Corrosion of Aluminum 3003-H14 in Tap Water, Salt Water, & Sulfuric Acid

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Abstract

Corrosion is a problem that many structural buildings suffer from as the materials oxidize with the atmospheric elements. The study investigates the surface characteristics of Aluminum 3003-H14 when coated with RUST-OLEUM High Performance Enamel. Placing the samples in a saltwater, tap water, and sulfuric acid solution were the parameters for corrosion. Microstructural observations revealed the formation of crystal particles on the coated surface with two of the solutions while different visuals were seen with the acidic solution. The chemical composition of the coated surfaces was analyzed to determine the durability of the enamel for the cost. The performance of the spray was limited with the time although it does require more dedicated time for accurate analysis. The cost and durability of the spray benefitted the corrosion protection of Al3003-H14.

1. Introduction

Aluminum alloys are in many applications due to their excellent mechanical, electrical and thermal properties coupled with lightness and high corrosion resistance in the pH range 4–9 [1]. Aluminum is protected by a spontaneously formed thin aluminum-oxide film that protects the underlying metal against corrosion [2]. The combination of water and salty air along the coastal areas allow the mixture to seep into metals, oxidizing the metal destroying the car. The moist saltwater air corrodes the cars much faster as having the metal submerged into water.

Corrosion occurs when atoms on the surface of the metal are oxidized by reacting with water. There are other substances that

can react causing corrosion, but water is one of the most common starters that begin a materials' corrosion process. In the case of saltwater, it is another starter which also corrodes metals. The salt in the water helps electrons flow freely from the metal to the oxygen, causing the reaction to occur faster. An increase in temperature also affects the rate of corrosion of the metal. Some metals have natural corrosion resistance such as aluminum. The layer is not reliable as it can be damaged or permanently removed, allowing oxidation of aluminum to begin breaking down the microstructure's integrity.

The automotive industry competes with lowering cost while maintaining rigorous environmental restrictions and simultaneously meeting higher safety requirements. The application of lightweight construction introduces high strength materials or lightweight materials which contain the highest promise. The weight reduction of automotive parts is one of the main decisive factors in material development as to meet legal requirements regarding the environmental protection [3].

With the high cost of aluminum raw materials, the development of a body-in-white (BIW) parts is in development yet keeps steel a bit more desirable. The corrosion-resistant sprays can help with the problem of metals losing their oxide layer or not having one at all. The corrosion-resistant sprays add a layer on top of the metals that ensures they remain intact from the oxidation reaction that corrodes the structures. While most manufactures repainting cost is expensive the durability of a commercially available spray paint allows the ability to repair affordable. Corrosion is a natural process that cost millions in damage, yet many methods and products have been dedicated to slowing down the destruction of materials.

2. **Experimental procedure**

2.1 Materials, sample preparation and chemicals

Aluminum alloy 3003-H14 (1.2% Mn) produced by Rose Metal Products (Michigan, USA) was used as the specimen in question. The samples used were cut in a square shape with dimensions 12.7mm x 12.7mm x 1.6mm with the TechCut 4x. Prior to enamel exposure of four aluminum pieces, samples were wiped down with acetone to remove any impurities on the surface. The samples were risen with DI and ethanol then placed in petri dishes allowing them to dry. In the absence of using N2 gas to speed up the drying process the samples were exposed to the environment briefly before entering the petri dishes.

The RUST-OLEUM High Performance Enamel (acetone, liquefied petroleum gas, N-butyl, acetate, aromatic hydrocarbons, and glycol ethers) coated four of the aluminum alloy samples. Precautions were taken to ensure the spraying of the samples occurred within the fume hood. While the coating on the samples was not distributed evenly the unevenness of the coating contains the human error that would occur in daily life. The sprayed samples were left to dry for 15 minutes, touched with tweezers then left to dry for 5 minutes more.

The following chemical was used for the experiment: H_2SO_4 (95.0-98.0%, ACS reagent, Sigma Aldrich) which was not diluted.

2.2 Immersion solution

The immersion solution of artificial sea water was prepared using 25mL of industrial water obtained through one of the research labs. The Instant Ocean is composed from: 19.268 g/L Cl, 10.767 g/L Na, 2.657 g/L SO_4^{2-}, 1.318 g/L Mg, .420 g/L K, .400 g/L Ca, .200 g/L HCO_3-, only amounted for 0.879g in the 25 mL of industrial water [4].

The other solution concerned only 25 mL of the industrial water as the 'tap' water. Although the consumption of the water was not consumable for humans. The minerals encompassing the water is unknown with unspecified concentrations of the elements.

