CAAP Quarterly Report

Date of Report: <*April* 10th, 2017>

Contract Number: <DTPH56-15-H-CAAP06>

Prepared for: <Government Agency: U. S. DOT PHMSA >

Project Title: <*Mitigating Pipeline Corrosion Using A Smart Thermal Spraying Coating System*>

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For quarterly period ending: <*April* 10th, 2017>

Business and Activity Section

(a) Generated Commitments

No changes to the existing agreement.

No equipment purchased over this reporting period.

No supplies purchased in this quarter.

(b) Status Update of Past Quarter Activities

Studies were conducted during this quarter to perform material characterization, corrosion tests, and analyze the corrosion test results for Al-Zn coating on steel substrate using wire arc spraying technology: 1) material characterization of the Al-Zn coating before corrosion tests; 2) corrosion test setup; 3) corrosion test results and material characterization of the Al-Zn coating after corrosion tests; and 4) coating thickness design. Further efforts will be put on coating samples with embedded sensors in both hard coatings and soft coatings, and compare the different corrosion performance of the coatings toward corrosion, also further study the corrosion damage localization and characterization in both hard and soft coatings. The detail progresses, which were completed in this quarter, are presented below:

1) Characterize the material property of the Al-Zn coated steel substrate using wire arc spraying technology before corrosion tests (Task 2 Subtask 2.3 & 2.4)

According to the results from updated materials selection study reported in our previous reports, Al-Zn has shown superior corrosion protective combined with acceptable mechanical stability. Wire Arc Spraying technique has also been used to make the coating system more cost effective. Figure 1 shows top surface of Al-Zn (85 wt% Al—15 wt% Zn).coatings deposited on steel substrate coupons at different thicknesses. This image shows smoothness of as-sprayed coating which does not require any machining or polishing after deposition. Steel substrate size were 1.5in (length) × 1.5in (width) × 0.25in (height). The thickness of coating were 2mm (Sample #1) and 0.1 mm (Sample #2). Deposition with different thickness were for comparison of coating thickness regarding mechanical and corrosion behaviors of the coatings.

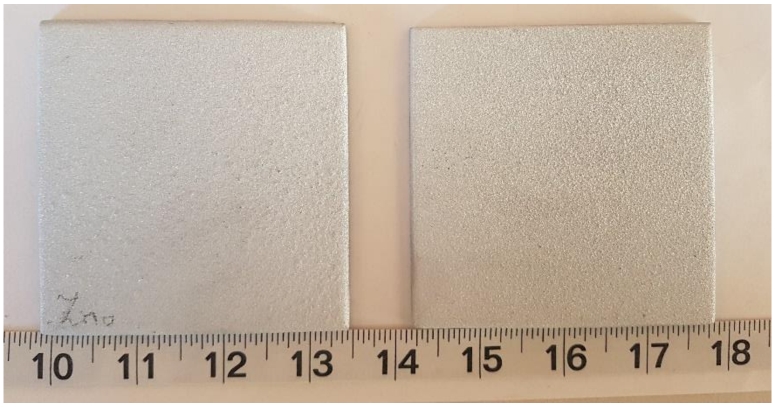

Figure 1. Wire Arc deposited Al-Zn coating on steel substrate, left 2 mm, and right 0.1 mm.

Figure 2 illustrates images taken from mounted coating samples (Sample #1 (left) and Sample # 2 (right)) illustrating different thicknesses of coatings on steel samples.

