Bioactivity and mechanical properties of nickel-incorporated hydrogenated carbon nanocomposite thin films

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In this paper, the influence of nickel incorporation on the mechanical properties and the *in vitro* bioactivity of hydrogenated carbon thin films were investigated in detail. Amorphous hydrogenated carbon (a-C:H) and nickel-incorporated hydrogenated carbon (Ni/a-C:H) thin films were deposited onto the Si substrates by using reactive biased target ion beam deposition technique. The films' chemical composition, surface roughness, microstructure and mechanical properties were investigated by using XPS, AFM, TEM, nanoindentation and nanoscratch test, respectively. XPS results have shown that the film surface is mainly composed of nickel, nickel oxide and nickel hydroxide, whereas at the core is nickel carbide (Ni₃C) only. The presence of Ni₃C has increased the sp² carbon content and as a result, the mechanical hardness of the film was decreased. However, Ni/a-C:H films shows very low friction coefficient with higher scratch-resistance behavior than that of pure a-C:H film. In addition, *in vitro* bioactivity study has confirmed that it is possible to grow dense bone-like apatite layer on Ni/a-C:H films. Thus, the results have indicated the suitability of the films for bone-related implant coating applications. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: amorphous hydrogenated carbon; nickel; reactive-biased target ion beam deposition; *in vitro* bioactivity; mechanical properties; nanoscratch

Introduction

Recently, much attention has been focused on analyzing the new form of carbon-based material for its biomedical properties. In general, carbon is the basic constituent of every biological entity and it possesses multifunctional properties suitable for biomedical engineering applications. In addition to its excellent biocompatibility, bone bioactivity is an essential factor to consider the carbon-based material for bone implant coating applications. Thus, according to Kokubo and Takadama's^[1] definition of *in vitro* bioactivity, a bioactive material is a material which has to exhibit chemical bonding to living tissues upon the formation of a bone-like hydroxyapatite layer selectively after it is immersed in a simulated body solution.^[1,2] Previously, many studies have shown that the *in vivo* apatite formation can be reproduced in a simulated body fluid (SBF) environment which has almost the same ion concentrations as those of human blood plasma.^[3] As a result, it was speculated that the bone-forming cells might preferentially proliferate and differentiate to produce apatite and collagen on the bioactive material surface. Thus formed apatite might bond to the surface apatite as well as to the surrounding bone. Consequently, a tight chemical bond is formed between the material and the living bone through the apatite layer.^[4] This means that the *in vivo* bone bioactivity of a material can be predicted from the apatite formation on its surface in SBF.

Along with the bone bioactivity property, appropriate mechanical properties are highly essential and ideal material for bone implant coating applications. In this regard, coatings composed of crystalline/amorphous nanophase mixture have recently attracted huge interest for its multifunctional properties. Especially, metal containing hydrogenated amorphous carbon (M/a-C:H) coatings have received considerable interest as nanocomposite coatings with nanosized crystalline metal or metal carbide clusters

embedded in the amorphous carbon matrix.^[4–6] These nanocomposite coatings possess unusual combinations of mechanical and tribological properties such as high hardness and toughness, superior wear resistance and low friction which are often not attained in nanocrystalline coatings.^[7] In addition to these properties, the biological behavior (bioactivity) of the coating is strongly influenced by the chemical properties at the surface. It has been reported that the biomedical properties of the a-C:H films can be modified by adding suitable carbide and noncarbide-forming materials which includes silicon (Si), titanium (Ti), calcium (Ca), phosphorus (P), boron (B), nickel (Ni) and nitrogen (N).^[8–16] Among these doping materials, carbide-forming metals play a significant role in altering the mechanical and the bioactivity of the coating to a greater extent. In general, these additives possess an ability to tune the surface-related properties of the a-C:H thin films suitable for biomedical applications. These studies show that the microstructure and the properties of the nanocomposite films were highly dependent on the type of metal and its concentration in the carbonaceous network.^[8–10]

