

Effects of Surface Treatments on Stainless Steel 316 Exposed to Potable Water Containing Silver Disinfectant

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Silver has been selected as the forward disinfectant candidate for potable water systems in future space exploration missions. To develop a reliable antibacterial system that requires minimal maintenance, it is necessary to address relevant challenges to preclude problems for future missions. One such challenge is silver depletion in potable water systems. When in contact with various materials, silver ions can be easily reduced to silver metal or form insoluble compounds. The same chemical properties that make ionic silver a powerful antimicrobial agent also result in its quick inactivation or depletion in various environments. Different metal surface treatments, such as thermal oxidation and electropolishing, have been investigated for their effectiveness in reducing silver disinfectant depletion in potable water. However, their effects on the metal surface microstructure and chemical resistance have not often been included in the studies. This paper reports the effects of surface treatments on stainless steel 316 (SS316) exposed to potable water containing silver ion as a disinfectant. Early experimental results showed that thermal oxidation, when compared with electropolishing, resulted in a thicker oxide layer but compromised the corrosion resistance of SS316.

Nomenclature

<i>AgF</i>	= silver fluoride
<i>DI</i>	= deionized
<i>I₂</i>	= iodine
<i>ISS</i>	= International Space Station
<i>KSC</i>	= Kennedy Space Center
<i>NASA</i>	= National Aeronautics and Space Administration
<i>SEM</i>	= scanning electron microscopy
<i>SS</i>	= stainless steel
<i>S/V</i>	= surface to volume
<i>XPS</i>	= X-ray photon spectroscopy

I. Introduction

SILVER is a proven broad spectrum biocide. The National Aeronautics and Space Administration (NASA) is interested in adopting silver biocide as a replacement for iodine (I_2) for long duration exploration missions. Silver ion (Ag^+) offers great benefits due to its high efficiency as a broad spectrum biocide, its low biocidal concentration that is relatively safe to human, and its promise as a standardized water disinfectant across international spacecraft platforms and mission architectures. However, silver ion as a water disinfectant for long duration exploration missions is not without challenges. One of such challenges is silver depletion due to material incompatibility. For long duration missions, silver losses can be expected as water is consumed and reprocessed for

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use. In addition, losses of silver biocides can also occur due their reactions with wetted materials of construction, and other interactions, such as adsorption and/or uptake by microbes and organic and inorganic materials in the system. These losses might be appreciable, especially during missions with long periods of dormancy. To meet requirements for exploration, different silver ion dosing systems, silver ion depletion mechanisms, and materials compatibilities have been investigated to ensure future mission success.¹

There have been several investigations on the subject of the material compatibilities.^{2,3,4,5,6,7,8,9} Alloys, such as stainless steels, nickel-based alloys, and titanium alloys, have been studied to determine the effect of the material on silver depletion. Different surface conditions were also compared to identify treatments to reduce silver ion loss. These studies were designed to represent the silver concentrations in potable water (200 to 500 ppb), and the conditional water (up to 500 ppm). Different surface (S) to volume (V) ratios, corresponding to the S/V range for the water storage tank and tubing components in a water distribution system were also examined. In general, more favorable results have been obtained at lower S/V ratios (0.14 to 0.2 cm⁻¹), with thermal oxidation,⁵ electropolishing,⁴ and silver pre-treatment,⁹ as shown in Table 1.

Silver pre-treatments introduce additional silver sources, thus should be evaluated among silver plating techniques. Thermal oxidation and electropolishing are comparable surface treatment methods; they should be tested for their effects on silver ion depletion at high S/V ratios, as such data is still needed. In addition, surface treatments directly change the surface oxide layers on metallic substrates, yet their effects on the metal surface microstructure and chemical resistance have not often been included in the studies. This paper reports the effects of surface treatments on SS316 exposed to potable water containing silver ion disinfectants. Early experimental results showed that thermal oxidation, when compared with electropolishing, resulted in changes of oxide layer thickness, microstructure, surface composition, as well as the corrosion resistance of SS316.

