Evaluation of Tribological Properties of (Ti,Al)CN/DLC Composite Coatings Deposited by Cathodic Arc Method

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ABSTRACT

In this study, Ti, Al and N doped DLC – referred to here after as “(Ti,Al)CN/DLC composite”- coating and pure diamond-like coating (DLC) were produced by cathodic arc deposition technique and the effects of the coating thickness on their tribological properties were evaluated. The coatings were characterized, using scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and Raman spectroscopy methods. The Raman and XRD patterns indicated that cathodic arc deposition method can potentially generate a composite coating consisting of TiC, Ti_3AlN, Ti_2N and Al_2Ti crystalline phases dispersed in the amorphous carbon matrix. Moreover, friction and wear of the coatings were investigated, using pin-on-disc wear test method in ambient air. The results of wear test showed a desired tribological behavior of the (Ti,Al)CN/DLC composite coatings with low amounts of the mean coefficients of friction (0.2) and wear rate (9×10^{-8} $mm^3/N.m$). In contrast with DLC coatings, it was also found that friction coefficient of the composite coated samples did not change significantly, when the thickness of the coating was increased from 1.5 to 3 μm.

1. Introduction

Austenitic stainless steels are widely used in industrial, biomedical and other applications mainly due to their excellent corrosion resistance; however, the low hardness and poor wear properties impose strong limitations in many cases. Thus, a coating that could offer better corrosion resistance, higher hardness and wear resistance is usually used to modify surface of austenitic stainless and other steels [1]. Thin coatings play a key role in tailoring surfaces to give them the hardness, wear resistance, chemical inertness, and electrical characteristics needed in a desired application [2]. High hardness, extremely low friction, high wear resistance, chemical inertness and excellent gas barrier properties make diamond like coating (DLC) suitable for use in a wide range of

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applications such as tribological, anti-corrosion, and gas barrier applications. Regardless of the type, structurally, almost all DLC films available today are amorphous. The four valence electrons of carbon ([He] $2s^2$ $2p^2$) are able to form three hybridization states enabling three major bond configurations; the sp^3 tetrahedral bonds like in diamond, the sp^2 planar graphite-like bonds and the sp bonds like in alkynes. The bulk or the main matrix of these films is usually made of a highly disordered network of sp^{3-} (mainly) and sp^{2-} bonded carbon atoms that give the material an outstanding hardness, while still retaining favorable low friction properties. However, these super hard materials have only a limited tolerance to deformation and overloading results in imminent brittle fracture and, thus, mechanical failure of the substrate-coating system [3]. Besides, the high residual stress in the DLC films after fabrication causes failure of the interface between the DLC film and the substrate [4]. Filtered cathodic vacuum arc (FCVA), mass selected ion beam deposition, and magnetron sputtering combined with energetic ion plating provide enough energy to grow DLC films. However the synthesized DLC thin films by various techniques exhibit a significant fraction of sp3-hybridized carbon. In these deposition methods, the film growth is driven by a random hail of atomic ions. Without additional lateral relaxation processes, this would inevitably cause a rapid increase of surface roughness as a function of film thickness. However, an efficient damping of these surface fluctuations is achieved through impact-induced downhill currents eroding hills on the film surface [4] and this explain the smoothness of DLC in terms of impact-induced thermal spikes accompanied by reduction of local interface curvature. In most tribological tests, a relatively high friction occurs in the beginning, but a much lover friction prevails as sliding continues. Such a reduction in friction always coincides with the formation of a thin transfer layer on the sliding surface of the counter face materials, which is also called graphitiation phenomena [3, 5]. Moreover, plastic deformation of the substrates results in poor durability of DLC coatings. It is essential to improve the adhesion strength at the film–substrate interface so that DLC films can be used in industrial applications [5]. There are several strategies for reducing residual stresses and improve adhesion of the coating to the substrate. One of these methods is using an intermediate layer between the substrate and coating, especially for steel substrates. High difference between thermal expansion coefficients of DLC coating and the steel substrate creates high stresses at the interface and hence coating adhesion to the steel substrate is low [3]. To overcome this problem a wide range of materials, including metals (Ti, Zr, W, Nb, Si and Cr,) or compound (carbides, nitrides and silicides) layers can be used as intermediate layer between the coating and substrate [3, 6-8]. Other approach is the use of alloying or doping with certain metals (Ti, Nb, Ta, Cr, Mo, W, Ru, Fe, Co, Ni, Al, Cu, Au and Ag), metalloids and gaseous species (such as B, S, Si, Cr, F, O and N) as well as the combinations of them to modify properties such as hardness, tribological properties, internal stress, adhesion, electrical conductivity or biocompatibility [3, 8-10]. For example, the co-alloying of B and F with DLC to produce films with a combination of high hardness and hydrophobic properties has been proposed recently based on the suppressing effects on the sp^2 graphitic cluster formation and hydrogen incorporation of B and F dopants, respectively [3, 11]. Adding Si, Ti and W into DLC films was proved to provide better friction and wear properties under lubricated sliding conditions and high resistance to scuffing under severe contact pressures. Among all other alloying elements, nitrogen occupies a special place in the field of DLC films. Nitrogenated DLC (also referred to as ‘carbon nitride films’) provides significantly higher hardness and superior tribological performance when used in magnetic hard disc applications [8]. Especially the manipulation of surface bio reactions by adding adequate elements such as titanium (Ti) or Si into the amorphous DLC matrix is expected to result in new fields of application. Alloying of DLC films has been done with many different the mentioned metals [3].

