EFFECT OF C\textsubscript{2}H\textsubscript{2} FLOW RATE ON THE DEPOSITION OF Ti-TiC-TiC/DLC GRADIENT NANO-COMPOSITE FILM ON NITI ALLOY

FUQIU MA, XILIANG LIU, DONG LIU and LI LI
Center for Biomedical Materials and Engineering, Harbin Engineering University, Harbin 150001, China
mafuqiu@hrbeu.edu.cn, liuxiliang5173@163.com, liudong@hrbeu.edu.cn, lili_hru@hrbeu.edu.cn

HUAFANG ZHANG
Beijing Aeronautical Manufacturing Technology Research Institute, Beijing 100024, China
zhuafg@tom.com

YUFENG ZHENG
Department of Advanced Materials and Nanotechnology, College of Engineering, Peking University,
No.5 Yi-He-Yuan Road, Beijing 100871, China
yfzheng@pku.edu.cn

Received 8 October 2008
Revised 21 July 2009

Ti-TiC-TiC/DLC gradient nano-composite films have been prepared on the NiTi substrates by the technique of plasma immersion ion implantation and deposition (PIIID) combining with plasma-enhanced chemical vapor deposition (PECVD). The influence of C\textsubscript{2}H\textsubscript{2} flow rate ranging from 30sccm to 50sccm on the chemical structure, microstructure, mechanical properties and corrosion resistance of resulting thin films are investigated by XPS, XRD, friction coefficient test, nano-indentation, electrochemical corrosion test and atomic absorption spectrometry. XPS and XRD results indicate that on the outmost layer, the Ti ions are mixed with the DLC film and form TiC phase, the binding energy of C 1s and the composition concentration of TiC depend heavily on the C\textsubscript{2}H\textsubscript{2} flow rate. With the increase of C\textsubscript{2}H\textsubscript{2} flow rate, the content of TiC and the ratio of carbon sp\textsuperscript{3}/sp\textsuperscript{2} decreases. The nano-indentation and friction experiments indicate that the gradient composite film at 30 sccm has a higher hardness and lower friction coefficient compared with that of the bare TiNi alloy. The microscratch curve tests indicate that Ti-TiC-TiC/DLC gradient composite films have an excellent bonding property with the substrate. Based on the electrochemical measurement and ion releasing tests, we have found that the Ti-TiC-TiC/DLC gradient composite films exhibit better corrosion resistance property and higher depression ability for the Ni ion releasing from the NiTi substrate in the Hank’s solution at 37°C.

Keywords: NiTi alloy; PIIID; PECVD; C\textsubscript{2}H\textsubscript{2}; Ti-TiC-TiC/DLC gradient nano-composite film.

1. Introduction

TiNi shape memory alloys are promising materials in dental, orthopedic and cardiovascular applications because of their unique properties (shape memory effect and superelasticity). However, for prolonged use in a human body, deterioration of the corrosion resistance of the materials becomes a critical issue because of the increasing
possibility of deleterious nickel ions released from the substrate to living tissues. Recent works had successfully fabricated Ta[1-2], TiN[3], TiC[4], ZrC[5], diamond like carbon(DLC)[6-7], Zr-ZrC-ZrC/DLC films[8] on bare TiNi alloy surface. In order to improve the adhesion strength, reduce the internal stress, and enhance the surface hardness, the gradient nano-composite Ti-TiC-TiC/DLC films were deposited on the NiTi alloy by the technique of ECR-plasma resource PIIID combining with PECVD in the present study, and the influence of the C$_2$H$_2$ flow rate on the microstructure, mechanical property and corrosion behavior of the resulting films have been investigated systematically.

2. Experimental Procedure

The experimental alloy had a composition of Ti-50.8at.%Ni, and all samples were cut into sizes of 10mm×10mm×1mm from the as-received heat rolled TiNi alloy sheet. The reverse martensitic transformation ending temperature was settled to 17°C through a series of heat treatment. For all samples, one side of 10mm×10mm surface was ground and mirror polished, then cleaned ultrasonically in acetone, methanol and distilled water, respectively, and finally dried by clean cold air immediately prior to transferring to the deposition chamber.

