Scientific paper

Deposition of DLC Film on Stainless Steel Substrates Coated by Nickel Using PECVD Method

Zahra Khalaj,[1] Mahmood Ghoranneviss,*[,1] Elnaz Vaghri,[1] Amir Saghaleini[1] and Mircea V. Diudea[2]

[1] *Plasma Physics Research Center, Science and Research Branch, Islamic Azad University,Tehran,Iran.P.O.Box:14665/678*

[2] *Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj, Romania*

** Corresponding author: E-mail: ghoranneviss@pprc.srbiau.ac.ir*
Tel: +98-21-44869624 ; Fax:+98-21-4869626

Received: 21-11-2011

Abstract

Research on diamond-like carbon (DLC) films has been devoted to find both optimized conditions and characteristics of the deposited films on various substrates. In the present work, we investigate the quality of the DLC films grown on stainless steel substrates using different thickness of the nickel nanoparticle layers on the surface. Nickel nanoparticles were sputtered on the stainless steel substrates at 200 °C by a DC-sputtering system to make a good adherence between DLC coating and steel substrates. Atomic Force Microscopy was used to characterize the surface roughness and distribution function of the nickel nanoparticles on the substrate surface. Diamond like carbon films were deposited on stainless steel substrates coated by nickel using pure acetylene and C_2H_2/H_2 with 15% flow ratio by DC-Plasma Enhanced Chemical Vapor Deposition (PECVD) systems. Microstructural analysis by Raman spectroscopy showed a low intensity ratio I_D/I_G for DLC films by increasing the Ni layer thickness on the stainless steel substrates. Fourier Transforms Infrared spectroscopy (FTIR) evidenced the peaks attributed to C–H bending and stretching vibration modes in the range of 1300–1700 cm^{-1} and 2700–3100 cm^{-1}, respectively, in good agreement with the Raman spectroscopy and confirmed the DLC growth in all samples.

Keywords: Diamond like carbon; RMS roughness; FTIR; Ni NP; stainless steel substrate.

1. Introduction

Diamond-like carbon (DLC) films are metastable amorphous hydrogenated or non-hydrogenated forms of carbon materials; they consist of a random network of sp^2 and sp^3 carbon sites with varying amounts of hydrogen dispersed within the lattice[1]. Since their first preparation by Aisenberg and Chabot in the early 70s,[2] DLC films have attracted word-wide attention due to their excellent properties which make them reliable to use in various fields of science and technology. Some of the remarkable properties of DLC films are their high wear resistance,[3] chemical inertness,[4] low friction coefficient[5] and particularly high hardness[6] which makes them one of the most suitable materials for coating surfaces. DLC coating would increase the surface hardness and its longevity[7] A wide variety of deposition techniques based on ion beam or plasma techniques have been developed for synthesizing DLC films.[8–11] DC- and RF-PECVD methods are two of the most popular deposition techniques of DLC films,[12–16] which allow the growth at low substrate temperatures and provide ion bombardment of the surface.[17] The PECVD process is based on the decomposition of a carbonaceous gas into species such as ions, radicals and atoms near the substrate surface. Using DC-PECVD technique, there is a lower stress value in comparison with RF-PECVD.[7]

Usually, there is a low adherence between DLC coatings and the metal substrate such as stainless steel. Many attempts have been made to increase the adherence of diamond like carbon coatings to the stainless steel substrates, since DLC coatings have a wide range of applications.[18–19] The major techniques to obtain a good adhesive strength include the fabrication of an adhesive layer between the DLC coating and substrates, and the reduction of the internal stress of the DLC coating.[18–20] In this work we report the growth of diamond like carbon films on

stainless steel substrates coated by nickel. The nickel nanoparticles would act as "glue" to make a good adherence between DLC coating and stainless steel substrate.[21] In addition, we found that the quality of the DLC films would be enhanced by increasing the nickel thickness and reducing the RMS roughness of the substrate surfaces. Atomic Force Microscopy (AFM), Raman spectroscopy and Fourier Transform Infrared spectroscopy (FTIR) were used to characterize the samples.

