Evaluation of Encapsulated Inhibitor for Autonomous Corrosion Protection

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ABSTRACT

This work concerns the development of smart coating technologies based on microencapsulation for the autonomous control of corrosion. Microencapsulation allows the incorporation of corrosion inhibitors into coating which provides protection through corrosion-controlled release of these inhibitors.

One critical aspect of a corrosion protective smart coating is the selection of corrosion inhibitor for encapsulation and comparison of the inhibitor function before and after encapsulation. For this purpose, a systematic approach is being used to evaluate free and encapsulated corrosion inhibitors by salt immersion. Visual, optical microscope, and Scanning Electron Microscope (with low-angle backscatter electron detector) are used to evaluate these inhibitors. It has been found that the combination of different characterization tools provide an effective method for evaluation of early stage localized corrosion and the effectiveness of corrosion inhibitors.

INTRODUCTION

The development of a smart multifunctional corrosion-protective coating system, based on a pH-sensitive delivery system, has evolved significantly over the last few years [1-4]. This effort has resulted in a coating that incorporates pH-sensitive microcontainers that can encapsulate corrosion indicators, corrosion inhibitors, and self-healing agents to achieve the desired functionalities of early corrosion detection, controlled release of corrosion inhibitor(s), and self-healing of mechanical damage.

One critical aspect of a corrosion protective smart coating is the selection of corrosion inhibitor for encapsulation and comparison of the inhibitor function before and after encapsulation. This paper presents a systematic approach being used to evaluate free and encapsulated corrosion inhibitors by salt immersion before they are tested in coating formulations.

2-Mercaptobenzothiazole (2-MBT) was selected as an example of an organic inhibitor for this study. 2-MBT is well known as an effective corrosion inhibitor for Cu and its alloys. The general understanding of its inhibitive properties is the formation of an insoluble metal complex, Cu(MBT) [5,6], which provides a protective film on metal substrate. It also has been investigated as an effective corrosion inhibitor for aluminum 2024 [7-11], possibly due to its interaction with copper-rich intermetallic particles.

Though 2-MBT has great potential as an effective corrosion inhibitor, it has been difficult to be incorporated into organic coating due to its high reactivity with resin systems. To overcome this challenge, 2-MBT has been encapsulated into different pH-sensitive microparticles to improve its coating compatibility. Before these microparticles are tested in organic coating for their corrosion protection of Al 2024, they are tested by salt immersion to compare their corrosion protection abilities for Al 2024, and also used to observe their interaction with pure copper in order to provide insight on their protection mechanism.

In this paper, inhibitor 2-MBT, encapsulated 2-MBT (Figure 1a) and inorganic inhibitor particle SiNaMBTPS (Figure 1b) immersion tests will be presented with some quick highlights on inhibitor performance in coating tests. A copper immersion test will also be presented to determine 2-MBT's interactions with the metal.

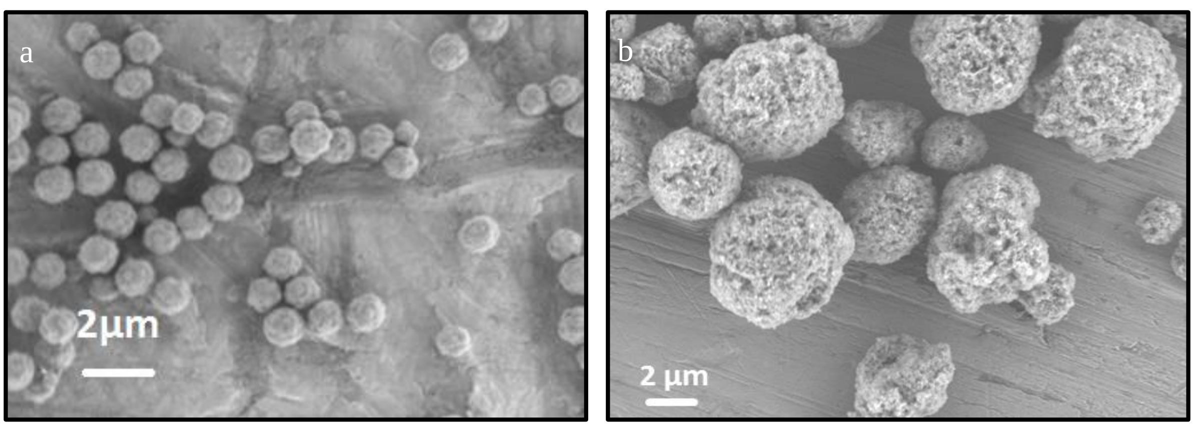


Figure 1: SEM images of (a) 2-MBT Particles and (b) SiNaMBTPS Particles

EXPERIMENTAL PROCEDURE

Aluminum 2024 Immersion Test

Aluminum 2024 T3 bare was used for the immersion test. Typical Aluminum 2024 composition is shown in Table 1. Samples were cut into 3.3mm long by 1.0mm wide by 0.1mm thick panels, and cleaned using water and detergent and dried before testing.

Table 1: Aluminum 2024 composition [14]

Component	Mg	Si	Ti	Cr	Mn	Fe	Cu	Zn	Al
Weight %	1.2-1.8	0.5	0.15	0.1	0.3-0.9	0.5	3.8-4.9	0.25	Remaining

Immersion testing was performed on the substrate. A control solution, 3.5% sodium chloride (NaCl), and three inhibitor solutions, 3.5% NaCl with 0.1% 2-MBT, 0.2% 2-MBT particles (50% 2-MBT) and 0.3% SiNaMBTPS particles (33% 2-MBT), were prepared for testing.

