Proceedings of International Conference on Heat Exchanger Fouling and Cleaning - 2013 (Peer-reviewed)
June 09 - 14, 2013, Budapest, Hungary
Editors: M.R. Malayeri, H. Müller-Steinhagen and A.P. Watkinson
Published online
www.heatexchanger-fouling.com

ANTIBACTERIAL EFFICIENCY OF TITANIUM DOPED DLC COATINGS

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ABSTRACT

Ti (titanium) doped DLC coatings with different Ti contents (1.3%, 1.8% and 3.2%) were prepared on stainless steel substrates by plasma-enhanced chemical vapour deposition (PECVD). The experimental results showed that the total surface energies of Ti-DLC coatings were almost same, about 44 mJ/m^2, but electron donor surface energy component γ^- values were changed in the range of 4.47-9.83 mJ/m^2. It was observed that after the coatings with bacteria were exposed to air for 15 minutes, some bacteria on the coatings were dead. The numbers of adhered bacteria (live, dead and total *E. coli* cells) decreased with increasing Ti content or γ^- values. The 3.2% Ti-DLC performed best, which reduced total bacterial adhesion by 75% and 66% respectively, compared with stainless steel and pure DLC coating. The removal percentage of the bacteria increased with increasing Ti content or γ^- values.

INTRODUCTION

Micro-biofouling has been recognized as a widespread problem in the design and operation of processing equipment, especially in heat exchangers. An effective and desired approach to reduce biofouling is to alter the surface properties of heat exchangers by surface coating techniques. Many attempts have also been made to reduce fouling by coating surfaces with polymers (e.g. silicone, PTFE) due to their non-stick properties. However, the poor thermal conductivity, poor abrasion resistance and poor adhesion to metal substrate of these polymer coatings currently inhibit their commercial use.

Diamond-like carbon (DLC) coatings have attracted great interest because of their properties such as excellent thermal conductivity similar to metals, low friction, extremely smooth surface, hardness, wear resistance and corrosion resistance (Grill, 1993), which make them suitable for heat exchanger applications. DLC itself does not have particularly good non-stick properties. The amorphous nature of DLC opens the possibility of introducing additional elements, such as Si, F, N, O and their combinations, into the coating whilst still maintaining the amorphous phase of the coating (Hauert 2003). Recently the incorporation of selective elements into DLC has been shown to be an effective method to alter the surface energy of the DLC coatings and to enhance the antibiofouling and other properties of DLC coatings. Zhao et al. (2007) showed that the silicon-doped DLC coatings reduced bacterial attachment significantly compared with pure DLC coatings. Numerous studies demonstrated that the heat transfer surfaces coated with fluorine-doped DLC coatings reduced scale adhesion and subsequent scale formation, compared with DLC coatings, untreated titanium and stainless steel surfaces (Müller-Steinhagen and Zhao, 2000; Bornhorst et al, 1999; Santos et al. 2004; Zhao and Wang 2005). Ishihara et al. (2006) demonstrated that the antibacterial performance of the pure DLC coatings was improved significantly by the incorporation of fluorine with *Escherichia coli*. In this study Titanium doped DLC coatings were prepared and evaluated for bacterial adhesion and removal.

MATERIALS AND METHODS

Ti-doped DLC coatings

DLC coating manufacture is well established, however there are no standard manufacturing processes for producing Ti-doped DLC coatings and it is still at the experimental stage. The selection of the doped elements were based on previous experience on producing non-stick doped DLC coatings and on the ability of manufacturers to produce the coatings with consistent quality after a period of experimentation and development using a PECVD process, which is feasible for application to heat exchangers. In the present study, Ti-doped DLC coatings with different Ti contents (1.3 at.%, 1.8 at.% and 3.2 at.%) were prepared on stainless steel substrates (25×25×1mm) by a magnetron sputter system consisting of a Ti target combined with plasma-enhanced chemical vapour deposition (PECVD) in order to investigate the effect of Ti contents on the adhesion and removal of bacteria.

Surface Energy of Ti-DLC Coatings

The surface energy of a solid surface gives a direct measure of intermolecular or interfacial attractive forces. van Oss et al (1988, 1994) proposed to divide the total surface energy of a material (γ_i^{TOT}) into 3 independent components, Lifshitz-van der Waals apolar (γ_i^{LW}), the electron acceptor (γ_i^{+}) and the electron donor (γ_i^{-}):

$$\gamma_i^{TOT} = \gamma_i^{LW} + 2\sqrt{\gamma_i^{+}\gamma_i^{-}} \quad (1)$$

In this study the contact angles on the Ti-DLC coatings were obtained using a sessile drop method with a Dataphysics OCA-20 contact angle analyser at the Biological and Nanomaterials Lab, University of Dundee.