In this study, an ECR-plasma resource system was applied to obtain gradient nano-composite films. The prepared samples were fixed onto the holder and then the chamber was evacuated to a base pressure of approximately $3\times10^{-3}$ Pa. Before PIIID, the samples were sputter-cleaned using argon plasma under a -600V DC voltage applied on the substrate. Subsequently, a 20KV(300Hz, 5µs) negative pulsed bias voltage was applied to all substrates, firstly the Ti was implanted into NiTi substrate for 10min by the technique of PIII and then a thin TiC film was deposited on the substrates for 5min by PIIID technique. After that the acetylene was introduced as a precursor gas for DLC deposition, with the negative DC voltage of -200 V, and various flow rate of C$_2$H$_2$, 30 sccm, 40 sccm and 50 sccm, deposition time of 40 min. As reference samples, some silicon wafer samples were also used as reference substrates undergoing the same whole experimental procedure as TiNi alloy substrate, and some Ti-undoped DLC films were also formed on the TiNi alloy substrates with the same DLC deposition procedure but without the preliminary Ti implantation and deposition procedures for comparison.

The chemical composition of the film was measured with a XPS system (Kratos, model Axis Ultra). The crystalline structure was analyzed using a Rigaku D/max-RB X-ray diffraction (XRD) system. The hardness and elastic modulus were measured with a nano-indentation tester (MTS, model Nanoindenter XP). The surface morphology of the film were observed by SEM (Amray, model 1910 FE). The adhesion of the experimental films to steel substrate was carried out on a conventional scratch tester (WS-2002 equipped with an acoustic emission detector). The corundum pin (0.2 mm in radius) was drawn across the surface of the films at a constant linear velocity of 4 mm·min$^{-1}$, while increasing the load linearly from 0 to 60~80 N, at a loading rate of 100 N·min$^{-1}$. A UMT-2 pin-on-disk tribometer was employed to measure the friction coefficient of the
deposited films at room temperature. Relative humidity in the measurement process was approximately 30%. A ball of 5 mm diameter made of GCr15 bearing steel (wt. C 0.95–1.05%, Cr 1.30–1.65%, Si 0.15–0.35%, and Mn 0.20–0.40%) was pressed against the films with a normal load of 10 mN. The tests were conducted under a sliding velocity of 2 mm·min⁻¹ and a sliding distance of 10 mm. Anodic polarization curves in Hank’s solution were generated at a sweep rate of 20mV/min from -0.6 V vs. SCE to 1.2V vs. SCE after 1h at the OCP to insure steady state. The nickel ion release was measured by an atomic absorption spectrometry (AAS) (Hitachi, model Z_5000) after anodic experiment.

3. Results and Discussion

Fig.1(a) shows the C1s XPS spectra of the Ti-TiC-TiC/DLC gradient nano-composite films deposited at different C₂H₂ flow rate on TiNi alloy substrate. The peak at 284.6 eV and 282.3 eV can be assigned to C-C bond and C-Ti bond, respectively. In order to determine the ratio of sp²/sp³, Gauss fitting analysis is employed. From Fig. 1(b)-(c) we can found that C 1s peak can be fitted into three peak, C-C sp² peak (284.7eV), C-C sp³ peak (285.6eV) and Ti-C peak (282.1eV), respectively. It can be seen that with the increase of C₂H₂ flow rate, the ratio of sp²/sp³ increases.

![Fig.1. C 1s XPS spectra of the Ti-TiC-TiC/DLC gradient nano-composite films deposited at different C₂H₂ flow rate and the corresponding Gauss fitting curves.](image)

Fig.2 depicts the XRD spectra of the Ti-TiC-TiC/DLC gradient nano-composite films deposited at different C₂H₂ flow rate on the Si wafer substrate. Besides the (200) and (400) peaks of Si, the (111) and (200) peaks of TiC and (100) peak of Ti can be observed. With the increase of the C₂H₂ flow rate, the intensity of TiC peaks decrease.