Although friction and wear performance of various co-alloying DLC coatings were studied and the researcher usually exhibit new alloying system as well as novel coat methods [3, 5], but there remain many unknown aspects, in this regard. In this study, Ti, Al and N doped DLC films were deposited by cathodic arc deposition method and the wear and friction performance were investigated for the first time. Since, we also could not find any published results concerning effect of thickness of the (Ti,Al)CN/DLC composite coatings on its tribological properties, the dynamic coefficient of friction (dynamic COF) and the mean linear wear continuously recorded and the results were compared with commercial DLC coating. It should be mentioned that the cathodic arc deposition method was employed here because it yielded high energy plasma that makes the coatings having high hardness and density [12].

2. Materials and Methods

Firstly, cylindrical samples with *10 mm* in height and 38 *mm* in *diameter* were prepared from a 316 stainless steel bar. Before coating, the surfaces of the samples were polished by alumina powder following by ultrasonic cleaning in a bath of acetone. Then, all the substrates were exposed to ion beam bombardment using ionized argon gas at a bias voltage (-800V), until surfaces were completely cleaned. Subsequently, an interlayer of titanium nitride (TiN) coating thickness of 0.5μm was coated on surface of all the samples. Finally, carbon films were coated on the surface of the prepared samples. DLC films were deposited on the prepared substrate by cathodic arc technique using a bias voltage of -350 V, under an acetylene gas atmosphere. (Ti,Al)CN/DLC composite films were also deposited under the aforementioned conditions, using a 33%Ti-67%Al composite alloy as target under an acetylene/20% nitrogen atmosphere. 3 and 5 μm thick coating were produced and based on the thickness of coatings, samples were named as 3 and 5 THK DLC, respectively (see Table 1). The phase constituents of the coatings were identified using X-ray diffraction (XRD) and Raman spectrometer methods. A Philips diffractometer was used to collect XRD difractogrames, using a monochromatic copper Kα (Wave length = 1.5418 Å). The operational tube voltage and current was 40 kV and 20 mA, respectively. The XRD peaks were labeled in the resulted spectra using x-ray expert software. The Raman spectra (Senterra 2009 tripe grating Raman spectrometer) were also measured, using the argon greens line at 514.5 nm, with a laser power of 20 mW and an exciting wavelength of 514.532 nm. Besides, the morphology of coatings was investigated, using scanning electron microscopy (SEM-Philips) and atomic force microscopy (AFM-Dualscop C-26) methods. A laser profilometer (Mitutoyo profilometer) was also used to measure the surface roughness average (Ra value) of samples. Moreover a pin-on disc tribometer was used to study tribological behaviors of the samples, against an AISI 52100 (65 Rc) pin at room temperature (25-29°C) and the relative room humidity (RH=28-30%). The applied normal force and speed of sliding were chose 10 N and 0.06 m/s, respectively. Uncoated AISI 316 stainless steel discs were also polished and cleaned for use as a reference material. Besides, the resulting wear surface was examined, using scanning electron microscopy (SEM) in order to find out the possible mechanisms of wear, more accurately.