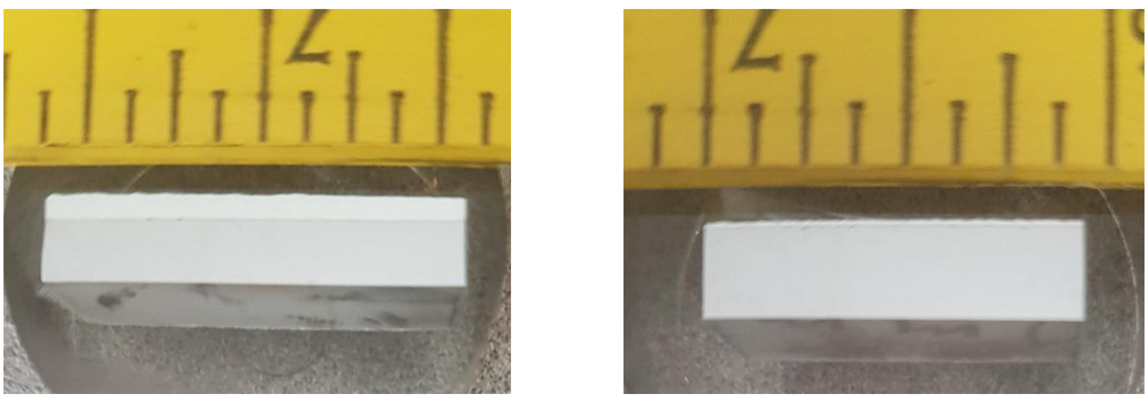

Figure 2. Mounted coating samples: Sample #1 (2mm, left) and Sample # 2 (0.1mm, right)

The microstructural properties, porosity level, mechanical properties, and corrosion resistant of the coatings were evaluated and compared with the former results obtained in the studies reported in the first quarters of the project. Fig.3 shows the optical micrographs taken from wire arc Al-Zn coatings with two different thicknesses (2mm and 0.1mm) sprayed on carbon steel substrates.

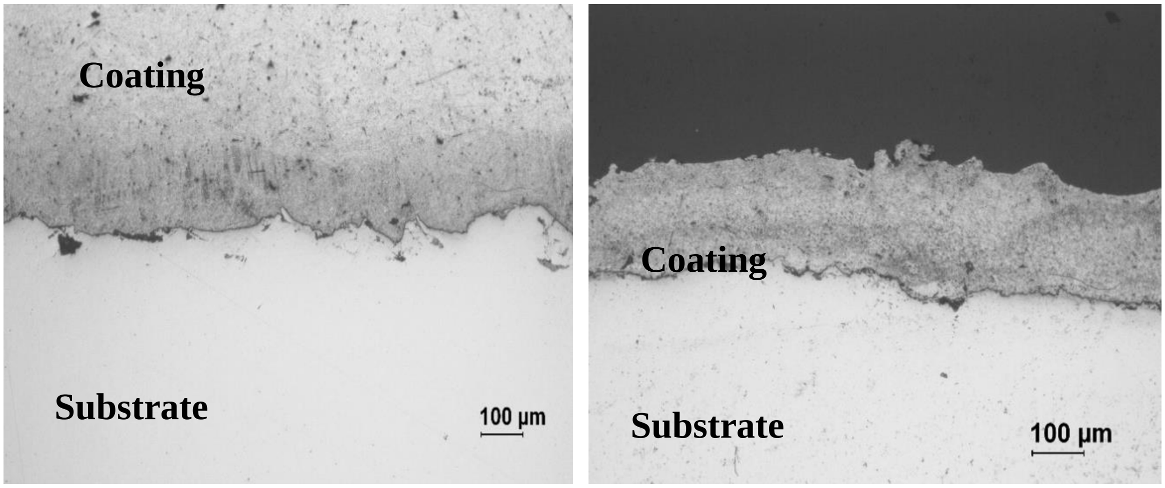

Figure 3. Wire arc sprayed Al-Zn deposited coating on carbon steel substrate in (left) 2mm and (right) 0.1mm thicknesses.

Figure 3 indicated that both coatings were dense with no visible delamination in the interphase of the coating-substrate exhibiting good bonding between the coating and the substrate. Table 1 shows the estimated porosity level for all the three trail materials which have been coated on the steel substrate including copper, Al-Brone as investigated before and Al-Zn results as measured in this quarter.. The results showed ~7% porosity for wire arc sprayed Al-Zn coating which was relatively higher compared to those of HVOF deposited copper coating (~3%) and HVOF deposited Al-bronze (~5.5%) which were investigated before.