2.3 Experimental setup

To test the durability of the enamel, spray the samples were exposed into the different water solutions for 4 days while the acidic solution only took 90 minutes. The water solution samples were placed into the same centrifuge tubes as the acidic samples were placed in the same jar. The cross-contamination of the specimens allowed the exchanging of reactions to occur among the samples. Once the samples were taken out of their solutions, they were placed into petri dishes to preserve any particles that had attached itself to the surface of the samples.

Solutions were made using the correct concentrations of Instant Ocean for the saltwater while the acidic solution amount was not measured accurately due to safety concerns.

The images below display the setup of the experiment. With combining both samples into the same container allows the unpredictability in life be accounted for as in many experiments might not simulate real world occurrences. In the case of the experiment the crosslinking of chemicals occurs daily in nature to which cannot be controlled.

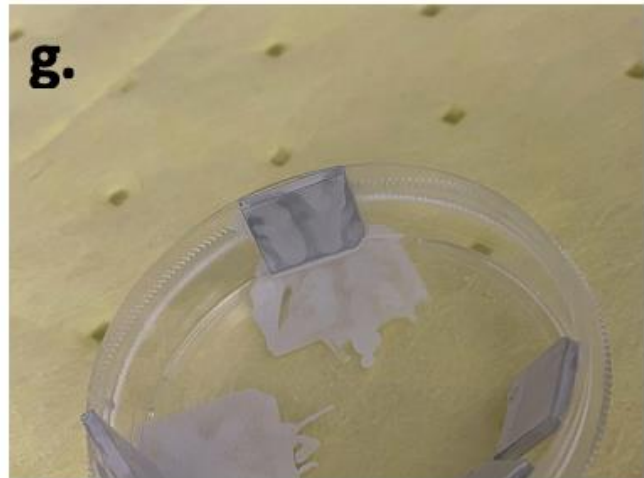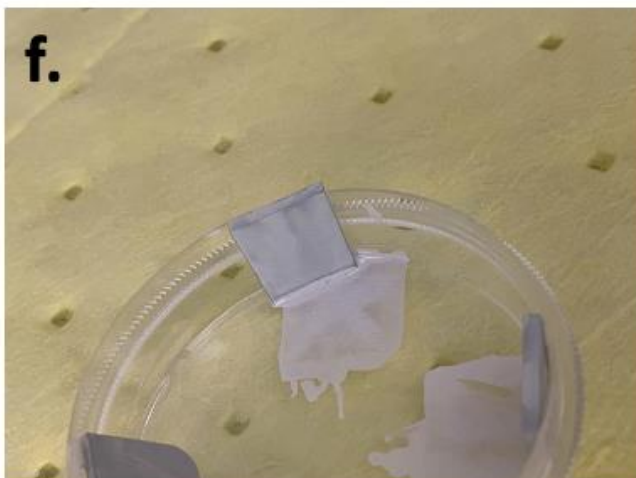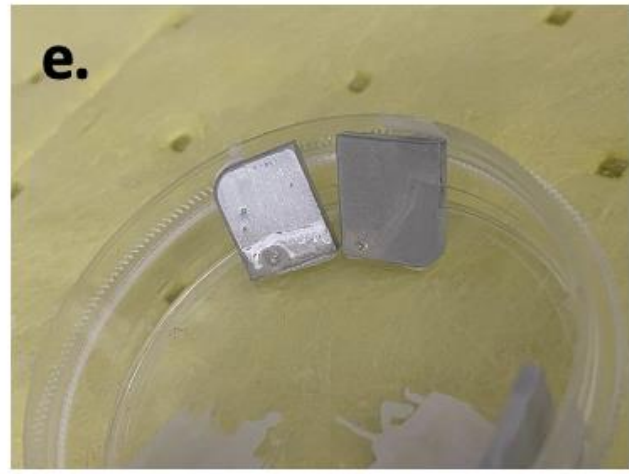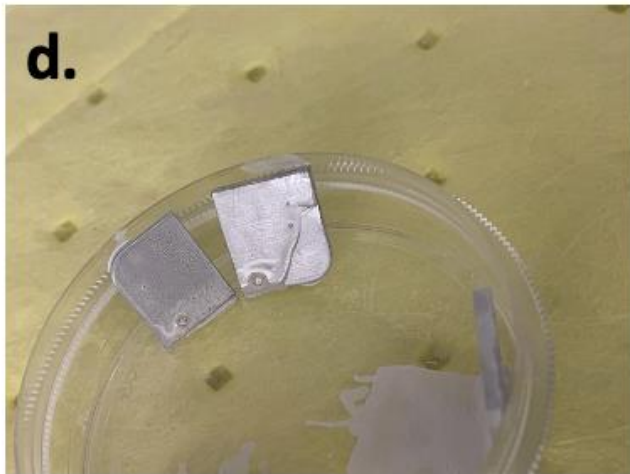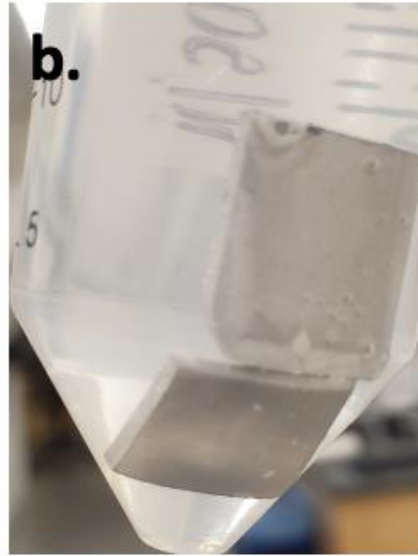**Fig. 1 .** (a) Tap water solution, (b) saltwater solution, (c) acid solution with the four different aluminum pieces. When selecting the samples similar sizes were placed together to ensure similar results between the samples. (d-g) the enamel protected samples