Each solution was poured into a glass containers, the 2024 panels were then added to the solutions. The solutions were loosely covered and left to sit for 14 days. The 2024 substrates were removed from the solutions after 14 days and sonicated to remove any loose deposition. Photos of the panels were taken before and following sonication. Optical Microscopy was performed on the panels using a Hirox KH-7700 microscope. Scanning Electron Microscopy (SEM) using lower secondary electron image (LEI) mode and the low angle backscatter detector (LABE) were performed on the panels using a JEOL 7500F SEM. Energy dispersive spectroscopy (EDS) was performed on the panels as well using a Thermo Scientific NORAN System 6.

Copper Immersion Test

Pure copper was cut into 5mm by 5mm pieces. The copper was polished using 3 micron media. Immersion testing was performed on the copper for 7 days using the same solutions used for aluminum 2024. The copper was removed from the solution and sonicated following the immersion. The panels were analyzed using optical microscopy, SEM and EDS using the same setup as the aluminum 2024 immersion.

Coating Evaluation

The aluminum substrate used for this test was a 3 in. x 6 in. panel of aluminum 2024-T3 bare supplied by Tri-Tech Metals. An epoxy-amine coating system was selected for this test as a model coating for the protection of aluminum alloy and to test the effectiveness of the added 2-MBT microcontainers for corrosion protection.
The substrate was prepped by abrading the surface to aid in adhesion and cleaning it using soap and warm water followed by an acetone wash and forced air drying. After prepping the substrate, the coating was applied using the #80 formed rod. The coating was allowed to cure for 7 days before being tested. Scribes in the shape of an “X” where made using a computerized engraving machine to ensure consistency from one panel to the next.
Microcontainers with corrosion inhibitors were incorporated into the epoxy-amine coating before it was applied for additional corrosion protection. Different coatings were made with various types of microcontainers loaded with various inhibitors to compare their corrosion protection performance. There were no noticeable issues with the incorporation of the microcontainers. The completed coatings were then placed in a salt fog chamber and tested according to the ASTM B117 standard [12].

RESULTS AND DISCUSSION

After the initial immersion test was completed, analysis was performed on the panels consisting of optical photos, SEM photos and EDS analysis. While the optical and SEM photos are purely visual analysis, the EDS is able to determine the composition of intermetallic particles in the 2024 aluminum alloy. Pitting corrosion tends to be the most common form of corrosion on the alloy and this is largely due to the intermetallic compound’s dissolution. The three intermetallic particles generally found in 2024 are Al-Cu, Al-Cu-Mg and Al-Cu-Fe-Mn. These compounds are considered coarse intermetallic particles and can be large in size [13].

AL 2024 Immersion Test

The results of the immersion tests are presented below. Camera and optical microscopy photos were taken following the immersion testing, as can be seen in Figure 2 below. The control panel is clearly discolored, while all three inhibitors samples are relatively corrosion free, by visual observation.

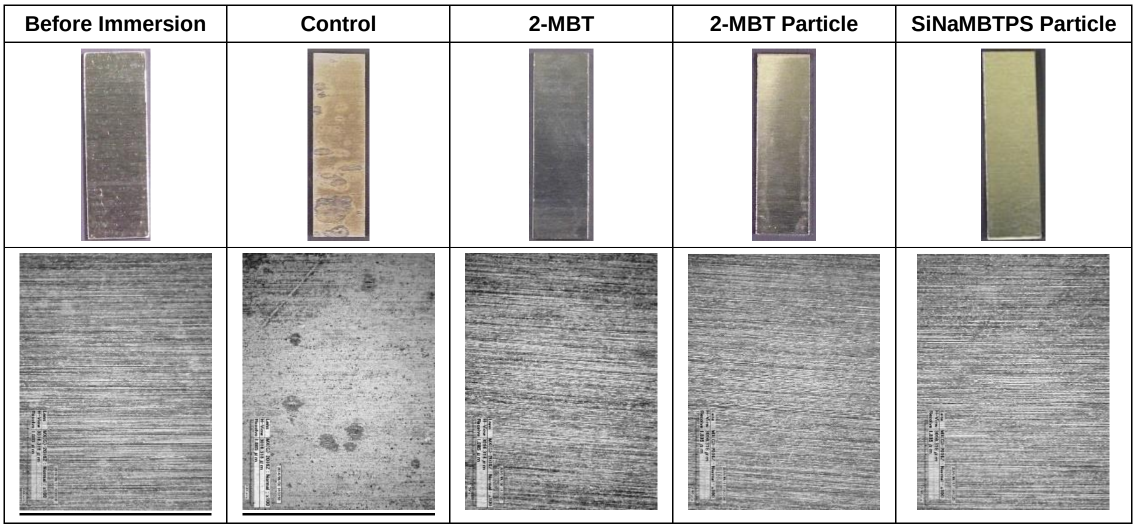


Figure 2: Camera and optical microscopy photos following immersion.

