

Calcareous deposition on thermally sprayed aluminum surfaces

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ABSTRACT

The formation of calcareous deposits on thermally sprayed aluminum (TSA)-coated surfaces immersed in natural seawater and connected to a cathodic protection system is a recurring issue. Calcareous deposition has occurred even though TSA coatings have a lower cathodic over potential compared with carbon and stainless steels, which should reduce the thermodynamic precipitation driving force. There is at present limited knowledge on the calcareous deposits' formation kinetics on TSA in natural seawater following prolonged exposure at different temperatures. In this study, bare 25Cr super duplex stainless steel (SDSS) and TSA-coated SDSS samples (with and without an silicone-based sealer) were exposed to natural seawater under potentiostatic cathodic protection (CP) and open circuit potential (OCP) conditions at different temperatures (i.e., 20, 35, 60 and 80°C) for 1.5 years. Samples were extracted at various intervals to construct growth kinetics curves under the various test conditions. The deposits were subsequently examined using scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction. Lastly, recommended CP protection potentials and current density values were obtained based on the findings of this study.

Key words: calcareous deposits, cathodic protection, thermal spray coatings

INTRODUCTION

In the oil and gas industry, thermally sprayed aluminum (TSA) coatings are commonly used, primarily, to reduce anode demand in cathodic protection systems and impart some degree of sacrificial protection in the topsides and splash zone areas ¹. The use of TSA coatings has advantages in systems where long service life is required. TSA coatings are also used to reduce the formation of calcareous deposits, normally a combination of CaCO_3 and $\text{Mg}(\text{OH})_2$, on heat exchanger piping, ². While the formation of calcareous deposits reduce the current demands of the cathodic protection (CP) system ^{3, 4}, there are some drawbacks. For example, the formation of calcareous deposits in subsea heat exchanges must be prevented or minimized, due to their low thermal conductivity, which would reduce the heat transfer efficiency.

The goal of this investigation was to quantify the precipitation rate and film characteristics (i.e., calcareous deposit thickness, composition and morphology) on different TSA-coated and bare 25Cr super duplex stainless steel (SDSS) surfaces as a function of temperature in natural Western Australian seawater. Long term tests were carried out on different substrates, namely, bare SDSS, SDSS coated with TSA (99.5% Al), and SDSS coated with a sealed TSA layer at the open circuit potential (OCP) and with a potentiostatic cathodic protection system. The thickness and morphology of the calcareous deposits were investigated at different substrate temperatures. In addition, optimal protection current density and corrosion potential are recommended based on the results.

EXPERIMENTAL PROCEDURE

Tubular SDSS samples—19.05 mm ($\frac{3}{4}$ " in) diameter—with the following sample conditions were tested¹:

- a) Bare samples (**B**),
- b) TSA-coated samples (**TSA**, without sealer),
- c) TSA-coated samples with sealer (**TSA/S**)

The tubes were coated with TSA and TSA with a sealer. Intertherm® 179 was used as the sealer, which is a heat-resistant silicone-based resin. Upon delivery, each tube was cut in two sets of: a) 3 units, 10 mm long and b) 14 units, 50 mm long samples. Short samples were used for as received coating characterisation, and the longer samples were used for the immersion tests.

The tests were carried out in filtered² natural seawater at four different temperatures, i.e., 20, 35, 60, and 80°C. The samples were immersed in four separate 200 L tanks (i.e., one per temperature). The tanks were placed in Curtin University SeaLab and exposed only to artificial light. The external tank's surfaces were painted to maintain maximum darkness inside the tanks. The water in the tanks was continuously replenished at a flow rate of 1.2 L/h, such that all the seawater was replaced every seven days.

A stirrer system was added to each tank—located in the centre of the containers—to maintain a uniform temperature distribution and to provide some degree of water circulation. The rotational velocity of the impellers was set at 60 rpm. Studying the effects of flow velocity was not in the scope of this research. Titanium Gr. 2 shaft stirrers were fixed to the lid with two PTFE supports. The Titanium shafts (1000 mm in length) had a semicircular end to act as a single impeller. The entire shaft was made from the same material in one piece.

Six sample holders per tank with a capacity of six samples each were used, as shown in Figure 1. The samples were positioned vertically inside the tank and held from the 3-inch caps over the lid. The sample holders were made using a tubular-shaped Teflon section with an outer diameter (OD) similar to that of the test coupons. Figure 1 depicts a 3D CAD rendering of a tank setup (without the heating and cooling elements for better visualisation) and the fully assembled sample-holders distribution.

The current density of the samples polarised at $-1.050 \text{ V}_{\text{SSC}}$ was measured during exposure. A rectifier was used to apply the cathodic potential. A voltage divider electrical circuit was used to measure the

¹ Specimen (TSA coated with sealer) with artificially created holiday/defects were also tested but not discussed in this article.