Table 1. Summary of the Silver Compatibility Studies. [1]

Study	Testing Material			Testing Condition		Silver Loss Rate	
	Composition	Geometry	Surface Treatments	Silver Solution	S/V (cm ⁻¹)	Quantitative	Qualitative
Callahan <i>et al.</i> , 2007	SS 21-6-9	Tube	passivated	0.5 ppm (AgF)	4.59	10-20%/day	high
			passivated & Ag plated	0.5 ppm (AgF)	4.59	10-20%/day	high
	Inconel 718	washer	passivated	0.5 ppm (AgF)	0.14	1.5%/day	med
Roberts <i>et al.</i> , 2007	SS 21-6-9	Coupon 10×10×1.5 mm	passivated	0.5 ppm (AgF)	0.14	3% 1 st day; 30% after 21 days	med
	Inconel 718	same	passivated	0.5 ppm (AgF)	0.14	>10% first day; 88% after 21 days	high
	SS 316L	same	passivated	0.5 ppm (AgF)	0.14	>10% 1 st day; 70% after 21 days	high
Adam 2009	SS 316L	washer	passivated	0.5 ppm (AgF)	0.2, 0.5, 1.0, 5.0, 8.2	90% loss: 411, 190, 180, 63 hours for S/V 0.2, 0.5, 1.0, 5.0	high
	Inconel 718	washer	passivated	0.5 ppm (AgF)	0.2, 1, 8.2	90% loss (days): 32.1 (0.2), 1.4 (1.0)	high
	Inconel 718	washer	electropolished	0.5 ppm (AgF)	0.2, 1, 8.2	90% loss (days): 108.3 (0.2), 17.7 (1.0), 0.5 (8.2)	med & high
Beringer <i>et al.</i> , 2014	Inconel 718	Test panels	thermal oxidized & Ag plated	0.35 ppm (AgF)	0.14	maintain about 1 year	low
	SS (E-Brite)	Test panels	thermal oxidized & Ag plated	0.39 ppm (AgF)	0.14	maintain about 1 year	low
Petala <i>et al.</i> , 2016, 2017, 2018*	SS 316L	Test Panels 76×12.7×1.6 mm	120 grit sanded passivated (P) passivated & electropolished (P&E)	Electrolytic Ag 0.5 ppm	5.0	near 100% loss for all samples after 7 days	high
	SS 15-5	same	thermal oxidized	0.5 ppm	5.0	100% loss after 7 days	high
	Ti6Al4V	same		0.5 ppm	5.0	100% loss after 7 days	high
	FEP & PTFE	same		0.5 ppm	5.0	> 60% loss after 7 days	high
	EPR	same		0.5 ppm	5.0	Near 100% loss after 7 days	high
*Russian water formula with high mineral content	SS 316L	Test Panels 76×12.7×1.6 mm	120 grit sanded passivated (P) passivated & electropolished (P&E)	Electrolytic Ag 10 ppm	5.0	Ag loss after 7 days: 316L P&E (21%) vs 316L P (94.75%) 316L (97%).	high
	SS 15-5	same	thermal oxidized	10 ppm	5.0	loss after 7 days: 78%	high
	Ti6Al4V	same		10 ppm	5.0	loss after 7 days: 100%	high
	FEP & PTFE	same		10 ppm	5.0	loss after 7 days: FEP 15%, PTFE 5%	med
	EPR	same		10 ppm	5.0	loss after 7 days: 60%	high
Wallace <i>et al.</i> , 2016, 2017	SS 316L	Washer	passivated	0.4 ppm (AgF) After 100 ppm for 24 hours	0.61	residual Ag at 28 days (ppb): 25 (control 350)	high
	Ti6Al4V	Panel 0.7×0.5×0.12 in	passivated by 20% HNO ₃	Same as above	0.15	residual Ag at 28 days (ppb): 225 (control 350)	med
	Ti6Al4V	Panel 0.7×0.5×0.12 in	Ag plated at 500 ppm	Same as above	0.15	residual Ag at 28 days (ppb): 325 (control 350)	low

II. Method and Materials

A. Material and Surface Treatments

Small stainless steel 316 flat strip coupons (length x width x thickness: 3x0.5x0.05 inch) were purchased from Aero Industries (Orlando, FL). The typical chemical composition of SS316 is shown below. All coupons were electropolished by Able Electropolishing (Chicago, IL), some samples were then thermally oxidized at 551°C for 4 hours.

