Mitigation of Silver Ion Loss from Solution by Polymer Coating of Metal Surfaces, Part II

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"Spacecraft potable water systems require a biocidal agent that effectively provides both immediate and residual disinfection over long periods of time. Ionic silver (Ag^+) is a leading candidate for this application, but suffers from rapid concentration loss due to interactions with the metal storage containers and tubing. In order to maintain biocidal efficacy in systems with long periods of dormancy and to reduce the required rate of Ag^+ injection, it is necessary to develop alternative materials and coatings for certified metal alloys that significantly reduce the Ag^+ loss."[1] In this work, we continue our investigation of vapor-deposited parylene (AF4, and now C) polymers as conformal barrier coatings under long-term (ca. 1-year) immersion in ca. 400 ppb Ag^+. The performance of internal coatings in tubing/two-ferrule fitting systems is characterized. We report successful "aging" and high concentration Ag^+ pretreatment of parylene coatings for quantitative reduction of Ag^+ loss rates. In addition, we observe long-term blister-free adhesion of mechanically anchored parylene-AF4 on nano-structured Ti-6Al-4V alloy and chemically bonded parylene-C on 316L stainless steel. Finally, we report preliminary experiments with mechanical and chemical anchoring of laboratory-deposited parylene-C on 316L.

Nomenclature

316L	=	Austenitic Fe-Cr-Ni-Mo stainless steel (low-carbon grade)
AdPro Plus™	=	AdPro Plus proprietary adhesion promotor (Specialty Coating Systems, Inc.)
Ag^+	=	Silver(I) ion
AgF	=	Silver(I) fluoride
A/V	=	Surface area/volume ratio
cm^{-1}	=	cm^2/cm^3
HAZ	=	Heat-affected zone
ISE	=	Ion-selective electrode
mL	=	milliliter
mm	=	millimeter
mM	=	millimolar
μm	=	micrometer
NaF	=	Sodium(I) fluoride
Parylene-AF4	=	Poly(α,α,α′,α′-tetrafluoro-p-xylylene)
Parylene-C	=	Poly(chloro-p-xylylene)
Parylene	=	Poly(p-xylylene) polymers
PP	=	Polypropylene
ppb	=	Parts per billion (mass)
ppm	=	Parts per million (mass)
SCS	=	Specialty Coating Systems, Inc.

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SEM = Scanning Electron Microscope
Silane A-174 = 3-(trimethoxysilyl)propyl methacrylate (silane adhesion promotor)
Ti-6Al-4V = Grade 5, alpha-beta titanium alloy

I. Introduction

IN our previous work,[1] we introduced vapor-deposited parylene barrier coatings for the mitigation of ionic silver (Ag^+) loss in metal-constructed potable water systems. Rather than recapitulate the motivation and background information here, the reader is directed to that work for familiarization. In addition, we again suggest Li et al.'s helpful review[2] to those new to the literature on ionic silver biocide. We reported[1] mixed success with parylene-AF4 (poly(α,α,α′,α′-tetrafluoro-p-xylylene)) on 316L stainless steel over immersion durations of 7, 28, and 56 days, with Ag^+ concentration and surface area/volume ratios (A/V) relevant to potable water systems (400 ppb, A/V ~1.5 cm^{-1}). Laser cutting (rather than waterjet cutting) resulted in a heat-affected zone (HAZ) at the coupon edge and significant deleterious effects on film adhesion. This made it difficult to distinguish loss to the barrier coating from that to the partially exposed metal coupon, and prevented robust conclusions from being drawn about the efficacy of high-concentration Ag^+ pretreatment and "aging" (exposure to potable-level Ag^+ solutions over weeks to months) to reduce silver ion loss rates on parylene-coated metal substrates.

While the parylene-AF4 surface itself appeared suitably inert/resilient and showed decreasing Ag^+ loss rates as it aged, important concerns about long-term adhesion emerged due to the rapid formation of blisters in the film (away from the HAZ) and visible corrosion on the metal coupon below the blister. Solutions to the adhesion problem were identified in the literature, including surface structuring of the metal substrate for mechanical anchoring,[3] and substitution with parylene-C (poly(chloro-p-xylylene)),[4] which was hypothesized to have more robust bonding to the proprietary AdPro Plus adhesion promotor employed due to the non-fluorinated aliphatic carbon (see Figure 1 for chemical structures).

In the present work, we continue our investigation of parylene barrier coatings—now including parylene-C and the more challenging geometry of a tube/fitting assembly. We examine the silver ion loss and adhesion of parylene films on 316L stainless steel (coupons and tubes with two-ferrule fittings) and nano-structured titanium (Ti-6Al-4V) coupons over long-term (ca. 1-year) immersion. The efficacy of high-concentration Ag^+ pre-treatment and "aging" in ca. 400 ppb Ag^+ to quantitatively reduce Ag^+ loss rates is demonstrated. We report initial experiments with the alkaline hydrothermal surface micro/nano-structuring of 316L on coupons and the interior of sealed tubes. Finally, we report preliminary work with in-house deposition of parylene-C for rapid turnaround experiments with mechanical and chemical (using generic Silane A-174) adhesion.

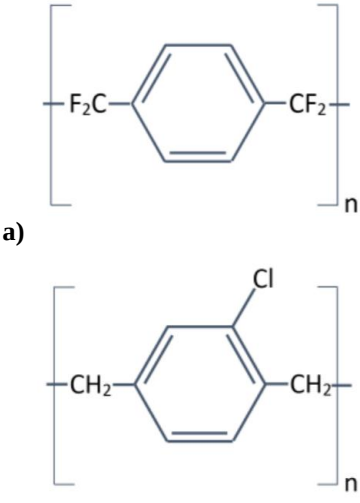


Figure 1. The chemical structures of a) parylene-AF4 and b) parylene-C.

