Use of Inert CVD Coating for Protein, Corrosion, and Moisture Resistance in Bioanalysis Applications

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ABSTRACT

Proteins and other biomedia are prone to adsorbing or fouling on stainless steel surfaces, leading to inaccuracies in clinical assays and detrimental downtime of the analytical system. This paper will introduce Dursan® [1, 2], a silicon-oxygen-carbon (carboxysilicon) coating that provides biochemical inertness, corrosion resistance, and low energy properties to stainless steel and other substrates. By using a vacuum thermal process instead of dip, spray, or line-of-sight deposition methods, the thermal chemical vapor-deposited (CVD) coating lends itself to ease of processing, high volume scale-up, and uniform deposition onto complex geometry components with narrow internal cavities, high aspect ratio features, and blind holes. Unlike solvent-based or crystalline deposition treatments, this amorphous, molecularly-bonded CVD coating can be flexed without risk of flaking or delamination.

After an introduction to the composition and deposition process, the protein resistant, corrosion resistant, and hydrophobic properties of this coating will be demonstrated and discussed. The CVD coating will also be compared to a fluoropolymer coating in the context of a medical diagnostic application [3].

Keywords: coatings, protein adsorption, corrosion resistance, hydrophobicity, non-stick

1 INTRODUCTION

The desire to enhance the surface properties of base materials is especially prevalent in life science applications [4]. In order to keep up with evolving patient needs and clinical innovations, manufacturers in the medical industry must constantly find ways to enhance the performance of their devices and instruments while simultaneously managing costs.

Though these manufacturers have employed coatings and surface treatments for decades, modern clinical challenges are fueling demand for increased robustness, sensitivity, and working lifetime of diagnostic instrumentation and componentry that has never previously been achieved. This has led to the need for new biocompatible coating technologies that can surpass existing performance standards and be efficiently integrated into the overall production process. The carboxysilicon CVD coating discussed here provides a versatile surface that is easy to apply to small or complex geometry components within the analytical flow path.

2 DISCUSSION

Numerous options exist for surface enhancements of equipment used in bio- and clinical analysis applications, but there are distinct advantages to utilizing carboxysilicon films applied via CVD. This material composition offers a low surface energy with little affinity for retaining biomolecules or other analytes of interest. CVD coatings are also very dense and provide a stable barrier to chemical attack in a variety of exposure conditions.

2.1 Coating Composition

The deposition process entails a thermal decomposition and reaction of gas-phase precursors to form the base coating layer of elemental silicon, oxygen, and carbon, which is naturally inert to a variety of chemical compounds. Further tailoring i.e. functionalization of the layer significantly lowers the surface energy at such that bulk material is much less likely to be irreversibly retained by the coated substrate. Through secondary ion mass spectroscopy (SIMS), Figure 1 illustrates a typical depth profile of the amorphous silicon, oxygen, and carbon base layer deposition.

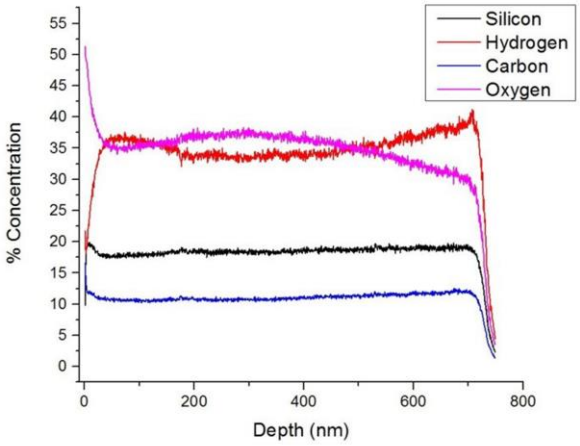

Figure 1: Secondary Ion Mass Spectroscopy (SIMS) depth profile of amorphous silicon, oxygen, and carbon coating base layer

Typical deposition thicknesses may range from 200-1000 nm; the example in Figure 1 has a surface depth of 750 nm. The elemental ratios are relatively consistent throughout the layer at 3:3:1.5:1 for Si:H:O:C. The uniform atomic distribution throughout the layer thickness is noteworthy, indicating a stable, uniform composition of the coating. This base coating deposition is further functionalized by alkyl groups to render the layer chemically inert and hydrophobic.

It is worth comparing the fundamental differences between a chemical vapor-deposited coating comprised of elemental materials and alternatives such as fluoropolymers. A compositional comparison is listed in Table 1.