Table 2. Stainless Steel 316 Composition (weight %).

	Fe	Cr	Ni	Mo	C	Mn	P	Si	N
Min	Balance	16	10	2					
Max	Balance	18	14	3	0.08	2	0.045	0.75	0.1

B. Silver Disinfectant Solutions

Two types of ionic silver disinfectant solutions, containing silver fluoride (AgF) and electrolytically generated silver ions, were prepared at 0.4 ppm weight percent (of Ag) using deionized (DI) water. AgF solutions were prepared from AgF stock solution following a JSC developed procedure.² Electrolytically generated silver ions were prepared using an Ionexx silver ionization unit (McAllen, TX) equipped with high purity silver electrodes (99.99%) and added into DI water to prepare the electrolytic silver solution, which was filtrated through a 0.2 micrometer filter before use.

C. Exposure of SS316 to Silver Disinfectant Solutions

SS316 coupons, with electropolishing and thermal oxidation surface treatments were exposed to both types of silver disinfectant solutions using the experimental setup shown in Figure 1. Three metal coupons were immersed in 10 ml solution in a small glass test tube with a diameter of 0.5 inch. The position of the coupons was adjusted so that the total wetted surface of coupons was 50 cm², which resulted in a surface to volume ratio (S/V) of 5 cm⁻¹. Metal coupons and nylon washers (as spacers) were held together by threaded nylon rods and bolts over the solution. Experiment preparations were performed under low light conditions, while the immersion tests were performed in the dark. At the end of the exposure period, all solutions were tested for silver ion concentration. Each exposure condition was tested in triplicate.



Figure 1. Experimental setup for metal coupon exposure.

D. Analysis Methods

An Orion Ion Selective Electrode (ISE) by ThermoFisher Scientific was used to test silver ion concentration of the silver disinfectant solutions before and after coupon exposure. Surface analysis was also carried out on the test coupons before and after exposure, using a ThermoFisher Scientific K-Alpha X-ray Photoelectron Spectrometer (XPS) system, and a JEOL JSM-7500F Scanning Electron Microscopy (SEM).

III. Results and Discussion

A. Silver Depletion after Three Weeks

The silver depletion test results for stainless steel 316 after three-week exposure are shown below. With a beginning silver concentration of 0.4 ppm, and a high S/V ratio of 5 cm⁻¹, the silver loss rate was high. For every test condition, the total silver ion loss was above 94%. Surface treatment conditions, electropolishing vs thermal oxidation, only have a small effect on the outcome.

Table 3. Silver depletion results after three weeks.

Testing Material			Testing Condition		Silver Loss Rate	
Composition	Geometry	Surface Treatments	Silver Solution	S/V (cm ⁻¹)	Quantitative (after 3 weeks)	Qualitative
SS316	Coupons 0.5"×3" thickness: 0.05"	electropolished	0.4ppm (AgF)	5	98.3%	high
			0.4ppm (electrolytically generated)	5	98.7%	high
		Electropolished and thermal oxidized	0.4 ppm (AgF)	5	94.4%	high
			0.4ppm (electrolytically generated)	5	96.0%	high

B. Surface Analysis Before Exposure

Figure 3 shows the scanning electron microscopy (SEM) pictures of SS316 surfaces of an as-received, an electropolished, and a heat-treated coupon. As-received samples have a visibly dull surface, while electropolished the SS316 surface is visibly glossy with a metallic luster. After heat treatment, the SS316 surface becomes less glossy, with a purplish hue. Under SEM, the as-received coupon surface is rough and severely corroded, especially at grain boundaries; the electropolished surface is very smooth with visible grain boundaries, indicating a very thin and transparent passive oxide layer; after heat treatment, the surface is no longer smooth, and grain boundaries no longer visible. The surface change on the heat-treated coupon can be attributed to the formation of a thicker surface oxide layer.

