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Investigations of Corrosion Protection of Natural Gas Pipeline Steel by Al Sacrificial Corrosion Coatings Using Electrochemical Technique

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ABSTRACT

The CO₂ internal corrosion is a major challenge facing the oil and gas industry. In order to protect the pipelines and equipment from the ravages of CO₂ corrosion, novel sacrificial coatings can be used. The objective of this study was to investigate the corrosion behavior of Al-based alloys as sacrificial coatings for protection of pipeline in a CO₂-saturated aqueous electrolyte (3.5 wt.% NaCl) at 4 bar CO₂ pressure (3 barg) and 40 °C. The corrosion resistance of Al-based alloys and thermal spray coatings was evaluated in an electrochemical reaction autoclave (ERAC) using electrochemical methods (potentiodynamic polarization, linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS)). The post-corrosion surface characterization was performed by scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). The obtained data show Al-based alloy demonstrated promising corrosion protection against CO₂ corrosion with no breakaway degradation issues.

Key words: Thermal spray coating, aluminum alloy, anti-corrosion coatings, cathodic protection, sacrificial coatings.

INTRODUCTION

The protection of oil and natural gas infrastructure against internal corrosion is an important issue facing the oil and gas industry. The internal corrosion in natural gas pipeline is primarily due to the presence of the corrosive gases such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), and if ingress occurs, oxygen (O_2), dissolved in the small amount of incidental water such as the water mist carryover after the gas dehydration process¹. While gas composition in natural gas transmission lines is generally agreed to by tariff agreement, Table 1 shows a typical chemical composition of the transmission gas². Liquid water may occasionally occur despite the gas normally being dehydrated to 7 lbs H_2O /MMscf (0.112 mg/l) or lower, done to reduce the risk of internal corrosion and hydrate formation. Upsets in gas dehydration units may release enough water for condensation to be feasible². If water is present, condensed (dewing condition) or associated with deliquescence (hygroscopic condition), the CO_2 , H_2S , and O_2 dissolve therein resulting in internal corrosion of steel pipelines. If the pipeline transporting gas is under a stratified or stratified-wavy flow regime, the top of the line corrosion will occur^{1, 3, 4}. The thin layers of water condensate usually form on the interior of pipe wall due to temperature gradients between the pipeline interior and the soil environment. The thickness of condensed water is very thin; it cannot be seen by naked eye. Another source of water on the internal steel wall is if a hygroscopic material such as salt is present on the steel surface. The presence of the residual salt inside the gas pipeline is due to non-appropriate rinsing of the pipeline after removal of brackish water used as an economical hydrotest medium. If the water content is below the thermodynamic dew point temperature, then a hygroscopic material like salt must be present for water and corrosion to occur.

The US Department of Transport reported numerous case histories of corrosion problems and failures in wet gas pipelines^{5, 6}. Several major fires, explosions, and costly unscheduled shutdowns has been reported because of the severe internal corrosion in the wet gas pipelines. The problems arising from CO_2 corrosion have led to the development of various methods of corrosion control and one of the most practical methods for protection is the addition of corrosion inhibitors⁷⁻¹² and organic coating^{12, 13}. However, the use of a conventional corrosion inhibitor in the gas pipeline is a big challenge because of the small amount of the water that makes the transport of the inhibitor along the pipeline difficult. Most popular polymer coatings used for internal corrosion protection are polyethylene, fusion bonded epoxy, polyurethane and polyamide^{12,13}. The design of an efficient polymer coatings material, which meet the health and environmental requirements, to mitigate internal corrosion is very challenging, due to climate, rate flow and properties of the gas travelling through the pipeline. With the time these polymers became saturated with the acid gases (CO_2 , H_2S and O_2), which lead to unpredictable behavior and corrosion related failures. Also, it has been shown that the pitting corrosion occurred as well when pinholes are present in the organic coating^{15,16}.

In order to solve this problem and protect the gas pipelines and equipment from the ravages of CO_2 corrosion, a novel sacrificial coating can be used. It has been reported that aluminum alloys were used in automobile, aerospace industries and marine structure¹⁷. The corrosion behavior of Al-5Zn-0.02In-1Mg-0.05Ti-0.5Mn (wt. %) alloys in 3.5 % NaCl has been investigated by Ma et al¹⁷. It was found that at initial stage of immersion, pitting corrosion predominate the corrosion around the precipitate MgZn_2 and Al_6Mn . Schmidt *et al.*¹⁸ assessed the corrosion protection performance of seventeen (17) different Zn and Al sacrificial coatings configuration during marine atmospheric exposure at Kure Beach, NC. It was found that the Zn coating by flame spray were more protective than arc spray coatings and the sacrificial performance was improved with the presence of water-based primer/topcoat system. Li et al.¹⁹