Coating	Composition
PTFE or PFA	100% polytetrafluoroethylene or perfluoroalkoxyacetyl
Parylene	poly(p-xylylene)
a-Si	amorphous silicon
a-SiOC-R; R=alkyl (Dursan®)	alkyl-functionalized carboxysilicon

Table 1: Common commercial coatings and compositions

2.2 Chemical Vapor Deposition (CVD) Process

Treating components with carboxysilicon-based coatings via thermal CVD processing is a highly scalable and reproducible process. Parts that receive CVD coating treatment are often made from stainless steel, but the process is compatible with several other substrates, including aluminum alloys, titanium, exotic or "super" alloys, glass, ceramics, and other high temperature materials.

Components are placed into a vacuum chamber which is connected to a gas source. The vacuum chamber is then placed inside a large oven. After vacuum is pulled, deposition gas begins to flood the entirety of the chamber, penetrating all accessible pathways, cavities, and holes, and depositing a base layer homogeneously across all surfaces of the parts inside. This process takes a number of hours and reaches temperatures as high as 450° C.

Aside from the non-line-of-sight advantages to CVD processing, the deposition creates a surface coating that is molecularly bound to the substrate. Unlike fluoropolymers such as PTFE or PFA, the coating can be bent or flexed and can withstand moderate mechanical agitations without risk of delamination. This is a critical feature to many medical applications, especially for in-vivo devices.

3 EXPERIMENTAL

The performance of the alkyl-functionalized carboxysilicon coating deposition confirms a low energy surface with a high water (avg. 90°) contact angle on smooth 304 stainless steel coupons (contact angles increase on rougher surfaces). Additionally, the coating displays a significantly lower corrosion rate in 15% NaClO (bleach) at room temperature than uncoated 316L stainless steel. The coating's tendency to irreversibly adsorb protein-containing media is proven to be lower than that of bare stainless steel, and more robust than AF1600, an amorphous fluoropolymer, as shown below.

3.1 Hydrophobicity

Static contact angle measurements were made on a Rame-Hart model 200 goniometer with DROPImage software. Deionized water with a purity of ca. 10 MOhm was used. "Smooth" stainless steel surfaces are mirror-polished whereas "rough" stainless steel surfaces have a brushed finish with ca. 125 Ra.

3.2 Corrosion Resistance

3.2.1. Salt Water Immersion (EIS Monitoring)

Room temperature salt water immersion test was performed by immersing Dursan-coated 304 stainless steel flat coupons in 5% NaCl static solution, and monitoring the Electrochemical Impedance Spectroscopy (EIS) response of the coupons over time. A Gamry paint test cell, consisting of a saturated calomel reference electrode, a graphite rod counter electrode, and a working electrode made of the investigated specimen, was used to obtain the EIS data. The measurements were performed using Gamry potentiostatic system 300 series G.

3.2.2. HCl Immersion (ASTM G31-12a)[5]

Hydrochloric acid immersion was performed at room temperature in 6M HCl (18-20%) for 24 hours, as well as at 50°C for 7 hours. At the end of each exposure, both uncoated and coated 316L stainless steel coupons were taken out of the solutions, rinsed and sonicated in DI water to remove any corrosion products, then dried and weighed to obtain the mass loss by comparing to the values measured before the exposure, and corrosion rate (mils per year) was calculated from the mass loss.

3.3 Resistance to Protein Adsorption[6]

The anti-biofouling properties of a chemical vapor deposited alkyl-functionalized carboxysilicon coating (Dursan) were compared to that of an amorphous fluoropolymer (AF1600) coating and stainless steel by studying non-specific adsorption of various proteins onto the coating surfaces using quartz crystal microbalance with dissipation monitoring (QCM-D). A wash solution with nonionic surfactant, polyoxyethyleneglycol dodecyl ether

(or Brij 35), facilitated 100% removal of residual bovine serum albumin (BSA), mouse immunoglobulin G (IgG), and normal human plasma proteins from the Dursan surface, whereas these proteins remained adsorbed on the bare stainless steel surface.

QCM-D Protein solutions were flowed (0.150 mL/min) over sensors maintained at 25±0.1°C using a peristaltic pump (Ismatec IPC-N4) attached to the Q-Sense E4 unit. Changes in frequency (f) and dissipation (D) at the 3rd, 5th, 7th and 9th overtones of the base resonance of Quartz crystal (5 MHz) were monitored over time

4 RESULTS

4.1 Hydrophobicity

Dursan-coated stainless steel surfaces that are smooth may have water contact angles averaging around 90°. Note, however, that a rougher surface with the same surface chemistry can increase the water contact angle to 121° (Figure 2). Comparatively, typical water contact angles for fluoropolymer-coated surfaces are approximately 115°.

