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ADHESION EVALUATION OF NANOSTRUCTURED COATINGS ON TITANIUM ALLOY FOR BIOMEDICAL APPLICATIONS

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Abstract. *The unsatisfactory wear resistance verified in biomedical applications of titanium alloy has been considered as the major concern in its long-term application inside the human body. The tribocorrosion performance of implants in body fluid has been improved by the deposition of innovative thin hard coatings on sliding contact surfaces. Accordingly, the coating adhesion to the implant materials turns into a fundamental concern for the success of these coatings development on the biomedical field. Therefore, adhesion of Diamond-like carbon (DLC) and Ti-(Si)-C-N biomedical nanostructured coatings on titanium alloy was evaluated by Rockwell-C and scratch adhesion test. Both coatings presented delamination mode failure, however, differences between test methods were observed. Also, the results revealed that the adhesion responses are affected by higher internal stresses on DLC coating and the chemical composition of Ti-(Si)-C-N coating.*

Keywords: *Adhesion, DLC, Ti-Si-C-N, Rockwell-C, Scratch Test*

1. INTRODUCTION

The unsatisfactory wear resistance verified in biomedical applications of titanium alloy has been considered as the major concern in its long-term application inside the human body. In prosthetic joints, the particulate wear debris and ion releasing induce an inflammatory state on the surrounded implant tissues which is triggered by a local movement of the artificial joint associated with tribocorrosion processes under body fluid (McGee et al. 2000). These reactions lead the patient to bone resorption and hypersensitivity symptoms which often result in premature revision arthroplasty within 15 to 20 years of implant placement procedure due to aseptic loosening diagnostic (Desai, Bidanda, and Bártolo 2008). Therefore, implant sliding contact surfaces have been coated with innovative thin hard films to improve the tribocorrosion performance of the prosthesis in the body environment. Accordingly, the coating adhesion to the implant materials turns into a fundamental concern for the success of these coatings development on the biomedical field. A proper coating deposition technique and extrinsic properties should guarantee the best adhesion possible to avoid delamination during usage stresses and then limit the debris generation that contributes as third wearing bodies on implant contact surfaces. Moreover, the obtaining of nanostructuring coatings and the employment of graded thin multilayer depositions instead of single layer coating have been verified to improve adhesion performance on thin hard coatings (Cavaleiro and De Hosson 2006; Xu and Pruitt 1999). Thus, good adhered nanostructured biocompatible multi-layered coatings are required to achieve the demanded extension in the lifetime of biomedical applications.

Among the new developments on nanostructured coatings to biomedical field, Diamond-like carbon (DLC) has been extended studied due to the high potential of its metastable amorphous structure. The DLC structure is composed of fractions of sp3 and sp2 carbon hybridizations, which allow a biocompatible material that is chemically inert, hard, wear- and corrosion-resistant and still a self-lubricant (Robertson 2002; Grill 2003; Hauert 2003). Furthermore, the enhanced mechanical properties of carbon films are strongly related to the high amount of sp3 content, but this condition generally results in poorly adhered coatings due to high residual stresses (Bull 1995). Therefore, the balance between desired mechanical properties with a good adhesion strength condition is one of the greatest challenges for this material application on thin coatings. Hopefully, some mechanical interlocking and chemical bonding approaches with the development of new deposition techniques have been verified to adjust the internal residual stress and then improve DLC coating adhesion to substrates. Also, the new nanocomposite generation as the quaternary Ti-Si-C-N is being considered as another promissory low friction nanostructured coating option to be applied on load bearing joints. This coating was developed by adding carbon into the deposition process of the ternary nanocomposite TiSiN coating which resulted in an optimum mechanical performance and self-lubricant coating due to its unique nanocomposite structure composed by nanocrystalline and amorphous nc-Ti(C,N)/a-Si_3N_4/a-C (Ma et al. 2007). The carbon content in this coating plays an important role to not only generates amorphous carbon sites that allows lubrication by graphitization process in load-bearing situations but to also refine the Ti(C,N) nanocrystals creating a much compact structure (Eriksson et al. 2012). Recent work (Wang et al. 2017) has demonstrated that with the increase of carbon content during deposition, the Ti-Si-C-N coating growing structure changes from columnar to a dense homogenous form. Although all the referenced studies, few are the reliable evaluations on how these characteristics mentioned can affect the adhesion strength of the DLC and Ti-Si-C-N nanocomposite coatings.