3. Results and discussion

Figures 1a and 1b show the X-ray diffraction pattern of the DLC and (Ti,Al)CN/DLC composite coatings, respectively. Because the DLC component of the composite film is amorphous and transparent to X ray radiation [3], only TiC, Ti_3AlN, Al_2Ti and Ti_2N crystalline phases were identified in the composite coating (see fig. 1b). It was shown that titanium carbide (TiC) which has a preferred orientation [13], increases toughness and wear resistance of carbon films by prevention of further propagation and growth of microcrack and nanocracks [14]. Formation of high elastic modulus Ti_3AlN and Al_2Ti crystalline phases [15, 16] in the composite coating was also predictable; since the target composite could provide the Ti and Al necessities for formation of these solid phases during the coating process. Ti_2N crystalline phase was also formed due to the high energy plasma which usually uses in the cathodic arc deposition method. Both of Ti_2N and Al_2Ti coating are frequently applied to the surface of steels to improve corrosion resistance [17].

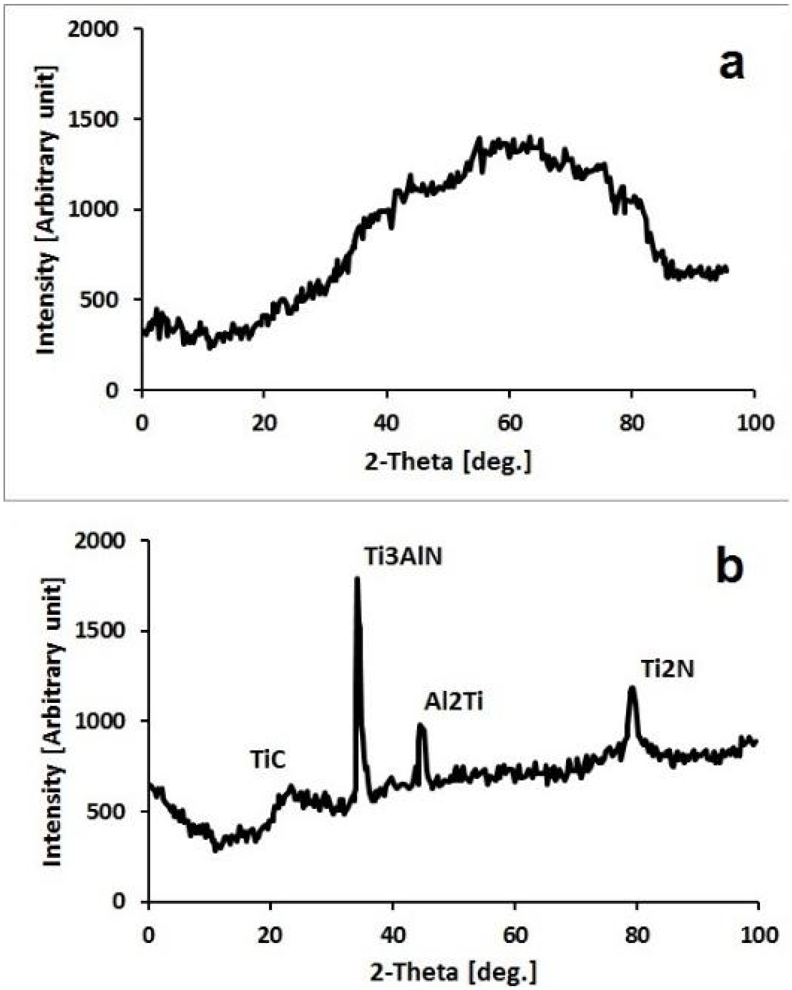


Figure 1. X-ray diffraction pattern of DLC coating (a) and (Ti,Al)CN/DLC composite coating (b).