2. Experimental Details and Methodology

2. 1. Substrate Pretreatment

In the present investigation stainless steel (AISI 304L, AMS Co., USA) in the size of 10 mm × 10 mm × 1 mm was used as substrate; it was cleaned ultrasonically in acetone and ethanol solutions to remove any residual contaminants prior to deposition. The samples introduced into the planar DC-sputtering system, which was then pumped down to a base pressure of 4×10^{-1} Pa. A nickel plate was used as a cathode and was placed in parallel with the oven which was grounded. The distance between cathode and anode was about 1cm. Argon was introduced into the chamber with a flow of 220 sccm. The nickel nanoparticles (Ni NP) were sputtered on stainless steel substrates when the substrate temperature increasing gradually up to 200 °C. Deposition time for nickel sputtering (t_s) was 40, 80, 120 and 160 minutes for S_1, S_2, S_3 and S_4, respectively.

2. 2. DLC Preparation

DLC coatings were prepared by DC-Plasma Enhanced Chemical Vapor Deposition (PECVD) system which manufactured by our group in Plasma physics Research Center. Figure 1 shows the schematic diagram of the PECVD system. Nickel-coated AISI 304L substrates were introduced into the PECVD chamber, which was then pumped down to a base pressure. All the samples were mounted in the furnace. Deposition of DLC films used C_2H_2 with a flow of 80 sccm for 50 minutes. Then a mixture of acetylene and hydrogen (15 vol. % C_2H_2/H_2) was inserted to the system with a total flow of 250 sccm. The working pressure was kept at 1600 Pa and deposition time was 120 minutes.

3. Results and Discussion

3. 1. AFM and SEM Studies

Using an Atomic Force Microscopy (AFM, XE-NSOM) in contact mode, we analyzed the surface morphology of Ni films deposited on AISI 304L substrates at 40, 80, 120 and 160 minutes, respectively. The bare stainless steel (S_0) used to compare the roughness of the surface with other sputtered samples (see Fig. 2). With the temperature rise, Ni nanoparticles are preferentially deposited on the bare AISI surface, resulting in the high-density nanoparticles layer, where the surface roughness reaches the comparatively minimum of about 1.17 nm for the growth time of 160 min. In Fig. 3, 2D and 3D topographies of the surfaces of the samples deposited at different time duration are shown. All images have been obtained in a scanning area of 3 μm × 3 μm. 2D and 3D AFM images show different RMS roughness of each sample's surface. Figure 3 (a-d) shows the morphology and roughness of stainless steel coated by nickel in the samples S_1 to S_4 respectively. Figure 4 shows the histograms of distribution of Ni particle size on the surface of stainless steel deposited at 40, 80,120 and 160 minutes, respectively. For all the samples, the Gaussian diagram showed a non-homoge-

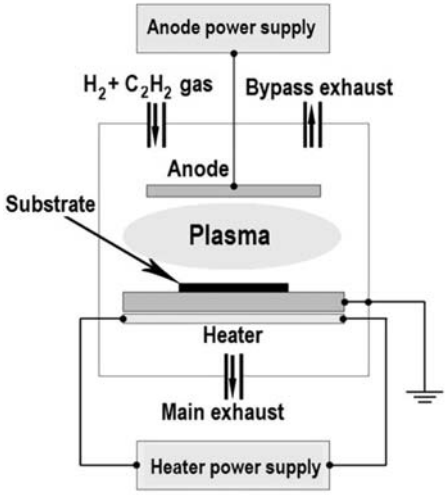

Fig. 1. Schematic diagram of the PECVD system for DLC films deposition.