<u>Before Immersion</u>

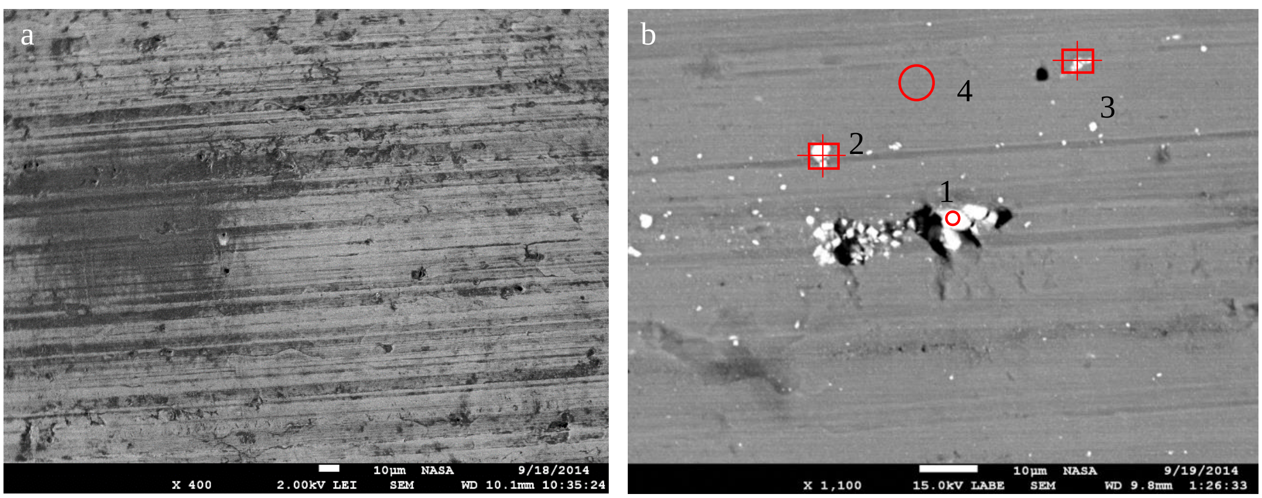


Figure 3: Before Immersion SEM (a) LEI 400x and (b) LABE 1100x point and shoot EDS

The 2024 panel before immersion was analyzed to provide comparison for immersed panels. In Figure 3b, it can be seen that there are three points on the photo situated on intermetallic particles. The points are point 1, 2 and 3. In table 4, the composition of each point can be identified. For the selected three points, each are rich in aluminum, copper, iron, and manganese. These intermetallic particles are determined to be the Al-Cu-Fe-Mn type. Point 4 shows a representative area of aluminum matrix. Because the before immersion panel is set to be the baseline for good performing inhibitors and particles, it is expected to see similar types of intermetallic particles with no pitting corrosion surrounding them.

Table 2: Before immersion point and shoot EDS analysis

	Al	O	Cu	Mg	Mn	Fe	C
Pt 1	48.18%	14.60%	10.23%	0.96%	2.61%	3.43%	19.97%
Pt 2	45.77%	10.64%	11.90%	1.52%	2.02%	3.59%	24.55%
Pt 3	61.30%	4.48%	7.70%	0.89%	1.35%	2.37%	21.91%
Pt 4	75.75%	6.79%	1.50%	0.77%			15.19%

<u>Control</u>

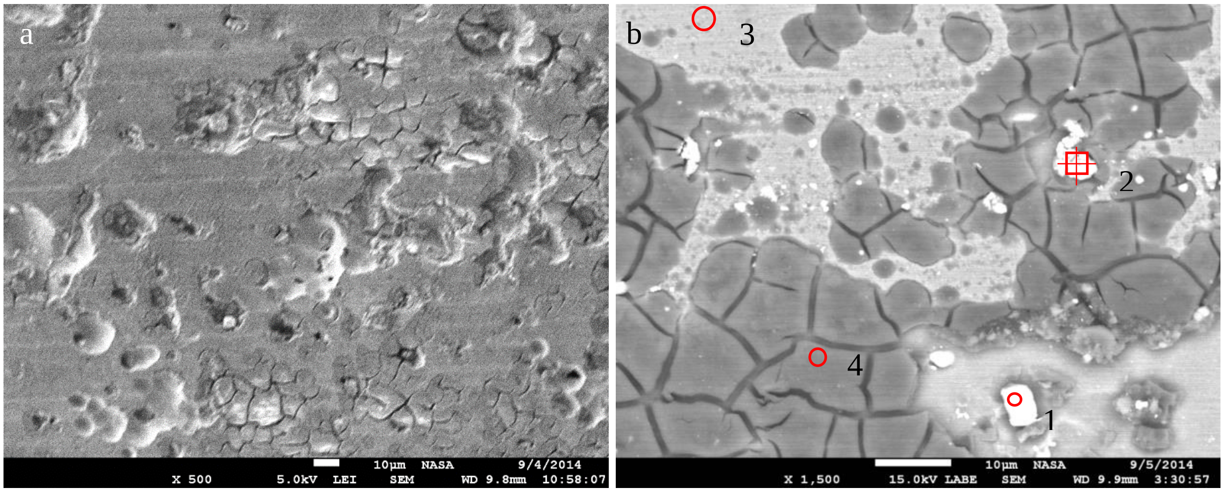


Figure 4: Control SEM (a) LEI 500x and (b) LABE 1400x point and shoot EDS

The control sample shows severe corrosion around the intermetallic particles and throughout the metal surface. There is a thick and cracked oxide layer on top of the sample. The two EDS points on intermetallic particles, points 1 and 2, can be seen in figure 4b. Point 2 is an Al-Cu-Fe-Mn intermetallic particle, with some trenching around the particle. Point 1 is a completely intact Al-Cu-Mg particle, with surrounding aluminum matrix selectively dissolved. The remaining points on the control are of a thick oxide layer formation (point 4) and the bare metal where the oxide layer peeled off (point 3). While Al-Cu-Fe-Mn is a typical cathodic intermetallic phase that causes pitting in surround matrix, Al-Cu-Mg can serve as an anodic site, go through selective dissolution itself, or serve as cathodic intermetallic phase that causes pitting corrosion around it, as seen here [13].