Figure 2 show Raman spectra of pure DLC and (Ti,Al)CN/DLC composite coatings. A broad Raman band with an intense peak in the range of 1500 -1630 cm $^{-1}$ (G peak) and a less intense peak in the range of 1280-1350 cm $^{-1}$ (D peak) are attributed to diamond-like carbon [1-4]. The positions, widths and relative intensities of these two features are found to vary with deposition conditions and film properties [3, 17]. As it is indicated in figure 2, the frequencies of the G peak of DLC shifted toward lower values in the (Ti,Al)CN/DLC composite coating.

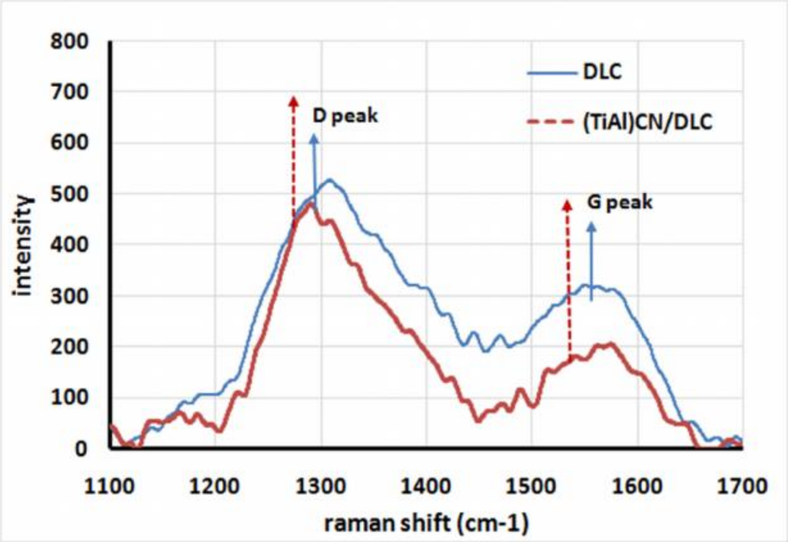
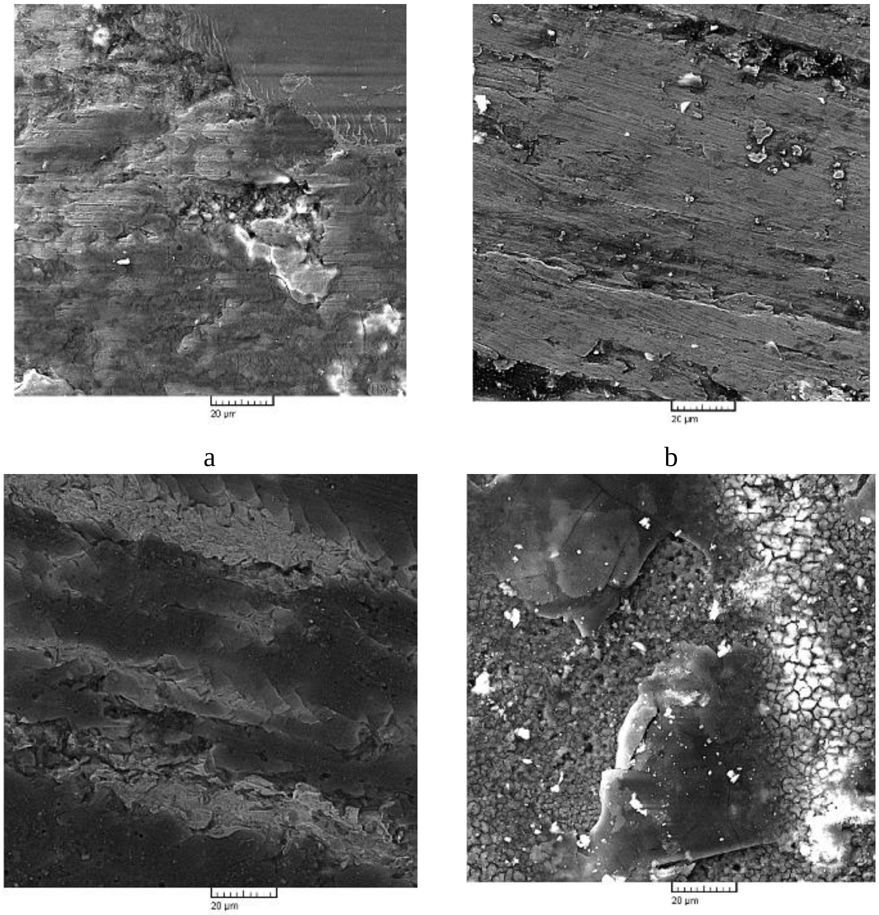