II. Materials and Methods

A. Coupon Fabrication, Tubing/Fitting Assembly, and Film Deposition

Stainless steel coupons of the same design as in Ref. 1 were cut from cold-rolled 316L sheets (0.060" thickness, 2B annealed/roll-finished/passivated, thyssenkrupp OnlineMetals). Waterjet cutting was used to minimize the formation of HAZ. No polishing or repassivation of the 316L coupons was done following fabrication.

6” long tubes were cut from ½” diameter seamless 316L ultra-high purity tubing stock (Swagelok). The tubing had a wall thickness of 0.049” and an electropolished internal surface with 0.25 µm average roughness. Each tube/fitting assembly included a tube section with a 316 (normal-carbon) stainless steel Swagelok two-ferrule cap (part no. SS-810-C, with included ferrules and nut) on one end. These were assembled in the standard (flats method) manner, with parylene deposition done at various stages of assembly in order to investigate practicality of post-deposition assembly. Figure 2 shows the various assemblies coated: a) a fully assembled tube with cap, b) a tube with ferrules set, c) a bare tube, and d) the end cap. A subset of the parylene-AF4 coated tubes were cut at the fitting-end post deposition with a rotary disc cutter to examine the effect of an exposed tube end on Ag^+ loss and film adhesion in water immersion. After deposition, any necessary further assembly was performed.

Figure 2. Swagelok two-ferrule fitting/tubes in various stages of assembly prior to deposition: a) fully assembled, b) ferrules pre-set, c) bare tube, and d) cap. Loose ferrules and nuts were not coated.

Ti-6Al-4V coupons were cut from (0.125”, McMaster-Carr) bar stock, wet-polished with 400 and then 1200 grit aluminum oxide paper and degreased. A surface nanostructure (following the procedures outlined in Refs. 3 and 5) was then grown by an ambient pressure hydrothermal process in 60 °C 5 M NaOH in deionized water for 18 hours. The structure was desodiated for 24 hours in aqueous 0.5 mM HCl at 40 °C to increase the titanium content. In both cases the solution was stirred at 200 rpm with the coupons suspended vertically. Finally, the structure was calcined for 1 hour in air at 400 °C. The resulting surface structure morphology was characterized in the scanning electron microscope (SEM).

B. Parylene Deposition

The above samples were washed in Dawn detergent and degreased in Crystal Simple Green. All coupons were rinsed in deionized water several times after cleaning. These were then sent to Specialty Coating Systems (SCS) for parylene-C and AF4 (brand name HT) deposition, with certain subsets receiving each type. Coupons were cleaned once more, in a deionized water/isopropyl alcohol solution and dried. Films of 25 µm (nominal) thickness were deposited, with the proprietary adhesion promotor AdPro Plus applied *in situ* from the vapor phase prior to deposition.

C. Ag^+/Water Chemistry

Potable water analogue with 470-520 µg AgF and 735 µg NaF in Z mL per 1,000 ml DI water (containing ca. 400-440 ppb Ag^+, 400 ppb Na^+, and 400 ppb F^-) was made by dilution from stock solutions with procedures similar to those given in Ref. 1.

D. Comparative Ion Loss Experiments

High concentration Ag^+ pre-treatment was done on a set of parylene-C coated 316L coupons. The coupons were immersed in ca. 100 ppm aqueous Ag^+ for 3 days, and then allowed to equilibrate in two sequential ca. 400 ppb aqueous Ag^+ solutions for 24 hours each prior to long term testing in the comparative ion loss experiments. The first solution showed a small increase in Ag^+ concentration, however no change was observed in the the second.

Coupons were partially immersed in the Ag^+ solutions (6.0 ml) in polypropylene (PP) flat bottom tubes (12 ml, 16 mm outer diameter, Globe Scientific) as described in Ref. 1. The A/V of the immersed portion was approximately 1.5 cm^{-1} for both the 316L stainless steel and nano-structured Ti-6Al-4V coupons. The 316L tubes were filled with 6.0 ml of solution (resulting in an A/V of ~ 4.0 cm^{-1}) and sealed with a polyethylene tube cap. These tests were done in quintuplicate except for the nano-Ti-6Al-4V coupons (done in triplicate). Ion-loss experiments were conducted at room temperature for a total of ca. 1 year, with Ag^+ loss determination and refills of fresh ca. 400 ppb Ag^+ solution done after 1, 2, 6, 10, 14, 26, 38, and 50 weeks from the start of the experiment. The pre-treated parylene-C coated 316L coupons were tested/refilled at 4, 8, 20, 32, and 44 weeks.

E. Ion Loss Determination

Ag^+ concentration was measured as described in Ref. 1. Due to difficulty making suitable controls for the 316L tubes, a method was developed to place upper bounds on Ag^+ loss by measurements of the Ag^+ solution at the time of filling.

F. Preliminary Experiments with Surface Structuring on 316L

The surface of the 316L coupons and the interior of the 316L tubing (1/4" diameter, 0.035" wall, else same as tubing above) were modified using high-pressure alkaline hydrothermal synthesis (as described in Refs. 6 and 7) to produce a micro-structure for mechanical anchoring. Using a Teflon lined reaction vessel (Parr 4748A), 316L coupons from above were processed in solutions of 0.5 M, 1 M, 2 M, and 5 M NaOH in deionized water in an oven at 250 °C for ca. 6.5 hours (including rise time), with a closed-door natural cool down. Tubes were filled with 0.5 M and 5 M NaOH, sealed with 37° A/N flare fittings (McMaster-Carr) on both ends, and processed as above. This was done to examine the practicality to treating sealed tubing without an autoclave or other pressure containment and to investigate the effects of limited volume reactant solution to surface area. In all cases excess expansion volume was available to prevent catastrophic failure due to the significant thermal expansion of liquid water. The robustness of a subset of samples was investigated by ultra-sonication in deionized water for 60 minutes.