Table 3: Control point and shoot EDS analysis

	Al	O	Cu	Mg	S	Ca	Mn	Fe	C
Pt 1	14.77%	27.31%	16.06%	3.43%		0.20%			37.86%
Pt 2	30.70%	17.28%	8.93%				1.29%	2.93%	38.87%
Pt 3	61.07%	12.88%	1.77%	0.84%					23.44%
Pt 4	27.05%	54.13%		0.26%	0.16%	0.17%	0.17%		18.05%

2-MBT

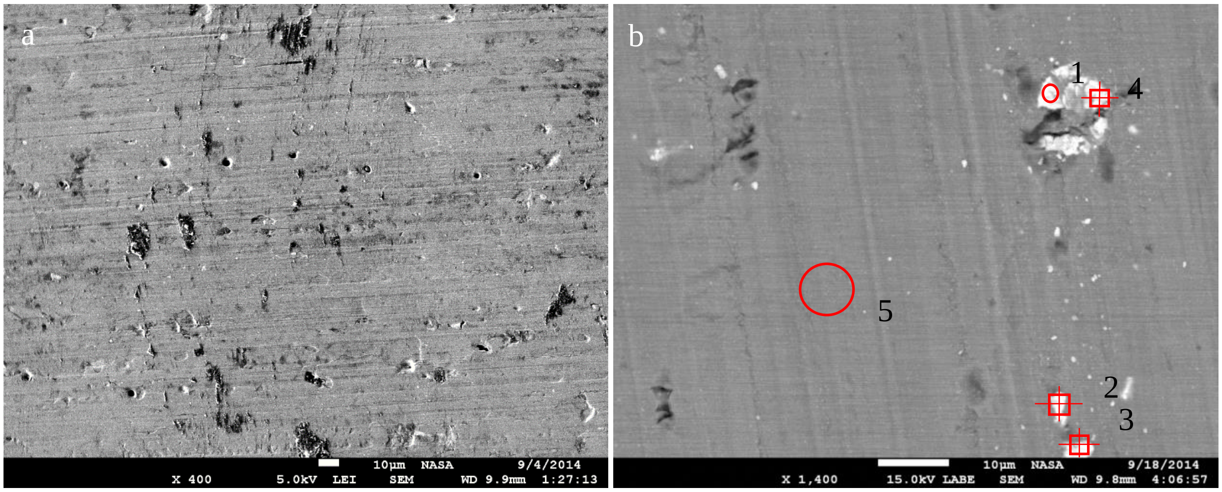


Figure 5: 2-MBT SEM (a) LEI 400x and (b) LABE 1400x point and shoot EDS

The panel in 2-MBT solution performed well and had good protection against corrosion. It had intermetallic particle Al-Cu-Fe-Mn on points 1, 3 and 4, as can be seen in Figure 5b and Table 4. It also had an intermetallic particle that was rich in silica, Al-Cu-Fe-Mn-Si, on point 2. The panel had a very clean appearance with no corrosion around the intermetallic particles or on the general surface (point 5).

Table 4: 2-MBT point and shoot EDS analysis

	Al	O	Cu	Mg	Si	Mn	Fe	C
Pt 1	48.24%	4.57%	10.74%	1.23%		2.35%	3.57%	29.32%
Pt 2	49.66%	4.05%	7.41%		0.74%	2.17%	4.60%	31.37%
Pt 3	52%	8.78%	12.36%	0.82%		2.53%	4.19%	19.32%
Pt 4	44.43%	11.28%	10.05%	1.44%		1.74%	3.64%	27.44%
Pt 5	78.69%	4.95%	1.43%	0.71%				14.22%

2-MBT Particles

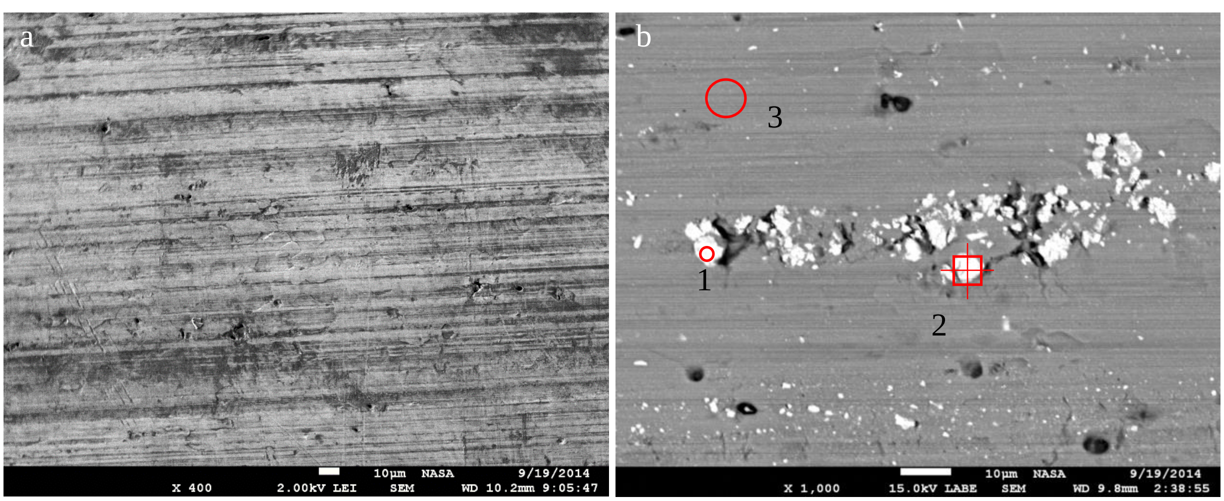


Figure 6: 2-MBT particles SEM (a) LEI 400x and (b) LABE 1000x point and shoot EDS

2-MBT particles performed well, with intermetallic particles Al-Cu-Fe-Mn on points 1 and 2, as can be seen in Figure 6 and Table 5. The panel itself was clean (point 3) with the exception of a few dark spots, which could be attributed to deposition from the particle.