Table 1. Porosity measurement of the thermally sprayed coatings.

Materials	**HVOF Copper**	**HVOF Al-Bronze**	**Wire arc AL-Zn**
Porosity Area %	3±0.5	5.5±0.7	7±0.6

The mechanical properties of the wire arc sprayed Al-Zn coating were evaluated using Knoob hardness test. The optical optical micrograph showing knoob indentation in coating microstructure is shown in Fig. 4. All indentation tests were performed under 200gF for 15 seconds.

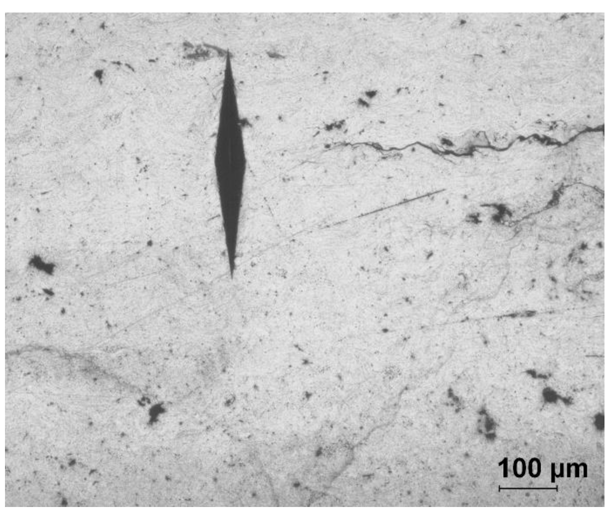

Figure 4. knoob indentation carried out on wire arc sprayed Al-Zn coating.

Table 2 compares the hardness of all the three trail materials which have been coated on the steel substrate including copper, Al-Brone, and Al-Zn. The average hardness values of the Al-Zn coatings regardless of their thickness were 41±1 HK which was lower compared to those of the other coatings examined in previous reports as tabulated in Table 2.

Table 2. Hardness estimation of the thermally sprayed coatings.

Materials	**HVOF Copper**	**HVOF Al-Bronze**	**Wire arc AL-Zn**
Hardness (HK)	96.5±1	139.4±2	41.2±1

2) <u>Corrosion test setup for the Al-Zn coated steel substrate using wire arc spraying technology (Task 2 Subtask 2.3 & 2.4)</u>

To evaluate the corrosion property of the wire arc sprayed Al-Zn coatings on steel substrate, electrochemical accelerated corrosion test to be conducted. Two PVC pipes with inner a diameter of 1 inch and a length of 3 inches were fixed on top of the coating surface using Loctite epoxy adhesive. The PVC pipes were filled with 3.5wt% NaCl solution as electrolyte for electrochemical corrosion test. To prevent any leakage during the test, samples were cured 24 hours in room temperature to maximum the bounding strength of adhesive. Figure 5 showed the schematic of corrosion test and Fig. 6 illustrates the actual test set-up in this study.

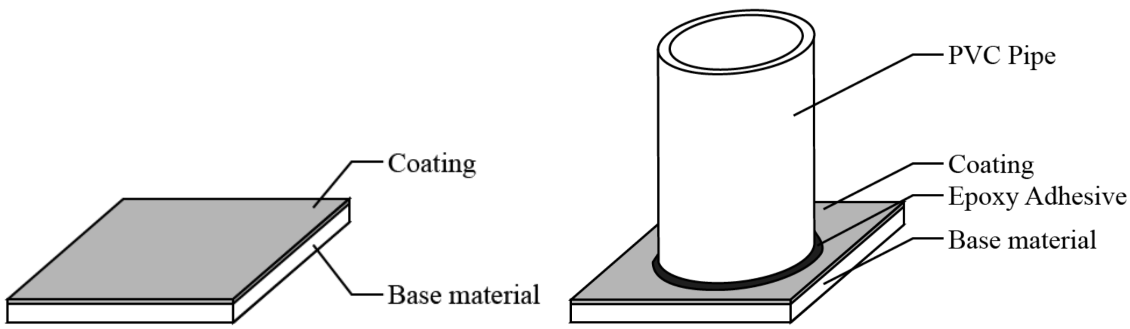

Figure 5. Sketch of sample layout.