2.4 Microstructural characterization

Surface characterization was performed using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) techniques. SEM images were taken with a ZEISS GeminiSEM 500 in Inlens mode at 10-15 kV [5,6] with a 4000X [6]. The uncoated samples were placed into the SEM as the coated samples were used for the XPS analysis.

The XPS was used to assess the composition of the samples' surface. The use of Point scan allows a XPS survey of the sample. With the conditions of 2 scans along with having the flood gun off the graphs obtained have been resolved of any elements the machine was skeptical about. The confirmation of the elements present contributes to the accuracy of the chemical compounds on the samples.

3. Results and discussions

The images with the SEM were done with different voltages ranging from 3 eV – 15 eV. The magnification for the images was kept constant above 4000X. The SEM images for the uncovered aluminum will reveal the surface topography of the samples. The XPS survey graphs will provide specific elemental analysis of the topographical elements on the surface. Both will aid in determining the durability of the enamel.
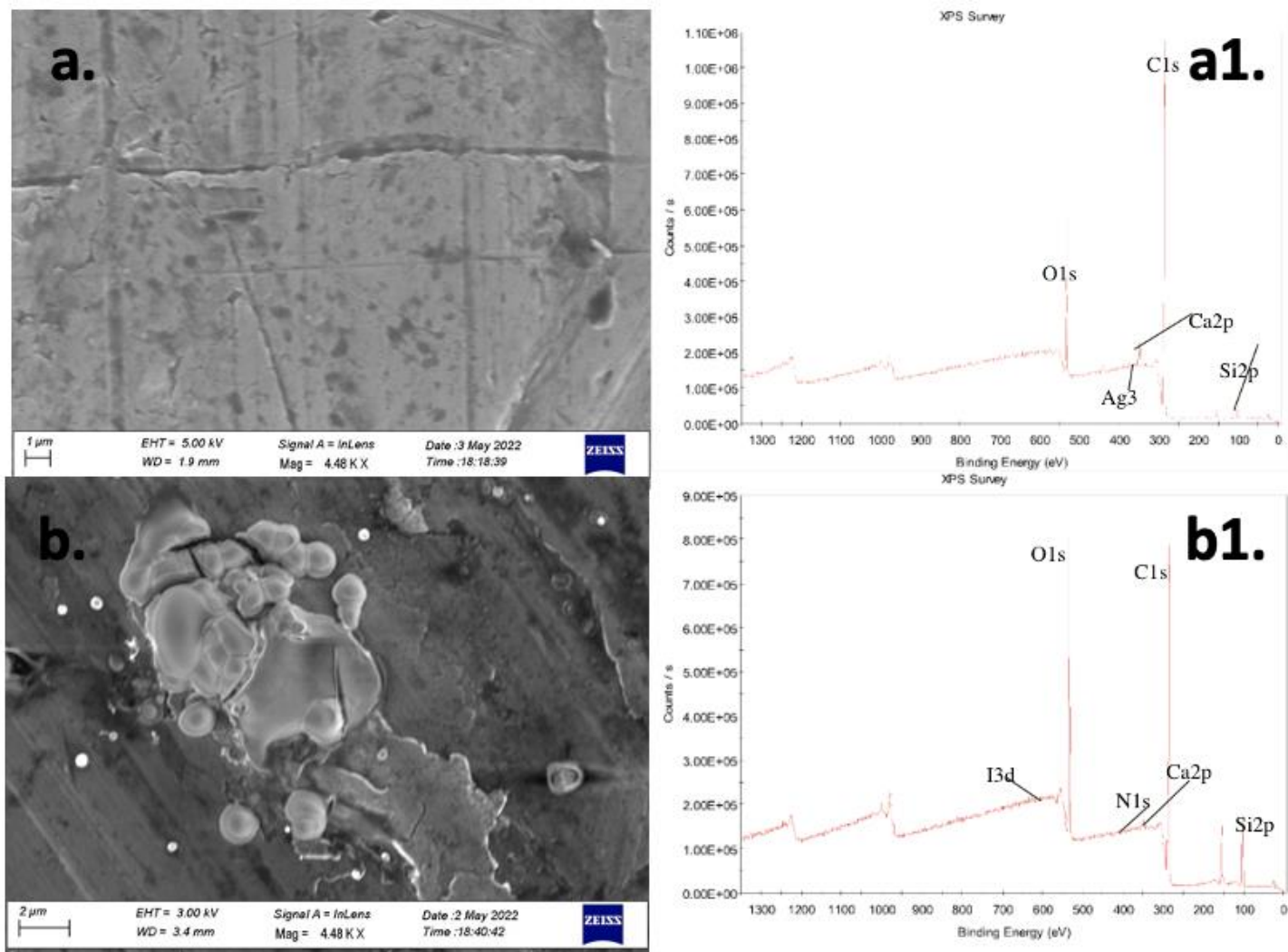
Fig. 2 . (a) SEM images of the uncoated samples and (a1) XPS graphs of the coated samples within the different solutions, (a) controlled [petri dish], (b) saltwater [Instant Ocean], (c, d) tap water [university water], and the (e, f) acidic variable [H₂SO₄]. The XPS graphs correlate to the corresponding SEM image with elements that have been deposited on the surfaces. (c) and (d) SEM images are of the same area under different voltages (c) 10kV and (d) 15kV.