Our present research interest is mainly focused to study the *in vitro* bioactivity (bone-bonding ability) and mechanical

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properties of pure a-C:H and Ni/a-C:H nanocomposite thin films. Several deposition methods such as hybrid reactive magnetron sputtering,^[13] pulsed laser ablation,^[14] electrodeposition^[17] and hybrid plasma enhanced chemical vapor deposition method^[18] have been employed to synthesize nickel-incorporated hydrogenated carbon thin films. Biased target ion beam deposition is a new deposition method mainly used for the fabrication of ultrathin (with high adhesion) films. The main advantage of this method is that it is possible to have a controlled atomistic intermixing between two phases to prepare nanoclusters using a low energy ion beam with few eV at room temperature. Reactive biased target ion beam deposition (RBTIBD) technique is capable of precise control on the concentration of metal, low contamination effect and thickness uniformity.^[19,20] Hence in the present work, the Ni/a-C:H films with different nickel fractions were deposited at room temperature by using RBTIBD method. The chemical composition, microstructure and surface topography of the Ni/a-C:H films were systematically investigated. It was interesting to see that most of the nickel reacts with carbon to form crystalline nickel carbide and, in addition to that, the incorporated nickel initiates more number of sp^2 than sp^3 hybridized bonding states in the a-C:H matrix. The influence of Ni incorporation on the mechanical properties and the *in vitro* bioactivity was investigated in detail.

Experimental details

Film deposition

Amorphous hydrogenated carbon and nickel-incorporated hydrogenated carbon thin films were deposited onto a *p*-type (100) Si substrate by using reactive-biased target ion beam deposition method (RBTIBD).^[21] After placing the Si wafers on the substrate holder, the deposition chamber was pumped down to the base pressure of 2×10^{-7} Torr and all the depositions were carried out at a working pressure of 6×10^{-4} Torr (approx.). Also, the substrate stage was placed at an angle of 45° and it was rotated about its axis at a constant speed of 3 rpm to achieve better uniformity. High purity (99.9995%) methane (CH_4) and Argon (Ar) gases were mixed in the ratio of 1:1 and introduced into end-hall ion source I to deposit pure a-C:H thin film. Similarly, for the deposition of Ni/a-C:H nanocomposite films, the hydrocarbon ion beam with an ion energy of 30 eV was directed towards the substrate to deposit a-C:H film, at the same time nickel was sputtered by using high purity Ar gas using another end-hall ion source II. The Ni sputtering yield was increased by increasing the negative bias voltage from -300 to -700 V. During the deposition, the argon/methane gas ratio and ion beam energy were fixed constant, only the Ni target bias voltage was increased to alter the Ni sputtering yield. The deposition duration was kept as 45 min in order to obtain a thickness of 100 nm (approx.) for all Ni/a-C:H thin films. The thickness of the films was measured to be around 100 ± 5 nm using the surface profilometer measurements.

Characterization techniques

The composition of the films was determined using a VG-Microtech Multilab 3000 X-ray photoelectron spectroscopy (XPS, operating with Mg $K\alpha$ (300 W) X-ray source and detecting chamber pressure of below 10^{-8} Torr). The spectra were collected at pass energy of 50 eV. An Ar⁺ ion beam was used to etch the samples' surface to a depth of about 15 nm, so as to remove contaminants before commencing the XPS measurement. The intensities were