Assays of Bacterial Adhesion and Removal

In this study, the suspension of *E. coli* with a 10^6 CFU/ml concentration was prepared and used for bacterial adhesion assays. Five replicate samples of each coating were immersed vertically in a glass tank containing 500 ml of a bacterial suspension and were incubated on a shaker at 20 rpm for 1 hour at 37˚C. The total number of bacteria on the samples was counted by a BX41 Olympus Fluorescence Microscope with QICAM High-Performance Digital CCD Camera after the samples were exposed to air for 15 minutes at 25˚C. The LIVE/DEAD *BacLight* bacterial viability kit was used for the enumeration of bacteria on the coatings. The kit consists of two nucleic acid stains: SYTO 9, which penetrates most membranes freely, and propidium iodide, which is highly charged and normally does not permeate cells but does penetrate damaged membrane. Simultaneous application of both dyes therefore results in green fluorescence of viable cell with an intact membrane, whereas dead cells, because of a compromised membrane, show intense red fluorescence. The number of bacteria is counted automatically using image analysis by *Image Pro Plus*. The green colour shows alive bacteria while the red colour shows dead bacteria. 8 fields (approximate 48000µm^2) were used for microscope image analysis. In this study all the Ti-DLC coatings had been treated with UV light for 1 hour before they were tested with bacteria.

In order to investigate bacterial adhesion strength, a home-made dipping device was designed by Zhao *et al.* (2008). It is designed to remove 10% ~ 90% bacteria from surfaces through moving the sample up and down into the water at constant speed (0.03 m/s) controlled by a motor. This process is identical to water flowing over the surface of the sample and the whole area of samples is flushed with water at constant shear stress. Therefore, the bacteria adhered weakly to the surfaces can be removed into the water tank. Finally, bacterial adhesion strength and removal percentage can be determined (Zhao et al 2008; Liu 2011).

RESULTS

Contact angle and surface energy

Table 1 shows the surface energy components of the coatings, which were calculated by van Oss acid-base approach with the contact angle data.

Table 1. Surface energy components of Ti-DLC coatings

Coatings	Surface Energy Components [mJ/m^2]			
	γ^{LW}	γ^{+}	γ^{-}	γ^{TOT}
Stainless steel	41.84	0.08	6.00	43.23
DLC	43.56	0.35	4.47	46.06
1.3%Ti-DLC	44.11	0.00	5.72	44.11
1.8%Ti-DLC	44.39	0.00	7.97	44.39
3.2%Ti-DLC	44.40	0.00	9.83	44.40

Bacterial Adhesion

The percentage of live cells on the suspension prior to adhesion was over 99%. Figures 1 and 2 show the attachment of *E. coli* cells on the stainless steel, DLC coating and Ti-DLC coatings for contact time 1 hour. After the coatings with bacteria were exposed to air for 15 minutes, some bacteria on the coatings were dead. Both pure DLC coating and the Ti-DLC coatings performed much better than stainless steel against bacterial attachment. The number of adhered bacteria (live, dead and total bacteria) decreased linearly with Ti content increasing (Figure 2). The 3.2% Ti-DLC performed best, which reduced total bacterial adhesion by 75% and 66% respectively, compared with stainless steel and pure DLC coating.

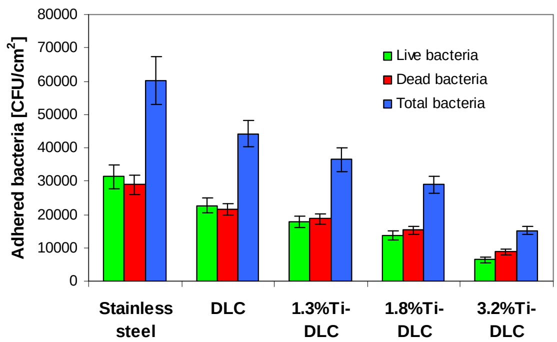

Figure 1 Attachment of *E. coli* cells on coatings

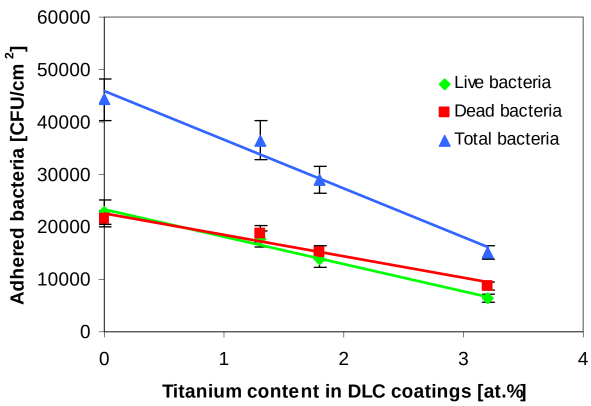

Figure 2 Effect of Titanium content on the attachment of *E. coli* cells on Ti-DLC coatings

