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CORROSION PERFORMANCE OF MIL-PRF-23377 PRIMER COATED ON LASER-INTERFERENCE STRUCTURED ALUMINUM ALLOY 2024

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ABSTRACT

Laser-Interference Structuring (LIS) is a technique that was proposed to treat aluminum surfaces for improving primer adhesion. LIS may not require a series of chemical treatments, such as those used in chemical conversion coating (CCC) and sulfuric acid anodizing (SAA), which make the pre-treatment of Al panels simpler and quicker for primer painting. Previous test results indicated that LIS surface preparation enhances coating adhesion on Al 2024. To assess the effect of LIS on corrosion resistance of coatings, Al 2024 panels prepared by LIS, CCC and SAA were coated with MIL-PRF-23377 primers and exposed to salt spray environment according to ASTM B117. The exposure is currently in progress and the corrosion attack on the coated panels will be evaluated by the degree of blister formation and rust creepage according to ASTM standards.

INTRODUCTION

Protective coating on Al-bodied US military assets requires proper inspection and repair for mission readiness. Typically, a coating repair process includes pre-treatment of the Al surface to enhance the adhesion of following primer layer and also improve corrosion resistance. Chemical conversion coating (CCC) and sulfuric acid anodizing (SAA) are common pre-treatment methods widely adopted for most Al alloys. These treatments, however, have multiple steps and involve toxic chemicals, such as Cd and hexavalent Cr, which increase the costs associated with safety and waste disposal. Therefore, non-chemical surface preparation techniques would be preferred. Classic mechanical surface preparation techniques, such as abrasion and grit blast, may leave residue of abrasive particles and other contaminants which should be avoided for sound adhesion of primer. Recently, an increase in the shear lap strength for single-lap joints made with laser-interference surface preparation of Al and carbon-fiber polymer composites was reported (*1*). This increase is likely due to the roughening caused by the laser-interference structuring (LIS) (*2*).

Currently, LIS is being investigated to simplify the pre-treatment process and reduce environmental risk because LIS can achieve surface preparation in relatively short time without using any chemicals. For successful field application of any pre-treatment, the corrosion performance of primer-coated Al needs to be investigated. There are several corrosion studies that were conducted on coated Al panels pre-treated with CCC and SAA (*3-11*), but no corrosion data is available for coated Al pre-treated with LIS. In this work, Al 2024 panels treated with LIS, CCC and SAA were coated with MIL-PRF-23377 primer, and the corrosion performance of the coated panels was compared using a standard salt spray test. The purpose of this work is to determine if the LIS surface treatment and primer coating provides corrosion resistance at least comparable to CCC + primer and SAA + primer for Al 2024.

EXPERIMENTAL

In this work, surfaces of aluminum alloy Al 2024-T3 were treated using a Q-switched Nd:YAG laser that was setup for laser-interference (*1, 2, 12-14*). LIS-treated Al 2024 panels were held on a LabView-moving platform controlled by two translational stages. Thus, the laser beam was rastered over the surface of Al 2024 panels. The laser rastering speed was 6 mm/s and the laser beam size was 5 mm. CCC- and SAA-treated Al 2024 were prepared by a company that provides Al pre-treatment service. For CCC, a commercial agent containing hexa-chromate was used. The surface area of all pre-treated Al panels was 2” × 3” and the thickness was approximately 1 mm. MIL-PRF-23377 primer was then painted on the pre-treated panels according to the procedure recommended by the manufacturer. The painted Al panels were cured at room temperature for 24 h then at 60°C for 24 h. The dry thickness of coating measured using a calibrated thickness meter was in the range of 14-32 um (0.6-1.2 mil). After primer curing, the coating was X-scribed using a box cutter, and then the edges of coated panels were masked with beeswax. The scribes were intended to fully penetrate the coating and expose Al substrate. The photos of coated Al panels with X-scribe are shown in Figure 1. The scribed Al panels were exposed to salt spray produced from 5 wt% NaCl solution according to ASTM B117 procedure. While running salt spray test, tap water was used to mix 5 wt% NaCl solution due to the limited access to deionized water. A recent chemical analysis on the tap water is included in Table 1. The coated panels also experienced several intermittent dry interruptions due to malfunction of the salt spray chamber. Nonetheless, all coated Al panels were kept in a single chamber with the same history of salt spray exposure.