Among the existing adhesion testing procedures in thin hard coatings, the most reported are the Rockwell-C indentation test standardized in the VDI 3198 norm (Dusseldorf 1992). In this test, the fracture resulted from a conical diamond indenter is evaluated through optical or scanning electron microscopy according to the Daimler-Benz adhesion quality ranking. Although Rockwell-C indentation test is the most common adhesion evaluation due to its simplicity, contestable qualitative results might be retrieved from the test because of the results interpretation from the user. Also, small differences in adhesion strength may not be demonstrated in this procedure due to a lack of the qualitative scale. Hence, scratch test is proposed to quantitatively assess the adhesion on hard thin coatings (Bull and G.-Berasetegui E. 2006). In this test, critical loads are defined when a failure, cohesive or adhesive, is observed due to an indenter pulling across the coating surface. Therefore, the objective of this study is to evaluate the adhesion of Diamond-like carbon (DLC) and Ti-(Si)-C-N nanostructured multilayer coatings deposited on titanium biomedical alloy by Rockwell-C and scratch adhesion tests. Several conditions have been applied to obtain these coatings which regard on the main characteristics that can affect the adhesion result, such as sp3/sp2 fraction in DLC coating and the nanocrystal sizes in the nanocomposite Ti-Si-C-N coating.

2. EXPERIMENTAL PROCEDURE

Substrate samples were obtained in 2 mm thick discs from electron-erosion cutting of a Ti-6Al-4V ELI (ASTM F136) annealed bar with 12.7 mm diameter and prepared by conventionally grinding and polishing. The multilayer nanostructured coatings were deposited using plasma enhanced magnetron sputtering (PEMS) and plasma immersion ion deposition (PIID) techniques developed by Southwest Research Institute (SwRI). Table 1 lists the coatings layering structure, thicknesses, obtaining techniques and precursor flow rates. More information about the deposition procedures can be found elsewhere (Wei 2010; Wei et al. 2006, 2010; A.M. Abd El-Rahman 2014).

Table 1. Nanostructured coatings layering structure, thicknesses, and deposition techniques.

Coating name	Layering structure	Coating thickness (µm)	Deposition technique	Precursor flow rate (sccm)
DLC (PIID)	SiC/DLC	5	PIID	20 (TMS[2]) + 80 (C_2H_2)
DLC (PEMS+PIID)	Ti/TiN/TiC/DLC	5	PEMS+PIID[1]	250 (C_2H_2)
Ti-C-N (0 TMS)	Ti/TiN/TiCN	10	PEMS	30 (C_2H_2)
Ti-Si-C-N (1.5 TMS)	Ti/TiN/TiSiCN	10	PEMS	1.5 (TMS[2]) + 30 (C_2H_2)
Ti-Si-C-N (3.0 TMS)	Ti/TiN/TiSiCN	10	PEMS	3.0 (TMS[2]) + 30 (C_2H_2)
Ti-Si-C-N (6.0 TMS)	Ti/TiN/TiSiCN	10	PEMS	6.0 (TMS[2]) + 30 (C_2H_2)
Ti-Si-C-N (9.0 TMS)	Ti/TiN/TiSiCN	10	PEMS	9.0 (TMS[2]) + 30 (C_2H_2)

(1) PEMS were employed to interlayers deposition only while PIID to DLC deposition;
(2) $Si(CH_3)_4$ (tetramethylsilane).

