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Andrea Ambrosini, Antoine Boubault, Clifford K Ho, Lam Banh, John R Lewis. Influence of application parameters on stability of Pyromark® 2500 receiver coatings. AIP Conference Proceedings, 2019, pp.030002. 10.1063/1.5117514 . hal-04372784

HAL Id: hal-04372784

<https://hal.science/hal-04372784>

Submitted on 4 Jan 2024

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Influence of Application Parameters on Stability of Pyromark® 2500 Receiver Coatings

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Abstract. Pyromark® 2500, manufactured by Tempil, is currently the industry standard for high solar absorptive receiver coatings for concentrating solar power towers. However, Pyromark has been reported to degrade if not applied properly or exposed to temperatures exceeding 700 °C over a period of time. However, it is not apparent if such degradation is due to a particular aspect or aspects of the deposition process, which may vary from plant to plant. Many variables factor in to the performance of Pyromark, e.g. deposition method, drying time, curing parameters (ramp rate, homogeneous heating, time at temperature...), and coating thickness. Identifying the factors with the most influence on coating performance and durability will help guide the application of Pyromark to receivers to minimize degradation over time. The relationships between coating quality and optical properties with deposition/curing parameters on Haynes 230 substrates were assessed using statistical analysis of variance (ANOVA) techniques for repeated measures. These ANOVA techniques were designed to detect differences in treatment effects on the response at each of the aging cycles. The analyses found that coating thickness, curing ramp rate, and dwell time had the most effect on coating quality.

INTRODUCTION

The efficiency of a concentrating solar power tower plant can be increased if the energy absorbed by the receiver is maximized. However, thermal radiation losses can be significant (> 7% annual energy loss) with receivers at elevated temperatures. For that reason, many CSP central receivers are coated with solar absorbant paints, such as high-temperature Pyromark 2500. Pyromark 2500, manufactured by Tempil, is a high-temperature silicone-based paint, with a high solar absorptance ($\alpha > 0.95$), that can be applied on steel, aluminum, alloys, and ceramics. However, Pyromark® has been reported to degrade if not applied properly or exposed to temperatures exceeding 700 °C over a period of time. [1-4] However, it is not immediately apparent if such degradation is due to a particular aspect of the deposition process, which may vary from plant to plant. Many variables factor in to the performance of Pyromark, e.g. deposition method, drying time, curing parameters (ramp rate, homogeneous heating, time at temperature...), coating thickness.

Other groups have investigated various aspects of Pyromark in relation to its stability and optical properties. Ho *et al.* reported on the development of comprehensive optical measurements of Pyromark and preliminary high-temperature (750 – 800 °C) aging studies of Pyromark coatings. In that report, it was found that aging at 800 °C resulted in a change in crystal structure of the paint, causing a decrease in absorptance. [3] Coventry *et al.* recently reported on the effect of substrate material and coating thickness on Pyromark performance, and found that Pyromark coating thickness had a significant influence on absorptance and stability. In general, they found that thinner coatings often perform better than thicker coatings under most conditions, save high temperature (850 °C) aging. [5] In the current work, the relationships between optical properties and deposition/curing parameters were assessed using statistical analysis of variance (ANOVA) techniques for repeated measures. These ANOVA techniques are designed to detect differences in treatment effects on the response at each of the aging cycles. Results include estimates of main

effects and interactions effects of the factors as well as their statistical significance. This will provide guidance as to which factors impact the response the most across aging cycles. Identifying the factors with the most influence on coating performance and durability will help guide the application of Pyromark to receivers to minimize degradation over time.

EXPERIMENTAL

Design of Experiments

A 96 run screening experiment was designed to study the effect of six production factors on four responses; stability (delamination), absorptance, emittance, and figure of merit, FOM. Three of the factors are curing parameters set by the furnace in the curing process. The other three factors are application factors related to how the substrates are coated with Pyromark paint before the curing process. At a high level, each of the 96 substrates was treated with a combination of levels of the six factors with the goal of screening out which factors affect the responses the most. To accomplish this, two levels (high and low) of each factor were chosen as follows:

- Application factors
 - Layer thickness (low, high): 25 μm , 76 μm
 - Substrate roughness: Rough $\approx 15 \mu\text{m}$ (grit blasted), Smooth = as-received
 - Substrate pre-oxidation: Oxidized = 800 $^{\circ}\text{C}/24\text{h}$ or Non-oxidized = as-received
- Curing factors
 - Temperature (low, high): 550 $^{\circ}\text{C}$, 750 $^{\circ}\text{C}$
 - Ramp Rate (low, high): 2 $^{\circ}\text{C}/\text{min}$, 20 $^{\circ}\text{C}/\text{min}$
 - Curing Duration (low, high): 1 h, 8 h

The experiment consisted of choosing the curing factor levels to set the parameters of the furnace and placing several substrates treated with different levels of the application factors into the furnace for curing. This process was repeated a total of 12 times, each time placing 8 substrates into the furnace. We can think of the experimental design as two designs: one to set the curing factors and one to set the application factors. For the application factors design, the 8 possible combinations of these three factors (3 factors, 2-levels each) were applied to the 8 substrates creating a 2^3 full factorial design within each furnace run. A 12-run design for the furnace runs was chosen, with each of the 8 possible combinations of the curing factors (3 factors, 2-levels each) observed at least once, and 4 of the combinations observed twice. The order of the furnace runs and the location of the substrates within the furnace were randomized. The choice of size (12 furnace runs \times 8 substrates = 96 samples) was based on a tradeoff between budget and the ability to detect reasonable effects. In the statistical literature, this type of design is known as a *split-plot* design. [6, 7]

Pyromark Deposition

Pyromark was painted via a spraying method based on the method developed by Ho *et al.* [3] The coupons were composed of Haynes 230 alloy and measured 2.54 sq cm. They were pre-treated according to the Application Procedures described above. The Pyromark[®] 2500 flat black paint was thin enough to spray without thinning. Prior to painting, the substrates were cleaned with methyl ethyl ketone (MEK) and allowed to dry for at least 1 h at room temperature. Between each coat, the samples were dried for 30 min at room temperature. It was determined that each coat added approximately 10.13 μm of thickness. After the final coat was applied, the coupons were dried at room temperature in the paint booth for 24 h. The final thicknesses were checked at multiple places on random coupons and were found to be within 20% of the target thicknesses, on average. The samples were cured in a programmable box furnace according to a combination of the curing factors listed above. After the predetermined curing duration, the samples were allowed to cool at a rate of 100 $^{\circ}\text{C}/\text{h}$. Samples were then aged at 700 $^{\circ}\text{C}$ for 96 h.

Optical Characterization and Figure of Merit

The solar-weighted directional absorptance ($\alpha_{1.5}$) was measured using a hand-held SOC 410 Solar reflectometer, which measures the reflectance in seven spectral bands from 335 – 2500 nm at a 20° incidence angle. The solar weighted reflectance was calculated using an air mass index of 1.5. [3] Hemispherical thermal emittance measurements (ϵ_H), were taken using an ET100 emissometer from Surface Optics Corporation weighted at 700 °C.

Typically, the metric used to evaluate selective absorber coatings is based on the net absorptance of energy relative to that of an ideal absorber. Cindrella [8] and Ho *et al.* [9] developed the following definition for the figure of merit (FOM) for the efficiency of selective absorbers, η_{sel} , which is equal to the ratio of the net radiative energy absorbed and retained by a surface to the net radiative energy absorbed and retained by an ideal selective absorber with an absorptance of one and an emittance of zero:

$$\eta_{sel} = \frac{\alpha_s Q - \epsilon \sigma T^4}{Q}$$

where α_s is the solar absorptance, Q is the irradiance on the receiver (W/m^2), ϵ is the thermal emittance, σ is the Stefan-Boltzmann constant ($5.67 \times 10^{-8} W/m^2/K^4$), and T is the surface temperature (K). For the purposes of the coatings synthesized at Sandia and NREL, Q was estimated at $\sim 60 W/cm^2$, and T was set to 973 K.

Solar Simulator Aging

Sandia's High-Flux Solar Simulator with Automated Sample Handling & Exposure System (ASHES) is a one-of-a-kind capability which can be used 24/7 with metal-halide lamps. [10, 11] ASHES provides accelerated lifetime aging tests for materials under high-temperature/high-flux conditions. A robotic sample-handling system can be used to move multiple (up to 12) 2.5 sq cm coupons automatically into and out of the concentrated flux sequentially to expose the samples to predetermined temperatures, fluxes, and/or durations. Select Pyromark® coated samples were exposed to an average flux of 600 suns. For each cycle, the sample was placed in flux with the robotic arm and held until the temperature of the coupon reached 700 °C, after which it was removed and placed on a holding stage. At this point the next sample was placed under flux, heated, removed, etc..., until all coupons had been exposed and the cycle started again with Sample 1.