(a) (b)

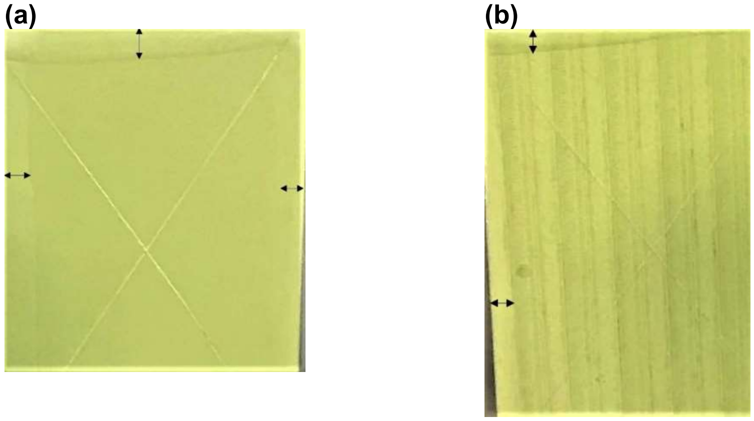

Figure 1. Pictures of two X-scribed Al panels (2” × 3”) coated with MIL-PRF-23377 primer for surface preparation prior to primer coating: (a) CCC and (b) LIS. Two-way arrows indicate the edges covered by beeswax.

Table 1. Results of chemical analysis on the tap water used in this work.

Properties and concentration of chemical species	Values
pH	7.93
Conductivity, μmho	267
Calcium Hardness, as $CaCO_3$, mg/L	79
Iron, as Fe, mg/L	0.06
Copper, as Cu, mg/L	0.01
Zinc, as Zn, mg/L	0.03
Sodium, as Na, mg/L	5.8
Potassium, as K, mg/L	1.6
Chloride, as Cl, mg/L	8.6
Sulfate, as SO_4, mg/L	16
Nitrate, as NO_3, mg/L	2.4
Phosphate, as PO_4, mg/L	<0.1
Silica, as SiO_2, mg/L	5.6

RESULT AND DISCUSSION

Two photos of an SAA-treated test panel after salt spray exposure are shown in Figure 2. Corrosion damage was not easily visible while the panel was still wet with NaCl solution from salt spray (Fig. 2a). After rinsing with water and drying the panel, white corrosion products were observed in local spots of the scribe (Fig. 2b). Similarly, the CCC-treated test panel presented in Figure 3 showed no visible corrosion features in the wet condition (Fig. 3a) but showed a few local corrosion products near the scribe after rinsing and drying (Fig. 3b). In both CCC- and SAA-treated panels, corrosion products near/on scribes extended less than 1 mm from the scribes, indicating that corrosion attack was not significant. A test panel treated with LIS shown in Figure 4 exhibited corrosion damage seemingly blisters. While undercutting corrosion may also produce corrosion damage near the scribes, blistering is considered more appropriate in this case because the damage spot is not extended along the scribes as the undercutting corrosion defects would have been. Moreover, the shape of damage close to complete hemisphere is unlikely produced by undercutting but by blistering. In the test panel in Figure 4, two blisters were observed in the wet condition (Fig. 4a), and after dried, corrosion products were observed at local spots including the blister sites (Fig. 4b). While corrosion on scribes appeared in all pre-treatment conditions, the formation of blisters was only observed in LIS-treated test panels. The susceptibility to blister formation could be attributed to the lack of chromate inhibitor (supplied from CCC) or the absence of barrier oxide (anodized Al_2O_3 in SAA) so that salt solution can permeate and corrode the Al substrate under the primer. The creepage rating of corrosion product on scribes, assessed by ASTM D1654, was higher than 8 in all test panels after 500 h salt spray exposure, indicating that corrosion was not significant in all pre-treatment conditions.