² Seawater was filtered before entering the tanks, to remove suspended solid particles, exclusively.

cathodic current. The circuit allowed for switching the resistor from 1 to 100 Ω to improve the accuracy of the measurements. A 10 Ω resistor was used to measure the current of the polarised samples. For the freely exposed samples, the OCP was recorded against a homemade Ag/AgCl/seawater reference electrode. After the acquisition, the potentials were converted to a conventional Ag/AgCl/KCl saturated reference electrode.

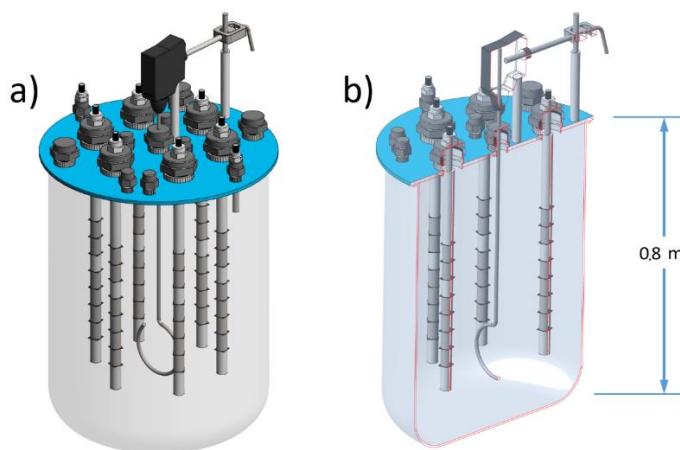


Figure 1: a) Tank design b) cut view.

The gravimetric study was carried out using an analytical balance. The samples' weight was determined before and after exposure to construct the calcareous precipitation rate curve; and was measured together with the wire connectors, before and after sample retrieval. Prior to the measurements, the samples were dried in a convection oven at 40°C for 24 h. This process was repeated until no change in weight was observed. At that point, samples were considered fully dried, and the values were recorded. Light optical microscopy (LOM) and Scanning Electron Microscopy (SEM) coupled with Energy-Dispersive Spectroscopy (EDS) were used to characterise the morphology and the composition of the calcareous deposits. Subsequently, crystallographic XRD measurements were performed with a Bruker D8-Advanced (Bruker, Billerica, MA) using Cu-K α radiation and collecting data over the 2θ range of 0° to 80°.

As shown in Figure 2, about 60% of each sample was mounted in an epoxy resin to protect the deposits located on the outer surface of the tubular specimens. The specimens were then cross-sectioned with a precision cut-off machine. Three 10 mm thick slices were obtained from each tubular sample, Figure 3a. Each slice was wet ground from 80 to 600-grit SiC paper. The specimens were rinsed with ultra-pure water, degreased with ethanol, and then dried with high purity nitrogen gas.

The thicknesses of the deposits over the TSA coatings and that of the TSA layer were measured with a LOM. Dark field images were taken to increase the contrast between the deposit and the mounting resin. Images were taken at different angular orientations to account for the seawater flow. Figure 3b illustrates a schematic of the top view of deposits. In each cross-section, a total of 12 independent measurements and 12 TSA thickness measurements were obtained per coated specimen.

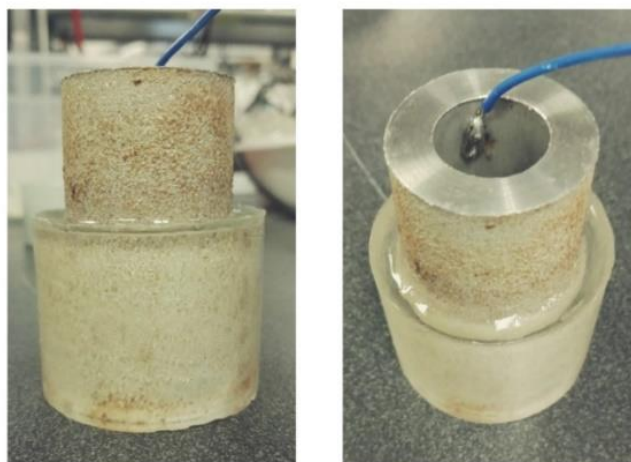


Figure 2: Pipe samples included in resin.