RESULTS AND DISCUSSION

Of the 96 substrates treated, 64 experienced visual delamination of the Pyromark paint coating to various degrees with only 32 of the coatings remaining completely intact. (FIGURE 1) Four “degrees of delamination” were identified: completely intact, partially delaminated, delayed delamination (complete delamination after measurements were taken), and complete delamination. Absorption and emittance of the original responses were still measured on the surviving samples after curing and also after aging for 96 h at 700 °C. Of the surviving samples, absorptance was measured at ≥ 0.96 with minimal change after aging at 700 °C.

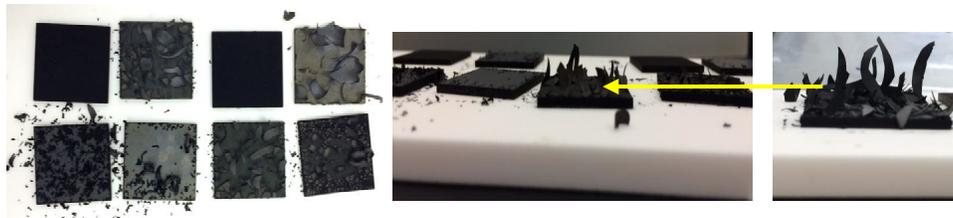


FIGURE 1. Examples of delaminated and intact Pyromark coatings after curing.

Analysis of the data (FIGURE 2) revealed that layer thickness, ramp rate, and substrate roughness have statistically significant effects on the degree of delamination. Similar to the results observed by Coventry [5], the thicker coatings ($\sim 75 \mu m$) showed a high incidence of delamination. The other factors did not significantly affect delamination. To achieve the highest likelihood of a completely intact coating, the low levels of layer thickness ($\sim 30 \mu m$) and ramp rate

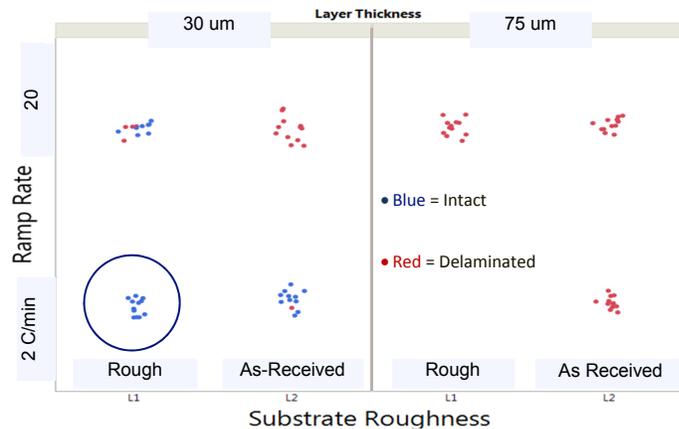


FIGURE 2. Plot showing effect of deposition parameters on coating quality. The blue circle indicates the region of optimal coating stability.

(2 °C/min) should be used, and the substrate should be roughened. At these levels, the data indicate that at least 95% of the substrates should remain intact with high confidence.

Despite the extent of delamination, the data still provides some useful information on the effects of the factors on the optical responses. Analyzing just the data from the intact coatings it was found that curing temperature affects the responses the most. On average, substrates cured at the low temperature (550 °C) had responses roughly 0.001 to 0.002 units higher than substrates cured at the higher temperature (750 °C). [1] These effects were statistically significant on absorptance (post-cure and post-aging), emittance (post-cure) and the FOM (post-aging). However, such a small magnitude of change, even though statistically significant, is not likely to have a practical effect on the coating performance.