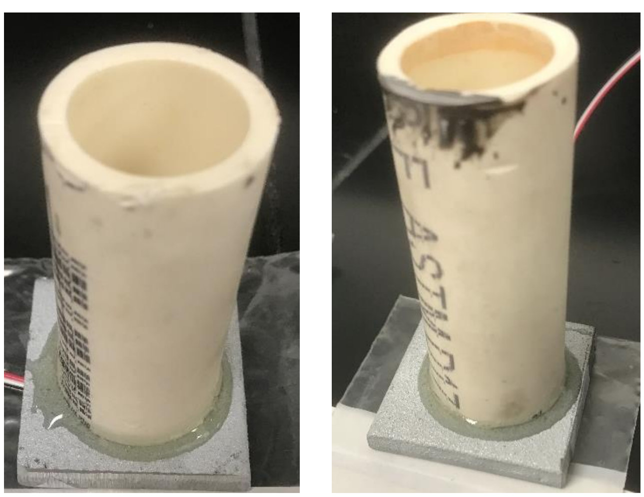

Figure 6. Photos of samples before electrochemical test (left: Sample #1; right: Sample #2).

Accelerated electrochemical corrosion test was carried out with a Gamry Reference 600 Ptentiostat/Galvanostat/ZRA instrument. Figure 7 shows the detailed layout of samples, instruments, and their connection in between. As mentioned before, 3.5wt% NaCl solution was filled in PVC pipe as electrolyte. Working electrode was first connected to a generic electric wire, and the wire was attached to the bottom side of sample for better connectivity (due to thickness of the samples, clips of working electrode cannot be applied to samples directly). Platinum was used as inert metal, and AgCl with KCl solution were used in reference bar. The reference bar was calibrated before test. White tapes were used to avoid reference bar and inert metal touching each other. For each sample, one Tafel test and one polarization test were conducted. The real picture of accelerated electrochemical corrosion test set-up in this study is shown in Fig. 8.

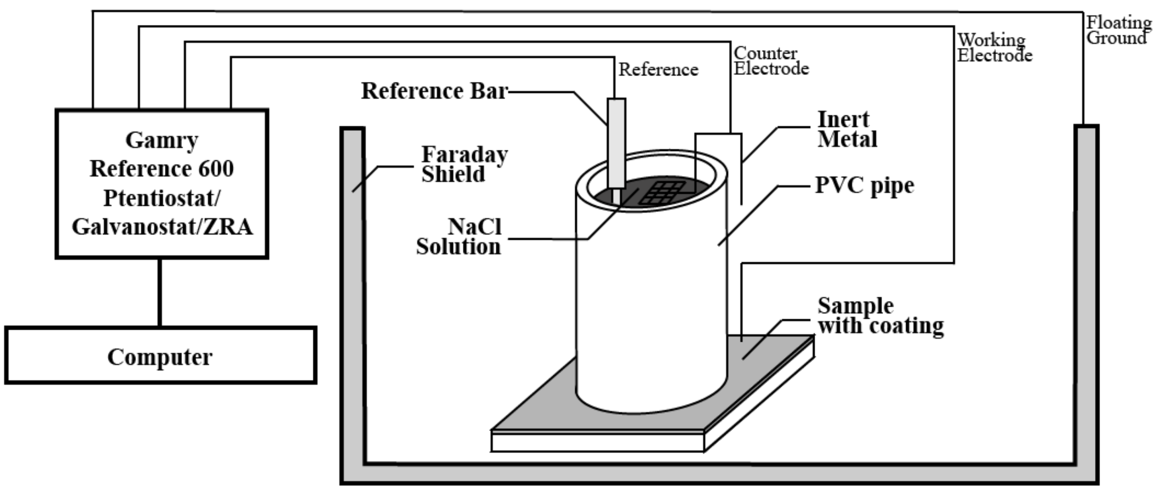

Figure 7. Sketch of the accelerated electrochemical corrosion test setup

Figure 8. Photo of Accelerated electrochemical corrosion test setup.