Following, adhesion was assessed by standard Rockwell-C indentation tests following VDI 3198 guidelines (Dusseldorf 1992). One indentation in each sample was performed with 150 kgf applied with a Rockwell-C diamond conical tip with 120° angle and 0.2 mm radius. The indentations were analyzed by scanning electron microscopy (SEM) and classified from HF1 to HF6 according to Daimler-Benz adhesion quality ranking. Scratch tests were also performed to adhesion evaluation following ASTM C1624-05 standard (ASTM 2013). Three linear progressive load scratch tests were performed on each sample using standard parameter values of 100 N/min loading rate, 10 mm/min horizontal displacement rate in a total scratch length of 5 mm resulting in final test load of 50 N. The cohesive and adhesion failures were identified by SEM and classified according to the scratch atlas presented in the standard. In order to evaluate how the different coating deposition conditions can affect the adhesion strength, the sp3/sp2 fraction in DLC coating and the nanocrystals size in nanocomposite Ti-(Si)-C-N coating were obtained by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) respectively. Moreover, energy dispersive spectrometer (EDS) was used during SEM analyses to verify adhesion test failures and the chemical composition of Ti-(Si)-C-N films. XPS analyses were conducted with 1486.7 eV Al Kα X-ray excitation source and calibrated by the C1s peak at 284.8 eV. Then the fractions of sp3/sp2 in the DLC coatings were calculated by the ratio between the Gaussian fitting curve areas of XPS spectra removing the Shirley-type background (Leung et al. 1999). While XRD analyses were conducted using a Shimadzu XRD-7000 facility in 2.5° theta Bragg-Brentano mode with 1.5406 Å wavelength excitation source. The scanning angle ranged from 10° to 100° at a scanning speed of 1°/min with a 0.02° step size. Finally, the Ti(C,N) nanocrystal sizes were estimated from the broadening peaks using the Scherrer formula.

3. RESULTS AND DISCUSSION

3.1 Diamond-like carbon coating

The adhesion strength of the DLC coated samples were first examined by the Rockwell-C indentation test. Figure 1 presents the SEM images of the indentations damages on each DLC sample with the conferred adhesion quality ranking. The DLC films presented poor adhesion strength with circular delamination exposing the coating interlayers, SiC and TiC for DLC (PIID) and DLC (PEMS+PIID) respectively. The DLC (PIID) sample was classified as HF5 due to its chipping delamination response, which is characterized by small size fractures caused through radial cracking. While the DLC (PEMS+PIID) sample shows a massive delamination beyond the indentation center point and thus, it was classified as HF6, the lowest adhesion position present in Daimler-Benz quality ranking. The result demonstrates the existence of a higher shear stress between the DLC film and interlayer in this sample compared to DLC (PIID). This is a characteristic imposed by the PEMS technique, a physical vapor deposition (PVD), that attributes high compressive residual stresses due to the ion bombardment on the sample surface. Even with the difference in the delamination shaping observed on the DLC coating samples, both revealed unacceptable failure according to VDI standard.

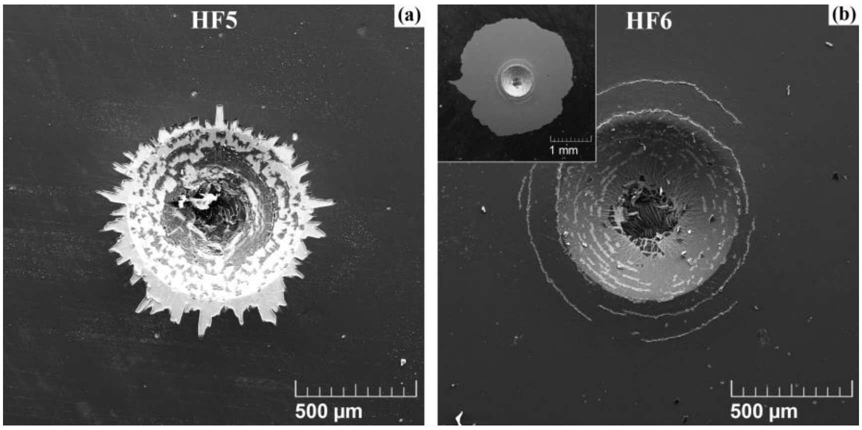

Figure 1. Rockwell-C indentations SEM images with adhesion HF classification of the coatings (a) DLC (PIID) and (b) DLC (PEMS+PIID) coating samples.