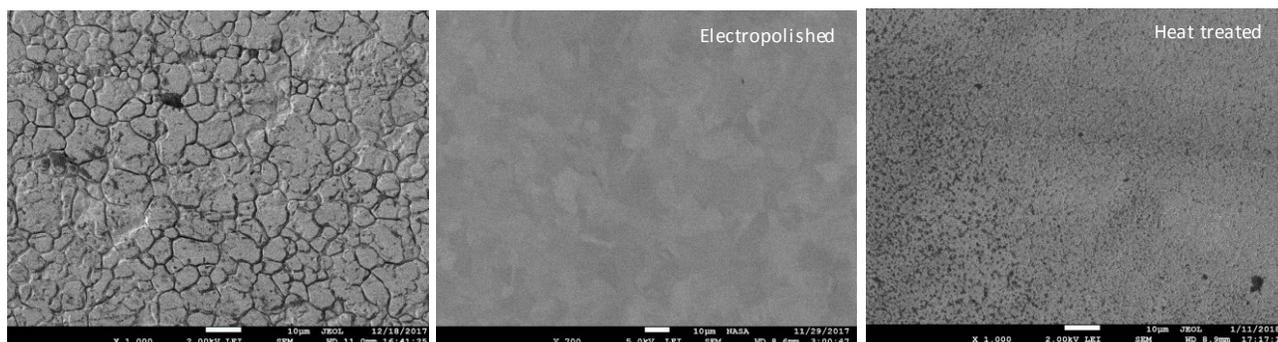


Figure 3. SEM images of the SS316 coupons before silver disinfectant solution exposure.

Figure 4 shows the depth profiles of electropolished SS316 (316EP). The sputter rate was 20 seconds per step for the spectrum on the left and 5 seconds per step for the spectrum on the right (showing more details near surface). The electropolished SS316 sample has a very thin oxide layer. The intensity of the O1s peak drops close to zero around a sputtering time of 40 seconds, corresponding to a 14 nm oxide layer under the given sputter setting. The oxide layer also shows a clear chromium (Cr) enrichment and a nickel (Ni) enrichment right below the oxide layer. The high Cr content in surface oxide film is a characteristic of stainless steel alloys, due to the contribution of Cr to the corrosion resistance of stainless steel.

Figure 5 shows the depth profiles of heat-treated SS316 (316EP+heat); the sputter rate was 20 second per step for the spectrum on the left and 5 seconds per step for the spectrum on the right. Heat-treated SS316 has a much thicker oxide layer. The intensity of the O1s peak intensity drops close to zero after 2000 seconds of sputtering, corresponding to an oxide layer of around 700 nm under the given sputter setting. The oxide layer also shows a slight enrichment of iron (Fe) on the very top surface of the oxide layer, but no signs of Cr enrichment. While this is a much thicker oxide layer, its corrosion resistance is questionable, due to its low Cr content in the oxide layer.

C. Surface Analysis after Exposure to Silver Disinfectants: Electropolished SS316

Figure 6 shows the SEM pictures of electropolished SS316 surfaces before exposure and after exposure to electrolytic Ag⁺ and AgF solutions. Both after-exposure surfaces of the electropolished SS316 coupons look similar to the surface before exposure. There might be a slight surface roughness change, but it is not obvious.

Figure 7 shows the XPS depth profiles of electropolished SS316 surface before and after exposure to electrolytic Ag⁺ solution. Figure 8 shows the XPS depth profiles of electropolished SS316 surface before and after exposure to

AgF solution. Both after exposure surfaces of the electropolished SS316 coupons are very similar to the surfaces before exposure, with a minor difference: the carbon content on the surface, which came from surface contaminants, which are much lower on the surface, indicating a cleaner surface after exposure, maybe a slight etching effect.