estimated by calculating the integral of each peak, after subtraction of the S-shaped background, and by fitting the experimental curve to a combination of Lorentzian (30%) and Gaussian (70%) lines by using XPSpeak software. The relative Ni atom concentration in the carbon matrix was calculated from XPS signals of Ni (2p) with respect to C (1s) core levels. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) investigations were carried out by a 200 kV Philips CM20 analytical microscope and a 300 kV JEOL 3010 microscope, respectively. Fast Fourier transform (FFT) was used to analyze the lattice spacing of the crystalline phase in the films. Surface topography and roughness of the deposited films were estimated over an area of $1 \mu m \times 1 \mu m$ by using atomic force microscopy (VEECO diCaliber instrument) in tapping mode. The hardness of a-C:H and Ni/a-C:H thin films was determined by nanoindentation (Triboindenter of Hysitron, Minneapolis, USA) in a load controlled mode. A partial unloading function (50% of the peak load) was used to obtain the depth-dependent hardness of the film between the loading ranges from 200 to 5000 μN . Images of the indents were captured using the same indenter in the scanning probe microscope (SPM) mode. Hardness of the films was calculated from the load-displacement curves using the Oliver–Pharr analysis.^[22] In order to find the true hardness of these thin films with more accuracy, Korsunsky fitting model was used. The advantage of this method is that it is possible to determine the substrate-effect free coatings hardness. For soft films on hard substrates, the influence of substrate is unavoidable during hardness measurement and, therefore, this method assumes importance in obtaining the true hardness of the film.^[23] This Korsunsky's model is based on energy expenditure during an indentation and the final equation is given by^[24]

$$H_c = H_s + (H_f - H_s)/(1 + k\beta^2) \quad (1)$$

where

β is the relative indentation depth, k is a constant related to the film thickness, H_f is film hardness, H_s is substrate hardness and H_c is the composite hardness. According to this model, the extrapolation of the curve to the vertical axes gives the hardness of the film. An average of 3 indentations was taken in each sample to determine the hardness value and fitted using Korsunsky model. The adhesion and friction coefficient of the nanocomposite thin films were evaluated by using a nanoscratch tester with a sharp diamond indent tip with a ramping load range between 0 and 1000 μN .

Stimulated body fluid treatment

The bioactivity of the thin film samples prepared by RBTIBD was evaluated by examining their apatite-forming ability in the simulated body fluid (SBF) medium. SBF was prepared by dissolving NaCl, $NaHCO_3$, KCl, K_2HPO_4 , $MgCl_2$, $CaCl_2$ and Na_2SO_4 in ultrapure water.^[25,26] The ion concentrations of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , HCO_3^- , HPO_4^{2-} and SO_4^{2-} were 142.0, 5.0, 1.5, 2.5, 147.8, 4.2, 1.0 and 1.0 mM, respectively. The solution was buffered at pH 7.4 using Tris (hydroxymethyl amino methane) and 1 M aqueous HCl at $37^\circ C$. Amorphous hydrogenated carbon and Ni/a-C:H thin films samples were soaked in 15 ml of SBF at $37^\circ C$ for 1, 7 and 28 days. Then the immersed samples were taken out, rinsed with ultrapure water and then dried in an oven for 30 min at $50^\circ C$. After SBF treatment, the morphology and structure of the apatite formed on the surface of the film was studied using FEI Quanta 200 scanning electron microscope and Expert pro-PAN-Analytical X-ray diffraction (XRD) system, respectively. All the bioactivity

Table 1. Surface chemical composition of Ni and oxygen on air exposed a-C:H and Ni/a-C:H films prepared at different target bias voltage

Sample	Target bias voltage	Ni concentration (at.%)	Oxygen concentration (at.%)
a-C-H	–	–	7.6
Ni - 1	–300 V	1.2	14.52
Ni - 2	–400 V	2.1	14.8
Ni - 3	–500 V	2.4	14.38
Ni - 4	–600 V	3	16.06
Ni - 5	–700 V	3.8	16.5

Figure 1. Typical C 1s XPS spectra for unetched pure a-C:H thin film.

experiments were performed in quintuplicate, by running five parallel independent tubes.