3) <u>Corrosion test results for the Al-Zn coated steel substrate using wire arc spraying technology (Task 2 Subtask 2.3 & 2.4)</u>

Figure 9 shows a general Tafel test result with detailed markers. Tafel curve was drawn by applying an incremental potential (x-axis) over counter electrode and working electrode, and measuring the current (y-axis, in logarithmic scale) in this system. The lowest point of the curve indicated that anodic reaction and cathodic reaction reach an equilibrium. The corresponding potential at that lowest point was open circuit potential or corrosion potential. The curve left to corrosion potential part was cathodic range, and in right side of the graph anodic range could be found. Tafel fit was conducted on the linear part of both cathodic and anodic range. Thus, two straight lines representing cathodic and anodic current should be carried out. The corresponding current to the intersection of these two straight lines is corrosion current. The slope of anodic range (called Tafel parameter A), together with corrosion potential and corrosion current, serve as three major indicators for corrosion resistance in Tafel test. Figure 10 showed Tafel test results of Sample #1 and #2.

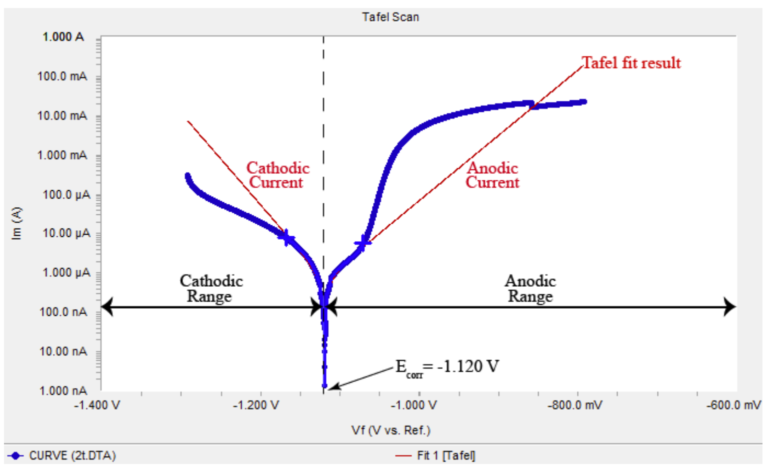

Figure 9. A general type of Tafel curve showing anodic and cathodic range.

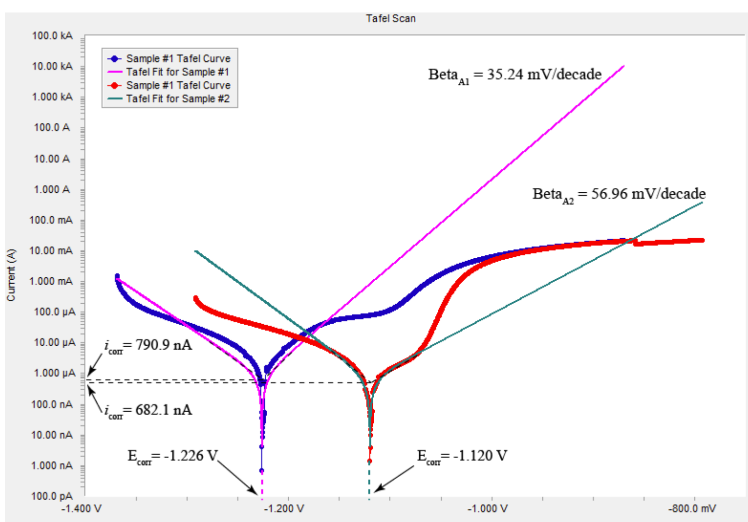

Figure 10. Tafel curve of Sample #1 and Sample #2.