Bacterial Removal

In order to assess the adhesion strength of the attached bacteria, each sample with bacteria was dipped 20 times vertically in a glass vessel containing 130 ml sterile distilled water at 37 °C at constant speed (0.03 m/s) controlled by a motor with a constant shear stress of 0.014 N m^{-2}. During the dipping process, some bacteria were removed from the coatings. Figure 3 shows the numbers of remaining bacteria (live, dead and total bacteria) on the coatings. Figure 4 shows that the numbers of remaining bacteria (live, dead and total bacteria) decreased linearly with Ti content increasing.

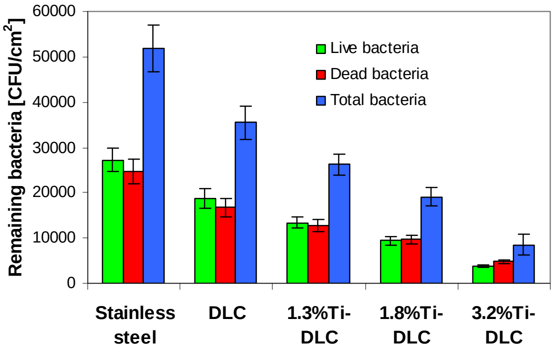

Figure 3 Remaining *E. coli* cells on the coatings after dipping process

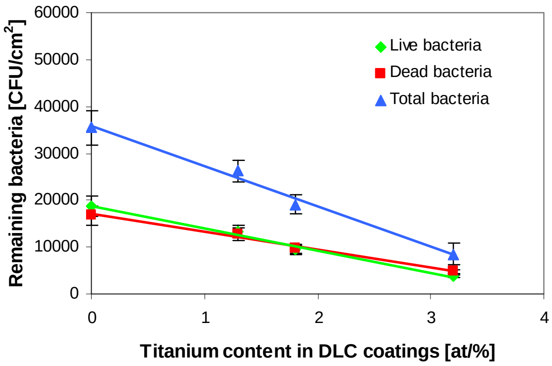

Figure 4 Effect of Ti content in DLC coatings on the remaining *E. coli* cells

Figure 5 shows that the removal percentage of *E. coli* cells from the Ti-DLC coatings after dipping process increased with Ti content in the DLC coating increasing. The removal percentages of live, dead and total bacteria on the 3.2% Ti-DLC coatings increased by 215%, 206% and 214% respectively, compared with stainless steel.

DISCUSSION

The improved anti-bacterial properties of Ti-DLC coatings with Ti content increasing could be due to electron donor γ^- increasing and titanium oxide (e.g. TiOx or TiO_2) increasing.

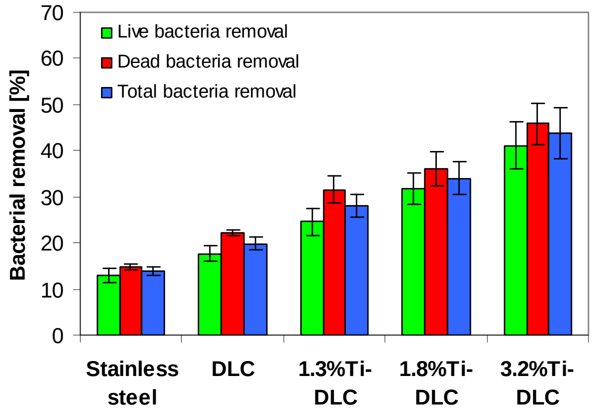

Figure 5 Removal percentage of *E. coli* cells from Ti-DLC coatings after dipping process

Table 1 indicates that the γ^- surface energy component of Ti-DLC coatings increased with Ti content increasing. In general bacteria are negatively charged (Liu and Zhao, 2011). It was reported that the larger the electron donor component γ^- of a surface, the more negatively charged the surface (Chibowski et al. 1994). Therefore bacterial adhesion should decrease with increasing electron donor γ^- values of the coatings if other parameters that affect bacterial adhesion are identical. In this study the total surface energies of Ti-DLC coatings were almost same, about 44 mJ/m^2, but γ^- values were changed in the range of 4.47- 9.83 mJ/m^2 (see Table 1). The adhered bacteria (Fig. 6) decreased linearly with the γ^- surface energy of the Ti-DLC coatings increasing; while bacterial removal (Fig 7) increased linearly with the γ^- surface energy of the Ti-DLC coatings increasing.