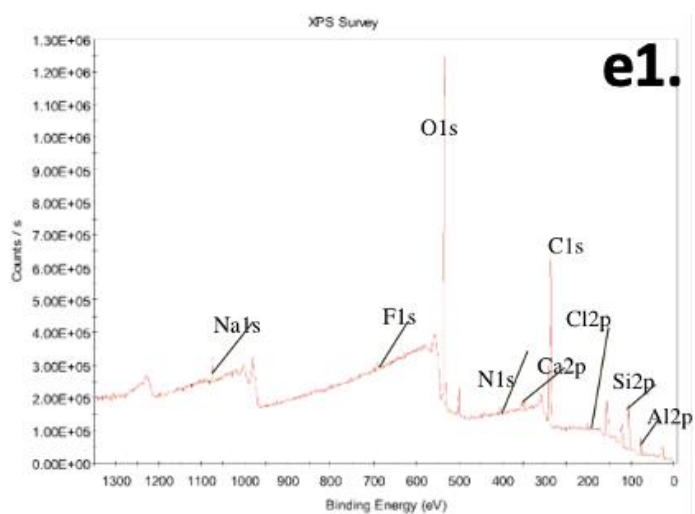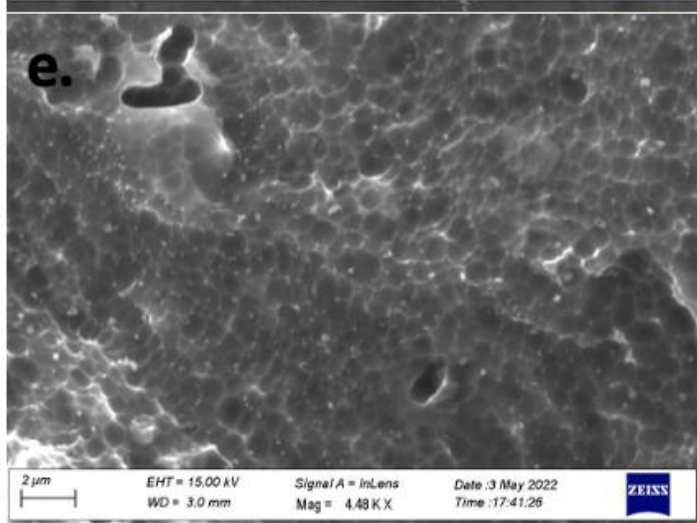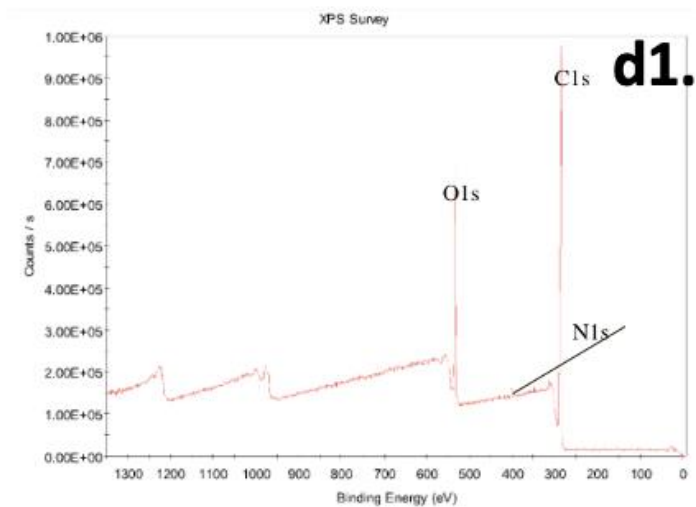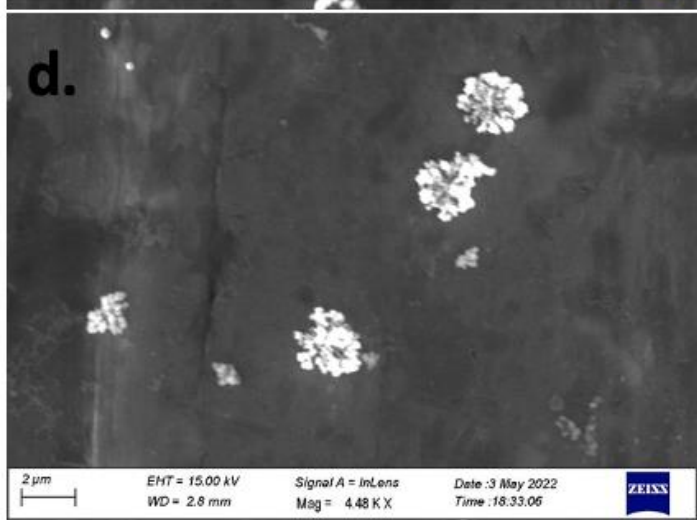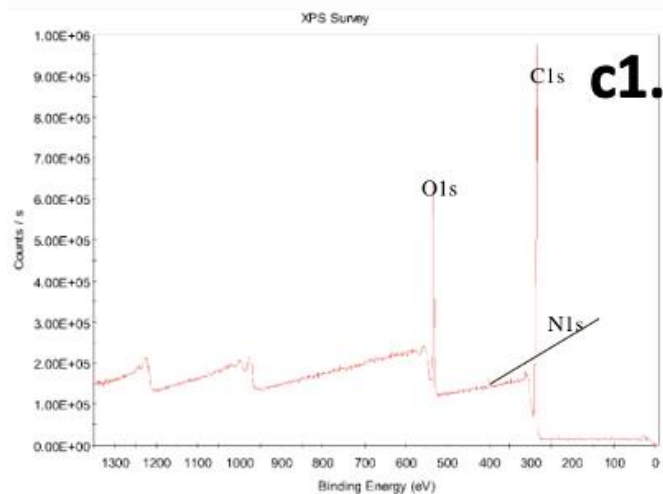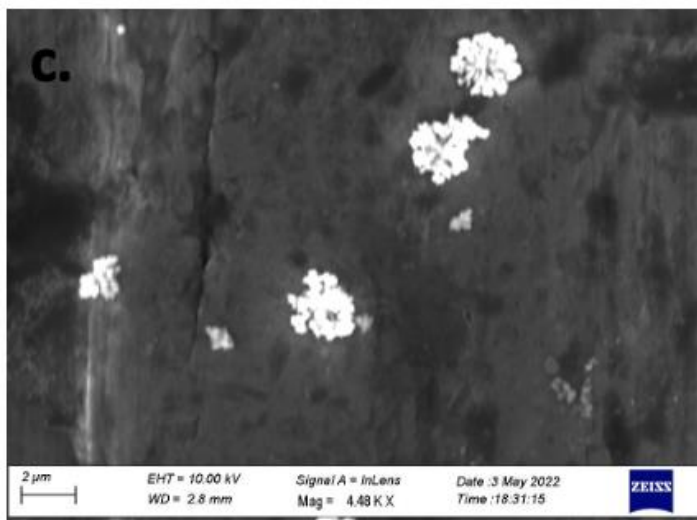
Fig. 3 . (e) and (f) are the acidic samples with (e) the uncoated sample and (f) the coated sample. The parameters for both images are under the exact circumstances, yet both contain drastically different images.
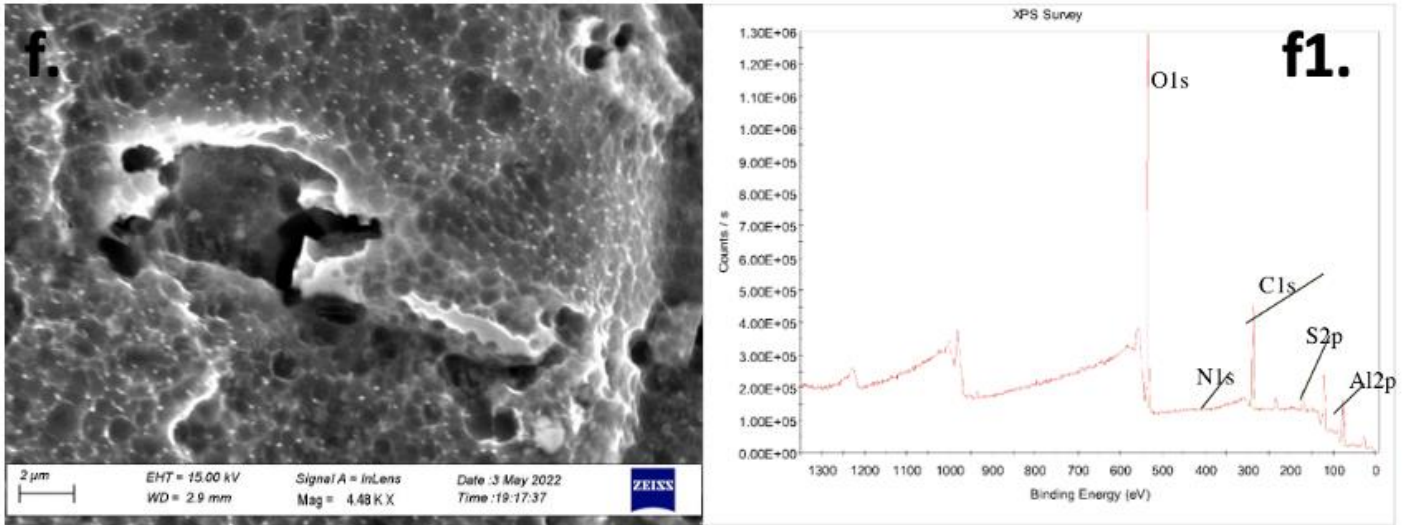
Fig. 4 . (f) the coated sample in acid. The hole seem is interesting as the efficiency of the acid decreases as time increases. The presence of the hole suggest that the part of the aluminum captured by the SEM might have had more sulfur anions reacting to the area causing the hole.