Table 1 listed the corrosion rate of each sample and parameters that contribute to the corrosion resistance. The corrosion rates of both samples were close to each other, which were around 0.11 mpy range.

Table 3. Measured Corrosion Rate and Major Corrosion Resistance Indicators for Coated Samples.

Sample Number	Corrosion Rate (mil per year)	Corrosion Potential (V)	Corrosion Current (A)	Anode Tafel Parameter β_A (mV/decade) $\times 10^{-3}$
Sample #1	0.1151	-1.226	7.90×10^{-7}	35.24
Sample #2	0.0993	-1.120	6.82×10^{-7}	56.96

Figure. 11 compared the Tafel graph of wire arc sprayed Al-Zn coating with other coating materials and the steel substrate material including the previously reported HVOF deposited copper coating and Al-Bronze. It can be seen that in Al-Zn coating the graph shifted to the more negative corrosion voltage (E_{corr}) and lower corrosion current density (I_{corr}) compared to the bare steel sample. This was expected and attributed to higher electronegativity of AL-Zn compared to the substrate which made the corrosion initiation took place at lower potentials. However, effective passivation process could be observed in the anodic part of the Tafel curve attributed to the formation of aluminum oxide protective layer which considerably hindered the corrosion process and resulted in overall corrosion rate of 0.11mpy. Compare to corrosion rate of bare steel (1~1.5 mpy), the arc-wire coating successfully lowered the corrosion rate more than 10 times.

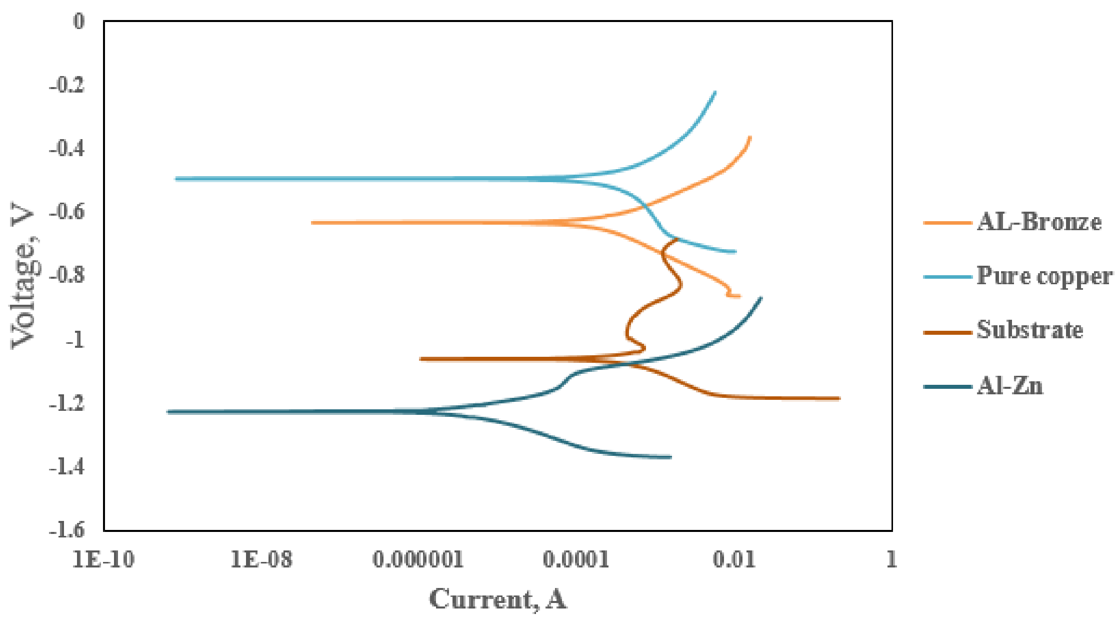

Figure 11. Tafel curves obtained for various thermally sprayed coatings in 3.5% NaCl solution. (The curve obtained from steel substrate is shown for the reason of comparison)