Table 5: 2-MBT Particles point and shoot EDS analysis

	Al	O	Cu	Mg	Fe	Mn	C
Pt 1	41.65%	13.83%	10.33%	0.72%	3.74%	2.04%	27.70%
Pt 2	48.51%	10.91%	12.63%	0.81%	4.41%	2.39%	20.33%
Pt 3	75.04%	3.74%	1.45%	0.98%			18.78%

<u>SiNaMBTPS Particles</u>

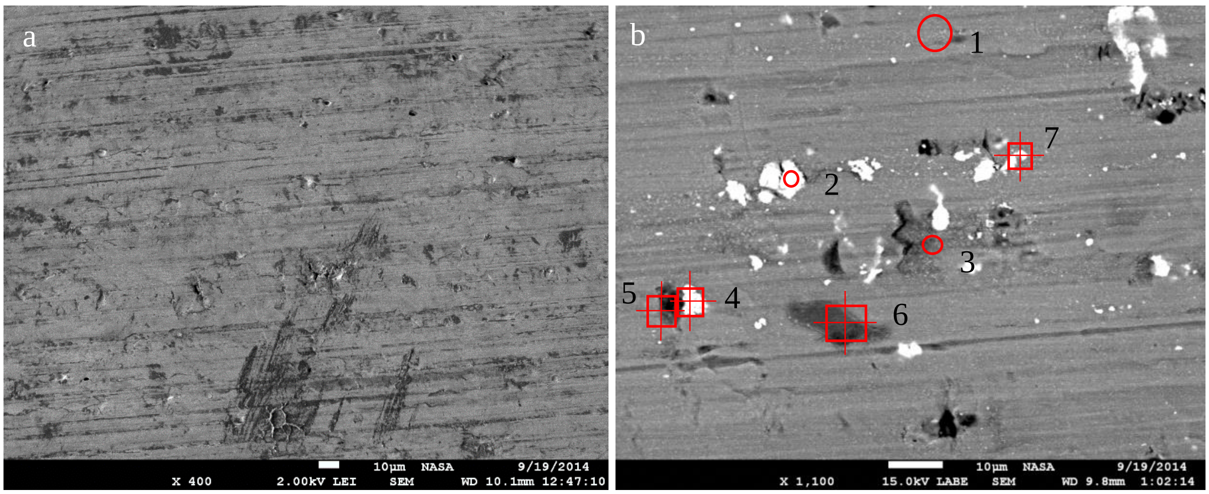


Figure 7: SiNaMBTPS particles SEM (a) LEI 400x and (b) LABE 1100x point and shoot EDS

The panel in SiNaMBTPS particle solution had some silicon rich spots (point 5 and 6), as well as some magnesium rich areas (point 3) and intermetallic particles, Al-Cu-Fe-Mn, which can be seen in Figure 7b and Table 6. The intermetallic particles Al-Cu-Fe-Mn were on points 2, 4 and 7. The panel performed well, there is no corrosion around the intermetallic particles. The silicon rich spots also are rich in carbon, with a dark appearance in LABE image, they are likely particle depositions on the surface.

Table 6: SiNaMBTPS Particles point and shoot EDS analysis

	Al	O	Cu	Fe	Mg	Si	Ca	Mn	C
Pt 1	83.98%	4.17%	1.55%		1.08%			0.36%	8.86%
Pt 2	68.98%	8.79%	12.72%	4.18%	1.45%			3.88%	
Pt 3	46.13%	25.60%	1.16%		3.56%				23.55%
Pt 4	55.11%	8.75%	5.26%	1.34%	0.91%			1.26%	27.36%
Pt 5	37.18%	30.11%	0.81%		0.73%	1.52%	0.10%	0.29%	29.26%
Pt 6	25.92%	8.99%	0.57%		0.33%	2.37%		0.10%	61.73%
Pt 7	48.27%	9.98%	11.70%	4.05%	1.68%	0.25%		2.07%	22.01%

In summary, encapsulated 2-MBT and free 2-MBT performed very well to protect Al 2024 substrate under testing condition. Deposition caused some carbon heavy spots on a few of the panels, but it didn't appear to cause any corrosion.

Part 2- Pure copper immersion test

Salt immersion test of pure copper was used to observe the interaction of free and encapsulated 2-MBT with pure copper in order to provide insight on their protection mechanism.

Each sample has a photo, an optical microscope photo at 100x zoom, a LEI SEM photo at 1400x zoom and a LABE SEM photo at 1400x zoom, as well as a table for point and shoot EDS compositions.

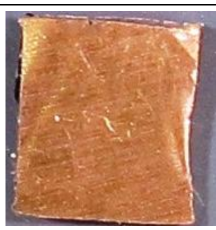
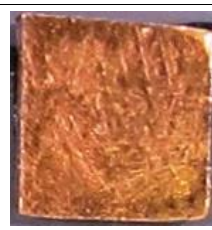
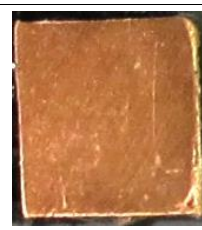
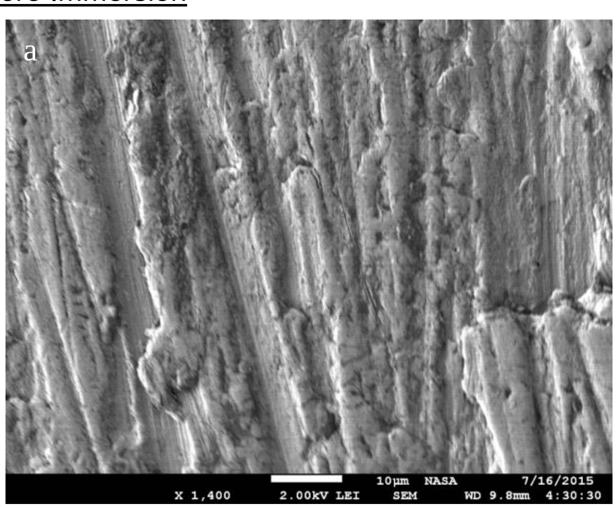
Before Immersion	Control	2-MBT	2-MBT Particles	SiNaMBTPS Particles
				
				

Figure 8: Photo and optical photos (100x) following immersion

A before immersion copper sample and a control copper sample are shown to evaluate the performance of the inhibitor and particles. The before immersion panel is shown for comparison. The control panel is discolored, with a gray-greenish tone. Among 2-MBT containing samples, both free 2-MBT particle and 2-MBT particle samples are largely intact, maintaining their shiny appearance, while the SiNaMBTPS particle sample has a somewhat darker tone.

