Corrosion resistance and cytotoxicity studies of DLC, TiN and TiCN films coated on 316L stainless steel

N Sunthornpan¹, S Watanabe² and N Moolsradoo¹

¹ Advanced Production and Industrial Technology Research Group, Department of Production Technology Education, Faculty of Industrial Education and Technology, King Mongkut’s University of Technology Thonburi, Bangkok 10140, Thailand
² Department of Systems Engineering, Faculty of Engineering, Nippon Institute of Technology, Saitama 345-8501, Japan

Email: nutthanun.moo@mail.kmutt.ac.th

Abstract. Corrosion resistance and cytotoxicity of diamond-like carbon (DLC), titanium nitride (TiN) and titanium carbo-nitride (TiCN) films coated on AISI 316L grade stainless steel were investigated. All films were deposited on the stainless steel substrates using a cathodic arc plasma deposition-physical vapor deposition (PVD) technique. Film compositions were measured using energy dispersive X-ray spectroscopy (EDS). Contact angle was measured using contact angle measurement. Corrosion resistance was determined using potentiodynamic polarization. Cell viability was analysed using cytotoxicity test. The results show that all films are more hydrophilic (80.75° to 87.79°) than uncoated stainless steel sample (96.63°). Moreover, TiCN, DLC and TiN films have good potential corrosion resistance values of -0.353 V, -0.58 V and -0.68 V, respectively. This is due to the formation of titanium carbides and the sp³ sites structure of DLC film. Meanwhile, DLC film appears to be the most biocompatible with the highest cell viability of 104%.

1. Introduction

Biocompatible stainless steels are now widely used in biomedical applications including vascular stents, artificial joints, artificial knees and bone plates [1-2]. However, problems from material deterioration are often detected over time. Corrosion of biomedical applications is unavoidable, since the body contains various ions that react electrochemically with the surface of metallic materials [3]. Previous investigation has focused mainly on the biological performance of diamond-like carbon (DLC) coatings with results indicating that DLC is more biocompatible and wear-resistant than stainless steel and titanium alloys [3-7]. Moreover, extensive research has improved the mechanical and tribological properties of many materials such as stainless steel by employing hard thin film coatings [8-11]. However, scant research has been conducted on the deposition of DLC, titanium nitride (TiN) and titanium carbo-nitride (TiCN) films to compare the corrosion resistance and cytotoxicity for biomedical applications. In this study, cathodic arc plasma physical vapor deposition (PVD) technique was utilized to prepare DLC, TiN and TiCN films on 316L grade stainless steel. Effects of film types and element contents were investigated regarding composition, surface contact angle, corrosion resistance and cytotoxicity.
2. Experimental Procedure
Medical grade AISI 316L stainless steel was used as the substrate material, and DLC, TiN and TiCN films were deposited onto it by cathodic arc plasma PVD technique. Total deposited thickness of all films was approximately 2 μm. Composition at the top surface of all films was measured using energy dispersive X-ray spectroscopy (EDS) at an acceleration voltage of 15 kV. Surface contact angle of all films was measured by contact angle measurement (Kyowa Interface Science Co., Ltd.) using distilled water at a volume of 1 μL. Corrosion resistance was determined using potentiodynamic polarization experiments in an aqueous 0.05 M NaCl solution. A Pt sheet and Ag/AgCl were used as the counter and reference electrodes, respectively, and potential voltage was varied from −3 V to +3 V at a scanning rate of 10 mV/s. Cytotoxicity testing of all specimens followed the ISO 10993-5 guidelines using Dulbecco’s Modified Eagle’s medium (DMEM) dilution method. All samples were placed in clean Duran bottles and sterilized at 121°C for 15 min. L929 mouse fibroblastic cells were cultured in a 96-well plate at a volume of 100 μL/well with 1x10^5 cells/mL concentration. Cells were incubated at 37°C, 5% CO₂ for 24 hours. Cell viability, performed in triplicate, was measured by MTT assay using a microplate reader.