Further, the adhesion strength was investigated by scratch test and figure 2 shows the cohesive and adhesive failures identified on the DLC coatings by SEM. The failures revealed similar mechanisms of delamination demonstrated by Rockwell-C adhesion test. Lateral cracking was observed as the cohesive failures alongside the scratch trail on the two samples. However, the cracks verified on DLC (PIID) are much more apparent compared to DLC (PEMS+PIID) sample due to its gradual increase in length and recurrence. When these cracks achieve a critical length, a spallation occurred in the interface between the DLC film and interlayer. The “shell” form of this spallation assign this adhesive failure as wedging spallation damage, that is a typical brittle failure mode generated by the internal stresses energy releasing due elastic recovery of the DLC film behind the moving indenter during the scratch test (Bull 1991). Moreover, a gross spallation was identified as the adhesive failure in DLC (PEMS+PIID) sample. Gross spallation occurs by an extensive crack propagation in a coating interface which provokes a large region delamination as demonstrated in the interface of DLC film and TiC interlayer.

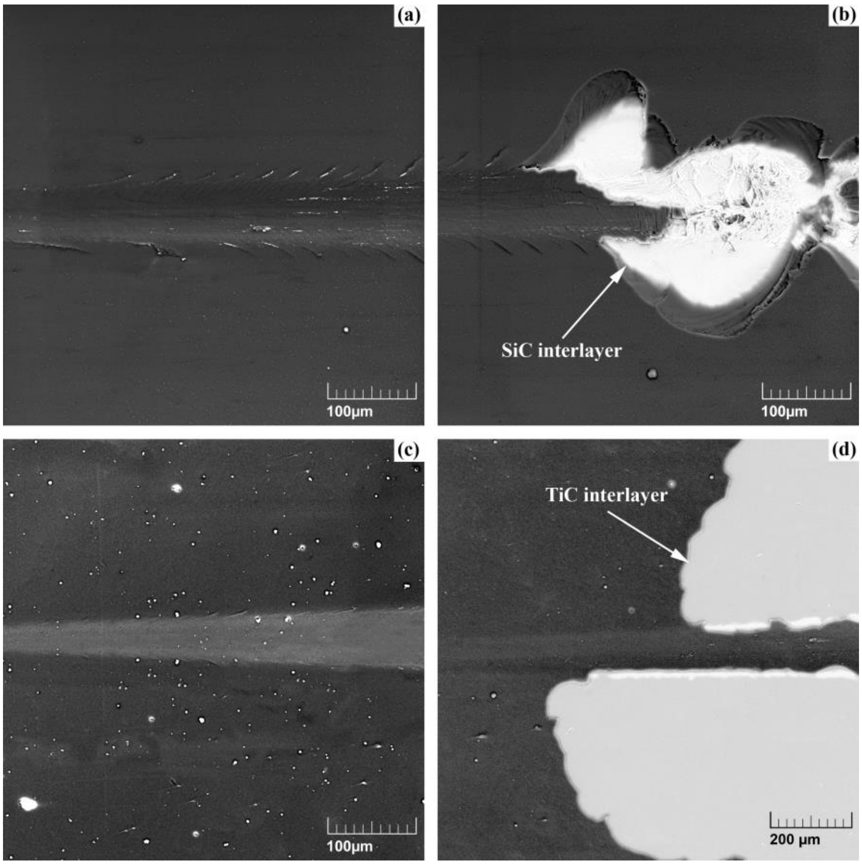

Figure 2. Scratch test SEM images of DLC (PIID) coating (a) cohesive failure, (b) adhesive failure; and DLC (PEMS+PIID) coating (c) cohesive failure and (d) adhesive failure.

Figure 3 shows the critical loads assigned at the first appearance of cohesive and adhesive identified by SEM. As revealed by the SEM failure images, after the first occurrence of a lateral crack at the mean value of 5.3 N (L_{C1}) in the DLC (PIID) sample, the cracks are gradually increasing until reach a critical size where occurs the wedging spallation at the mean value of 14.4 N (L_{C2}). On DLC (PEMS+PIID) sample, the critical loads revealed low values with no statistically significant difference at mean values of 4.7 N and 5.7 N for L_{C1} and L_{C2} respectively. Although the DLC (PIID) condition has presented higher value for the spallation failure which is an important feature to prevent debris releasing on biomedical applications, low values of cracking are a concern because may expose the substrate surface provoking corrosion and ions releasing.