Figure 2. Raman spectra of DLC and (Ti,Al)CN/DLC coatings.



a b

c d

Figure 3. SEM micrographs of worn surface of 1.5THK DLC (a), 3THK DLC (b), 1.5THK (TiAl)CN/DLC (c) and 3THK (TiAl)CN/DLC (d) samples.

It has been shown that the G peak (vibration of sp^{2-} carbon atoms) moves towards lower frequencies when the internal stresses of the coating reduced [18]. So it would be predicable that the composite coating will perform superior wear resistance, because of the internal stress of the composite coating is not as much of pure DLC film. For DLC coatings, prevalent micro grooving/striation along the sliding direction was observed on the disk wear surfaces (Fig. 3a, b). Thus, adhesive wear could be easily identified as dominant wear mechanism [19] in this coating. The SEM observations (Fig. 3a, b) also show that the DLC film is bulged and pull away from the substrate. As it was mentioned before, the DLC films suffer mostly from the inherently its high brittleness of the material. Besides, as the Raman spectrums showed, there is a very large compressive stress in the DLC films. The adhesion strength of DLC films deposited on stainless steel substrates has been found to be inversely proportional to the magnitude of residual stresses [3]. These reasons cause the film to be bulge and peel off from the substrate, thus restricting the applications for thin DLC films.

Figure 4 show the dynamic coefficient of frictions (COFs) of the uncoated and coated samples during the wear tests. Besides, the mean coefficients of friction (μ) and the calculated total linear wear rates as well as the surface roughness average values (Ra) of all the samples are listed in Table 1. These results show that the bare 316 stainless steel (figure 4a) and the (Ti,Al)CN/DLC composite coated samples (figure 4d and 4e) have the lowest wear resistance (with the maximum amount of μ) and the highest wear resistance (with the minimum value of μ), respectively. The amounts of dynamic initial COFs of the DLC coated samples were low (figure 4b), due to the graphitiation phenomena (see introduction). Moreover, it was recently suggested that [20], a thin transfer polymeric layer on the sliding surface of the counter face materials could be formed in the presence of hydrogen during the wear test of DLC films. After longer sliding, amounts of dynamic COF of DLC coating increased and its fluctuations expanded to a wider range. It was observed that friction coefficient of DLC increases when it slides in ambient air, due to reaction of DLC with oxygen and moisture [21]. It was reported that sudden rises in friction coefficient occur over 5%RH (room humidity) due to the agglomeration of wear debris particles at sliding interface of DLC films. These debris particles are generated mainly by the oxidation of the pin and coat materials at the contact interface. Their detrimental effects on friction become much more pronounced and frequent at humidity levels of more than 30%RH [3, 19, 22]. So it was revealed that the high RH (28-30%) during the wear test of DLC coating deteriorated its lubricating properties and this led to sever wear of the carbon film.