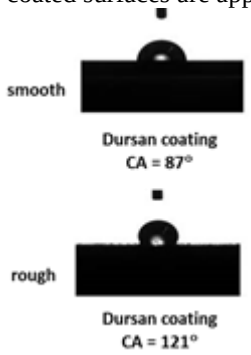

Figure 2. Water contact angle on Dursan-coated surface of varying roughness

4.2 Corrosion Resistance[7]

4.2.1. Salt Water Immersion (EIS)

304 flat stainless steel coupons coated with Dursan were exposed to 5% static NaCl solution at room temperature in an EIS cell, and the EIS response was measured periodically to monitor the sample's integrity over time. Figure 3 represents the EIS response of a Dursan-coated coupon over the period of 8 months, showing excellent stability and minimal change of the spectra over time. The result indicates that the coating is very effective at preventing salt solution from penetrating through the barrier coating to interact with the metallic substrate, which would initiate corrosion reactions under the coating and lead to degradation of the system's corrosion resistance.

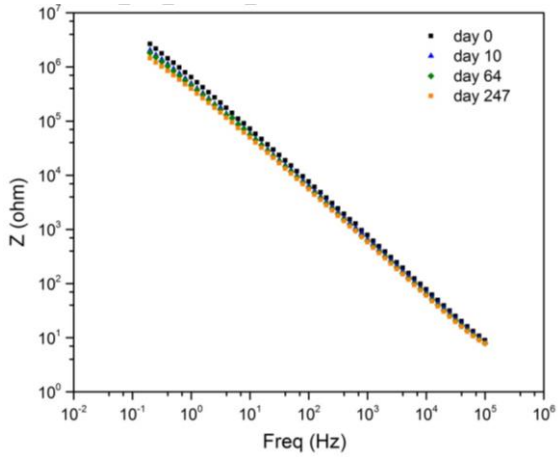

Figure 3. EIS (Electrochemical Impedance Spectroscopy) measurement of Dursan in 5% NaCl solution over 247 days

4.2.2. HCl Immersion

The corrosion resistance of Dursan-coated stainless steel was evaluated and compared to the uncoated control in 6M hydrochloric acidat room temperature. Figure 4 shows the photographic difference between a bare 316L stainless steel coupon and a Dursan-coated sister coupon, after 24 hours of room temperature immersion in 6M HCl. The average corrosion rates in mils per year (mpy) were shown in the same figure, indicating that the coated sample offers an improvement factor of over 170x under this test condition.

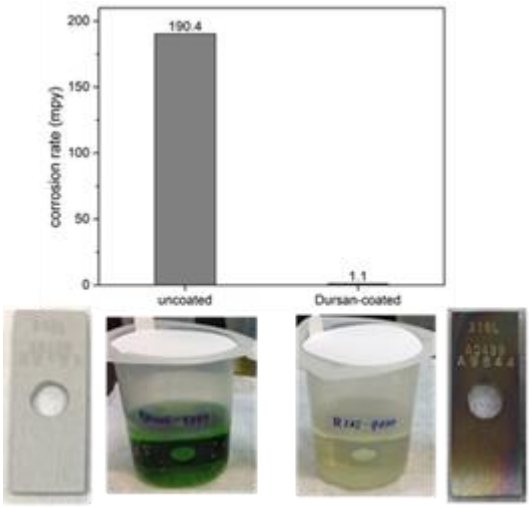

Figure 4. Uncoated and Dursan-coated 316L stainless steel exposed to 6M HCl at room temperature

4.3 Resistance to Protein Adsorption[6]

Using the surface of a quartz crystal microbalance (with dissipation; QCM-D) sensor provides a sensitive method for measuring the degree of molecular adsorption to the sensor face. The sensor is typically fabricated out of stainless steel. Since the QCM-D sensor varies in

vibrational frequency as molecules pass by it (or bind to it), this system can detect not only the presence of a reagent, but also its absence and any intermediate changes in concentration.