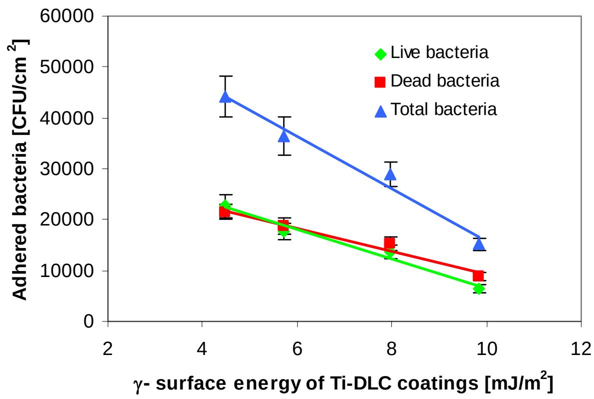

Figure 6 Effect of γ^- surface energy of Ti-DLC coatings on the attachment of *E. coli* cells

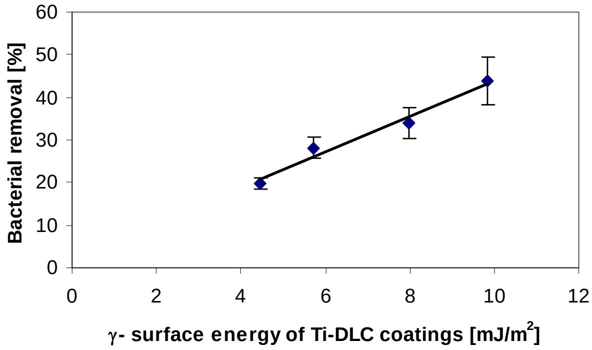

Figure 7 Effect of γ^- surface energy of Ti-DLC coatings on the removal of *E. coli* cells

The microbiocidal effect of TiO_2 photocatalytic reactions was first reported by Matsunaga et al (1985). The microbiocidal mechanisms of TiO_2 photocatalysts have been investigated in detail by Huang et al (2000) and Wang et al (2000). It is suggested that TiO_2 photocatalysts generate strong oxidizing power when illuminated with UV light with wave-lengths of less than 385 nm. The initial oxidative damage takes place on the cell wall when contact with the TiO_2 photocatalytic surface. Then the further oxidative damage takes place on the underlying cytoplasmic membrane, leading to cell death. Kikuchi *et al.* (1997) showed that TiO_2 films coated on different substrates such as glass, tiles and stainless steel possessed antibacterial functions under weak ultraviolet light in living areas and the viable number of *Escherichia coli* significantly decreased on the illuminated TiO_2 film. Li and Logan (2005) reported that bacterial adhesion on TiO_2 coated surfaces reduced significantly after exposed to UV light. In this study all the Ti-DLC coatings had been treated with UV light for 1 hour before they were tested with bacteria. Figure 2 also shows that the ratio of dead *E. coli* cells to total *E. coli* cells on the coatings increased slightly with Ti content increasing.

CONCLUSIONS

1) A series of new Ti-doped DLC coatings with different contents of titanium (1.3 -3.2%) were designed and produced on stainless steel substrates. The experimental results showed that the total surface energies of Ti-DLC coatings were almost same, about 44 mJ/m^2, but γ^- values were changed in the range of 4.47- 9.83 mJ/m^2 .
2) It was observed that after the coatings with bacteria were exposed to air for 15 minutes, some bacteria on the coatings were dead. The numbers of adhered bacteria (live, dead and total *E. coli* cells) decreased with Ti content or γ^- values increasing. The 3.2% Ti-DLC performed best, which reduced total bacterial adhesion by 75% and 66% respectively, compared with stainless steel and pure DLC coating.
3) The removal percentage of the bacteria (live, dead and total *E. coli* cells) increased with Ti content or γ^- values increasing. The removal percentage of live, dead and total bacteria on the 3.2%Ti-DLC coatings was increased by 215%, 206% and 214% respectively, compared with stainless steel.
4) The Ti-DLC coatings may be toxic to bacteria due to the formation TiOx or TiO_2. More research work will be performed to confirm this.