After initial success with mechanical anchoring with nano-structured titanium, we sought to produce a putative Cr_2O_3 based nano-structure on 316L with similar features and length scale by including a Cr(III) complex precursor in the alkaline hydrothermal synthesis, also reported (with mixed results) in Refs. 6 and 7. The synthesis and structure of the Cr(III)-glyoxylate complex are described in Refs. 8 and 9. Here, we produced the complex by refluxing $Cr(NO_3)_3 \cdot 9H_2O$ dissolved in a slight excess of ethylene glycol at 130 °C until completion of the reaction was observed (no further visible emission of nitrogen oxides). The product was then washed with acetone and filtered under vacuum, ground to a fine powder, and dried in air at 60 °C. 316L coupons were treated as above at 250 °C for 6.5 hours with 0.02 wt% Cr-precursor in 0.5 M NaOH and 0.2 wt% in 2 M NaOH.

A nanofoam structure on 316L, which can be produced with (more practical) standard autoclave conditions (121 °C, 15 psi), was produced following Ref. 10. 316L coupons were treated with 10 M NaOH at 121 °C for 22 hours in the reaction vessel described above.

The morphology of the resulting structures produced above on 316L were characterized with SEM. A subset of the structured 316L samples were ultrasonicated in water to determine mechanical resilience, with prior/post SEM imaging.

G. Silane A-174 Treatment and In-house Parylene-C Deposition

The effectiveness of Silane A-174 adhesion promotor on 316L was investigated. Coupons were treated by immersion for 30 min in a 100:100:1 volume mixture of isopropyl alcohol/deionized water/Silane A-174. The silane was allowed to hydrolyze for 2 hours prior to coupon immersion. Silane activity was checked with the potassium permanganate test prior to use. Coupons were then immersed in isopropyl alcohol under agitation for 30 seconds and then dried. In one experiment the coupons were blown dry with clean nitrogen, in another they were dried in a hot air oven at 65-80 °C for 15 minutes.

The operation of the Specialty Coating Systems Labcoter 2 (model no. PDS 2010) was investigated for fast turnaround in-house deposition of parylene-C. The relationship between parylene-C dimer (Specialty Coating Systems) charge mass and resultant film thickness was investigated by running depositions with constant processing parameters with 15, 30, and 45 g of dimer. Nominal processing parameter setpoints were kept constant, with the dimer vaporization furnace at 135 °C, pyrolysis furnace at 690 °C, and 30 milliTorr deposition pressure. The base pressure of the system was approximately 9 milliTorr. Coating thickness was calculated by measuring the mass gain of glass microscope slides used as witness samples.

H. Film Adhesion Testing

The adhesion of the parylene films in the comparative ion loss experiment sample set was characterized non-destructively by visual inspection for blistering at each ion loss determination/ tube refilling. The adhesion of parylene-AF4 to one of the 316L tube assemblies (with cut end) was investigated by destructive disassembly and sectioning of the tube.

Film adhesion with SCS deposited parylene-C and AF4 on bare 316L and with in-house deposited parylene-C on bare, hydrothermally modified (0.5 M NaOH at 250 °C for 6.5 hours), and Silane A-174 treated 316L coupons not subjected to water immersion was characterized destructively. A modified version of the ASTM Test Method D3359: method B cross-cut tape test[11] was used. A square 5 x 5 grid (line spacing ~1 mm) was cut using a knife blade and

then tape (Intertape 51596) was applied over the grid, rubbed with a rubber eraser, allowed to set for 90 seconds, and peeled against itself at 180°. The result was then inspected under magnification and scored according to the standard.

Prelimary immersion experiments with 316L samples with the hydrothermal microstructure and nanofoam coated with SCS parylene-AF4/AdPro plus were done to compare the efficacy of these treatments with bare 316L and nano-structured Ti in preventing blistering.

I. Preliminary Experiments with Ag^+ Compatibility with PEEK Engineering Polymer

For an alternative strategy to metals coating, we are interested in the replacement of metals with high-performance engineering polymers such as polyetheretherketone (PEEK). A preliminary Ag^+ compatibility test was done similarly to the ion loss tests above on a ¼" diameter extruded PEEK rod (A/V= ~ 1.6 cm^{-1}), with refilling and Ag^+ measurements done after 1, 2, 3, 4, and 5 weeks of immersion.

III. Results and Discussion

J. Coupon Fabrication, Tubing/Fitting Assembly, and Film Deposition

No significant HAZ was observed on the waterjet 316L coupons. The HAZ and scale formed by laser cutting (and possibly welding) at excessive temperatures/without inert shielding gas is deleterious. These effects might be reduced by removal of scale/oxide by pickling or electropolishing and may be the subject of future inquiry.

The external surface of the tubes and the internal surface of the caps of assembly method 2b were also coated, eliminating the clearance between them and preventing proper assembly of the tubes with pre-set ferrules (Figure 2). In the case of the bare tubes (Figure 2c), it was necessary to forcefully hammer the tubing into the cap prior to placing the ferrules and tightening the nut. The tubing employed was of slightly larger (several 0.001") diameter than typical tubing employed with Swagelok fittings, and this further exasperated the problem. Two-ferrule fitting systems (e.g. Swagelok) have issues which need to be overcome if this method is to be applied, and it appears that other connection types including 37° flare, face seal o-ring, and clamped sanitary gasket fittings may be more suitable in terms of polymer coated systems.

The surface nano-structure was successfully produced on the Ti-6Al-4V coupons and is shown in Figure 3 (reproduced from Ref. 1). The structure appears well suited for mechanical anchoring as the well-penetrating parylene-AF4 can wrap around it, strongly interlocking the film and substrate.

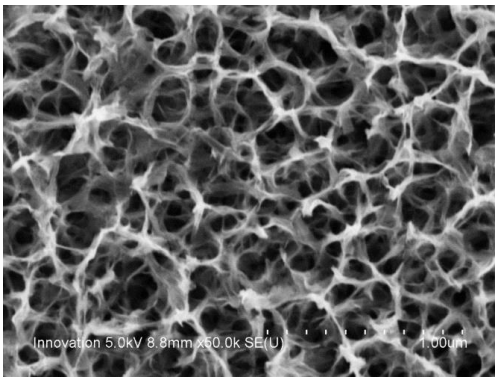


Figure 3. Electron micrograph showing surface nano-structuring on Ti-6Al-4V for mechanical film anchoring (from Ref. 1).