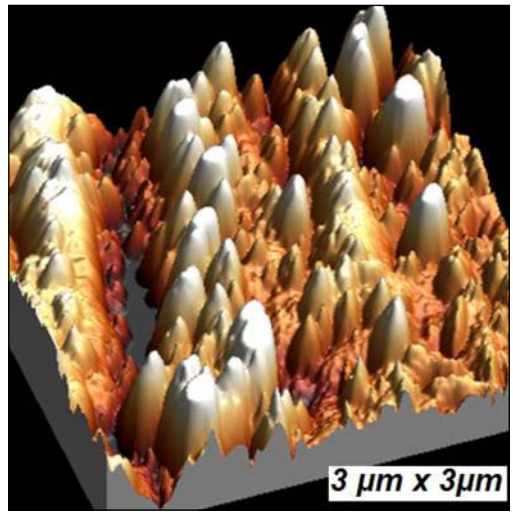

Fig. 2. 3D AFM image of the bare stainless steel

neous distribution of the nickel nanoparticles on substrates. This may be due to the Ni sputtering at temperature of 200 °C that led to more agglomeration of the nickel nanoparticles by increasing the deposition time. The histogram of the nanoparticles distribution can be used to interpret the distribution function of particle size.[22] By the Gaussian diagram,[22] we can easily observe that the average particle size distribution of all samples is less than 50 nm. The Root-Mean-Squared roughness (R_{rms}) of surface is one of the most important parameters for the characterization of the surface structure.[7] The results of MS studies are listed in Figure 5.

The AFM results show the RMS roughness of the samples decreasing from S_1 to S_4. The lowest RMS roughness was in S_4, corresponding to a temperature and deposition time of 200 °C and 160 minutes, respectively.

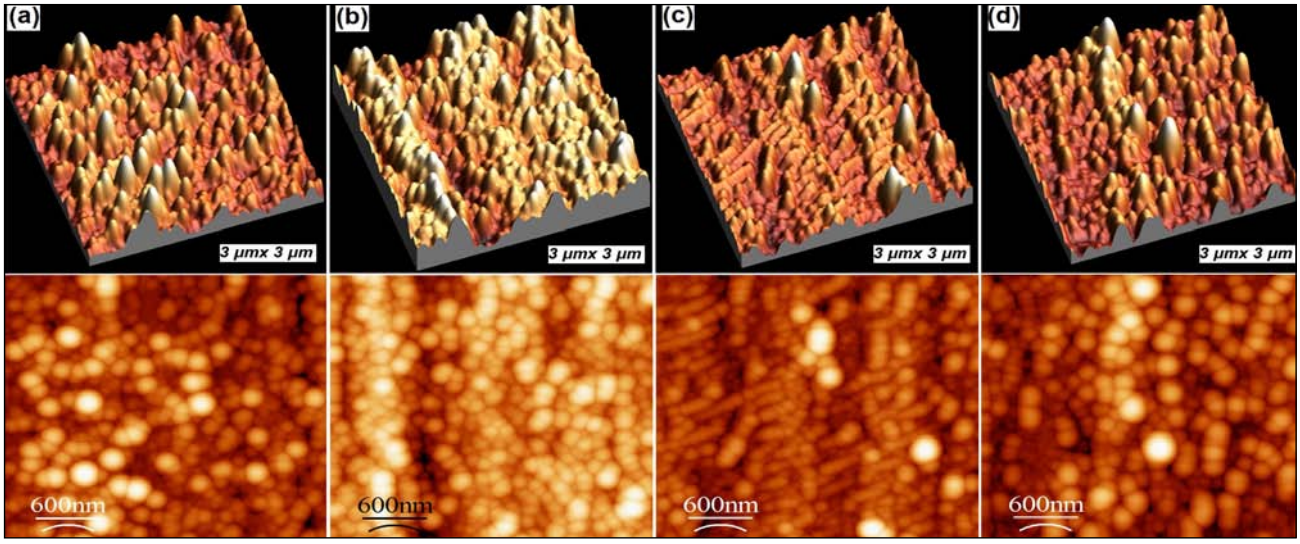

Fig. 3. 2D and 3D AFM images of the stainless steel coated by Ni at (a) 40 min (b) 80 min (c) 120 min and (d) 180 min, respectively.