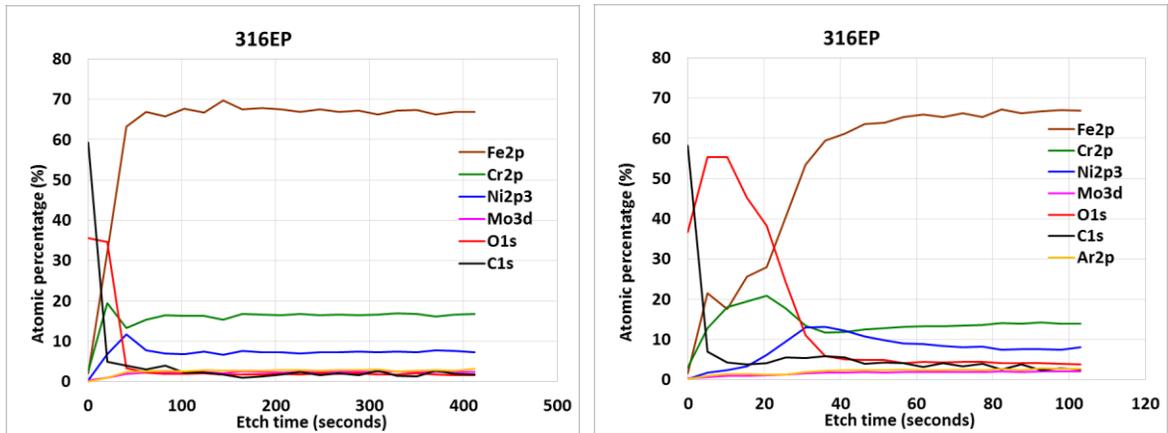


Figure 4. XPS depth profiles of the electropolished SS316 coupons before exposure.

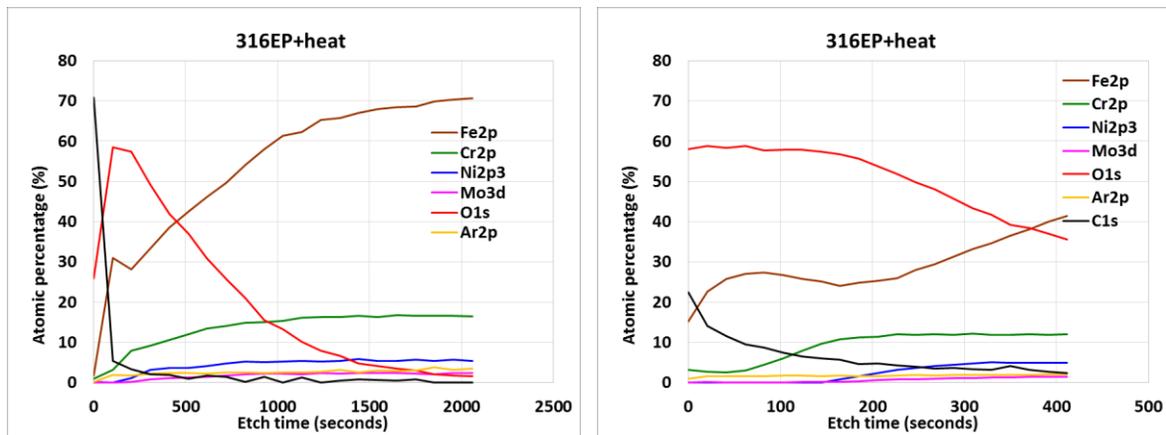


Figure 5. XPS depth profiles of the heat-treated SS316 coupons before exposure.

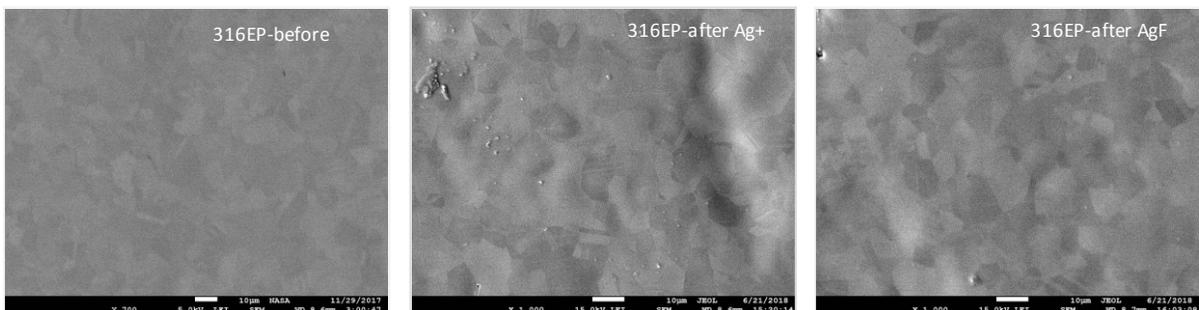


Figure 6. SEM images of the electropolished SS316 coupons before and after silver disinfectant solution exposure.