Results and discussion

Surface chemical composition analysis

The chemical composition and bonding nature of pure a-C:H and Ni/a-C:H thin films were studied by using XPS analysis. The relative elemental concentration of nickel gets increased from 1.2 to 3.8 at.% with increase in target bias voltage from –300 to –700 V. We have prepared five different samples with different Ni concentration and these corresponding films are named as Ni-1, Ni-2, Ni-3, Ni-4 and Ni-5. Table 1 shows the Ni concentration and the corresponding target bias voltage. The atomic percentage of oxygen increases with an increase in the Ni concentration. This increase is due to unreacted Ni metal being exposed to air after deposition.

C 1s and Ni 2p_{3/2} XPS spectra of air exposed Ni/a-C:H films

The effect of Ni incorporation on the chemical bondings of a-C:H matrix was studied in detail. Figure 1 shows the C 1s XPS spectrum of air-exposed pure a-C:H thin film. It was found that the deconvoluted C1s spectrum of pure a-C:H film was mainly composed of three different components with binding energy values at ~284.5 eV, ~285.2 eV and ~286.2 eV corresponding to C sp², C sp³, and C–O bonds, respectively. Figure 2(a) shows the C 1s XPS spectrum of Ni/a-C:H film. It was found that the deconvoluted

Figure 2. Deconvoluted C 1s XPS spectra for Ni/a-C:H (Ni-2.4 at.%) nanocomposite thin films with different etching times: (a) Unetched, (b) etching time 2 min, and (c) etching time 4 min. **Figure 3.** High-resolution Ni 2p_{3/2} XPS spectra for Ni/a-C:H (Ni-2.4 at.%) nanocomposite thin films with different etching times: (a) Unetched, (b) etching time 2 min, and (c) etching time 4 min.

C 1s spectra of Ni incorporated a-C:H thin film was also composed with C sp², C sp³ and C–O bonds. In addition to these peaks, Ni₃C phase was also noticed due to the Ni incorporation in the carbon matrix. Irrespective of the nickel concentration, nickel carbide phase was found in all the Ni/a-C:H nanocomposite thin films. Our result is in agreement with the results reported by others on the nickel containing a-C:H film.^[27,28] Upon comparison, the presence of sp² and sp³ hybridization and their relative concentrations in a-C:H and Ni/a-C:H thin film and this is to find the influence of Ni on the carbon matrix. It was found that with increasing Ni, the relative fraction of C sp³ bonds decreases from 44.1 to 25.5%. On the other hand, the C sp² presences have relatively increased from 45.8 to 50.4%, as an evidence of progressive graphitization in the nanocomposite films.

Figure 4. TEM image of Ni/a-C:H: (a) plan view TEM image, (b) HRTEM image, and (c) FFT pattern of Ni-3 (Ni-2.4 at.%) nanocomposite thin film.

To assess quantitatively the presence of different nickel bonding states in air-exposed Ni/a-C:H nanocomposite films, the broad Ni 2p_{3/2} core level spectra was deconvoluted (shown in Fig. 3(a)). It was found that all the films were composed of three different components with binding energy values at ~852.9 eV, ~856.1 eV and ~861.2 eV, corresponding to Ni, Ni₂O₃ and Ni-OH bonds, respectively.^[28] The presence of Ni and their corresponding nickel oxide phase gets increased with increase in target bias voltage. These results indicate a fact that a greater part of the surface-exposed Ni is oxidized. A broad O1s spectra inbetween 529 to 534 eV was observed from air-exposed Ni/a-C:H films (not shown here). Thus, observing the O 1s spectra it was found that most of the atmospheric oxygen bound to Ni and carbon to form nickel oxide, carbonyl and C=O bonds on the films surface.

C 1s and Ni 2p_{3/2} XPS spectra of Ar etched Ni/a-C:H films

Once the films are exposed to air after deposition, a gradual oxidation takes place in the first few days. In addition to that, the oxygen contamination on the surface of air-exposed Ni/a-C:H films

Figure 5. Surface topography of Ni/a-C:H thin film showing 3D images and surface line profile plot of (a-b) Ni-1 (c-d) Ni-3 and (e-f) Ni-5 nanocomposite thin films.