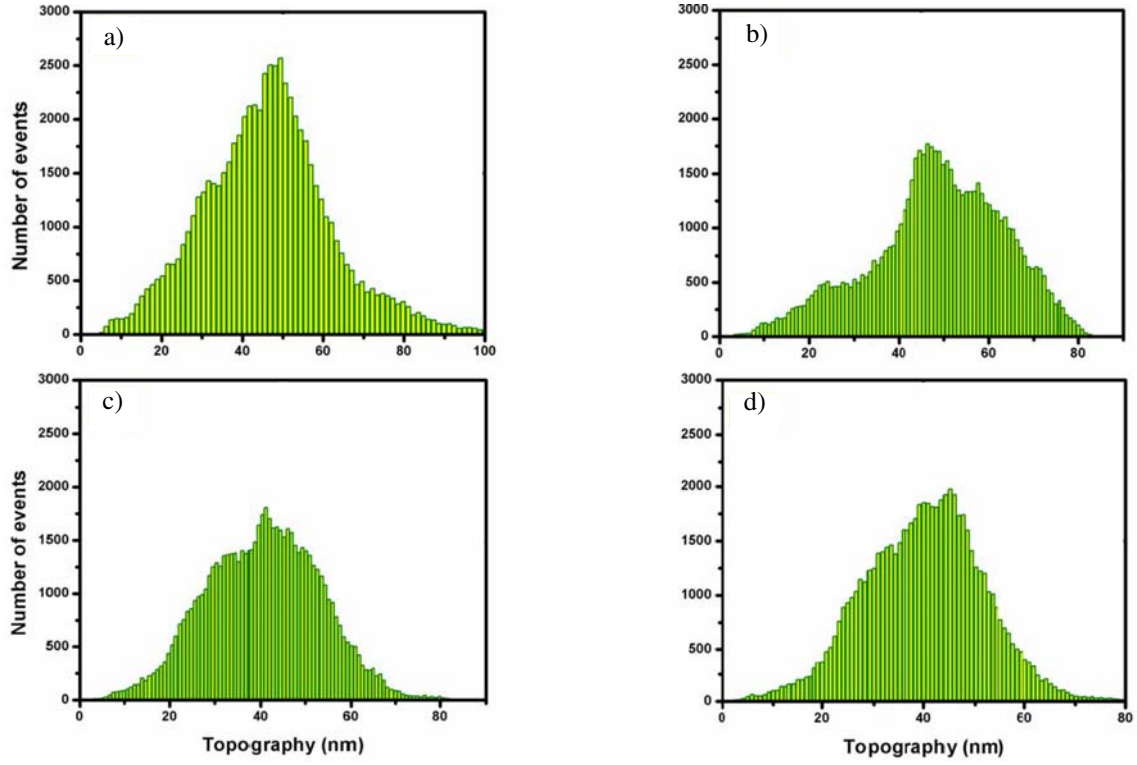

Fig. 4. Histograms of the size distribution of Ni nanoparticles on AISI 304L substrates deposited at: (a) 40 min (b) 80 min (c) 120 min (d) 160 min, respectively

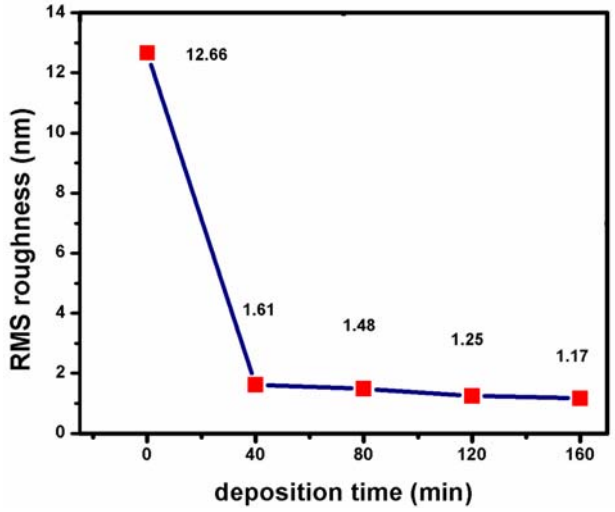

Fig. 5. Variation in the roughness of the Ni coating on AISI 304L substrates for different time duration