K. Parylene Deposition

The parylene-C and AF4 films were deposited on the comparative ion loss samples (coupons and tubes/caps) as described above.

L. Ag^+/Water Chemistry

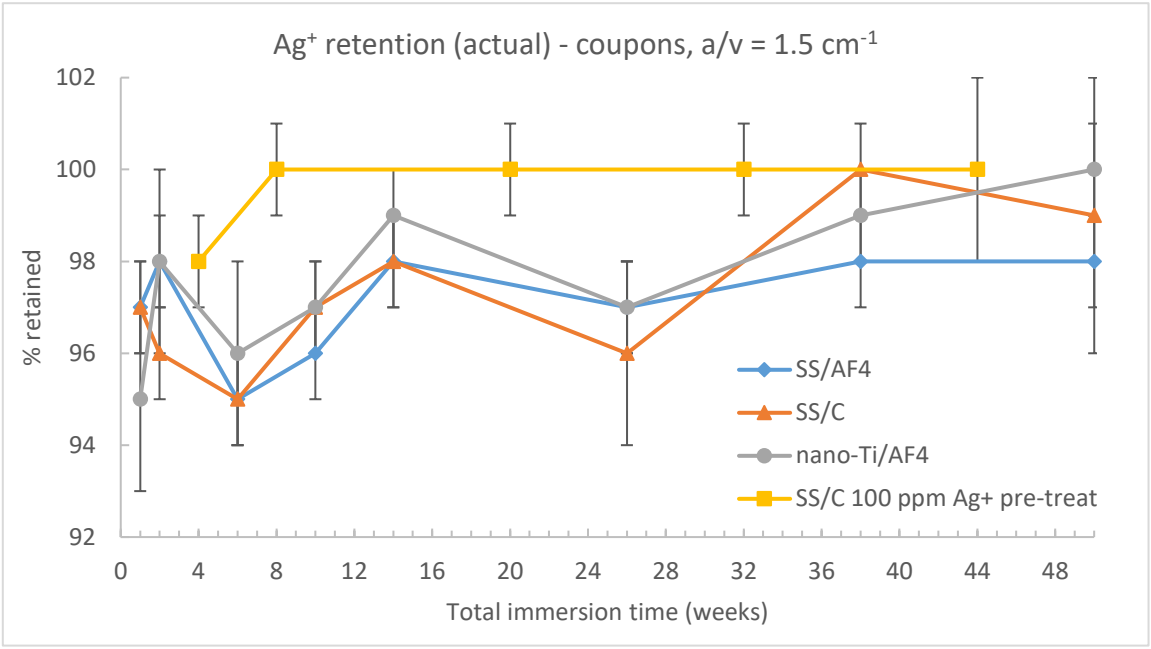
The solutions were prepared as described above.

M. Comparative Ion Loss Experiments

The results of the comparative ion loss experiments through 50 weeks of total immersion (given as % retention) are given in Figures 4 (actual) and 5 (normalized to 4-week immersion). The vast improvement with waterjet vs. laser cut coupons is readily apparent in comparison with our initial work.[1] We see long term loss rates of on the order of only a few % per month with both parylene-C and AF4 coated 316L stainless steel. From the normalized retention data, we see that the kinetics of Ag^+ loss decrease significantly with "aging," as the parylene (both AF4 and C) film saturates with silver. High-concentration Ag^+ (100 ppm) pre-treatment appears to almost quantitatively eliminate Ag^+ loss, and we suggest other investigations with polymer coatings and structural materials should include experiments to determine the proper concentration for pre-treatment and confirm its applicability.

Examining the results with the 316L tube/cap specimens, we see slightly larger initial losses, as is to be expected with the larger A/V ratio employed; again we see the effects of "aging" with normalized retention rates increasing

a)