<u>Before Immersion</u>



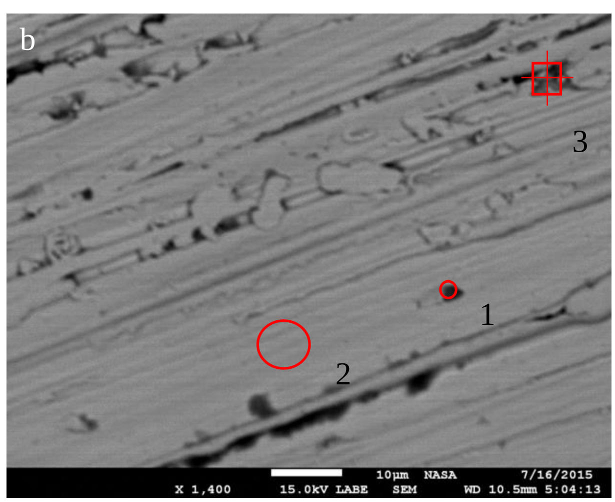


Figure 9: Copper before immersion (a) LEI 1400x and (b) LABE 1400x point and shoot EDS

The copper surface before immersion shows a clean surface without many features besides polish lines, the overall surface is free of oxide (point 2), with some occasional inclusion of polishing media rich in Si and C (point 1), which can be seen in Figure 9 and Table 7.

Table 7: Copper before Immersion Point and Shoot EDS Analysis

	Cu	Al	O	Si	Ca	C
Pt 1	25.29		28.42	5.52	2.02	38.74
Pt 2	98.24	1.76				
Pt 3	38.49	2.74	3.14			55.63

<u>Control</u>

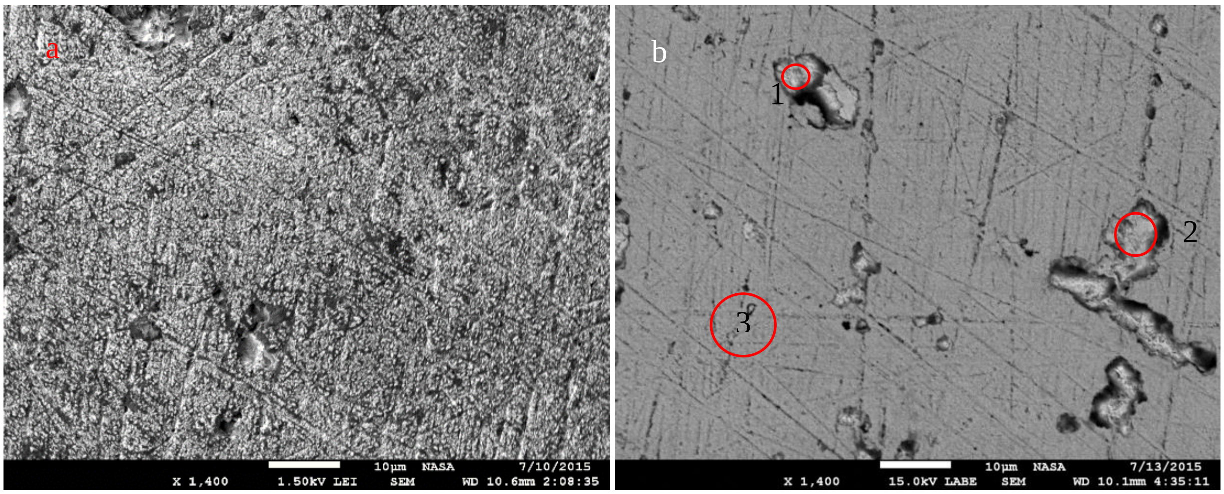


Figure 10: Copper control SEM (a) LEI 1400x and (b) LABE 1400x point and shoot EDS

The copper control sample surface shows a heavily corroded surface, with a grainy look. The overall surface is covered by oxide (point 3) and there are some pits around 10 microns or larger (point 1 and 2), as shown in Figure 10 and Table 8.

Table 8: Copper Control Point and Shoot EDS Analysis

	Cu	N	O	Si	C
Pt 1	37.46		8.18	0.53	53.83
Pt 2	29.62		8.12	0.57	61.68
Pt 3	67.03		32	0.97	