Figure 6. (a) Film-only hardness for Ni/a-C:H films with different Ni concentration fitted using Korsunsky model. (Only Ni-1 and Ni-5 data were presented to avoid confusion and clumsiness in the figure. Dotted lines represent fit). (b) Shows the variation of 'Film-only hardness' with different nickel concentrations, obtained from composite hardness after Korsunsky fit. (c) Variation of elastic modulus with varying nickel percentage in the a-C:H films.

prevents us from evaluating the precise chemical composition of the nanocomposite thin films. In the present work, the oxygen contamination on the surface of the film was removed by etching the film by using Ar ions with energy of 1 KeV for 2 and 4 min. Figure 2(b) and (c) depicts the C 1s XPS spectra of Ni/a-C:H (Ni-2.4 at.%) nanocomposite thin film etched for different durations (2 and 4 min). Again, the deconvoluted C 1s spectra of Ni/a-C:H thin film shows four components: C sp², C sp³, C–O and Ni₃C. But by comparing the etched and unetched thin films, it was found that the intensity of Ni₃C gets increased relatively. This result indicates that the surface-exposed Ni is oxidized. The presence of Ni₃C was not prominent in unetched samples. Etched samples showed the prominent feature to be the Ni₃C phase (shown in Fig. 2). From the Ni 2p_{3/2} spectrum (Fig. 3(b) and (c)) of the etched thin film sample, it was again proved that most of the oxide phases disappeared completely.

Structural analysis

Figure 4 shows the plan view and HRTEM image of Ni/a-C:H (Ni-2.4 at.%) thin film. The plan view TEM image (Fig. 4(a)), shows the presence of nanoclusters in a random distribution and embedded in the amorphous hydrogenated carbon matrix. In addition, the HRTEM image depicted in Fig. 4(b) shows that the metal nanoclusters are randomly distributed in the amorphous a-C:H matrix with an average size of ~2 nm. Furthermore, by using the FFT pattern (Fig. 4(c)), it was found that the incorporated Ni appears in the form of crystalline Ni₃C (101) phase in the amorphous hydrogenated carbon matrix. A similar nickel carbide phase formation was also noticed by others.^[13, 28–30]

Surface topography analysis

Surface roughness and surface topography are the key factors influencing the bioactivity of amorphous hydrogenated carbon thin films. Hence, surface topography and roughness of pure a-C:H and Ni/a-C:H thin films were studied by using AFM. Figure 5(a)–(f) shows the typical AFM (3D) images of Ni/a-C:H films with variable Ni concentrations measured over 1 μm × 1 μm area by AFM. The pure a-C:H film shows a very smooth surface with a surface roughness value of around 0.25 nm. With the incorporation of Ni concentration into the a-C:H matrix, the surface roughness increases to a maximum value of around 1.3 nm for Ni/a-C:H (Ni-3.8 at.%) film. In addition to that of surface roughness and surface topographic study, the line profile analysis was performed to retrieve the detailed information about the surface uniformity of the Ni/a-C:H thin films. Three lines are randomly chosen in three different places on the surface of the film to analyze their uniformity. It was clear that the film with higher Ni fraction shows more rough patterns than that of other Ni/a-C:H nanocomposite thin films.

Mechanical properties

The hardness (H) and elastic modulus (E) details of Ni/a-C:H thin films were obtained and the results are shown in Fig. 6. It was interesting to note that at an indentation depth of 30 nm, Ni incorporated a-C:H films exhibited a lower hardness value than that of pure a-C:H thin film ($H = 26.5$ GPa) and Si substrate, and this is irrespective of Ni concentration. This observation indirectly supports the increase in the concentration of sp² carbon bonds in the Ni/a-C:H films, which was confirmed through XPS analysis.