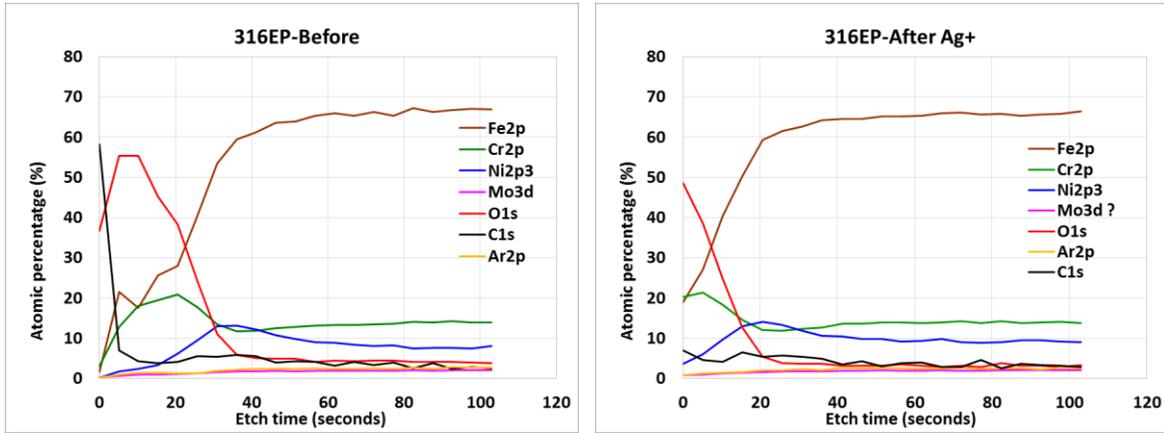


Figure 7. XPS depth profiles of the electropolished SS316 surfaces before and after electrolytic Ag⁺ exposure.

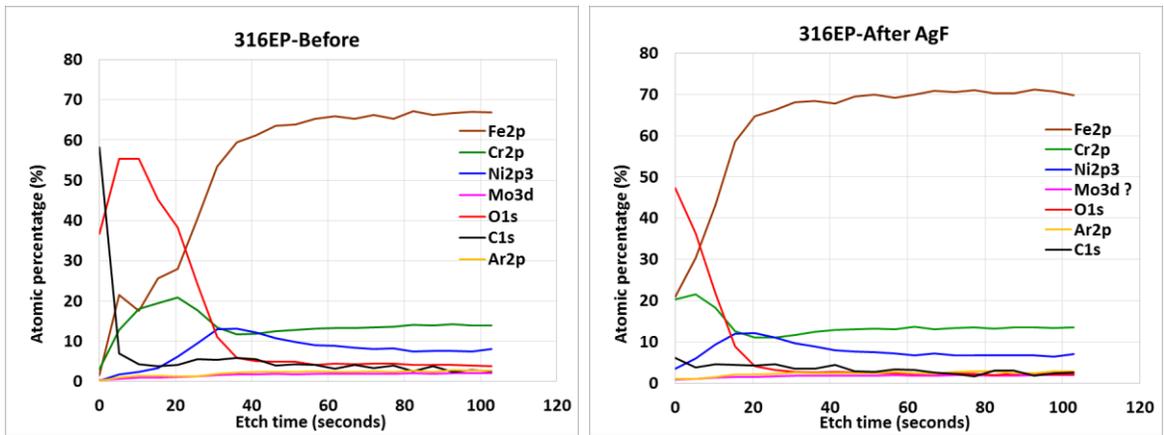


Figure 8. XPS depth profiles of the electropolished SS316 surfaces before and after AgF exposure.