The images obtained with the use of the SEM and XPS allow the justification of the durability to corrosion the enamel is given the cost. Within fig. 1. the XPS surveys obtained show no exposure of aluminum. The notion of aluminum not being detected within the same solution as the uncovered sample, supports the durability of the enamel to withstand saltwater. The elements found on the surface of the coated sample with the XPS differs but provide information on what chemicals are being left on the surface.

During the experimental process with the acidic solution – after the 90 minutes of the sulfuric acid telling the two samples apart was difficult as the acid eroded the enamel away from the sample. With the XPS, differentiating between both became easier as the notion of sulfur would be evident in the aluminum specimen that was not exposed to the sulfuric acid. The reaction between aluminum and sulfuric acid releases hydrogen gas and forms aluminum sulphate.

$$2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2$$
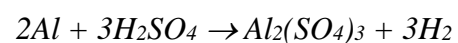
With identifying the presence of sulfur on one of the acidic samples allowed the images captured with the SEM to be correctly matched.

In fig. 1a. the surface of the uncoated aluminum contains no notion of deposited minerals. However, with the XPS the coated sample displayed Ag, Ca, Si, O, and C as elements detected. With having detected Ca the importance of calcium buildup is a common occurrence that can cause damage to cars. With washing cars, the buildup of calcium can be reduced and prevent another problem from escalating.

BEs of The Elements by XPS

Mean BEs from NIST SRD-20 Database v3.4
Standard Deviation for NIST Mean BE
Range (Spread) Between High and Low NIST BEs
Number (#) of BE Values Reported in NIST Database
MS-Excel Based Calculation of Confidence Level (95%)
for NIST Mean BE Value

Because the NIST database did not report BEs for some alkali
and alkaline elements, a common salt was substituted.