2-MBT

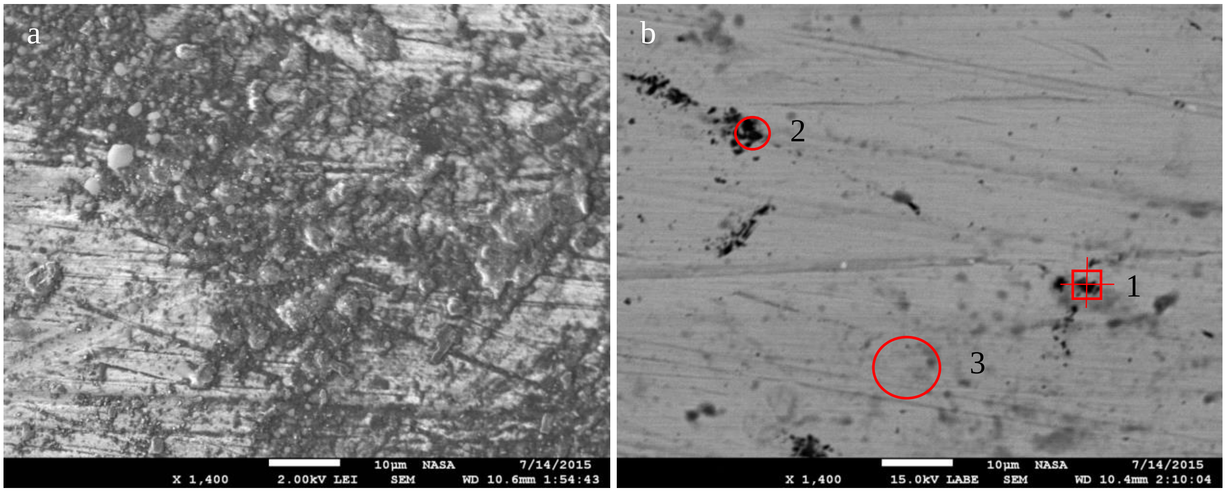


Figure 11: Copper 2-MBT SEM (a) LEI 1400x and (b) LABE 1400x point and shoot EDS

Table 9: Copper 2-MBT Point and Shoot EDS Analysis

	Cu	Al	O	Si	C
Pt 1	8.04		0.9	14.3	76.76
Pt 2	25.14	0.7		12.11	62.06
Pt 3	29.67	0.52	1.61		68.2

The copper sample in the 2-MBT solution had good performance, with very little corrosion. In the LEI SEM photo in Figure 11a, it can be seen that there was a large amount of deposition on the copper. This can also be determined because of the large amount of carbon present in the EDS composition in Table 9 (points 1, 2 and 3). The overall area has a lower oxygen content, compared with the control, which confirms that 2-MBT protects copper from the corrosion environment.

2-MBT Particles

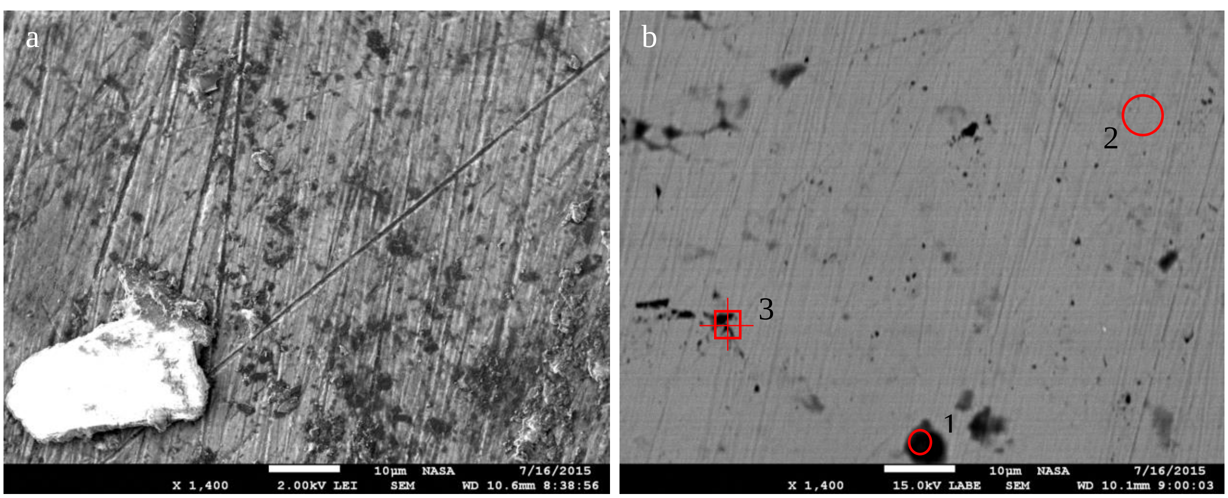


Figure 12: Copper 2-MBT particles SEM (a) LEI 1400x and (b) LABE 1400x point and shoot EDS

Table 10: Copper 2-MBT particles Point and Shoot EDS Analysis

	Cu	O	Al	Si	S	Ca	C
Pt 1	5.91	7.09		0.62	0.26	0.87	85.26
Pt 2	44.55	3.99		1.67			49.79
Pt 3	3.57	0.93	0.13	18.73	0.58		76.06

The copper sample in the 2-MBT particle solution had excellent performance, with little to no discoloration on the copper, which can be seen in Figure 8. It is very comparable to the before immersion panel, visually. In the LEI SEM photo, Figure 12a, it can be seen that there is deposition on the sample, and also in the EDS composition in Table 10.