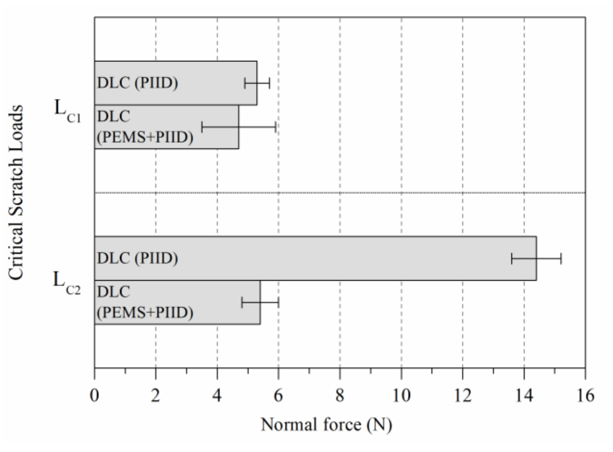

Figure 3. Critical loads from scratch test on the DLC coating samples.

In order to verify a number of sp3 bond sites presented in each condition of DLC deposited, an XPS analysis was conducted and the C1s spectra are represented in figure 4. As expected, DLC (PEMS+PIID) condition have a higher amount of sp3 content due to the use of a deposition technique based on ion bombardment. The sp3 content is very correlated to the compressive internal stresses on DLC films which in turn heavily affect the adhesion behavior of these coating systems. The Rockwell-C and scratch adhesion strength tests have confirmed to be affected by the amount range of sp3 content applied. However, the scratch test gives a lot more information about how the failure mechanism is being modified by this coating property. At this point, both DLC exanimated presented unacceptable adhesion by the standards of the test, but the study has demonstrated how important is the control of the internal stresses in DLC coatings to be successfully applied in biomedical applications.

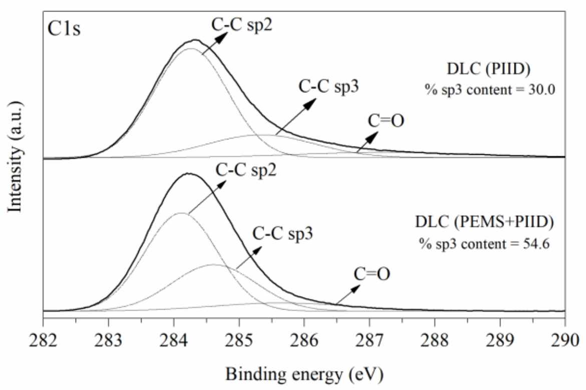

Figure 4. XPS C1s spectra with Gaussian fitting curves and calculated sp3 bonding content for the DLC coating samples.

3.2 Nanocomposite Ti-Si-C-N coating

The nanocomposite Ti-(Si)-C-N coating samples have been submitted to Rockwell-C adhesion test first and the SEM images are shown in figure 5. All of the samples presented somehow delamination defects around the indentation with chipping characteristics closer to DLC (PIID) sample. As noted in the images, a trend to better quality rankings can be verified with the increase in TMS deposition flowrate, which corresponds to a raise on carbon and silicon content. The sample condition deposited with 9.0 sccm of TMS have been attributed to the HF2 quality ranking, which is considered acceptable according to VDI guidelines. This behavior can be ascribed to a grain size effect, as this condition has more silicon and carbon content, the size of nanocrystals tend to reduce in the nanostructure due silicon and carbon contribute to the amorphous matrix and the amorphous carbon sites respectively. Therefore, with smaller grains, more are the grain boundaries with high free energy regions which may be favorable to enhance the adhesion strength between the nanocomposite film and the interlayer.