Figure 7. Surface topographies and their corresponding line profile on the residual indent impression of (a) a-C:H, (b) Ni-1 and (c) Ni-5 thin films.

Since the hardness values of Ni/a-C:H films are less than that of silicon substrate used, we have followed Korsunsky's model to find the 'film-only hardness' from composite hardness (film + substrate hardness). Korsunsky's fit to the H values versus normalized depth obtained using O&P method for Ni-1 and Ni-5 samples are shown in Fig. 6(a). The composite hardness of all the Ni/a-C:H films increases from 7 to 9.5 GPa with increase in indenter penetration depth. At higher indentation depths, the hardness values were approaching towards the hardness of the substrate (10 GPa for Si). The film only hardness of a-C:H films with different nickel concentrations is shown in Fig. 6(b). It is clear that hardness values decrease with increasing nickel content in the films. The hardness of Ni-1 film was

3.8 GPa, whereas it decreased to 3.3, 2.9, 2.7 and finally 2.5 GPa for Ni-2, Ni-3, Ni-4 and Ni-5 films, respectively. Among Ni-incorporated thin films, very low hardness value of 2.5 GPa was observed for high Ni-incorporated a-C:H thin film. The decrease in the hardness value is mainly due to the increase in sp^2 content.

The mechanical hardness directly affects the materials plastic and elastic behavior of the films.^[22] So as to investigate this effect, we conducted two different experiments to monitor the plastic and elastic behavior. The plasticity of the films was tested by using indentation test and also through pile-up formation around the indented zone after indentation. In the present case, we have observed a large amount of material around the sides of the

Figure 8. Variations of friction coefficient as a function of nickel concentration in Ni/a-C:H thin with a ramping load from 0 to 1000 μN in 30 s. Inset with the friction coefficient value of Ni/a-C:H films is given for eye guidance.

indenter. The height was almost one-third of the indentation depth. It was also found that the pile-up height increases with increasing nickel content in the a-C:H films (Fig. 7(a)–(c)). However, no pile-up formation was observed for Ni-free a-C:H film as shown in Fig. 7(a). From the above results it is clear that the incorporation of Ni in a-C:H film, enhances the plastic behavior. In general, similar kind of plastic behavior was usually observed in low-strain hardening materials as reported elsewhere.^[31]

Elastic modulus, E , which is a measure of stiffness, followed the same trend as that of hardness, a well known relationship.^[32] A decrease in E observed from ~ 140 to ~ 100 GPa with increasing nickel content from 1.2 to 3.8 at.%, respectively, as shown in Fig. 6(c). Nevertheless, the values presented in Fig. 6(c) are calculated from O&P method, hence, we believe that they are also overestimated values because of the pile-up effect. To report precise values, elastic modulus was calculated from the projected contact area method using the image of residual indent impression; they are 88.7 GPa for the Ni-1 films and decreased to 81.5 for Ni-2, 73.4 for Ni-3, 69.1 for Ni-4, and finally 56.7 GPa for Ni-5. This may be due to the presence of soft nickel carbide nanoclusters in the hard amorphous a-C:H matrix which changes the overall behavior of the film from diamond-like to graphite-like amorphous carbon thin film.

The friction and adhesion behavior of a-C:H and Ni/a-C:H thin film with different Ni fractions were studied using nanoscratch test under ramping load from 0 to 1000 μN . Figure 8 shows the friction coefficient as a function of lateral displacement from 0 to 10 μm . In general, both the pure a-C:H and Ni/a-C:H films possess low friction coefficient values. In addition to that, both the films are highly scratch resistant without any peel-off from the substrate at higher loads. The typical value of friction coefficient is 0.464 for pure a-C:H, 0.2458 for Ni is 1, and 0.04182 for Ni is 5. It was clearly seen that the film with very high Ni content of around 3.8 at.% shows a very low friction coefficient value compared to that of other films. Hence, these results indicate that a-C:H films are becoming more smooth with the increase in the incorporation of Ni content. Further, no scratch track was observed. Hence, it was clearly shown that the Ni/a-C:H films prepared through RBTBD method are highly smooth with good scratch resistance.