Based on the results from the first Design of Experiment (DoE), a second DoE was created in order to narrow the pertinent parameters in order to determine optimum deposition conditions. In the follow-up experiment, 90 coupons were treated in 15 furnace runs with six coupons per furnace run. The levels of each variable studied in the experiment were:

- Layer thickness: 25-33 μm (3 layers), 38-46 μm (4 layers), 50-58 μm (5 layers)
- Curing Rate (° C/min): 5, 10, 15
- Curing Temperature (°C): 550, 650, 750

The goal in choosing the levels for thickness and curing rate was to narrow down the parameter range in which delamination would not occur. For example, the first experiment indicated that 2 layers of paint resulted in an intact coating, but 8 layers were too many. Since this variable is not precisely controlled in the field, we want to understand the maximum number of coatings that would provide acceptable results. A center point for curing temperature (650 °C) was added to the levels from the original experiment in an attempt to detect any curvature effects on the continuous responses.

Of the 90 additional coupons tested, only 11 (12%) were completely delaminated compared to the 39 out of 96 (40%) in the original experiment. Further, the percentage of coupons with at least some level of delamination decreased from 67% to 50% from the original experiment to the follow-up.

Statistical Analysis of Delamination

Statistical analyses were performed to determine the factor settings that reduce the likelihood of delaminated substrates. To simplify the interpretation of results, we collapsed the various levels of delamination to just two levels: *intact* and *some level of delamination*. The latter group includes coupons that had various levels of delamination (completely delaminated, partially delaminated, some cracking of the paint, delamination along the edge, etc.). An

¹ The average increase varies by the response being analyzed, but the average is consistently higher on the low temperature setting. It should be noted that while statistically significant, this small difference may not be practical. Also, the statement applies to substrates that remained at least partially intact for the measurements. These were most likely to be the rough substrates with low layer thickness and cured at the low ramp rate.

analysis using just the data from the second-round experiment was conducted, in addition to an analysis with data from both experiments combined. These analyses tell the same story - fewer layers of paint results in higher likelihood of intact coatings with further improvement provided by slower curing rate and lower curing temperatures. These analyses also confirm the results from the first round of experiments, strengthening the confidence we have in those conclusions.

Regression trees were used to partition the factor space into groups most predictive of the two-level response (intact vs. some level of delamination). Regression trees recursively partition the data according the relationship between the factors (e.g. layer thickness, curing rate, and curing temperature) and the response (e.g. intact vs. some level of delamination) to produce splits that best predict the data. A ten-fold cross-validation was performed to reduce the chance of over fitting the observed data. [12] This analysis suggests that robust factor settings are *two or three layers of paint, curing rate ≤ 10 °C/min, and a curing temperature of ≤ 650 °C.*

Another method to analyze this data is to use logistic regression. Logistic regression models the probability of belonging to the intact group as a function of the factor levels. Statistical tests are performed to decide if the effect size for each of the factors is statistically significant. Starting with the model including effects up to two-way interactions and polynomials of degree two, we drop all insignificant effects and end up with a model that includes only the main effects of layer thickness, curing rate, and curing temperature. This model estimates a 95% lower bound of about 0.80 for the probability of remaining intact when the factor settings are *three layers of paint, curing rate of 5 °C/min, curing temperature of 650 °C.* This analysis agrees with the results from of the nonparametric regression tree approach.

The 75 surviving coatings from the second round of experiments were aged at 700 °C for 96 hours. These included the coatings that remained completely intact or had some minimal edge delamination or cracking. Levels of delamination after aging could be sorted into: completely intact, flecked (e.g., spotted), and partial delamination. One interesting question to explore is “For a given coating that remained completely intact after curing, are there processing parameters that affect the coating integrity after it is aged?” To answer this question involved considering the 45 aged coatings that were completely intact after curing. A regression tree was fit to this data using two splits. The tree appears in FIGURE 3. The first split is on Layer Thickness with 3 layers in one group and 4 or 5 layers in the second group. Note that only 17 of the 45 coatings received 4 or 5 layers of paint. This is a consequence of using only the coatings that remained intact after curing – we already know that 4 or more layers of paint results in fewer intact coatings. However, this split on Layer Thickness does still suggest that given a completely intact coating after curing,