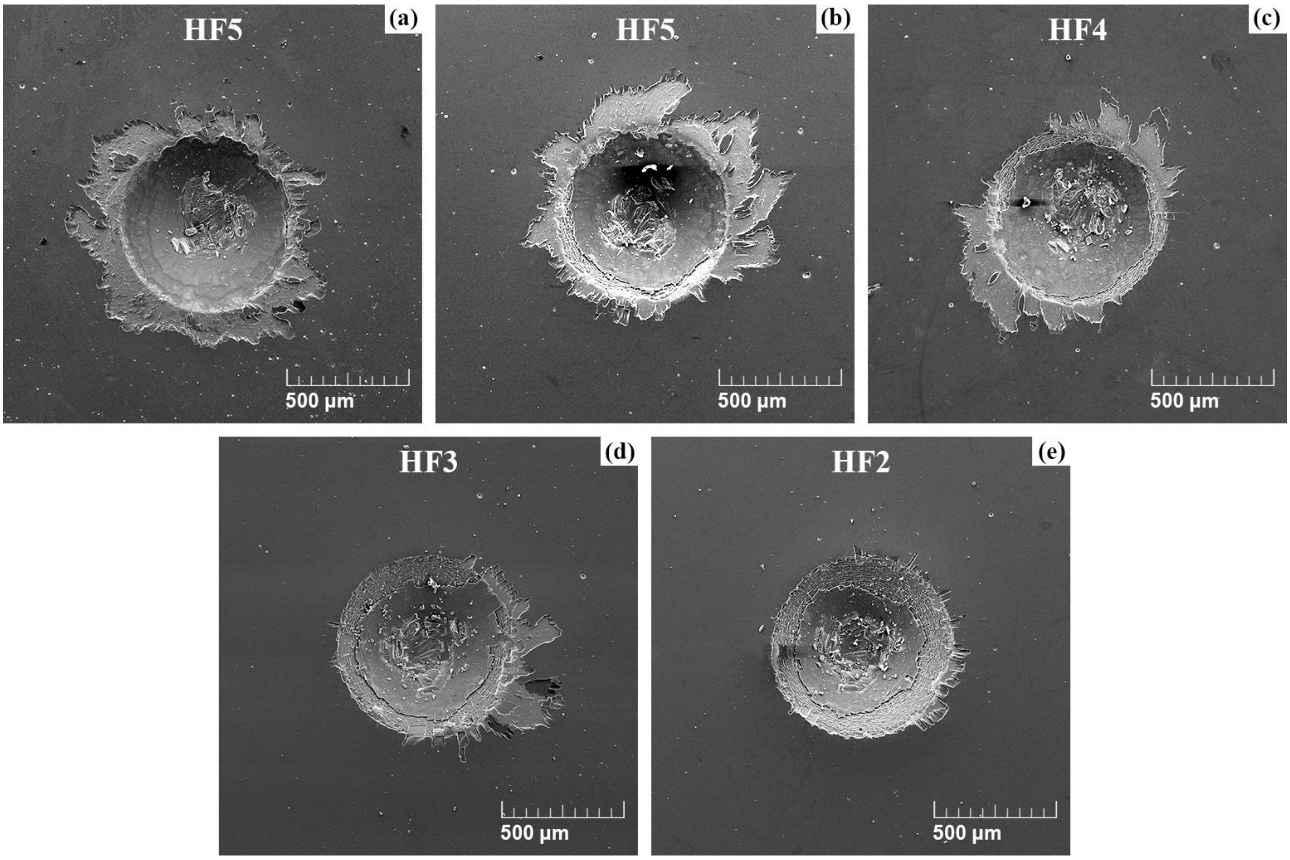

Figure 5. Rockwell-C indentations SEM images with adhesion HF classification of the coatings (a) Ti-C-N (0 TMS), (b) Ti-Si-C-N (1.5 TMS), (c) Ti-Si-C-N (3.0 TMS), (d) Ti-Si-C-N (6.0 TMS) and (e) Ti-Si-C-N (9.0 TMS) coating samples.

