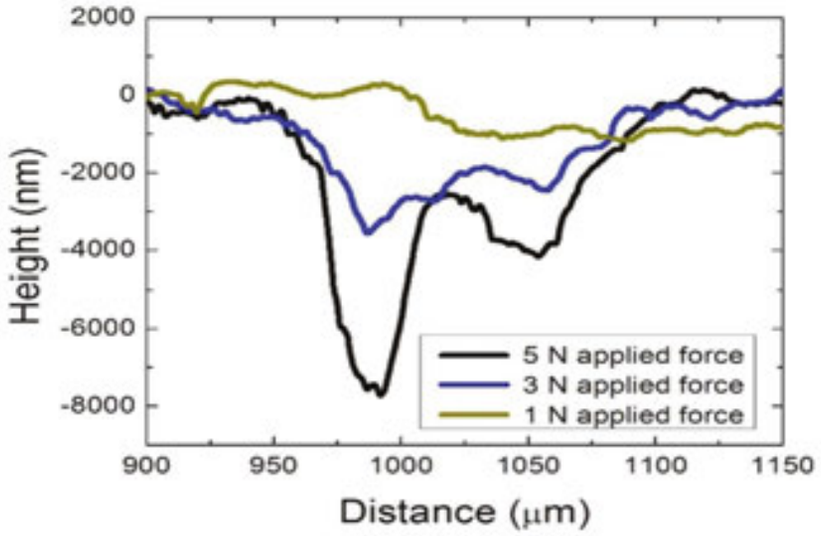


Figure 10. Depth profile of the wearing traces after tribological characterization.

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

Figure 10 presents the depth profile of the wearing traces after the tribological characterization. The roughness was determined by AFM analysis, with a range of 20–34 nm, confirming along with SEM measurements the nanometric granular structure of the obtained thin film. SEM investigations show a high-quality film surface, without major defects.

6. Surface-free energy properties for binary and ternary composites

Wetting of solid substrates by liquids is a fundamental phenomenon with relevance to both the technological and natural worlds. Applications include the spreading behavior of liquid coatings as well as chemical reactors and thus the understanding and characterization of the solid surfaces wettability is of great interest. The wettability of solid-fluid-vapor interfacial phenomena is determined by the estimation of the contact angle between a solid surface and a liquid drop. This measurement is often used, being a useful and sensitive tool for assessing the wettability of a surface, the solid surface energy, and liquid surface tension [41, 42].

The contact angles and free surface energy were determined by means of Surface Energy Evaluation system (SEE System). The device is based on the usage of a charge-coupled device (CCD) camera, which observes a liquid drop on the studied surface, by using sessile drop method. The tangent angle of the drop with the solid surface is measured by selecting three points on the contour of the drop, two for solid-liquid, and one for liquid-vapor interfaces.

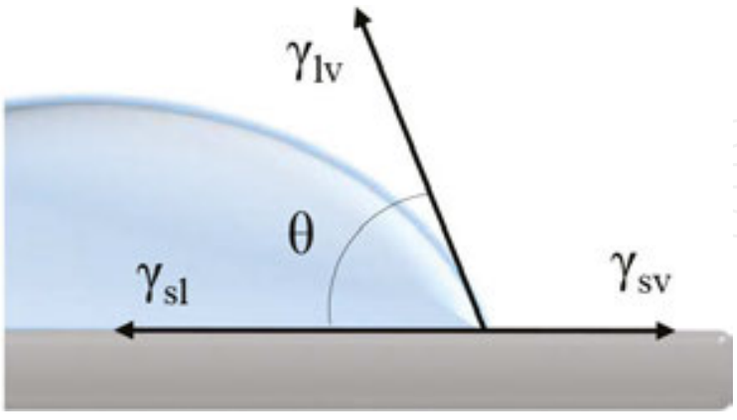


Figure 11. Drop profile and tangent angle of the drop with the solid surface.

This technique is generally applied only to low-energy solid surfaces, as most available liquids as water and ethylene glycol have relatively low surface tensions and wet solids with higher surface energy [43].

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In **Figure 11**, the tangent angle of the drop with the solid surface defined as "contact angle" method is presented. It can be interpreted as a mechanical force balance on the three-phase contact line; the surface tension is an energy per unit area, equivalent to a force per unit length acting on the contact line. Horizontal balance of forces is given by Young equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\Theta \tag{1}$$

In order to perform the measurements, the samples were set on a holder in front of the CCD camera, and the static contact angles were measured from the front view. The averaged results were calculated from 10 values and measured on different location on sample, and the drop volume was of 0.4 μl. The constant small volume of the drops used for the measurements is necessary in order to minimize the gravitational effect.

The water contact angles Θ results on the thin films are plotted in **Figure 12**. These results were further analyzed using Owens Wendt method, which allows us to determine the electron-donor and electron-acceptor parameters of the free surface energy. The total free surface energy is a sum of polar (γ^{AB}) and dispersion (γ^{LW}) components:

$$\gamma = \gamma^{LW} + \gamma^{AB} \tag{2}$$

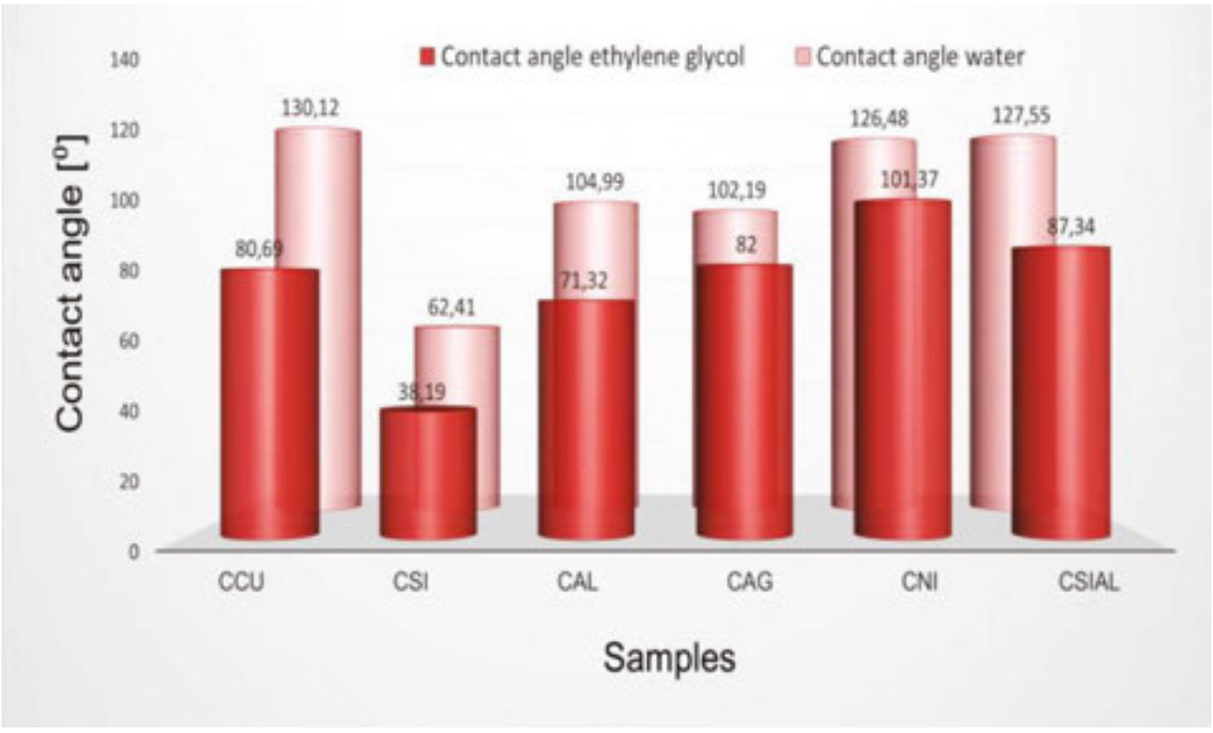


Figure 12. Contact angle measurements.

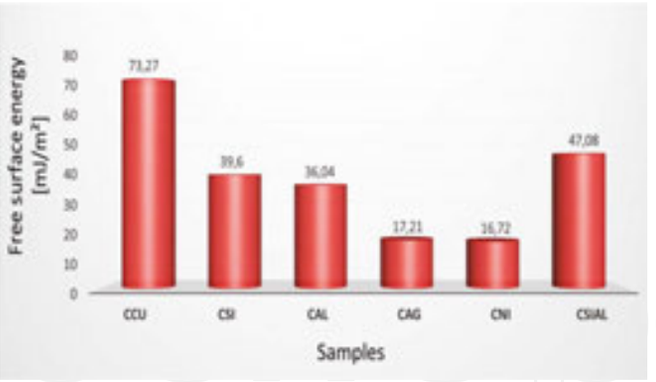


Figure 13. Comparative view of surface-free energies.

where γ^{LW} refers to the total Lifshitz-Van der Walls interaction and γ^{AB} refers to the acid-base interaction [15, 44]. The comparative view of the surface free energy values calculated is presented in **Figure 13**.

The surface free energy can be different from sample to sample due to the nonuniformity of the samples. In order to reduce this, we take instants of the drops for the various liquids used on one sample only, and we calculate the contact angle from these instants.



Figure 14. Images of droplet-stilled water on different thin films.

http://dx.doi.org/10.5772/63367

Typical image frames acquired by the image analysis system described are displayed in **Figure 14**. The figure shows a printout of the side view for a sample during experimental measurement for stilled water on the substrate. These data were digitalized and measured using the software, the omissions of other images obtained, for ethylene glycol, were deliberate to avoid redundancy of images.

Contact angle can reflect the wettability of the materials, and it is influenced by many aspects such as surface characters, roughness, and temperature. Roughness was affected by manufacture craft of the substrate material; however, surface free energy was variable because surface free energy represented the interface molecular between materials and the analyzing liquid. The values of the contact angle reported above indicate a hydrophobic character of the surfaces except for the CSi thin film that has a hydrophilic character.

7. Conclusion

The TVA deposition technique has been successfully used to obtain thin films that presented high purity, low roughness, and good adhesion on the substrates. Also, it is suitable for obtaining carbon-containing binary and ternary composite structures.

The combined deposition of carbon and metal improves basically the film adhesion and the friction coefficient. The structure of C-Me films changes with the metal and its content, as verified by TEM and EDS analysis. HRTEM images and SAED (Selected Area Electron Diffraction) reveal that C-Me structures consist of a distribution of nanocrystallites embedded within an amorphous matrix.

From the tribological analysis, the friction coefficient of the ternary structure showed a 2–3 times decrease with a slight increasing tendency in the range of 0.17–0.58 with an increase in loading force compared with the uncoated substrates. The calculated wear rate was in the range 1.23×10^{-5} and 6.16×10^{-5} mm^3/Nm. The ternary structure hardness was high in the range 3600 to 5000 N/mm^2, decreasing with the depth measurement increase.

Material characteristics presented here enhance the mechanical parts with special features such as higher resistance to wearing and gripping and excellent conformity of the layer with the geometry of the coated parts. These results could have a great impact on the development of advanced materials and many manufacturing industries, as well as expanding the technologically important field of interface science where the control of the film-substrate interface would be critical.

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI–UEFISCDI, project number 160/2012, PN-II-PT-PCCA-2011-3.2-1453.

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