	1	2		13	14	15	16	17	18
	LiCl	Be		B	C	Si3N4	SiO2	MF	Ne(+)
Mean BE (NIST)	56.03	111.57		187.28	284.63	397.82	532.88	684.12	962.40
Std. Dev. (NIST)	0.21	0.25		0.85	0.42	0.48	0.42	1.04	0.75
BE Range (NIST)	0.40	0.50		2.00	1.52	1.72	2.30	3.50	1.80
# of NIST Values	3	3		5	15	35	51	20	4
95% Confid Level	0.52	0.63		1.06	0.23	0.17	0.12	0.49	1.19

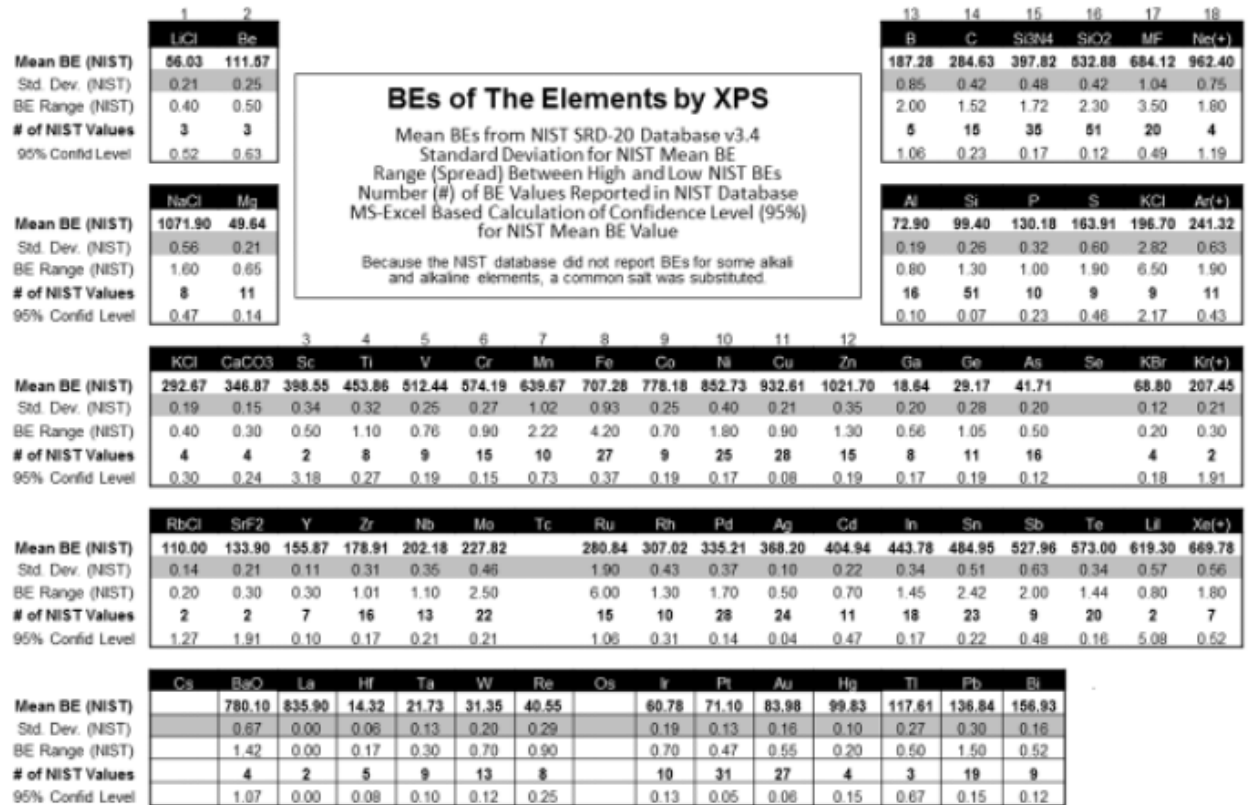|	NaCl	Mg		Al	Si	P	S	KCl	Ar(+)
Mean BE (NIST)	1071.90	49.64		72.90	99.40	130.18	163.91	196.70	241.32
Std. Dev. (NIST)	0.56	0.21		0.19	0.26	0.32	0.60	2.82	0.63
BE Range (NIST)	1.60	0.65		0.80	1.30	1.00	1.90	6.50	1.90
# of NIST Values	8	11		16	51	10	9	9	11
95% Confid Level	0.47	0.14		0.10	0.07	0.23	0.46	2.17	0.43