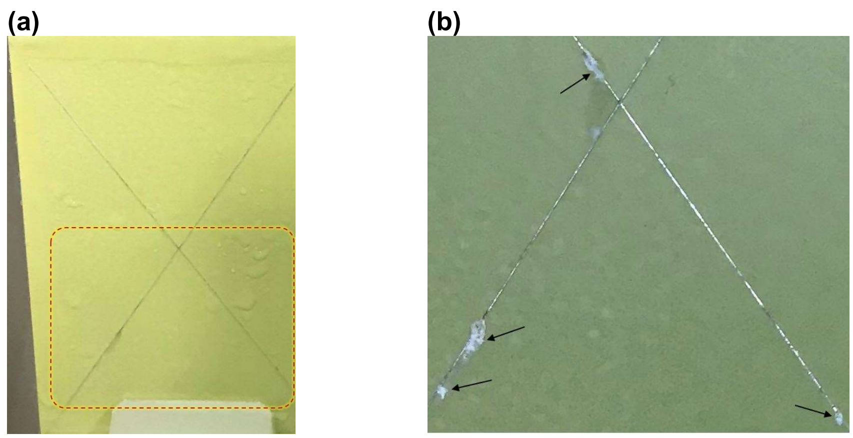

Figure 2. Pictures of a 2" × 3" test panel with SAA pre-treatment after 500 h salt spray exposure: (a) wet panel and (b) zoomed-in view of the selected half-panel region after water-rinsing and drying. The arrows indicate white Al corrosion product.

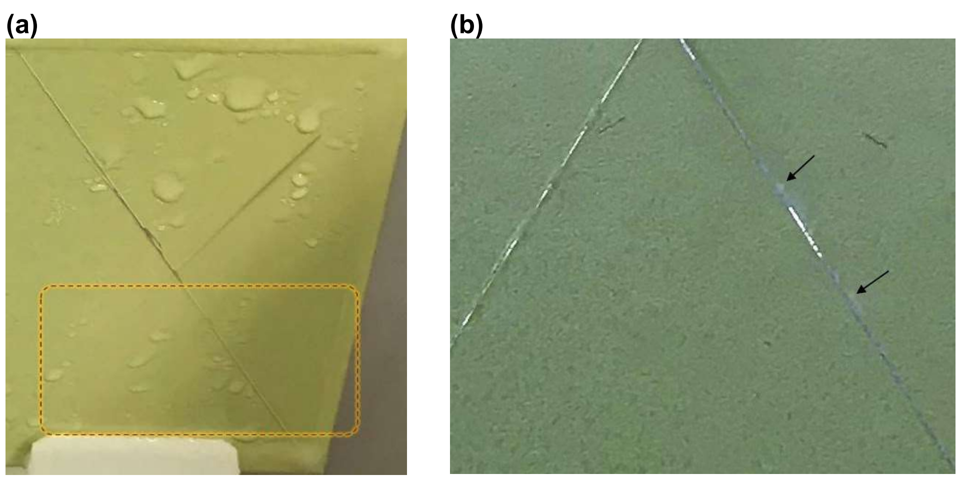

Figure 3. Pictures of a 2" × 3" test panel with CCC pre-treatment after 500 h salt spray exposure: (a) wet panel and (b) zoom in in the selected half-panel region after water-rinsing and drying. The arrows indicate white Al corrosion product.

Blister formation in a test panel treated with LIS is shown in Figure 5 with increasing time of salt spray exposure. While no apparent blister was observed after 24 h exposure, a visible blister formed near the upper-right scribe after 96 h exposure (Fig. 5a). This blister did not grow up to 208 h but became larger after 500 h (Fig. 5b and 5c). Another blister, that was not present up to 208 h, was observed near upper-left scribe after 500 h (Fig. 5c). Similarly, other test panels (not shown here) treated with LIS exhibited 1-2 blisters near scribes after 500 h exposure. However, no blisters formed in the undamaged-coating area away from scribes. This could suggest that without coating damage, MIL-PRF-23377 primer on LIS-treated Al 2024 is resistant to blister formation. Further investigation on the mechanism of blister formation near scribes is being conducted and will be described in a future report.