To follow closely the evolution of the Ni nanoparticles growth on SIAI 304L substrate, a mechanism image of the surface morphology is shown in Fig. 6. The mechanisms of adhesion can be mainly divided into two groups: 1) mechanical interlocking 2) chemical bonding.[23] Mechanical interlocking can be divided into locking by friction and locking by dovetailing.[23] As the typical images show, by decreasing the RMS roughness, the surface becomes smoother. Due to the high degree of chemical bonding and good friction coefficient of Ni nanoparticles layer[23] in this case, there is more adherence to the AISI substrate.

Scanning Electron Microscopy (SEM) images in Figure 7 shows the minimum and the maximum of the thickness of the Ni layer which was coated by DLC in the same condition. Figure 7(a) related to the S_1 in which the thickness of the Ni layer and DLC film are 1.96 μm and 2.13 μm respectively. The thickness of the DLC becomes 970.7 nm in S_4 when the Ni thickness rises to the 2.68 μm (see Fig 7(b)).

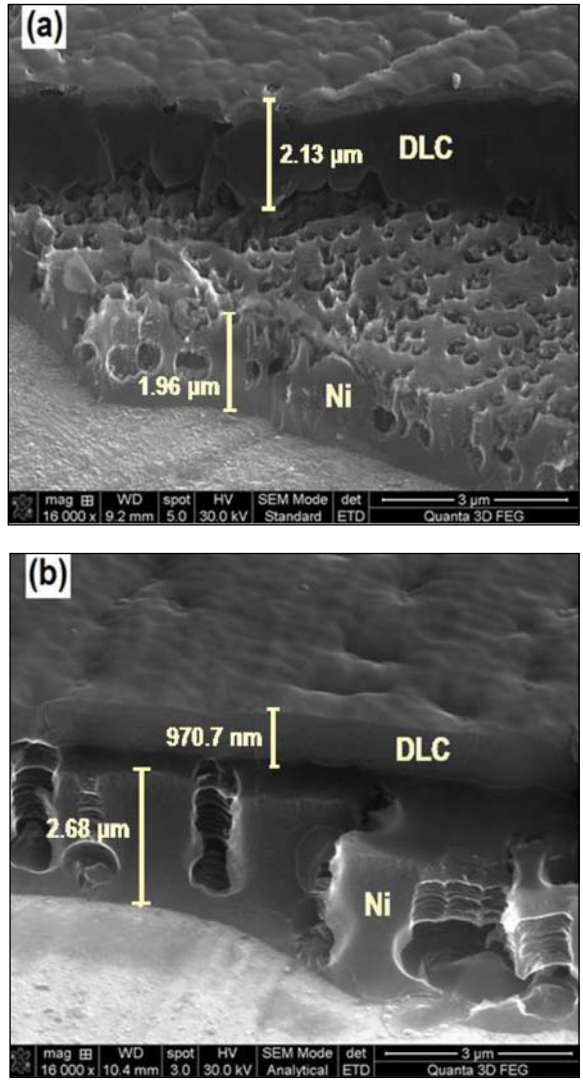

Fig. 7. Typical cross section SEM images of the DLC deposited on Ni coated steel: (a) S_1 (b) S_4

3. 2. Raman and FTIR Studies

Raman spectroscopy is an effective technique for the characterization of DLC structure due to its availability and non-destructive nature.[24] The Raman spectra of the DLC deposited films, measured by 532 nm excitation wave length of Nd:YLF laser are shown in Fig. 8. All carbon materials such as DLC coatings indicate common features in Raman spectra, named as D and G peaks. The G peak (labeled 'G' for graphite) corresponds to any pair of sp^2 sites in both rings and chains while the D peak (labeled 'D' for disorder) is assigned to the breathing modes of sp^2 atoms only in aromatic rings not in chains.[25–29] The Raman spectra of the DLC films grown on nickel coated