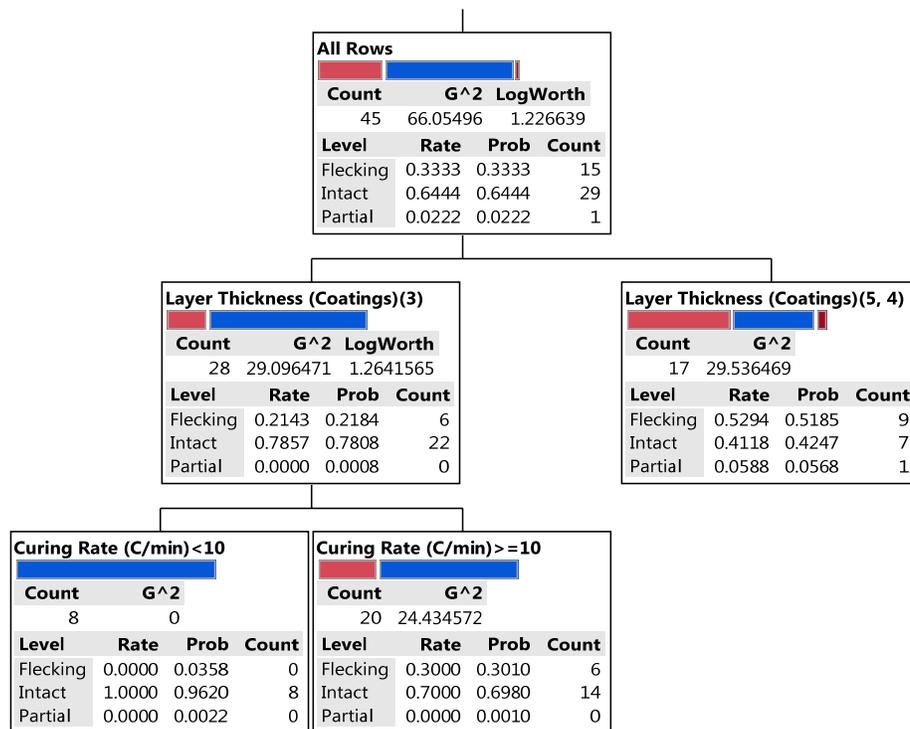


FIGURE 3. Regression Tree fit on delamination status after aging. The data include only the coatings remaining intact after curing and so inferences are conditional on this subset of coatings.

Flecked/Partial Delamination after aging is slightly more likely to occur with 4 or more layers of paint. That is, even if a substrate treated with 4 or 5 layers of paint remains completely intact after curing, it is more likely to lose coating integrity after aging than substrates treated with fewer layers of paint. Similarly, the split on Curing Rate suggests that rates of 10 °C/min or more are also slightly more likely to experience Flecking after aging even if intact coating after curing). These results indicate that the settings suggested above will also be robust settings for aged coupons.

Solar Simulator Testing:

A subset of intact samples was tested under rapid thermal cycling on the ASHES solar simulator at the NSTTF. Due to time constraints, only 5-16 cycles were run on nine Pyromark samples for these initial tests. However, even limited, these tests provide interesting insights into the coating stability.

A representative heating profile for several samples is seen in FIGURE 4. Most samples heat up within 25-40 seconds. However, several coatings take much longer, up to several minutes. Upon post-test examination, these samples were noticeably lighter after exposure and little trace of the Pyromark could be found. This is also reflected in the absorbance measurements seen in FIGURE 5 and listed in Table 1. Almost all of the Pyromark coatings show physical degradation to some extent, with the exception of Samples C05 and C21. They also show a slight decrease in absorbance, but less visible degradation. There does not seem to be trend between coating degradation and deposition parameters.

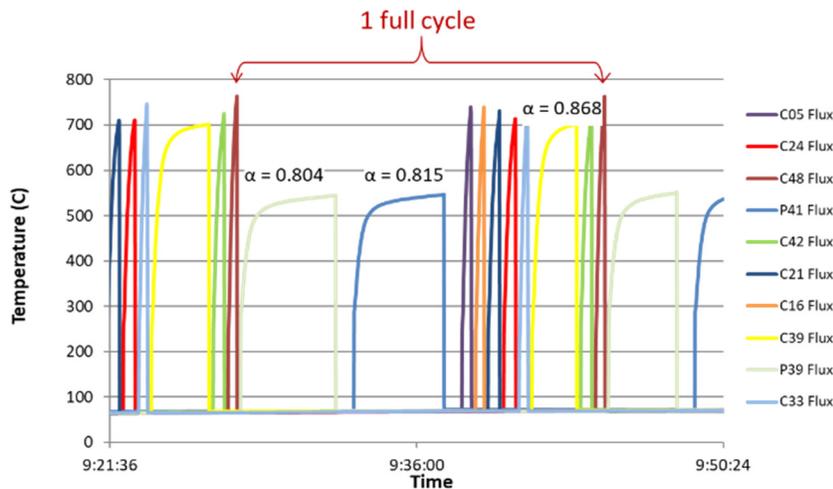


FIGURE 4. Example of heating profile for several samples on solar simulator.