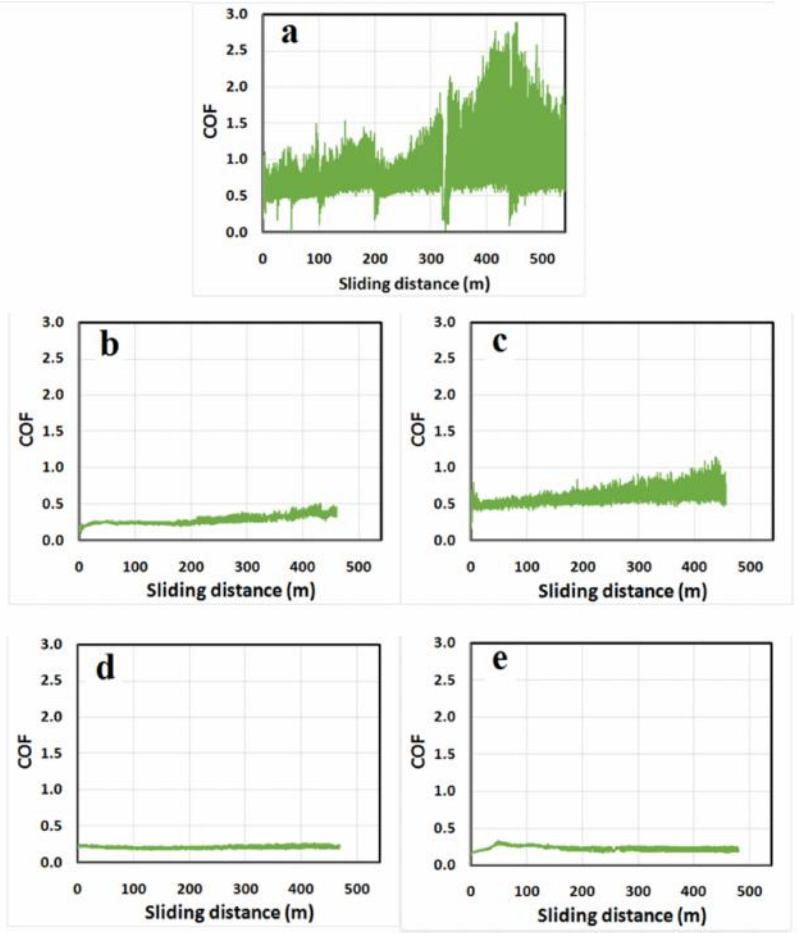


Figure 4. Dynamic COF curves of 316 stainless steel substrate (a), 1.5THK DLC (b), 3THK DLC (c), 1.5THK (Ti,Al)CN/DLC (d) and 3THK1.5THK (Ti,Al)CN/DLC samples against AISI 52100 roll bear in ambient air

Effects of increasing thickness on the tribological behavior of DLC and (Ti,Al) CN/DLC coatings were also studied. The dynamic COF curves of 1.5THK DLC and 3THK DLC samples were shown in figures 4b and 4c, respectively. The comparison between these curves shows that the friction coefficient of the DLC coatings was noticeably amplified by enlargement of its thickness, while the surface roughness average values (Ra) of these samples did not change noticeably (see Table 1). Besides, SEM images of wear surface of the DLC samples after the wear test (figures 3a and 3b) show that although both of the DLC coatings wore, the wear damage of coating of 3 THK DLC sample is obviously larger than the 1.5THK DLC one's. Detachments on surface of DLC coating, 1.5µm thick, indicates that adhesive wear mechanism was principally activated. While image of wore surface of the thicker coating (figure 3b), shows more parallel tracks and this demonstrates that the abrasive wear mechanism was also activated. Simultaneous activation of the two mentioned wear mechanisms could be the reason of higher wear rate of thicker DLC (Table 1). Although, it was reported an optimal thickness of 2 µm for the layers of the DLC film, however, it is difficult to make a general statement, as the layers were produced differently and have different intermediate layers (, even if the coatings are of the same type) [3].

Table 1. Wear properties of the coated and uncoated samples.