Fig.3(a) and (b) show the variation curves of hardness and elastic modulus of the Ti-TiC-TiC/DLC gradient nano-composite films with the indentation depth. With the increase of the penetration depth, the hardness and elastic modulus of the films at first increase rapidly, and then decrease gradually until reaching a stable value which is significantly higher than that of uncoated TiNi alloys substrate. With the increase of the C₂H₂ flow rate, the hardness and elastic modulus of the Ti-TiC-TiC/DLC gradient nano-composite films decrease.
Fig. 4 shows the scratch test results of the Ti-TiC-TiC/DLC gradient nano-composite film deposited at different C$_2$H$_2$ flow rates. The film deposited at 30sccm exhibits the lowest slope, and has the best bonding strength, with the critical peel-off stress around 50N, whereas the films deposited at 40sccm and 50sccm have the critical peel-off stress around 35N and 27N.

Fig. 5 shows the friction coefficient of the Ti-TiC-TiC/DLC gradient nano-composite film deposited at 30sccm. The friction coefficient gradually stabilizes at a relatively low
value of 0.12, compared to that of Zr-ZrC-ZrC/DLC gradient nano-composite film, 0.21[8].

Fig.6 shows the open circuit potential, Tafel and anodic polarization curves in Hank’s solution for the Ti-TiC-TiC/DLC gradient nano-composite films deposited at different C$_2$H$_2$ flow rates. From Fig.6(a), it can be seen that the open circuit potential for the 30sccm is the most stable one among the three samples with a value of -0.08V, whereas the 40sccm sample has the highest potential value of -0.04. From Fig.6(b) it can be found that the 40sccm sample has the best corrosion resistance, with self-corrosion potential and current density be -0.195V and 3.176×10$^{-7}$A·cm$^{-2}$. From Fig.6(c), it can be noticed that three curves are very close, with no secondary passivation feature.

Fig.6. OCP(a), Tafel (b) and anodic polarization (c) curves for the Ti-TiC-TiC/DLC gradient nano-composite films deposited at different C$_2$H$_2$ flow rates.
Table 1 summarizes the Ni⁺ concentration in the Hank’s solution after the anodic polarization tests by AAS measurement. No Ni⁺ ions were detected for the three Ti-TiC-TiC/DLC gradient nano-composite films, whereas 6.337 mg/L is the Ni⁺ concentration for the bare TiNi alloy sample before surface modification.

<table>
<thead>
<tr>
<th>negative bias voltage/flow rate of C₂H₂</th>
<th>Ni⁺ concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200V/30sccm</td>
<td>0/undetected</td>
</tr>
<tr>
<td>200V/40sccm</td>
<td>0/undetected</td>
</tr>
<tr>
<td>200V/50sccm</td>
<td>0/undetected</td>
</tr>
<tr>
<td>Uncoated NiTi</td>
<td>6.337</td>
</tr>
</tbody>
</table>

4. Conclusion

Ti-TiC-TiC/DLC gradient nano-composite films have been successfully deposited on NiTi alloy substrate by PIIID combining with PECVD technique. The composite film is composed of nano-TiC phase and amorphous DLC phase. With the increase of the C₂H₂ flow rate, the ratio of carbon sp²/sp³, the content of TiC phase and the hardness decreases. The gradient film has an excellent tribology, adhering and electrochemical corrosion resistance. After anodic polarization tests, there is no Ni⁺ ion in the Hank’s solution for the Ti-TiC-TiC/DLC gradient nano-composite films. For specimens deposited at 30 sccm, the Ti-TiC-TiC/DLC gradient nano-composite film has the best adhesion to the substrate, highest surface hardness and excellent corrosion resistance property.

References