3. Results and Discussions

3.1. Relative atomic content and average surface roughness
Relative atomic content and average surface roughness measured on the top surface of all films and the uncoated sample are shown in table 1. DLC film shows higher C content (89.52 at.%) than TiCN (30.92 at.%) and TiN films (2.87 at.%), respectively, while TiCN film has greater surface roughness (0.66 μm) than TiN (0.19 μm) and DLC films (0.17 μm), respectively.

| Film             | Relative atomic content (at.%) | Average roughness (μm) | Contact angle (°) | Corrosion resistance |
|------------------|-------------------------------|------------------------|-------------------|----------------------|
|                  | C    | Ti   | N    | Fe  | Cr  | E_{corr} (V) | I_{corr} (A/cm²) |
| DLC              | 89.52 | -    | -    | 7.10 | 2.13 | 0.17         | 84.6            | -0.580 | 4.94E-6    |
| TiN              | 2.87  | 42.52 | 54.45 | 0.43 | -    | 0.19         | 87.8            | -0.686 | 1.35E-5    |
| TiCN             | 30.92 | 48.81 | 20.20 | 0.08 | -    | 0.66         | 80.7            | -0.353 | 2.80E-6    |
| AISI 316L        | 5.87  | -    | -    | 61.67 | 16.63 | 0.18        | 96.6            | -0.925 | 2.63E-5    |

3.2. Surface contact angle
Contact angle measurements on the top surface of all films and the uncoated sample are shown in table 1. Contact angle of uncoated AISI 316L (96.6°) is higher than all films (80.7° to 87.8°), while TiN film shows a higher contact angle (87.8°) than DLC (84.6°) and TiCN films (80.7°), respectively. This is because surface roughness affects the measured contact angle [12], the rougher the contact surface, the smaller the observed contact angle.

3.3. Corrosion resistance
Potentiodynamic polarization curves of all films and the uncoated sample are shown in figure 1. Results of uncoated AISI 316L show lowest corrosion potential (E_{corr}) and highest current density (I_{corr}) than all films, with considerable improvement in corrosion resistance. Moreover, TiCN film shows the highest corrosion potential (-0.353 V) than DLC (-0.580 V) and TiN films (-0.686 V), respectively. Corrosion resistance increases with addition of titanium which increases carbide stabilization by combining with carbon to form stable titanium carbides. For DLC film, low electrical conductivity results from low I₀/I₇.
ratio of the DLC coating which reduces electron transport and exchange of electrical charges necessary for electrochemical corrosion at the sample surface [14]. Moreover, carbon is inherently chemically inert while titanium and carbon formed very strong and inert carbide bonds in the implanted samples with high corrosion resistance [15]. The non-crystalline structure of DLC coating also plays a part in improving resistance to pitting corrosion [9, 15-16].

Figure 1. Potentiodynamic polarization curves of films.

Figure 2. Cell viability of films using DMEM elution method.

Figure 3. Morphology of L929 fibroblastic cells cultured on (a) DLC, (b) TiN, (c) TiCN, (d) uncoated AISI 316L stainless steel.

3.4. Cytotoxicity test
Cell viability of films conducted by cytotoxicity testing is shown in figures 2 and 3. Cytotoxicity evaluation is required to confirm biomedical applicability for implantable materials. From the results, DLC film shows cell viability of 104%, which is slightly lower than uncoated AISI 316 L (107%), but higher than TiCN (103%) and TiN films (92%). However, none of the specimens demonstrate cytotoxicity. Cell viability between 90% and 110% observed from the films has passed the criteria of ISO10993-5 standard, which suggests that the cell viability has to be over 70% in order to be biocompatible. There is also no visible change in cell morphology as they still exhibit typical fibroblastic morphology [16]. Moreover, the non-cytotoxicity results agree with those reported by Gotzmann et al. [6], Serro et al. [7], Antunes et al. [9], Sui et al. [13] and Dearnaley et al. [17].

4. Conclusion
Effects of film types and element contents on composition, surface contact angle, corrosion resistance and cytotoxicity of DLC, TiN and TiCN films were investigated. From the results, TiN film shows a higher contact angle (87.8°) than DLC (84.6°) and TiCN films (80.7°). This is because surface roughness affects the measured contact angle. Moreover, TiCN, DLC and TiN films have good potential corrosion resistance values of -0.353 V, -0.58 V and -0.68 V, respectively. This is due to the formation of titanium
carbides and the sp³ sites structure of DLC film. Meanwhile, DLC film appears to be the most biocompatible with the highest cell viability of 104%, which is higher than TiCN (103%) and TiN films (92%).

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