D. Surface Analysis after exposure to silver disinfectants: heat-treated SS316

Figure 9 shows the SEM pictures of heat-treated SS316 surfaces before exposure, and the coupon surfaces after exposure to electrolytic Ag⁺ and AgF solutions. The two after-exposure surfaces of the heat-treated SS316 coupons look similar to each other, but there are clear changes of surface features for both exposed coupon surfaces. There are features indicating surface deposition and both surfaces show signs of grain boundary attack, or intergranular corrosion.

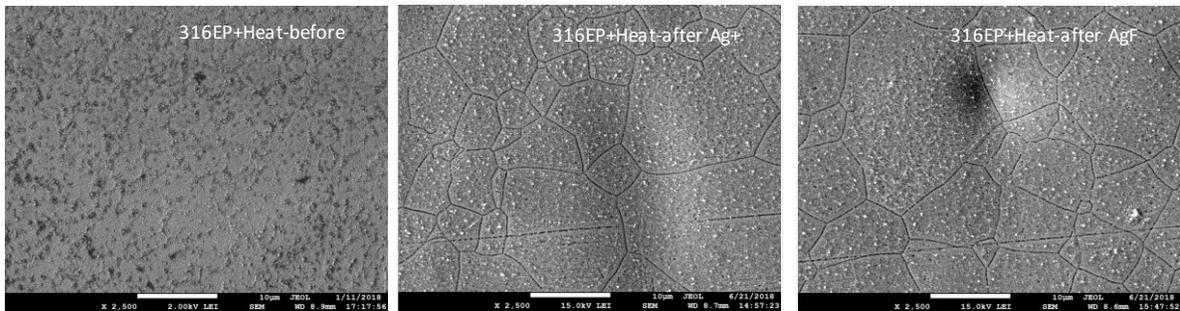


Figure 9. SEM images of the heat-treated SS316 coupons before and after silver disinfectant solution exposure.

Figure 10 shows a close up look at these surfaces. The SEM images show the presence of intergranular corrosion over the entire observed sample surface, as well as some pitting corrosion inside the grains.

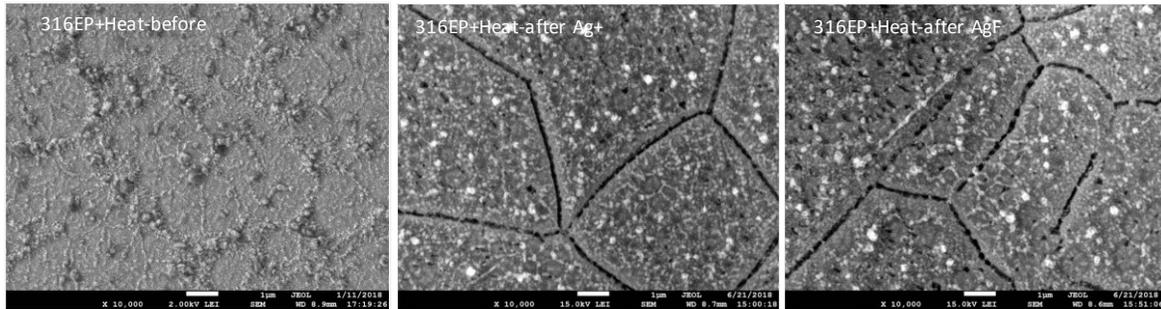


Figure 10. SEM images of the heat-treated SS316 coupons before and after silver disinfectant solution exposure.

Figure 11 shows the XPS depth profiles of the heat-treated SS316 surface before and after exposure to electrolytic Ag^+ solution. Figure 12 shows the XPS depth profiles of heat-treated SS316 surface before and after exposure to AgF solution.