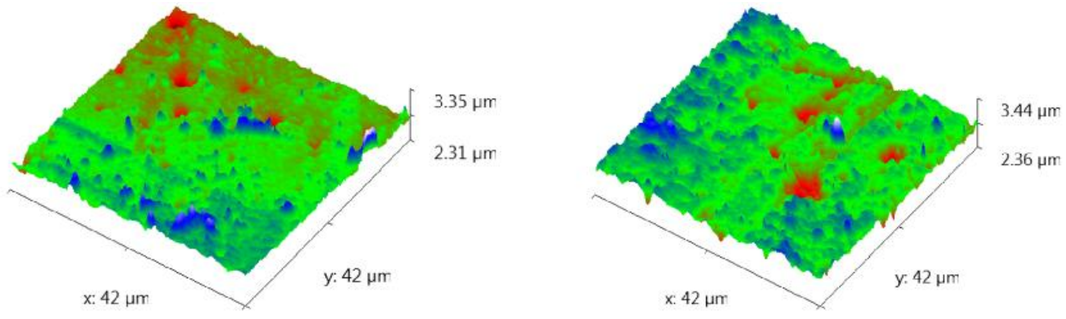
The Sample name	Coating Thickness [µm]	Friction coefficient (µ)	Wear rate [mm^3/N.m]	Roughness average R_a [µm]
316 SS	-	0.75	2.7×10^{-5}	0.106
1.5THK DLC	1.5	0.33	1.19×10^{-7}	0.031
3THK DLC	3	0.62	5.7×10^{-7}	0.035
1.5THK (Ti,Al)CN/DLC	1.5	0.21	9×10^{-8}	0.032
3THK (Ti,Al)CN/DLC	3	0.22	1.12×10^{-7}	0.082

SEM images of wear surface of the (Ti,Al)CN/DLC composite coatings are shown in figures 3c and 3d. In contrast with DLC coatings (figures 3a and 3b), no delamination was happen in the composite coating and it seems that only adhesive wear mechanism was activated. As compared to DLC, the increased thickness did not apparently relate to change of the wear mechanism of the (Ti,Al)CN/DLC composite coatings. Figures 4d and 4e present a peak with a dynamic COF of more than 0.2 which occurred at the beginning of the test, followed by a period of a steady state COF values. Table 1 also show that wear rate of 3THK (Ti,Al)CN/DLC sample is slightly larger than 1.5THK (Ti,Al)CN/DLC one's. Perhaps, it could be explained by higher roughness average (Ra) of the thick composite film (see Table 1). In order to achieve a thick coating of 3 microns, the substrate should be ion-bombarded for a long time and the surface roughness was increased, consequently. As will be discussed later, this also could be duo to presence of crystalline phases in the amorphous carbon film and these two might be reasons of a relatively higher coefficient of friction of the 3THK (Ti,Al)CN/DLC sample, in the beginning of wear test (figure 3e).

The dynamic COF of the (Ti,Al)CN/DLC composite coated samples, 1.5 and 3 thick, are also shown in figures 4d and 4e, respectively. These results show that the composite coated samples have a steady-state friction coefficient in the range 0.2-0.22 without any apparent tendency to rise with increasing sliding distance. The incorporation of titanium [3, 23], aluminum [24] and nitrogen [3, 25 and 26] into DLC coating has been separately studied. Alloying with titanium is effective in reducing of friction coefficient in ambient humid air to below 0.1, with a limited deterioration of the wear resistance [23]. The substitution of nitrogen for carbon in the graphite basal planes affects both curvature of planes and their reactivity, which is one of the key processes for the formation of fullerene-like CN_x solid films at elevated temperatures, whereas pure carbon films sputtered under the same conditions result in a porous under dense soot-like material [3, 25]. It also suggested that, upon nitrogen incorporation in a hexagon, it is for the adjacent carbon atom energetically more favorable to change from a sp^{2-}hybridized to a sp^{3-}hybridized state, which could provide for the required out-of-plane bond. For that reason, nitrogen-doped hetero fullerenes also known as aza-fullerenes, e.g., $C_{59}N$ instantaneously dimerize [3]. This results in an extremely fracture tough, elastic, and compliant material, which deforms by reversible bond rotation and bond angle deflection rather than slip and bond breaking [26]. It could be concluded that three major roles were assigned to nitrogen. The first role is that nitrogen incorporation induces curvature. The second role of nitrogen is the promotion of interplanar cross-linking and the precise nature of the cross-linking mechanisms is, however, still under discussion. The third major role of nitrogen is the formation of C_xN_y ($x,y \leq 2$) species [3]. Gilmore and Hauert [27] demonstrated the tailoring of DLC films by F and Si incorporation to yield a coating with a low and stable friction coefficient independent of the relative humidity. They reported that, the dependence of coefficient of friction on the relative humidity can be changed from a positive correlation for pure DLC to a negative correlation if more than 6 at. % silicon is incorporated in the film. Co-alloying of Ti, Al and N doping agents could lead to such a favorite friction and wear properties of the (Ti,Al)CN/DLC composite coatings. It was suggested that interface between the crystalline phase and amorphous diamond-like phase could prevents crack growth and this could be the reason of less delamination of the composite coatings [6].