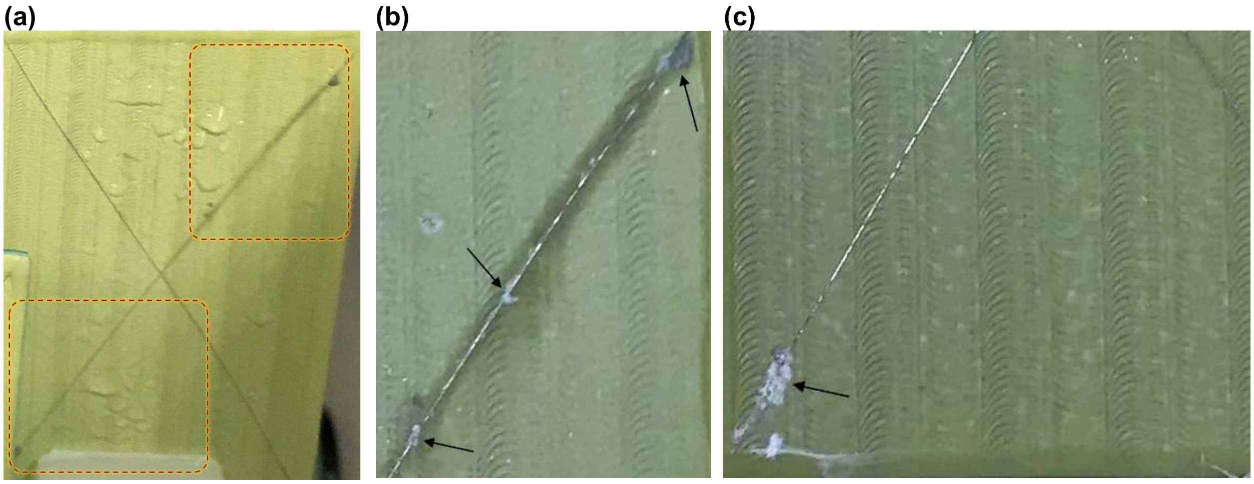

Figure 4. Pictures of a 2” × 3” test panel with LIS pre-treatment after 500 h salt spray exposure: (a) wet panel, (b) zoom in in the selected top-right panel region after water-rinsing and drying, and (c) zoom in in the selected bottom-left panel region after water-rinsing and drying. The arrows indicate traces of blisters and white Al corrosion product.

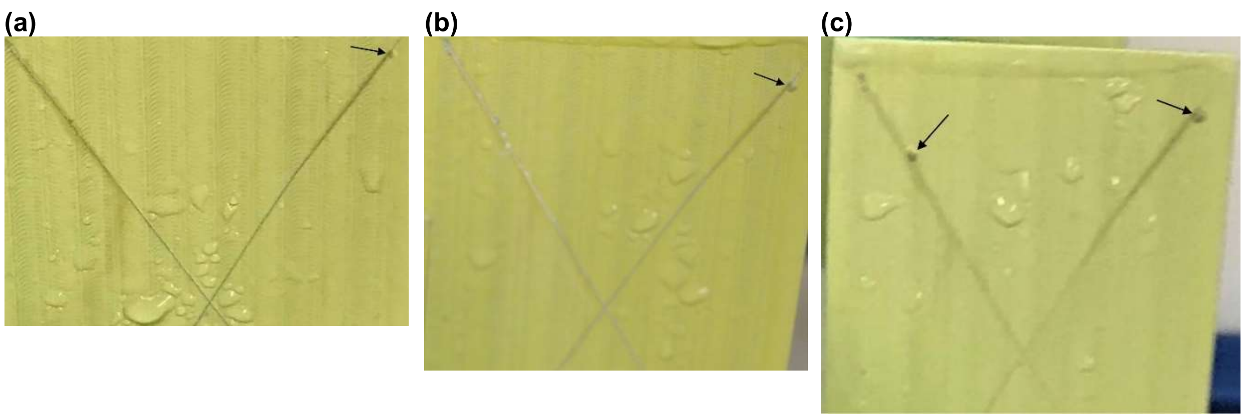

Figure 5. Pictures of a 2” × 3” test panel with LIS pre-treatment after (a) 96 h, (b) 208 h and (c) 500 h salt spray exposure. The test panel was not dried when the pictures were taken. The arrows indicate the location of visible blisters.