Moreover, the nanocomposite Ti-(Si)-C-N coating samples were submitted to scratch adhesion test and the cohesive and adhesive failures SEM images are presented in Figure 6. The cohesive failures identified were assigned as lateral cracking, however in the conditions with 6.0 and 9.0 sccm of TMS deposition flowrate the cracks could not be verified through SEM. On these two coatings, the first critical loads (L_{C1}) were checked with the changes in acoustic emission signals and tangential load responses acquired during the tests. The wedging spallation adhesive mode failure exposing the TiN interlayer were verified for all samples with minimum visual differences. The quantitative scratch test results are presented in Figure 7. In opposition to Rockwell-C adhesion test, the best condition by adhesion test was the Ti-Si-C-N deposited with 3 sccm of TMS for both failures. Although the cohesive failures of the conditions with 6.0 and 9.0 sccm of TMS could not be identified in SEM images, the occurrence of these failures appears in lower loads compared to the best pointed 3 sccm of TMS condition. This behavior could indicate that an increase of silicon amorphous matrix and amorphous carbon regions, from some point, can fragilize the nanostructure due to a greater distance between the nanocrystals. Thus, fewer nucleation regions to cracking can exist but the adhesion strength drops considerably at the same time.

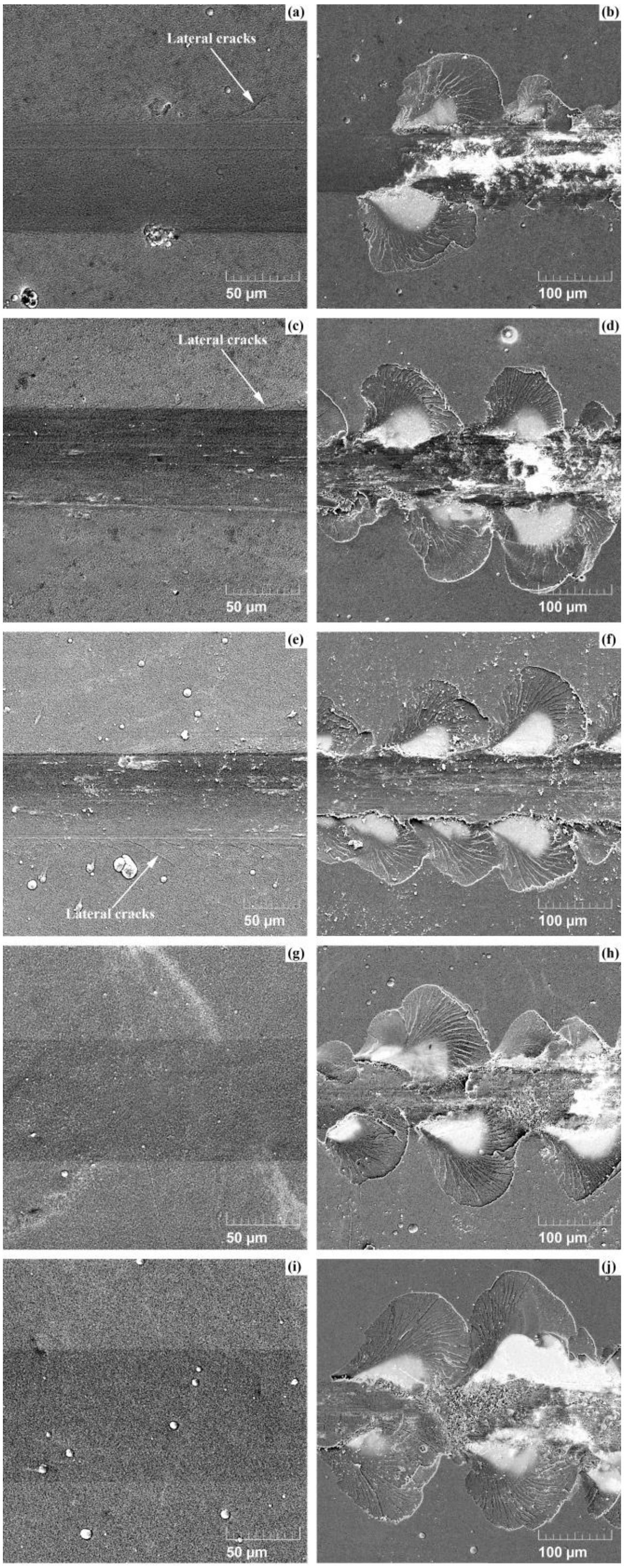

Figure 6. Scratch test SEM images of coehsive (left) and adhesive (right) failures from (a) (b) Ti-C-N (0 TMS), (c) (d) Ti-Si-C-N (1.5 TMS), (e) (f) Ti-Si-C-N (3.0 TMS), (g) (h) Ti-Si-C-N (6.0 TMS) and (i) (j) Ti-Si-C-N (9.0 TMS).