Another factor that must be considered is the surface roughness of the coatings. The surface smoothness becomes crucial for obtaining low friction in case of these films. So, it is technologically important to control the roughness development of these films to obtain low friction [28]. The comparing of the relative surface roughness average (Ra) amounts of substrate and DLC coatings (Table 1) show that the Ra values of the coatings significantly reduced. It is believed that [4, 28] the industrial polished substrates are typically rough and one has to suppress the initial surface roughness during deposition to obtain smooth films on such rough substrates. It was observed that the shape of the hills turned from sharp pyramids to round bumps and the hills were broadened sub-nanometer crater formation in the vicinity of the impact site of carbon ions can lead to surface fluctuations during the coating process which further are efficiently dampened by erosion of the hills into neighboring valleys.

Figures 5a and 5b shows a three-dimensional AFM image of DLC and (Ti,Al)CN/DLC coatings, respectively. Comparison of these two images and the relative Ra values of 1.5 THK DLC and 1.5THK (Ti,Al)CN/DLC samples (see Table 1) show that doping of the carbon film did not change Ra considerably. Also, they concluded that amorphicity is another important prerequisite for achieving ultra-smoothness. The intensive Ar+ ion impingement induces formation of such amorphous front layer during coating. This layer prevents roughening of the growing film which otherwise may occur due to presence of the TiC [28], Ti_3AlN, Al_2Ti and Ti_2N nanocrystallites at the growth front. Thus, the intensive and continuous ion impingement causes impact induced downhill flow of adatoms in the presence of the amorphous front layer. This surface diffusion mechanism competes with the mechanisms like geometrical shadowing and noise induced roughening and also suppresses initial high Ra of the substrate to evolve surface smoothing. It seems that the presence of crystallinity or ordered areas on a nanometer scale in will lead to roughening of the film, especially when the thickness of the composite film was increased. Thus, the intensive and continuous ion impingement causes impact induced downhill flow of adatoms in the presence of the amorphous front layer. This surface diffusion mechanism competes with the mechanisms like geometrical shadowing and noise induced roughening and also suppresses initial high Ra of the substrate to evolve surface smoothing.



a

b

Figure 5. Three-dimensional AFM image of a) 1.5THK DLC, b) 1.5THK (Ti,Al)CN/DLC samples.

4. Conclusion

Pure DLC and (Ti,Al)CN/DLC composite coatings were deposited on 316 stainless steel substrates by cathodic arc deposition method. The coatings were characterized and their tribological behavior was evaluated. The results showed that the friction and wear properties of the (Ti,Al)CN/DLC coating-which is an amorphous matrix composite coating- is quite attractive, as compared to that of the conventional DLC coatings. Furthermore presence of multiple crystalline phases in the structure of diamond-like carbon of the composite coating not only do not change its surface topography, but also lead to reduce amount of residual stresses and hence increase the wear resistance. Unlike the DLC coating, the roughness of the composite film was noticeably increased by increasing its thickness. It was improbability that increasing the Ra values of composite coating due to increasing its thickness did not lead to change its friction coefficient and wear rate. However, contrary to (Ti,Al)CN/DLC composite coatings, the application of DLC films suffers mostly from the inherently higher brittleness of the material as well as its higher internal stress. In general, the results indicated that cathodic arc deposition method can potentially generate a nanocomposite consisting of TiC, Ti_3AlN, Ti_2N and Al_2Ti nano-sized intermetallic phases dispersed in the amorphous carbon matrix. Future work will focus on more exploration of the structure as well as evaluation of other properties (such as corrosion) of the (Ti,Al)CN/DLC composite coating.

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