investigated the effect of the presence of CO₂ at different concentration on corrosion behavior of aluminum at immersed in deionized water at 50°C. It was found that the presence of CO₂ at concentration of 0.84 µmol/L and pH 4.35 decreased the corrosion rate of aluminum. This may be attributed to the adsorption of HCO₃³⁻ from dissociated H₂CO₃ generated by CO₂ dissolved in water, providing protection and inhibiting the dissolution of the oxide film on the aluminum surface. Figueroa *et al.*²⁰ investigated the effect of the sacrificial coatings (Zn-14%Ni and Al-based Serme Tel 1140/962) on hydrogen embrittlement and re-embrittlement of ultra-high strength steel (AerMet 100, 300M). It was found that the Zn-14% Ni coatings caused the most re-embrittlement compared to Al coatings as they had the most active potential and contained more defects that left the steel exposed to the hydrogen uptake. Corrosion behavior of thermally sprayed aluminum coatings applied on Mg/Al alloys immersed in 3.5 % NaCl has been investigated by Pardo *et al.*²¹. The authors found that the thermal spray aluminum coatings revealed a high degree of porosity and poor corrosion protection, which resulted in galvanic acceleration of the corrosion of the magnesium. Galvanic corrosion property of contacts between carbon fiber cloth materials and A356 aluminum alloy in a 3.5% NaCl solution was also evaluated. It was found that the galvanic corrosion was mitigated by applying oxide coating (plasma electrolytic oxidation (PEO) technique) on aluminum surface²².

Regardless of the large number of sacrificial metallic coatings investigations^{23, 24}, no research has been reported on protection of the oil and gas pipeline from internal CO₂ corrosion using sacrificial coating. The main objective of this study is to investigate the corrosion behavior and understand the mechanism behavior of Al-based alloys as sacrificial coatings for protection of pipeline in a CO₂-saturated aqueous electrolyte (3.5 wt.% NaCl) at 40 °C and 4 bar CO₂ pressure and prove the concept of protection of the carbon steel from CO₂ corrosion using thermal spray coating.

Table 1. Typical Pipeline Gas Specifications ²

Characteristic	Specification
Water content	4–7 lbs H ₂ O/MMscf of gas
Hydrogen sulfide content	0.25–1.0 grain/100 scf
Gross heating value	950–1200 Btu/scf
Hydrocarbon dewpoint	14–40 °F at specified pressure
Mercaptans content	0.25–1.0 grain/100 scf
Total sulfur content	0.5–20 grain/100 scf
Carbon dioxide content	2–4 mol%
Oxygen content	0.01 mol% (max)
Nitrogen content	4–5 mol%
Total inert content (N ₂ + CO ₂)	4–5 mol%
Sand, dust, gums, and free liquid	None
Typical delivery temperature	Ambient
Typical delivery pressure	400–1200 psig

EXPERIMENTAL PROCEDURE

Materials and Chemicals

The chemical composition of the alloys (UNS A91100, UNS A95052, UNS G10180) and UNS G10180 carbon steel coated with the thermal spray coatings (UNS A91350, UNS A95356) is provided in Table 2. The Thermal spray metallic coatings samples were provided by TMS Metalizing Systems (Bremerton WA)[†]. Al alloy (UNS A91350 and UNS A95356) wires were used to prepare the metallic coating using arc thermal spraying method. Carbon steel 1018 (UNS G10180) was used as the substrate for thermal spray coatings. The SEM cross section and EDS mapping analyses for thermal spray coatings and their characteristic are shown in Figure 1 and

Table 3, respectively. SEM images (Figure 1) shows very dense coating surface with a minimum number of pores. It seems that the UNS A91350 coating was more porous than the UNS A95356 (Table 3). The porosity of thermal spray coating was identified by image analysis of the SEM images using ImageJ software. The porosity can be easily detected by image analysis due to the high degree of contrast between the dark pores (voids) and the more highly reflective coating material. The thickness of the coating for the UNS A91350 and the UNS A95356 is 284 μm and 200 μm , respectively. The thermal spray coatings used in this research were not sealed with topcoat layer. The electrolyte was prepared by dissolving 3.5 g of sodium chloride (NaCl) in 96.5 g of deionized water, which was then saturated with CO_2 by sparging with CO_2 .

Table 2. Nominal composition (wt.%) of the tested alloys and the thermal spray coating

Alloys	Elements												
	C	Cu	Cr	Mg	Zn	Mn	P	S	Ti	Si	Ni	Fe	Al
UNS A91100	-	0.13	0.01	0.01	0.01	0.01	-	-	0.01	0.12	0.01	0.51	>99.0
UNS A95052	-	0.004	0.189	2.43	0.007	0.033	-	-	0.013	0.086	-	0.245	Bal.
UNS A91350	-	0.05	0.01	-	0.05	0.01	-	-	-	0.1	-	0.4	>99.5
UNS A95356	-	0.1	-	5	0.1	-	-	-	-	0.25	-	0.4	Bal.
UNS G10180	0.2	-	-	-	-	0.9	0.04	0.05	-	-	-	Bal.	-

Table 3 . Characteristic of thermal spray coating

Coatings	Thickness (μm)	Particle size (μm)	Wire diameter (mm)	Voltage (V)	Current (A)	Porosity (%)
UNS A91350	284	63.5-127	4.7526	32	350	≈ 8.5
UNS A95356	200	63.5-127	3.175	32	300	≈ 8.5