Figure 9. SEM photographs of the surfaces of (i) a-C:H and (ii) Ni/a-C:H thin films after immersing in the SBF solution for 1, 7 and 28 days.

In vitro bioactivity analysis

Biomimetic apatite coatings precipitated on the surface of a-C:H and Ni/a-C:H (Ni–2.4 at.%) thin film samples during the SBF treatment were analyzed by SEM and XRD. Figure 9 shows the SEM images of a-C:H and Ni/a-C:H samples immersed in SBF solution and analyzed after 1, 7 and 28 days of immersion. After 24 h of immersion, both the a-C:H and Ni/a-C:H films have shown no formation of bone-like apatite on the surface. However, similar immersion for 28 days have resulted a dense apatite coverage over larger area on the Ni/a-C:H films surface. In the case of pure a-C:H, the apatite layer was formed with poor coverage. The observed result thus indicate a fact that the bioactivity of a-C:H gets improved because of the presence of metal clusters on the surface of nanocomposite thin film. It is usually believed that the OH functional groups formed on the surface of the thin film, play an important role in the nucleation of apatite.^[33] Recently, Qiwei *et al.*^[34] have investigated the bioactivity of surface-modified Titanium dioxide thin films and found that the OH group present on the film surface in the form of Ti-OH helps to initiate the growth of apatite. Similarly, enhanced bioactivity was noticed from Tantalum thin film which was again attributed to the formation of Ta-OH on the film surface.^[35] As XPS results have also shown the presence of OH group in the form of Ni-OH, such OH functional group formed on the films surface initiate the growth of apatite. Formation of bone-like apatite layer on the surface of the film promotes the bone bonding with living tissues and thereby helps to increase the longevity of the implant. To confirm the apatite composition, EDX analysis was performed. It was observed that the Ca/P ratios of as-grown apatite is in accordance with nonstoichiometric biological apatite.^[36]

The phase composition and the crystallinity of the apatite formed on the film after exposure to SBF solution were investigated by XRD analysis. The as-grown apatite was scratched from the

Figure 10. XRD spectra of apatite formed on the surface of the Ni/a-C:H thin films after SBF soaking.

sample and its crystallinity was investigated. Figure 10 shows the XRD pattern of bone-like apatite grown on the surface of Ni/a-C:H film after 28 days of immersion. It was clearly seen that the as-grown apatite was high-crystallinity hydroxyapatite (HAp). All the diffraction peaks were readily indexed to the pure hexagonal phase with lattice parameters of $a = 9.418 \text{ \AA}$ and $c = 6.884 \text{ \AA}$, which was in accordance with that of HAp crystals (JCPDS card # 09-0432).

Conclusion

Amorphous nickel incorporated hydrogenated carbon films with low Ni concentration ranging from 1.2 to 3.8 at.% were synthesized by using RBTBD method. It was observed that the elemental concentration of Ni in the films increased with an increase in the target bias voltage. At about 2.8 at.% of Ni, uniform sized, randomly dispersed NiC nanoclusters were seen in the a-C:H matrix. These NiC clusters were Ni_3C in phase at the core. However, at the top surface, the clusters were contaminated by atmospheric oxygen and, therefore, its oxide and hydroxide phases appeared. The presence of nickel hydroxide phase at the surface of Ni/a-C:H film is the reason which favored the growth of apatite and increased the growth rate of the apatite layer. At the core, the presence of NiC nanoclusters have increased the sp^2 content in the a-C:H matrix, which in turn reduced the mechanical hardness and friction coefficient of the Ni/a-C:H films. The result thus obtained provides valuable insights into the potential use of Ni/a-C:H material to support apatite growth with promising mechanical properties suitable for bone cell growth on bone implants.

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