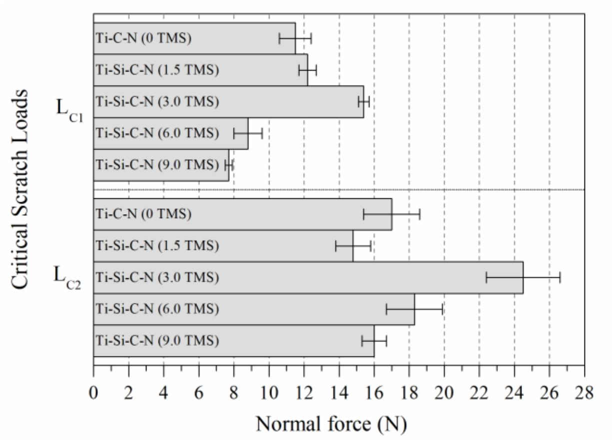

Figure 7. Critical loads from scratch test on the Ti-(Si)-C-N coating samples.

In order to confirm that the nanocrystals decrease the amount of carbon and silicon content, an EDS and XRD analyses were conducted and the results are presented in table 2. As shown, at the first condition with the introduction of carbon the nanocrystals have a bit increase in size. This can be reasonable due to the carbon just not form amorphous carbon region in the structure only but also bond with Titanium atoms to form nanocrystals of TiC(N) with different stoichiometry. Therefore, with more introduction of carbon into the film deposition, the surplus starts to accumulates in high free energy spaces as grain boundaries and start to form lubricious amorphous carbon regions and, at the same time, reducing the size of the nanocrystals.

Table 2. The composition of Ti-(Si)-C-N films as determined by EDS with estimated crystal size.

Coating name	Si content (at. %)	Carbon content (at. %)	Crystal mean size (nm)
Ti-C-N (0 TMS)	0.0	20.2	3.5
Ti-Si-C-N (1.5 TMS)	1.5	22.7	3.6
Ti-Si-C-N (3.0 TMS)	3.1	25.8	3.2
Ti-Si-C-N (6.0 TMS)	7.2	28.5	3.0
Ti-Si-C-N (9.0 TMS)	8.4	34.5	2.7

The studies on adhesion strength in nanocomposite Ti-(Si)-C-N have demonstrated different results between the two adhesion tests applied. Qualitative results as the Rockwell-C and scratch SEM images can conceal important failure mechanisms and may not be sensitive to all small differences of the coating composition for example. Also, the qualitative results presented can be the best approach to indicate the best deposition condition during coating development phase. Although these results still must be verified in the application environment where other factors could impose a different response, the results have proved that quantitative analyses of scratch test can provide more information and reliability to further experiments on nanocomposites thin coatings.

4. CONCLUSIONS

Adhesion strength of DLC and Ti-(Si)-C-N nanostructured multilayers coatings deposited on titanium biomedical alloy have been evaluated through usual Rockwell-C and scratch adhesion tests. Main characteristics of each coating were explored as a sp3/sp2 fraction in DLC and nanocrystal sizes in the nanocomposite Ti-(Si)-C-N. Both characteristics have been proven to affect strongly the adhesion strength of the coatings. On DLC coatings, the internal compressive stress resultant of more sp3 content bond sites was verified as a strong point in order to have a successful application of this coating in biomedical applications. While on Ti-(Si)-C-N coatings, the nanocrystal size which in turn is correlated to the chemical composition presented different adhesion results for each test. The scratch test seems to expose more information about the adhesion failure mechanism and therefore the quantitative results could point the best deposition condition in order to have an enhanced adhesion strength. Furthermore, the study revealed that the common Rockwell-C adhesion test may not possess a ranking resolution to afford small differences in coating characteristics, as demonstrated with the range of Ti-(Si)-C-N nanocrystal studied. Still, the study demonstrated the necessity of more attention to the techniques that verify the adhesion strength in order to perceive small variations on the deposition of biocompatible nanostructured multi-layered coatings to achieve an extended lifetime in biomedical applications.

5. ACKNOWLEDGEMENTS

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