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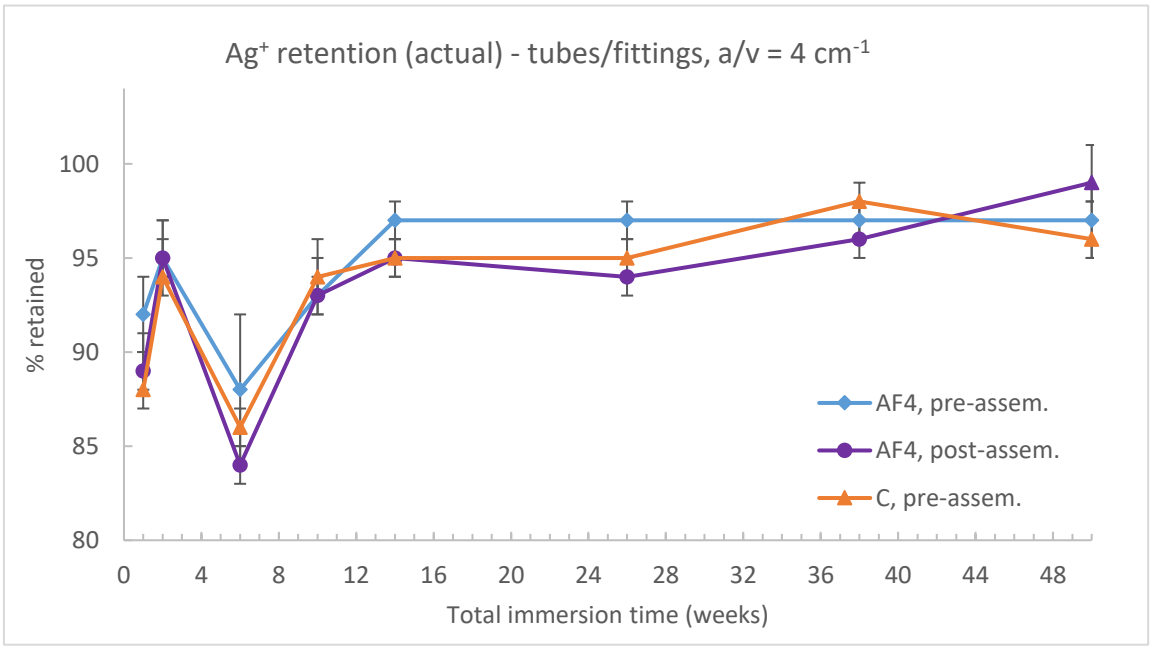
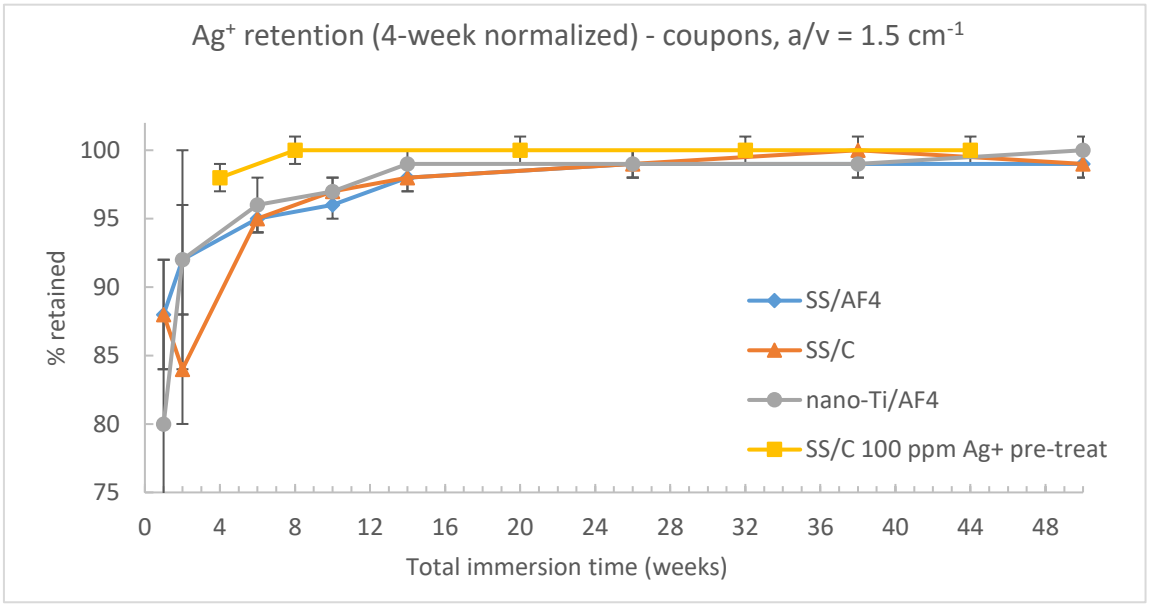


Figure 4. Results of comparative ion loss experiments (actual), a) coupons and b) 316L tubes/fittings (coupon data is vs. polypropylene control tubes, tube/fitting data is the lower bound of retention).

significantly over time. This occurs more slowly than with the lower A/V coupons, likely due to the larger area that must be saturated.

The parylene-AF4 coated tubes with the cut ends showed significant Ag^+ loss over all periods (typically >80%, not shown). As discussed below, these films appeared to rapidly lose effective adhesion. These results strongly suggest that for cut method of sealing cut ends must be developed. Further experiments with C coated tubing are required to understand the magnitude of Ag+ loss to the exposed metal at the tube end vs. under the delaminated film.

a)



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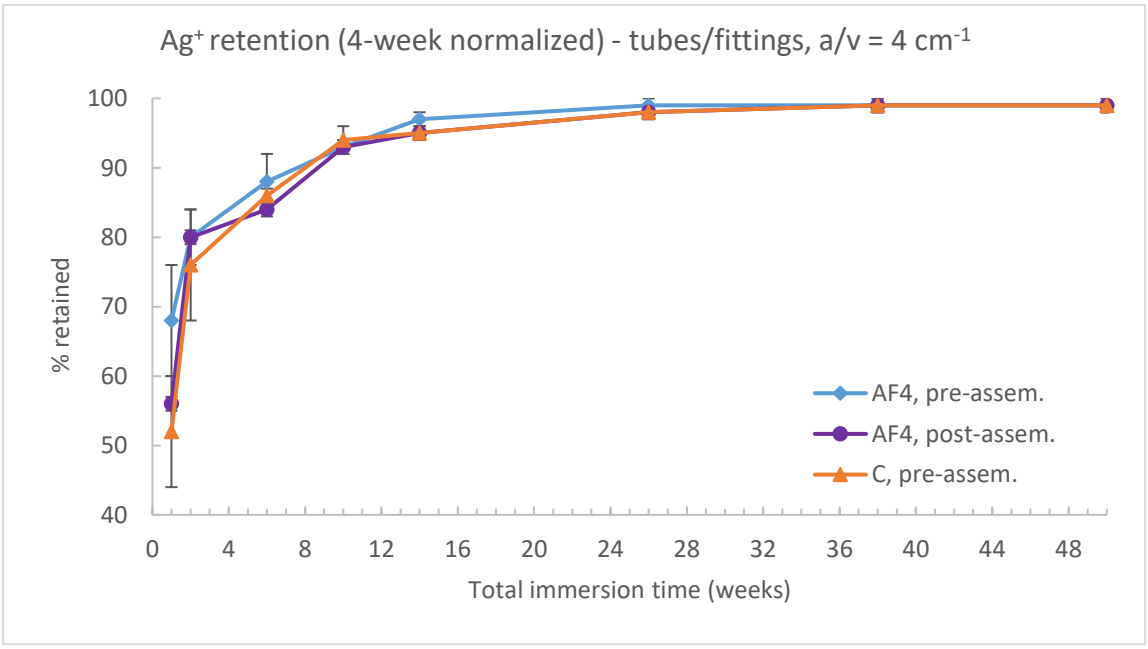

Figure 5. Results of comparative ion loss experiments (normalized to 4-week immersion), a) coupons and b) 316L tubes/fittings (coupon data is vs. polypropylene control tubes, tube/fitting data is the lower bound of retention).