The corrosion parameters resulted from the potentiodynamic polarization test have been listed in Table 4. As it can be seen in this table, Al-Zn coating showed very low value of corrosion current density (I_{corr}=0.736μA/cm^2) and high value of the anodic Tafel constant (46.08×10^{-3}mV/dec) among the other coatings, both of which indicated higher corrosion resistance of this coating. Overall, wire arc sprayed Al-Zn coating possessed the lowest corrosion rate of 0.11mpy among the other materials produced and tested in this study. In an open water system a corrosion rate of around 1 mpy for steel is normal and if it has a corrosion rate of around 10 mpy, action should be taken right away. A corrosion rate of 0.11mpy is well below the concerned rang of corrosion and the coating is able to protect the steel substrate well.

Table 4. Corrosion performance comparison between different coating materials

Material	Corrosion Potential, E_{corr} (mv)	Corrosion Current Density, i_{corr} ($\mu A/cm^2$)	Anodic Tafel Constant, β_a (mV/dec)	Cathodic Tafel Constant, β_c (mV/dec)	Corrosion Rate (mill/year)
Substrate	-1062	638.3	435.4×10^{-9}	104.3×10^{-3}	1.82
Al-Bronze	-632.7	0.641	3.74×10^{-3}	3.39×10^{-3}	0.66
Cu	-495.1	1.956	5.586×10^{-3}	4.923×10^{-3}	0.22
Al-Zn	**-1173**	**0.736**	**46.08×10^{-3}**	**21.3×10^{-3}**	**0.11**

The in-situ investigation on samples before and after corrosion test is shown in Fig. 12 (a) and (b). The Al-Zn coating with 2 mm thickness (Sample # 1) showed strong resistance to corrosion propagation as seen in Figure 12. Corrosion cells could not have a deep penetration from surface into the core of coating.

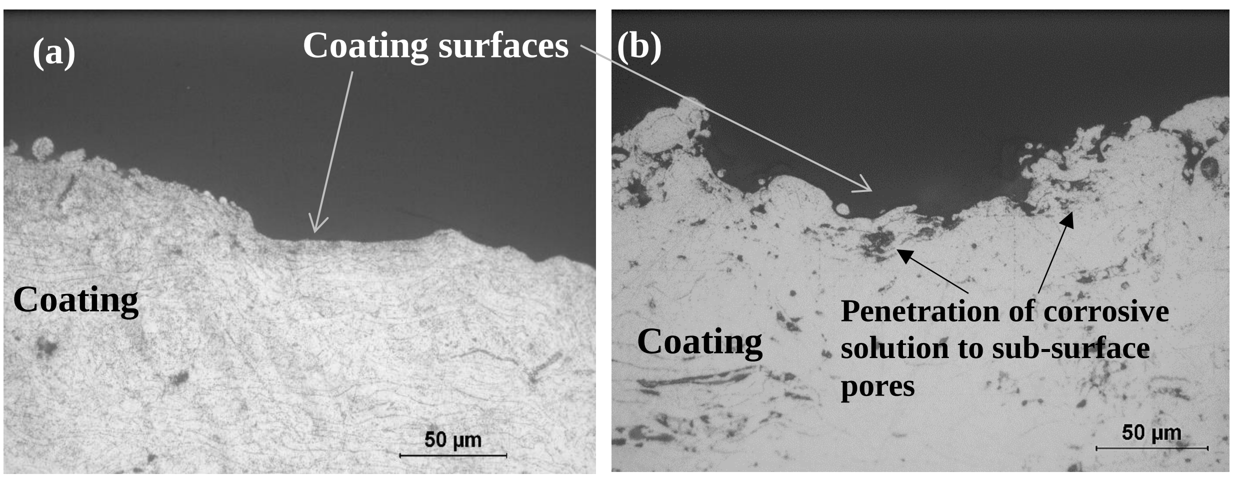

Figure 12. Microstructure of the Al-Zn coating (Sample #1) (a) before and (a) after corrosion test.