<u>SiNaMBTPS Particles</u>

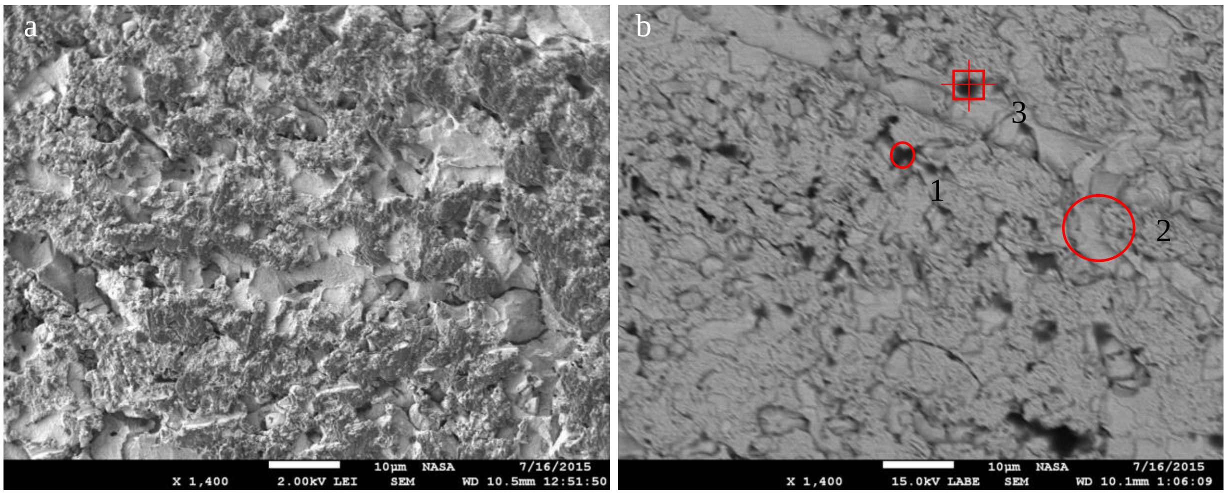


Figure 13: Copper SiNaMBTPS particles (a) LEI 1400x and (b) LABE 1400x point and shoot EDS

Table 11: Copper SiNaMBTPS Point and Shoot EDS Analysis

	Cu	O	Si	S	Cl	C
Pt 1	12.98	2.07				84.95
Pt 2	46.95	7.56	0.18	0.47		44.84
Pt 3	4.44	4.21	0.05		0.07	91.23

The copper sample in the SiNaMBTPS particle solution had discoloration on the panel edges and appeared to have a very thick layer of deposition on it, which can be seen in Figure 13a. The EDS photo also had a very different appearance when compared to all of the other copper samples tested. The carbon content was slightly higher than the other samples, likely due to the large amount of deposition on the panel.

The copper immersion test showed that 2-MBT does help to protect against corrosion. Each form of 2-MBT prevented corrosion and had a drastically less corroded appearance than the control. They each seemed to form a layer on the copper, shown by the carbon deposition visible on the panel in the SEM-LEI photos and in the composition of the point and shoot EDS analysis. While SiNaMBTPS copper appeared to have the thickest layer, it did cause some discoloration on the copper, but otherwise, not much corrosion occurred. Of the 3 copper panels tested, the 2-MBT particle had the cleanest appearance.

Coating Testing

Both particles have been tested in coating in a salt fog chamber for 2000 hours, results can be seen in Figure 14 below. In the coating testing, SiNaMBTPS performed better than the 2-MBT particles. The performance difference between the two encapsulated 2-MBT particles is not yet clear, but based on our previous test, it is possibly that SiNaMBTPS has a fast release rate, and was able to form adequate protection with copper-rich intermetallic particles which leads to its better performance.

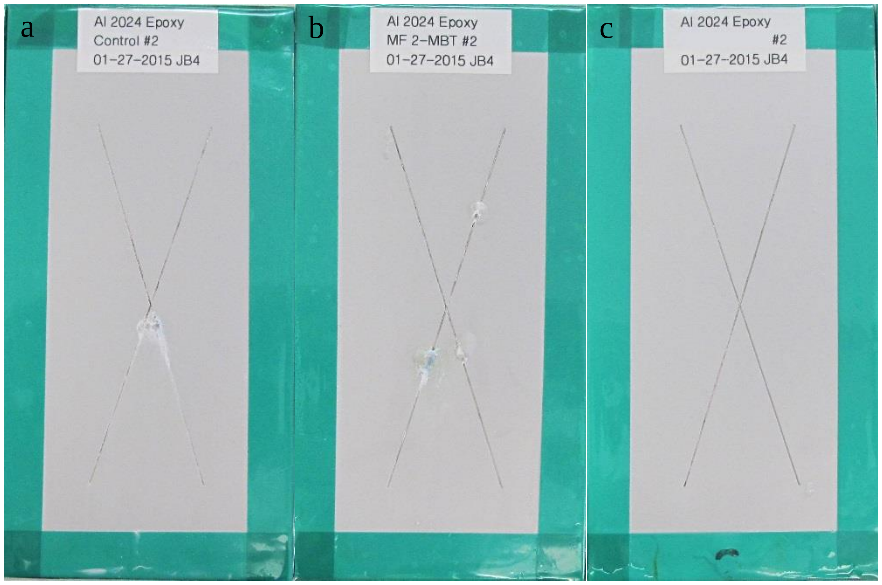


Figure 14: 2000 hour (a) control, (b) 2-MBT particle and (c) SiNaMBTPS particle salt fog results

CONCLUSIONS

Immersion testing was used to evaluate inhibitors and microparticles before they are incorporated into coatings. The tested 2-MBT inhibitor and particles performed well on the aluminum 2024 alloy. There was little to no corrosion on each panel and the intermetallic particles appeared to be intact, based on their compositions. The similar performance of the inhibitor and particles indicate that microencapsulation can be used to improve the coating compatibility of the inhibitors without sacrifice their protection properties.

The 2-MBT inhibitor and two particle variations seemed to form protective films with the copper panels, and protect it from corrosion in salt water. The panel in 2-MBT particles had a clean appearance, while the panel in the SiNaMBTPS particle solution had a very thick film or deposition layer over it and showed some discoloration.

Both 2-MBT particles showed good compatibility with the epoxy coating and perform better than control. The SiNaMBTPS particles performed better than the 2-MBT particles, possibly due to their fast release rate, which enables them to form good protection over copper-rich intermetallic particles.

ACKNOWLEDGENMENTS

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