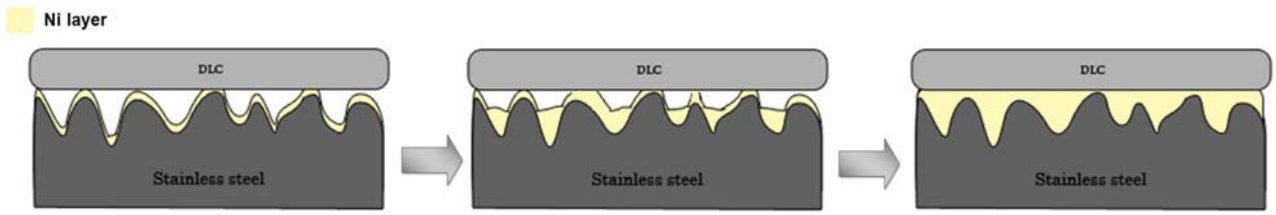

Fig. 6. The contact mechanism of a DLC sliding on a Ni coated stainless steel with different surface roughness

AISI 304L substrate display two major features for each sample separately, corresponding to D and G bands, respectively[30–32] (see Table 1).

Table 1. The statistic data of DLC growth on different substrate

Sample no.	D band (cm^{-1})	G band (cm^{-1})	I_D/I_G
S_1	1342.44	1539.74	1.45
S_2	1339.25	1535.15	0.96
S_3	1339.11	1536.41	0.94
S_3	1339.48	1537.99	0.86

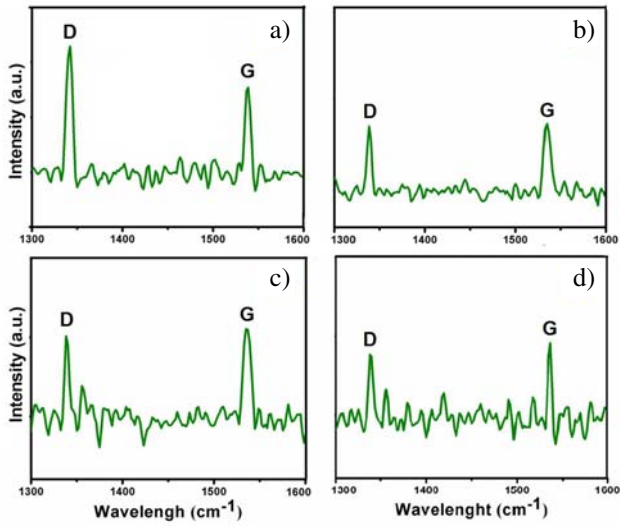

Fig. 8. Raman spectra for DLC coating on: (a) S_1 (b) S_2 (C) S_3 (d) S_4.

In amorphous carbons, the intensity ratio I_D/I_G is related to the size of the sp^2 phase organized in rings.[29,32] The intensity ratio I_D/I_G for the DLC coating on S_1 and S_2 substrates was 1.45 and 0.96, respectively and decreased to 0.94 and 0.86 case of S_3 and S_4 substrates, respectively, as resulted by Raman spectra analysis. If the ratio I_D/I_G becomes lower or zero, the sp^2 phase is organized rather in chains whereas a higher ratio I_D/I_G indicates an increase of the sp^2 phase in aromatic rings[33] but also a higher overall sp^3 content.[29,33,34] These results suggest that the quality of DLC structures can be improved by reducing the Ni surface roughness. In addition, the sp^2 phase was organized rather in chain structures in S_4 compared with the other samples.

Fourier transform infrared spectroscopy (FTIR) was used for analyzing the bonding structure of the DLC films. The FTIR absorption spectra obtained from the DLC films deposited on S_1 to S_4 substrates recorded in the range of 400–4000 cm^{-1}, are shown in Fig. 9.