N. Ion Loss Determination

The performance of this method was similar to that as described in Ref. 1.

O. Preliminary Experiments with Surface Structuring on 316L

Electron micrographs of the surface-structured 316L stainless steel specimens are shown in Figure 6. The 316L coupon and electropolished tubing treated with 0.5 M NaOH are shown in Figures 6a and 6b, respectively. It is evident

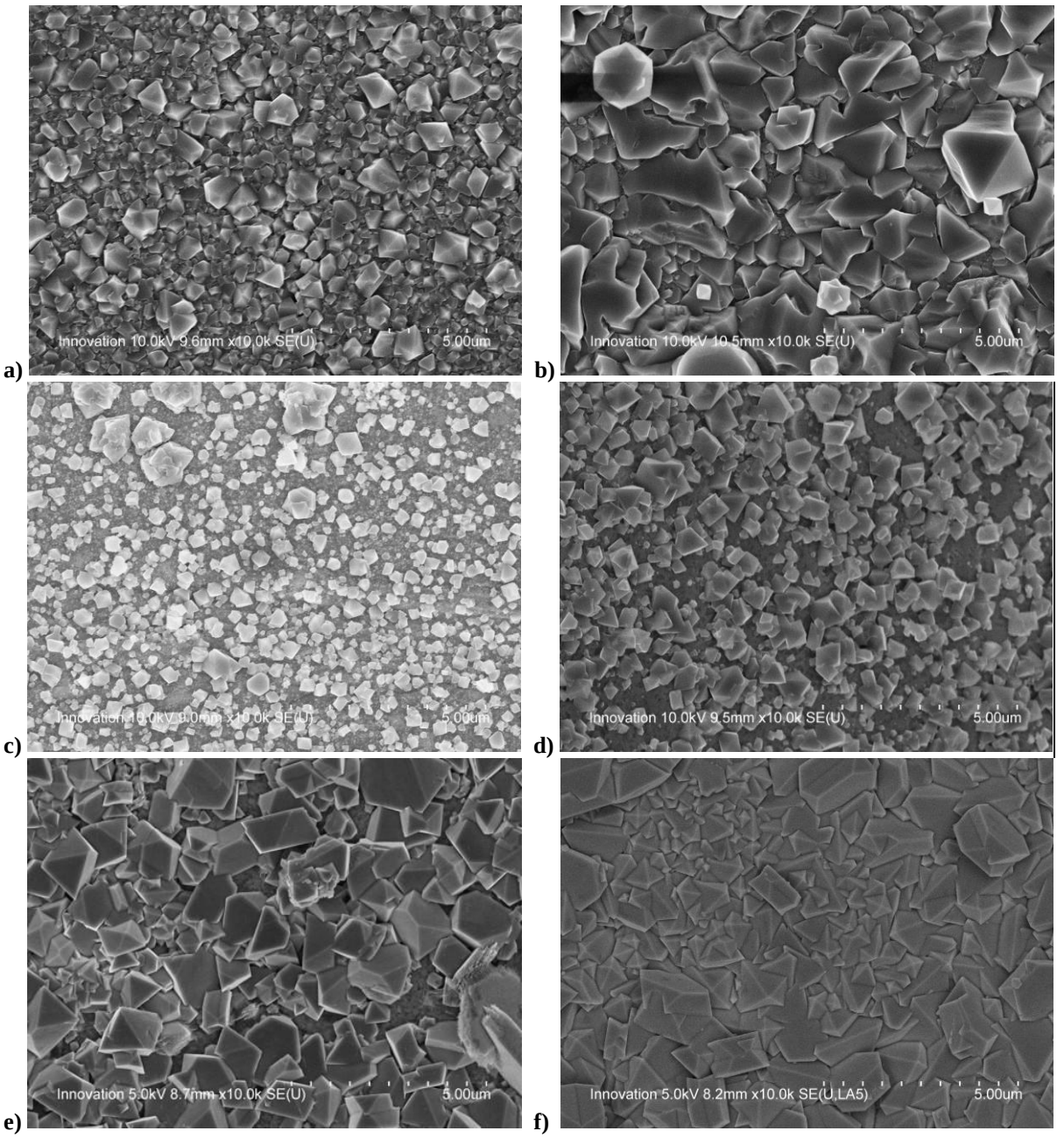

Figure 6. Electron micrographs of hydrothermally treated 316L a) coupon and b) section of electropolished tubing, immersed in 0.5 M NaOH, and sealed electropolished tube filled with c) 0.5 M NaOH and d) 5.0 M NaOH. 316L coupons treated with higher concentration e) 2 M NaOH and f) 5 M NaOH.

that the morphology of the resultant surface microstructure is strongly dependent on the grain structure of the substrate (and possibly its surface roughness). The effect of the limited volume (and thus NaOH mass) of alkaline reactant solution in sealed tubes is easily visible by comparing Figures 6c and 6d (0.5 and 5 M NaOH, respectively). It is evident that the surface microstructure is tuneable by adjusting the concentration of NaOH in solution, and likely by processing time/temperature as well (see Figures 6a, 6e, and 6f for coupons treated in 0.5, 2, and 5 M NaOH, respectively). Ultrasonication did not appreciably change the surface structure grown on the 316L coupons and tube interiors (micrographs not shown). However, further experiments are necessary to determine the resilience of the structure under film peeling. Interestingly, with 316L coupons at lower NaOH concentrations (0.5 and 1 M), the growth of well-adhered large (>10 μm) platelets was observed (not shown). These may be deleterious, but the

suppression with higher NaOH concentration results in a morphology less ameniable to mechanical anchoring, as shown in Figures 6e and 6f.

The nanofoam 316L is shown in Figure 7a. It has been reported that the pore size can be enlarged with increased processing temperature.[12]

The putative Cr_2O_3 nanostructure on 316L (2 M NaOH, 0.2 wt% precursor) is shown in Figure 7b, and may provide good anchoring sites. The length scale of these features might be controllable by tuning the concentration of NaOH, the Cr-precursor, and processing temperature. While the nanostructure was successfully produced with the higher reactant concentrations, there was an uneven coloration on the coupon, suggesting that agitation of the solution or further tuning of the chemistry is necessary to ensure uniformity. No nanostructure was produced on the sample treated with 0.5 M NaOH and 0.02 wt% Cr-precursor (not shown).