The formation of very small pits on the surface resulted by corrosion could be seen from comparison of the micrographs obtained before and after corrosion. As it is mentioned before, corrosive solution could not penetrate into the coating and consequently subsurface was well protected against corrosion. In order to have better estimation of the corrosion products compositions and also depth of the penetration of the corrosive elements (Cl^-), further microstructural characterizations including XRD and EDS are needed to be conducted in the nest step of the evaluations (Task 3.2).

4) <u>Al-Zn Coating thickness design (Task 2 Subtask 2.4)</u>

Since, the unit of 1mpy=0.0254 mm/y, from Tables 3 and 4, the Al-Zn coated sample with 0.1 mm thickness (Sample #2) has a corrosion rate of 0.0993mpy, which yields to 0.0025mm/y. Therefore, a thickness of 0.1mm thin of wire arc sprayed Al-Zn coating on top of base steel material could protect the steel substrate from corrosion for about 40 years. Sample #1 with 2 mm layer of coating has a corrosion rate of 0.1151mpy, which yields 0.0029mm/y. A thicker coating of 2mm wire arc sprayed Al-Zn coating could protect the steel substrate again corrosion for over 690 years if no other external factors such as external damages are to be considered. Thus, for practical application, depends on the design life of the coatings and the pipes in service, the thickness of the coatings can be determined based on the initial expected corrosion rate. For a design service life of 100 years, a thickness of around 0.28mm (280μm) of wire arc sprayed Al-Zn coating is recommended if no sealing technology is applied.

Tables 3 also showed that the thickness of the coating will not significantly influence the corrosion rate of the coatings. However, the measured data in Table 3 does show that a thinner coating (Sample #2) has slightly slower corrosion rate when compared to a thicker coating (Sample #1). Sample #2 which has a thinner coating has slightly better corrosion resistance because: 1) Sample #2 has less corrosion rate; 2) Sample #2 has a corrosion potential closer to zero, which indicates it is more difficult for corrosion formation to initiate on this sample; 3) Sample #1 has a lower corrosion current, which matches the calculated lower corrosion rate, indicating the corrosive chemical reactions have less reaction rate; and 4) Higher Tafel parameter β_A indicates that for each one decade increase in current, it requires more potential or energy, thus the corrosive chemical reaction rate tends to be lower. However, since only less than 15% difference was observed between Sample #1 and #2 and only one pair of samples were tested, we cannot yet conclude that for all arc-wired sprayed Al-Zn coatings, thicker coating yields better corrosion resistance. Thus, average corrosion rate is suggested to use for coating thickness design for practical application for conservative design purpose. More samples will be tested in next quarter to further investigating the influence of various coating thickness and the variance of corrosion rate for designed coatings together with intelligent fiber optic sensors embedded in. The accelerated electrochemical corrosion test and fiber optic sensors will cross-validate each other about the arc-wire coating performance against corrosion.

(c) Description of Problems/Challenges

Effective Materials Selection process, Deposition of Al-Zn coating with optimized properties. We could successfully solve all the problems and issues we ran into in this quarter.

(d) Planned Activities for the Next Quarter

The planned activities for next quarter are listed as below:

1) Optimizing coating thickness design and coating samples with embedded sensors and perform corrosion tests on the samples (Task 2.5);
2) Experiment data analysis of monitored hard and soft coatings coated steel corrosion progress (Task 3.2);
3) Localize corrosion locations on both hard coatings and soft coatings through embedded sensor network (Task 3.2);
4) Corrosion damage characterization (Task 3.2).