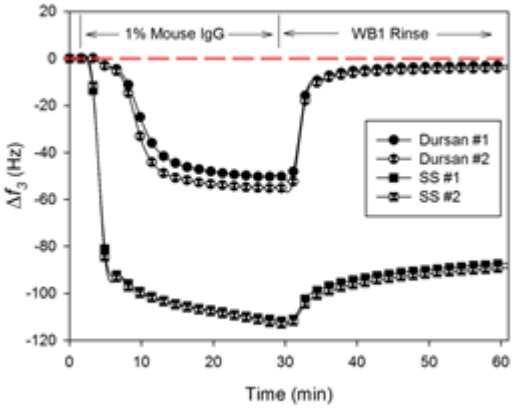

Figure 5. QCM-D results comparing Dursan-coated and bare stainless steel sensors.[6]

Figure 5 illustrates the introduction of mouse immunoglobulins (Mouse IgG) across a stainless steel QCM-D sensor that was coated with Dursan. Both upper traces in the figure show a downward deflection (i.e. lower vibration frequency) from interaction with the Mouse IgG. Then at 30 minutes, a wash buffer (WB1) was introduced. As the Mouse IgG readily rinsed away from the Dursan-treated sensor, the detector frequency returned to its "zero" state.

When using an untreated stainless steel sensor, the WB1 rinsing protocol was not effective at removing the Mouse IgG, and therefore a frequency deflection persists, signifying an irreversible adsorption to the stainless steel.

A PTFE-coated (AF-1600) sensor was also evaluated. This sensor showed similar beneficial biofouling performance in comparison to the Dursan-coated sensor. However, when the AF-1600 sensor was cleaned via solvent sonication, there was visible damage to that coating, whereas there was no visible damage to the Dursan-coated sensor (Figure 6).

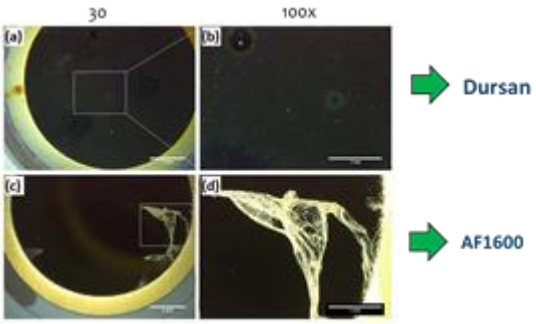

Figure 6. Optical micrographs illustrating before and after effects of solvent sonication of Dursan- and AF1600-coated QCM-D sensors[6]

As a result of the damage to the AF1600-coated sensor from standard sonication cleaning, the resulting tests with normal human plasma (NHP) indicate an increase in biofouling character (Figure 7). The Dursan-coated sensor after sonication cleaning did not show any change in anti-biofouling character, signifying a significant advantage in robustness of Dursan over the AF1600 surface.

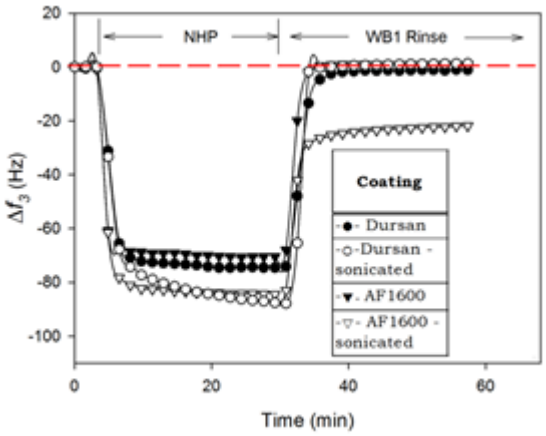

Figure 7: QCM-D results comparing Dursan- and AF1600-coated sensors before and after sonication cleaning[6]

5 CONCLUSIONS

Today, coatings and other surface treatments are well-accpeted means of improving the properties of stainless steel and other materials used in bioanalytical and clinical laboratory applications. While basic substrate selection may suffice in some instances, the demand for materials with a low surface energy – specifically with a low affinity for adsorbing proteins and other bio-molecules - is growing in importance as companies strive to produce analytical sampling systems and instruments that can perform accurate assays without corrosion, retention, and carryover issues.

Many solutions exist for coatings in bioanalytical applications, but depositing alkyl-functionalized carboxysilicon coatings onto instrument componentry via chemical vapor deposition (CVD) combines advanced processing capabilities with high performance surface characteristics. The CVD process is highly robust, reproducible and scalable based on commercial requirements from medical device and clinical instrument manufacturers.

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