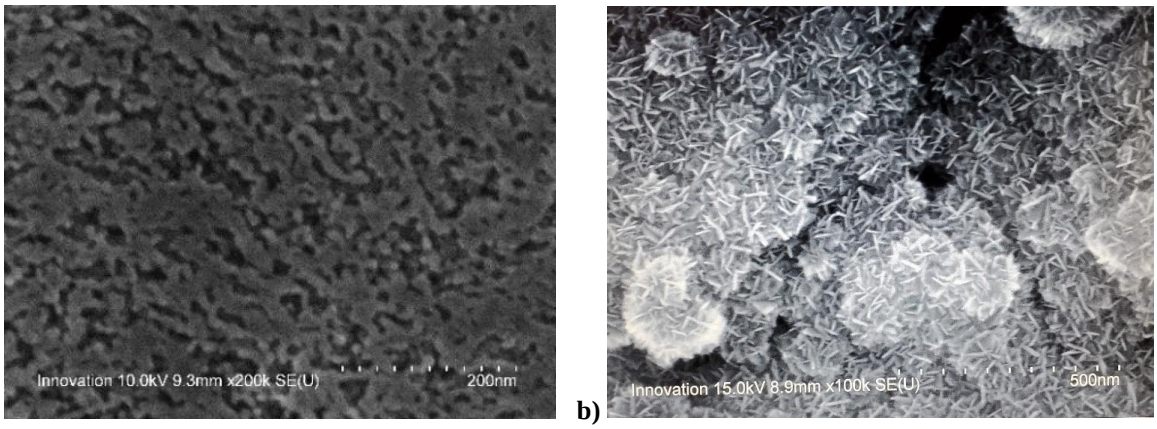

Figure 7. Electron micrographs showing a) nanofoam and b) Cr_2O_3 nanostructure on 316L

P. Silane A-174 Treatment and In-house Parylene-C Deposition

Silane A-174 treatment was completed as described above. This method may require improvement as it appeared unsuccessful, as described below. The silane solution used passed the potassium permanganate test, producing a yellow/brown color rather than the pink/purple expected with depleted solution.

The deposited film thicknesses were approximately 8, 16, and 24 μm for the dimer charges of 15, 30, and 45 g respectively. This expected linearity will be helpful if experiments with coatings of various thickness are desired. However, with increasing dimer charge, run times become excessively long (>6 hours for 45 g). Additional tuning of process parameters, particularly the deposition vacuum setpoint, may be necessary to improve film quality/transparency and/or adhesion.

Q. Film Adhesion Testing

As expected, blistering was visible on all parylene-AF4 coated 316L coupons after only one week of immersion. As the total duration of immersion increased, the blisters grew until apparently stabilizing in size (~2-3 mm in diameter). Significant discoloration due to corrosion was visible below the film (see Figure 8a). The growth of the blister might be driven by strain relaxation or hydrogen gas evolution resulting from corrosion. Interestingly, as we see above, blistering does not appear to result in an increase in Ag^+ loss; as the delamination is localized (preventing liquid transport), barrier properties are maintained. No visible blistering on parylene-C coated 316L or AF4 coated nano-structured Ti-6Al-4V coupons was observed after 50 weeks. A cross-cut tape test on parylene-C and AF4 coated 316L coupons after one week of water immersion resulted in excellent adhesion retention (4B-5B on the ASTM D3359 method B scale) and total loss of effective adhesion (0B) respectively. This suggests that blistering with AF4 may be a good indicator for bulk adhesion failure and the inverse. The proximate cause of blister nucleation following general adhesion failure is unclear, but such sites may be caused by contaminant particles or defects in the coupon surface or adhesion promotor layer.

The sectioning experiment with the immersed (6-month) parylene-AF4 coated 316L tube showed that (given the near total loss of adhesive strength) the cylinder formed by the coating could be removed in one piece. We could not determine if the delamination had been significant prior to disassembly due to the force and rotation required to remove

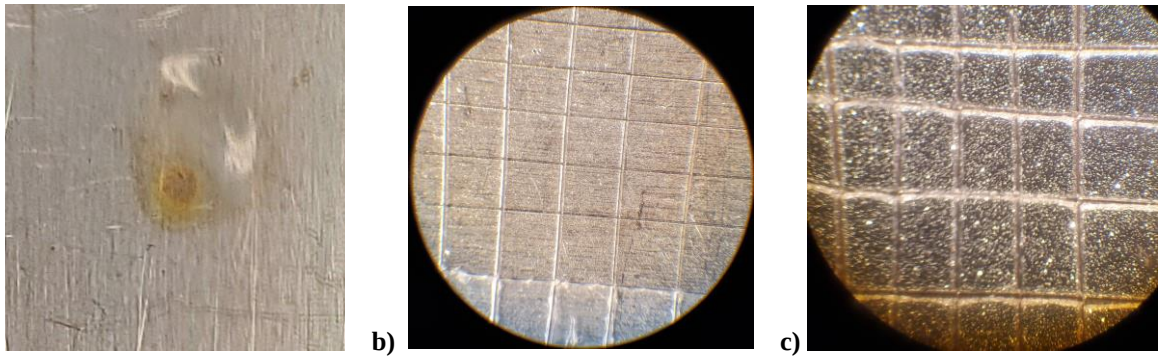

Figure 8. a) Blister in parylene-AF4 after aqueous immersion. Results of cross-cut tape tests with in-house deposited parylene C on b) untreated 316L showing complete film loss, and c) hydrothermally treated 316L showing good film anchoring to the coupon.

the tube from the fitting cap. However, these results suggest long term resilience of the film itself immersed in water. These results make clear the importance of adhesion in internally coated systems where the substrate geometry does not prevent significant film deformation.