	3	4	5	6	7	8	9	10	11	12							
	KCl	CaCO3	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	KBr	Kr(+)
Mean BE (NIST)	292.67	346.87	398.55	453.86	512.44	574.19	639.67	707.28	778.18	852.73	932.61	1021.70	18.64	29.17	41.71		68.80	207.45
Std. Dev. (NIST)	0.19	0.15	0.34	0.32	0.25	0.27	1.02	0.93	0.25	0.40	0.21	0.35	0.20	0.28	0.20		0.12	0.21
BE Range (NIST)	0.40	0.30	0.50	1.10	0.76	0.90	2.22	4.20	0.70	1.80	0.90	1.30	0.56	1.05	0.50		0.20	0.30
# of NIST Values	4	4	2	8	9	15	10	27	9	25	28	15	8	11	16		4	2
95% Confid Level	0.30	0.24	3.18	0.27	0.19	0.15	0.73	0.37	0.19	0.17	0.08	0.19	0.17	0.19	0.12		0.18	1.91

	RbCl	SrF2	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	LiI	Xe(+)
Mean BE (NIST)	110.00	133.90	155.87	178.91	202.18	227.82		280.84	307.02	335.21	368.20	404.94	443.78	484.95	527.96	573.00	619.30	669.78
Std. Dev. (NIST)	0.14	0.21	0.11	0.31	0.35	0.46		1.90	0.43	0.37	0.10	0.22	0.34	0.51	0.63	0.34	0.57	0.56
BE Range (NIST)	0.20	0.30	0.30	1.01	1.10	2.50		6.00	1.30	1.70	0.50	0.70	1.45	2.42	2.00	1.44	0.80	1.80
# of NIST Values	2	2	7	16	13	22		15	10	28	24	11	18	23	9	20	2	7
95% Confid Level	1.27	1.91	0.10	0.17	0.21	0.21		1.06	0.31	0.14	0.04	0.47	0.17	0.22	0.48	0.16	5.08	0.52

	Cs	BaO	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi
Mean BE (NIST)		780.10	835.90	14.32	21.73	31.35	40.55		60.78	71.10	83.98	99.83	117.61	136.84	156.93
Std. Dev. (NIST)		0.67	0.00	0.06	0.13	0.20	0.29		0.19	0.13	0.16	0.10	0.27	0.30	0.16
BE Range (NIST)		1.42	0.00	0.17	0.30	0.70	0.90		0.70	0.47	0.55	0.20	0.50	1.50	0.52
# of NIST Values		4	2	5	9	13	8		10	31	27	4	3	19	9
95% Confid Level		1.07	0.00	0.08	0.10	0.12	0.25		0.13	0.05	0.06	0.15	0.67	0.15	0.12

Fig. 5 . Binding Energy chart of XPS elements; provided by XPS International,
https://www.xpsdata.com/xpsdata.htm

The XPS data was reconfirmed by fig. 5. as the elements detected by the machine contained the probability of being inaccurate. It allows the investigation of why some minerals were deposited to be solved as the reaction with the solution and the enamel be the reason why for the different minerals.

The reactions that occur with the enamel and solutions allow different

deposits of minerals, fig 3 (c,d) depict the particles attached to the uncoated aluminum surface. The strength of the attractive forces keeping the particles on aluminum are unknown as it was an unconsidered parameter. With the addition of heat into the mixture, the forces could have released the hold around the particle allowing them to detach or could have enhanced the process which further destroys the material. The durability investigation of the enamel with

aluminum elicits the cost effectiveness of the product.

For the cost of effectiveness, the enamel requires more test aimed at corrosion to develop faster layers to the metal while keeping the same strength.

4. Conclusion

The corrosion behavior of aluminum alloy Al3003-H14 in tap water, artificial saltwater, and an acidic solution was investigated for its' surface topography. The elements that were found with the saltwater solution displayed no perception of aluminum with the coated sample. The enamel held up against the artificial saltwater created protecting the aluminum. With the input of human error concerning the coating, the aluminum bonded well to the spray allowing the natural oxide layer of the aluminum to be untampered with.

Although the enamel held up for 4 days, further research is needed to fully confirm if the cost of the spray corresponds positively to the durability. Another notion is that while these samples were submerged in saltwater, the salt particles in the air are much more destructive rather than in a solution. Moreover, the enamel was not place under the circumstances of evaporating saltwater – an investigation into the difference of submerged and evaporated saltwater is another path to expand on.

With knowing the elements on the surface, the experiment can explore further into sprays which can react with the elements left into another oxide layer – if desired. Given more time a deeper analysis concerning the change in pH and salinity can be investigated with the solutions. Equipment for investigating the concentrations would need a budget as tools are not cheap.

The next step for the project can expand in many areas as corrosion is a problem yet to have been solved for metals.

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