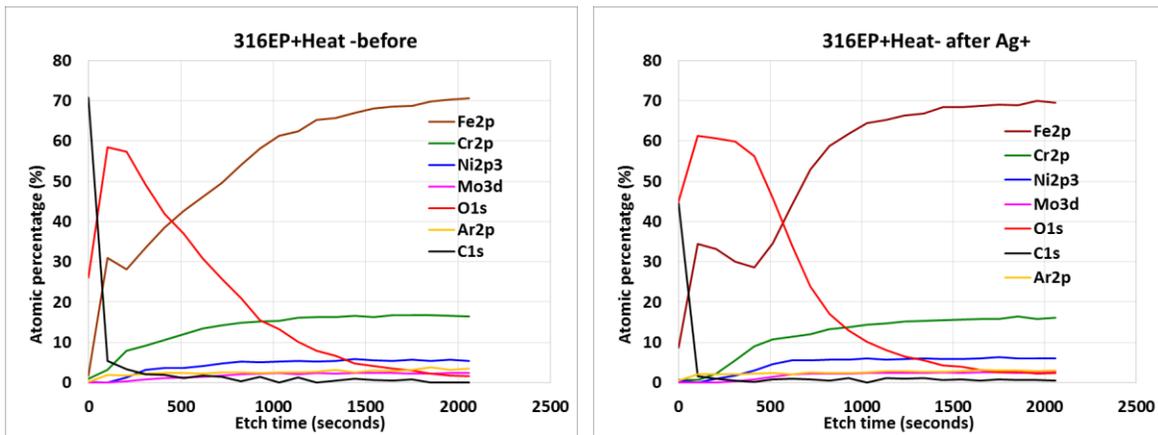


Figure 11. XPS depth profiles of the heat-treated SS316 surfaces before and after electrolytic Ag^+ exposure.

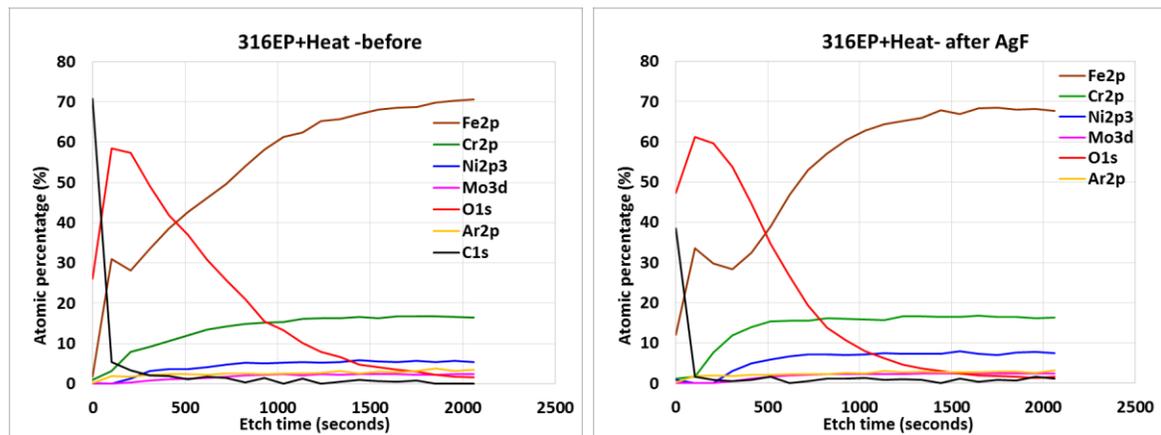


Figure 12. XPS depth profiles of the heat-treated SS316 surfaces before and after AgF solution exposure.

Both after exposure surfaces of the heat-treated SS316 coupons are very similar to the surfaces before exposure, with a very minor difference: the oxide layer (where oxygen content is about 60%) is thicker after exposure to electrolytic Ag⁺ solution; a similar trend can be observed in the case of AgF solution exposure, but it is less noticeable. The oxide layer thickness changes often indicate new oxidation or corrosion processes, consistent with the SEM observations.

IV. Conclusions

The material compatibility of stainless steel 316 with silver biocide was studied. The two surface conditions included electropolished with and without an additional thermal oxidation process. The surfaces were exposed to silver ion disinfectant from two silver ion sources: electrolytically generated and AgF solution. The surface treatments were compared for their effects on silver depletion. Under testing conditions that included a Ag⁺ ion concentration of 400 ppb and a surface to volume ratio of 5 cm⁻¹, the silver biocide was almost completely depleted from the water after three weeks of exposure. SEM and XPS analysis showed that thermal oxidation changes the oxide layer thickness, composition, and morphology. This early experimental results showed that thermal oxidation, when compared to electropolishing, resulted in a thicker oxide layer, but compromised the corrosion resistance of SS316.

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