The peaks attributed to C–H bending and stretching vibration modes appeared in the range of 1300–1700 cm^{-1} and 2700–3100 cm^{-1}, respectively.[35–38] The peak appearing at about 912 cm^{-1} can be associated with the

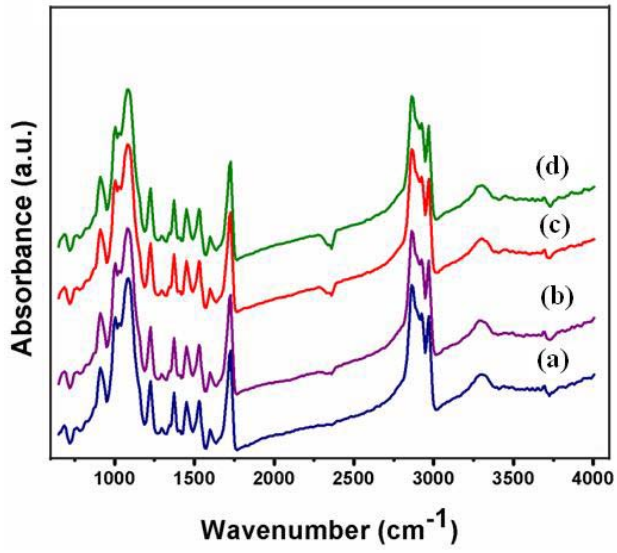

Fig. 9. FTIR spectra of the C–H vibrational region for DLC grown on nickel coated AISI 304L substrates: (a) S_1 (b) S_2 (c) S_3 (d) S_4

olefinic sp^2 C–H_2 vibration mode whereas the peak at around 1451 cm^{-1} could be assigned to C–H bending mode (see Table 2).

Table 2. Summary of the characteristic $sp^n CH_m$ (n and m = 1, 2, 3) vibration modes of DLCs grown on Ni coated steel: (a) S_1, (b) S_2, (c) S_3, (d) S_4.

Sample	Wave number (cm^{-1})	Assignment
S_1, S_2, S_3, S_4	912	Olefinic sp^2 –CH_2
	1227	sp^2/sp^3 C–C
	1451	Olefinic sp^2–CH_2 and sp^3 –CH_2
	2922	asymmetrical sp^3 C–H_2
	2862	$sp^n CH_m$ (n and m = 1,2,3)
	2968	Asymmetric sp^3 –CH_3

These results suggest the films grown on Ni coated steel substrates have DLC structure, are in good agreement with the Raman analysis.

4. Conclusions

In this study, a DLC coating with an adhesive Ni layer was deposited onto AISI 304L substrates. The Ni nanoparticle layers were successfully deposited onto substrate surfaces for 40, 80, 120 and 160 minutes, respectively. The surface roughness of the Ni coated steel substrate in 40 min (S_1) was higher than the others. The RMS roughness of the surface decreased and the surfaces become smoother with increasing the deposition time. Raman analysis enabled evaluation of the intensity ratio

I_D/I_G for the DLC coating on the realized substrates S_1 to S_4. The results showed that by reducing the RMS roughness and increasing the Ni thickness on the AISI 304L substrate a lower intensity ratio I_D/I_G can obtain which is connected to a higher overall sp^3 content and also the sp^2 phase organized rather in chain structure. This results in the production of high quality DLC films on stainless steel substrates.

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Povzetek

Raziskave prevlek na osnovi ogljika, podobnega diamantu (angl. Diamond-Like Carbon, DLC), so bile posvečene optimizaciji pogojev priprave in lastnosti prevlek na različnih podlagah. V delu so opisane raziskave prevlek DLC na podlagah nerjavnega jekla. Za izboljšanje adhezijesmona podlage napršili plasti nanodelcev niklja različnih debelin pri 200 °C. Hrapavost površine in porazdelitev velikosti delcev niklja smo analizirali z mikroskopom na atomsko silo. Prevleke DLC smo nanesli s kemijsko metodo nanosaiz parne faze (angl. DC-Plasma Enhanced Chemical Vapor Deposition, PECVD). Strukturo DLC v vseh vzorcih smo analizirali z Ramansko in infrardečo spektroskopijo s Fourierjevo transformacijo.