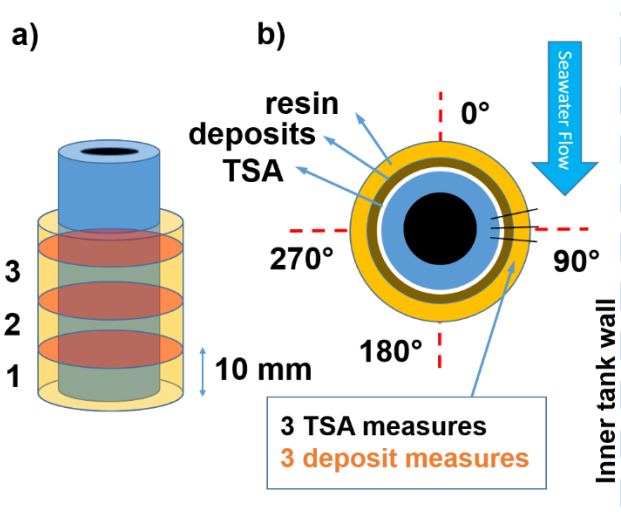
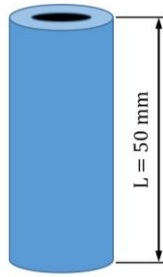


Figure 3: a) Cutting slides scheme b) Measurement scheme (one measurement were taken at 0, 90, 180 and 270° for three transverse slices through the specimen).

Two approaches were used to determine the thicknesses of the calcareous deposits as a function of immersion time, i.e., a) measuring cross sections, b) estimation from weight gain (assuming a constant thickness) using the calculation method give in Figure 4. For this study, we used both methods, but considering the non-homogeneity of the deposits, the deposit thickness values were derived from the overall weight gain and are reported in this paper.



$$Vol_{deposit} = \Delta wt \left[\frac{(1 - \%B)}{\delta_A} + \frac{\%B}{\delta_B} \right]$$

$$Vol_{deposit} = \frac{\pi L}{4} [(OD + x)^2 - OD^2]$$

$$x = 2t = \left\{ \left[4 \Delta wt \left(\frac{(1 - \%B)}{\delta_A} + \frac{\%B}{\delta_B} \right) + \pi L OD^2 \right] \frac{1}{\pi L} \right\}^{1/2} - OD$$

Where: Δwt : weight gain

$\%B$: volume fraction of Brucite

$\delta_A = 2.83 \text{ g/cm}^3$ (Aragonite)

$\delta_B = 2.34 \text{ g/cm}^3$ (Brucite)

OD : bare tube + coating diameter

t : deposit thickness

Figure 4: Calculation of deposit thickness from the weight-gain measurements.

RESULTS

Characterisation of the TSA coating

Figure 5 shows a LOM micrograph of a TSA sample (11A). In the Figure, pores and surface undulations associated with the TSA deposition process can be seen. These features were observed in the remaining samples as well. In this regard, the Direct Comparison procedure (Test Method A) of the ASTM E2109-01 (2014) standard was used to estimate TSA porosity. The analysis revealed that the porosity was between 8 to 10 % percent for both the TSA and TSA/S samples. Overall, TSA-coated samples presented an as received average coating thickness of $188 \pm 55 \mu\text{m}$, while TSA/S samples presented an average thickness of $193 \pm 66 \mu\text{m}$. Details of the measurements are shown in Table 1.

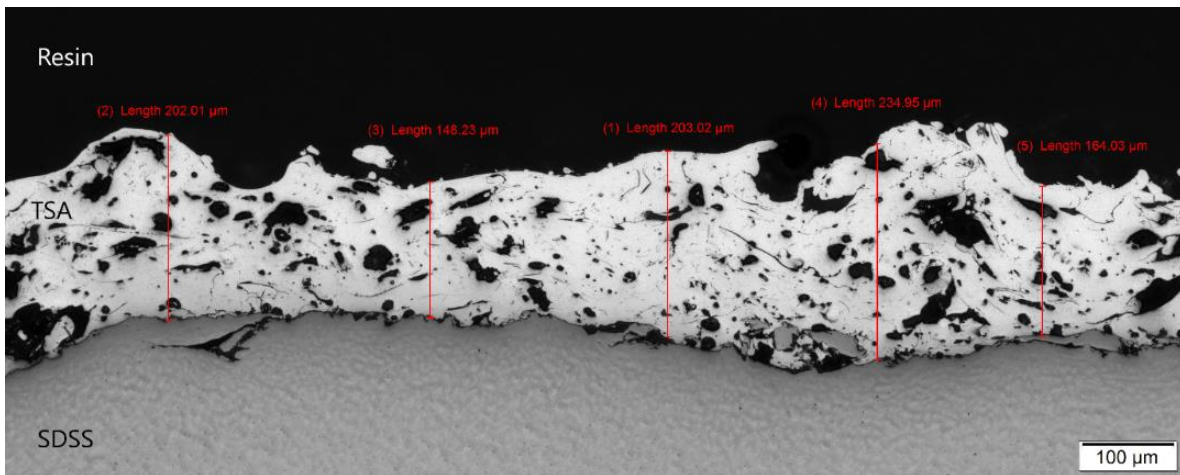


Figure 5: Optical micrograph of sample 11A, showing coating thickness measurements in red.