Further experiments are required to more rigorously characterize the long term adhesion of parylene-C (with AdPro Plus) and AF4 (on nano-Ti) as destructive testing of long-term immersed coupons was not possible due to the limited number of specimens. It may be possible to conduct accelerated life testing at elevated temperatures if appropriate Arrhenius rate constants can be found. Regardless, the encouraging total lack of blistering with C coatings after 50 weeks suggests that the AdPro Plus adhesion promotor enables long-term (several-year) bonding.

Preliminary adhesion experiments using the cross-cut tape test (non-immersion) with alternatives to the AdPro Plus gave mixed results Bare 316L had total loss of film (0B adhesion, see Figure 8b). The hydrothermally treated 316L coupon coated in house with parylene-C had very good adhesion (4B/5B, see Figure 8c) under the tape test, with minimal peelings due to tape removal. However, the cut film could still be peeled from the edge with a knife blade, suggesting that the structure did not allow for a fully robust anchoring of the parylene-C film. Preliminary immersion tests with AF4 coated hydrothermally produced microstructured and nanofoam 316L showed blistering after one week. Further testing is necessary without the adhesion promotor to see if the AdPro Plus clogged the anchoring sites. Further experiments are necessary to investigate the efficacy of the nanostructure produced with the Cr-precursor.

Initial work with Silane A-174 based adhesion on 316L was unsuccessful (0B), and did not result in an appreciable improvement over bare metal (where the cut film was easily peeled off without damage). This may be due to insufficient active hydroxyl groups on the surface oxide or hydrolysis of the silane due to the neutral pH of the solution used. These hypotheses may be tested by changing the substrate to glass or acidifying the silane solution to accelerate the hydrolysis kinetics. Again, further work is required with these strategies.

R. Preliminary Experiments with Ag^+ Compatibility with PEEK Engineering Polymer

Figure 9a shows the results of the first Ag^+ retention experiments with PEEK. We hypothesize that the large initial Ag^+ loss is due to the highly electronegative oxygen atoms on the ketone and ether sub-units (see Figure 9b for the chemical structure of PEEK), which may serve as strong silver adsorption sites. As these sites are rapidly saturated,

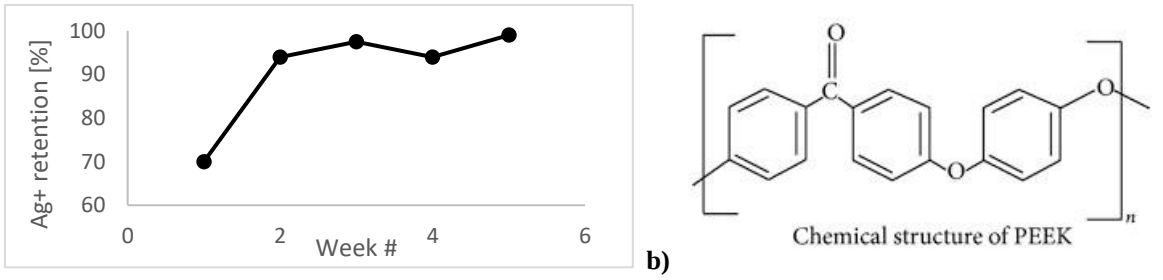

Figure 9. a) Ag^+ %-retention with PEEK vs. time, b) the chemical structure of PEEK.

we see retention increasing to near 100%. If these results are generalizable to other thermoplastics (less inert than PTFE, PP, etc.) such materials may be suitably compatible if pre-treated prior to use.

IV. Future Work

Given the largely encouraging results reported above, the authors are conducting extensive continuing work in this area. The long term immersion experiments reported herein will be continued indefinitely. The performance of parylene on 316L stainless steel weldments (with various surface treatments), Inconel 718, and polished Ti-6Al-4V will be investigated in a new set of experiments. In addition, long-term organic leaching of parylene films/adhesion promotors will be characterized. The effects of elevated temperature on film adhesion will be investigated. Film resilience and adhesion under relevant radiation is also of future interest.

A test bed will be constructed to characterize the performance of parylene barrier coatings in a simulated potable water system, including the effects of pressure cycling, flow, and repeated dis/reassembly. The suitability of parylene coatings on components with complex geometries and deformable surfaces, such as bellows, and on sensors, will be investigated. Finally, the authors are very interested in further investigating the suitability of high-performance engineering polymers such as PEEK as general replacements for metal alloys in potable water systems. This alternative strategy would eliminate the need for barrier coatings and may allow for significant reductions in system mass.

V. Conclusions

In this work, we have shown that parylene (both AF4 and C) coatings are suitably inert and can reduce Ag^+ loss rates at potable water system relevant Ag^+ concentrations and A/V ratios to approximately 1-2% per month after "aging" or high-concentration Ag^+ pre-treatment, vs. greater than 95% in only 7 days on uncoated 316L. We report that parylene-C appears to have reliable long-term (>1 year) adhesion to 316L stainless steel (using AdPro Plus promotor), with no blistering observed during that period. Following these results, we argue that parylene-C is a very strong candidate for silver ion loss mitigation on metal components. Parylene-AF4 may still be of interest as it offers greater radiation tolerance and crevice penetrating abilities during deposition, possibly allowing enhanced mechanical anchoring (to prevent blistering/delamination). The successful anchoring of AF4 on nano-structured Ti-6Al-4V coupons reported above argues for continuing work with other alloys and processing strategies, including on 316L, which we have begun to address here.

Off-the-shelf double-ferrule (Swagelok) fittings are not necessarily compatible with thin polymer barrier coatings due to the limited diameter tolerances between the tubing and fittings/ferrules and the possibly deleterious assembly process. A double ferrule connection would need to be designed specifically to take into account the thickness of the parylene layer. In a future work, we will investigate alternatives, including 37° A/N flare, sanitary clamp, and o-ring face seal fittings. Some of these fittings may allow for post-deposition assembly and repeated disassembly/re-assembly of connections without damaging the barrier coating.

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