CONCLUSION

MIL-PRF-23377 primer coated Al 2024 with CCC, SAA or laser-interference pre-treatment were exposed to salt spray up to 500 h to investigate the corrosion performance for a new laser-based surface preparation technique. All test panels exhibited corrosion along coating-penetrating scribes regardless of pre-treatment type, but the creepage by corrosion was not significant as assessed by ASTM D1654 for any of the pre-treatments. Blister formation near scribes was only observed in the test panels treated with LIS, but no blister formed on scribe-free coating area. This suggests that primer coating on laser-interference treated surface would be resistant to blister formation if no coating damage is present. No blisters were observed at all for the CCC and SAA pre-treated samples.

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REFERENCES

1. A. S. Sabau *et al.*, A Laser Interference-Based Surface Treatment of Al and Carbon Fiber Polymer Composites for Enhanced Bonding. *SAMPE Conference and Exhibition, Long Beach, CA*, (2016).
2. A. S. Sabau, C. M. Greer, J. Chen, C. D. Warren, C. Daniel, Surface Characterization of Carbon Fiber Polymer Composites and Aluminum Alloys After Laser Interference Structuring. *JOM* **68**, 1882-1889 (2016).
3. S. Spadafora, F. Pepe, in *TRI-SERVICE CONFERENCE ON CORROSION*. (USAF WRIGHT-PATTERSON Air Force Base, ORLANDO, FL, USA, 1994).
4. S. Cohen, S. Spadafora, "A COMPARISON OF THIN FILM SULFURIC ACID ANODIZING AND CHROMIC ACID ANODIZING PROCESSES " (NAVAL AIR WARFARE CENTER, Warminster, PA, USA, 1995).
5. X. Wang, G. S. Frankel, Protection Mechanism of Al-Rich Epoxy Primer on Aluminum Alloy 2024-T3. *CORROSION* **73**, 1192-1195 (2017).
6. G. S. Frankel, R. G. Buchheit, M. Jaworowski, G. Swain, "Scientific Understanding of Non-Chromated Corrosion Inhibitors Function," (The Ohio State University, DoD information center, 2013).
7. Z. Feng, G. S. Frankel, C. A. Matzdorf, Quantification of Accelerated Corrosion Testing of Coated AA7075-T6. *Journal of The Electrochemical Society* **161**, C42-C49 (2014).
8. NCAP, "Non-Chromate Aluminum Pretreatments Phase I Report " (2003).
9. B. Placzankis, C. Miller, J. Beatty, "Accelerated Corrosion Analysis of Aluminum Armor Alloy 2519 With Nonchromate Conversion Coatings for DOD Applications " (U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, USA, 2001).
10. B. Placzankis, C. Miller, B. Mullis, "Examination of Nonchromate Conversion Coatings for Aluminum Armor From Three Final Candidates Using Accelerated Corrosion and Adhesion Test Method," (U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, USA, 2001).
11. P. Smith, C. Miller, "Performance of Chromate-Free Pretreatment Options for CARC Systems," (U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, USA, 2007).
12. A. Lasagni, M. D'Alessandria, R. Giovanelli, F. Mücklich, Advanced design of periodical architectures in bulk metals by means of Laser Interference Metallurgy. *Applied Surface Science* **254**, 930-936 (2007).
13. C. Daniel, F. Mücklich, Z. Liu, Periodical micro-nano-structuring of metallic surfaces by interfering laser beams. *Applied Surface Science* **208-209**, 317-321 (2003).
14. C. Daniel, F. Mücklich, *Quantification of periodic surface structures by white-light interferometry*. (2004), vol. 41, pp. 277-285.