NOMENCLATURE

γ^{LW} Lifshitz-van der Waals component of surface energy, mJ/m^2.
γ^{TOT} Total surface energy, mJ/m^2.
γ^- Electron-donating parameter of the acid-base component, mJ/m^2.
γ^+ Electron-accepting parameter of the acid-base component, mJ/m^2.

REFERENCES

Bornhorst, A., Müller-Steinhagen, H., Zhao, Q. 1999. Reduction of Scale Formation By Ion-Implantation and Magnetron Sputtering on Heat Transfer Surfaces, Heat Transfer Engineering, Volume 20 (2):.6–14

Chibowski E, Holysz L, Wójcik W. 1994. Changes in zeta potential and surface free energy of calcium carbonate due to exposure to radiofrequency electric field. Colloids and Surfaces A 92:79-85.

Grill A. 1993. Review of the tribology of diamond-like carbon, Wear. 168:143-153.

Hauert R. 2003. A review of modified DLC coatings for biological applications Diamond and Related Materials, 12:583-589.

Huang Z, Maness P C, Blake DM, Wolfrum EJ, Smolinski SL, Jacoby WA Bactericidal mode of titanium dioxide photocatalysis, Journal of Photochemistry and Photobiology A: Chemistry. Journal of Photochemistry and Photobiology A: Chemistry. 2000;130:163-170

Ishihara, M., Kosaka, T., Nakamura, T., Tsugawa, K., Hasegawa, M., Kokai, F. , Koga, Y. 2006. Diamond and Related Materials 15:1011.

Kikuchi Y, Sunada K, Iyoda T, Hashimoto K, Fujishima A. Photocatalytic bactericidal effect of TiO_2 thin films: dynamic view of the active oxygen species responsible for the effect. J. Photochem. Photobiol. A: Chem. 1997;106:51–56

Li BK, Logan BE. The impact of ultraviolet light on bacterial adhesion to glass and metal oxide-coated surface. Colloids and Surfaces B: Biointerfaces. 2005;41: 153-161

Liu, C and Zhao Q. (2011), The CQ Ratio of Surface Energy Components Influences Adhesion and Removal of Fouling Bacteria, Biofouling, 27 (3):275–285

Liu C. and Zhao Q. (2011), Influence of Surface-Energy Components of Ni–P–TiO2–PTFE Nanocomposite

Coatings on Bacterial Adhesion. Langmuir, 27(15):9512–9519.

Matsunaga T, Tomoda R, Nakajima T, Wake H, Photoelectrochemical sterilization of microbial cells by semiconductor powders Photoelectrochemical sterilization of microbial cells by semiconductor powders. FEMS Microbiology Letters. 1985; 29:211-214

Müller-Steinhagen, H., Zhao, Q., Helali-Zadeh, A., Ren, X. 2000. The Effect of Surface Properties on CaSO4 Scale Formation During Convective Heat Transfer and Subcooled Flow Boiling, Canadian Journal of Chemical Engineering, Volume78 (1):12–20.

Santos O., Nylander T., Rosmaninho R., Rizzo G., Yiantsios S., Andritsos N., Karabelas A., Müller-Steinhagen H., Melo L., Boulangé-Petermann L., Gabet C., Braem A., Trägårdh C., and Paulsson M., 2004, Modified stainless steel surfaces targeted to reduce fouling–surface characterization, Journal of Food Engineering, Volume 64, Issue 1, Pages 63-79

van Oss, C.J. (1994). Interfacial Forces in Aqueous Media. Marcel Dekker, New York.

van Oss, C.J., Good, R.J., Chaundhury, M.K., (1988). Additive and nonadditive surface-tension components and the interpretation of contact angles. Langmuir 4, 884-891.

Wang XP, Yu Y, Hu XF, Gao L. Hydrophilicity of TiO_2 films prepared by liquid phase deposition Hydrophilicity of TiO_2 films prepared by liquid phase deposition Thin Solid Films. 2000; 371:148-152

Zhao Q, Liu Y, Wang C, Wang S 2007. Evaluation of bacterial adhesion on Si-doped diamond-like carbon films. Applied Surface Science, 253:7254-7259

Zhao Q, Liu Y, Wang C, Wang S, Peng N, Jeynes C. 2008. Reduction of bacterial adhesion on ion implanted stainless steel surfaces, Medical Engineering & Physics, Volume 30 (3):341–349

Zhao Q, Wang X. 2005. Heat transfer surfaces coated with fluorinated diamond-like carbon films to minimize scale formation. Surface and Coatings Technology, 192:77-80.