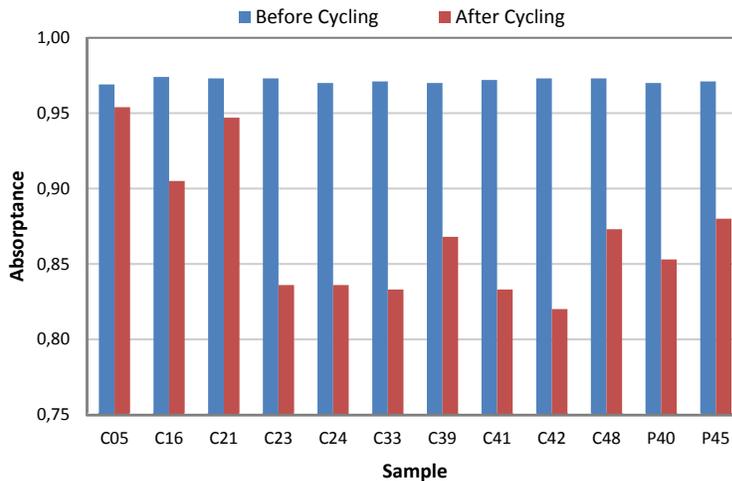


FIGURE 5. Change in absorbance of coatings tested on the solar simulator.

TABLE 1. Optical properties of Pyromark and thermal spray coatings before and after testing on solar simulator.

Coupon #	Thickness (# Coats)	Curing Rate (°C/min)	Curing Temp (°C)	Before			Solar Sim (700 °C)			
				α	ϵ	FOM	α	ϵ	FOM	# Cycles
C05	3	5	750	0.969	0.877	0.896	0.954	0.863	0.882	11
C16	3	10	550	0.974	0.901	0.899	0.905	0.795	0.839	16
C21	3	15	550	0.973	0.897	0.898	0.947	0.823	0.878	11
C23	3	15	550	0.973	0.897	0.898	0.836		0.836	5
C24	3	5	650	0.970	0.900	0.895	0.836	0.768	0.772	13
C33	3	10	750	0.971	0.885	0.897	0.833	0.721	0.773	16
C39	3	5	550	0.970	0.900	0.895	0.868	0.795	0.802	8
C41	3	5	550	0.972	0.895	0.897	0.833	0.77	0.769	10
C42	3	10	650	0.973	0.898	0.898	0.820	0.767	0.756	13
C48	3	15	650	0.973	0.895	0.898	0.873	0.781	0.808	16
P40	2	2	750/8h	0.970	0.863	0.898	0.853	0.760	0.790	5
P45	2	20	750/8h	0.971	0.865	0.899	0.880	0.790	0.814	5

CONCLUSIONS

A statistical analysis of Pyromark application parameters was undertaken in order to identify which parameters were most influential for successful Pyromark deposition, i.e. intact coatings. The results show that thin coatings (preferably < 35 μm), slow ramp rates, and lower-temperature dwell result in the most stable coatings. There was little difference in measured FOM vs deposition parameters between Pyromark coatings that remained intact during the initial deposition and after aging 96 h at 700 °C. The results imply that careful attention to the deposition

methodology of Pyromark onto commercial power tower receivers can improve the quality and durability of the coatings.

Ten intact coatings were tested on the ASHES system at Sandia under 600 kW/m², rapidly cycling between ambient and 700 °C for several cycles. Despite being stable after isothermal aging in a box furnace, many of the coating degraded swiftly on the solar simulator. A possible explanation for this degradation is that the much faster heating and cooling rates exacerbate any thermal expansion differences between the coating and substrate, resulting in delamination. However, for this hypothesis to be verified, additional testing and post-mortem coating analyses are required and will be completed in future investigations.

ACKNOWLEDGMENTS

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This material is based upon work supported by the U.S. Department of Energy SunShot program.

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