[†] Trade name

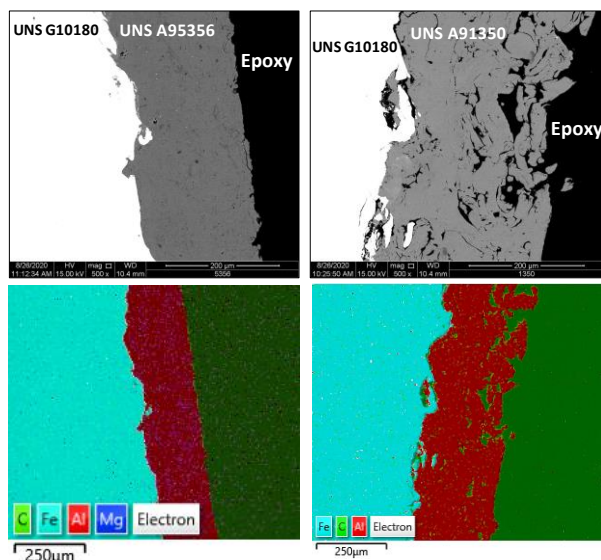


Figure 1: Backscattered SEM micrographs of the Cross-section and EDS mapping analysis of the UNS G10180 coated with thermal spray coatings (UNS A91350 and UNS A95356)

Electrochemical Measurements

In order to investigate the corrosion behavior of aluminum-based alloys in simulated field conditions in natural gas transmission pipeline, the corrosion tests were conducted in a one liter electrochemical autoclave made of Hastelloy® C-276 alloy (UNS N10276) with three electrodes configuration setup (Figure 2). The autoclave is specially designed to investigate an aqueous corrosion at high pressure and temperature. Rectangular specimens made of the alloys shown in Table 2 with an exposure of the area of 1.37 cm² (0.98 cm x 1.4 cm) were used as working electrode. Platinum with KCl/AgCl liquid junction and platinum electrode were used as a reference and counter electrode, respectively. The potential difference between the reference electrode and saturated calomel electrode (SCE) is 48 mV. Therefore, all potentials reported in this study were converted and referred to SCE. Each working electrode were sequentially polished using, 320, 400 and 600 grit silicon carbide paper, rinsed with isopropanol in an ultrasonic cleaner for 2 to 3 minutes and air dried, before the immersion in the autoclave. A volume (0.5 L) of 3.5 wt.% NaCl was introduced in Teflon™ liner that was placed inside the autoclave vessel heated to 40 °C. To eliminate dissolved oxygen, the solution was sparged with CO₂ for 2 hours. After the insertion of the sample, the oxygen in the gas phase was removed by pulling vacuum and back filling with carbon dioxide (CO₂). This procedure was repeated three times to reduce the residual air in the gas phase. The final pressure of CO₂ in the system was achieved by introducing CO₂ to the liquid phase until pressure become stable (4.08 bar). The pH of the measured pressurized solution was around 4 ± 0.1 before and after experiments. Investigation of corrosion behavior of the metallic coating was performed by electrochemical methods using potentiodynamic polarization (PDP), linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS). All electrochemical measurements were conducted after one hour of immersion and after a steady open circuit potential (OCP) was reached. Potentiodynamic polarization curves were recorded from -0.2 V_{vs} OCP up to 1.5 V_{vs} OCP at a scan rate of 1 mV/s. Resistance of polarization R_p was measured using LPR by polarizing the working electrode from -5 mV to +5 mV_{vs} OCP; using a scan rate of 0.125 mV/s. The Tafel value (β_a and β_c) for these experiments were determined by Tafel's extrapolation method. The corrosion current I_{corr} was calculated considering the Stern-Geary assumption (equation 1)²⁵.

$$I_{corr} = \frac{1}{R_p} * \frac{\beta_a * \beta_c}{2.303(\beta_a + \beta_c)} \quad (1)$$

The corrosion rate was calculated using the following equation ²⁶ as follow:

$$CR \text{ (mm/y)} = K * \text{—————} \quad (2)$$

Where *CR* is corrosion rate in mm/y, *K*: conversion factor 3.15×10^8 (24 h/d * 365 d/y * 10 mm/cm * 60 min/h * 60 s/min). *M*: Molar mass of alloys (55.84 g/mol for UNS G10180 and 26.98 for Al alloys). *A*: area in cm². *n*: number of electrons transferred (3 in case of Al alloys and 2 in case of UNS G10180). *ρ*: density of substrate (7.87 g/cm³ for UNS G10180 and 2.8 g/cm³ for Al alloys). *I*_{corr}: corrosion current in A. *F*: Faraday constant: 96485 C/mol. The EIS measurements were carried out over a frequency range of 10 kHz to 10 mHz using an AC amplitude of 10 mV (rms). LPR and EIS data were measured every hour during a total exposure time of 24 hours. Electrochemical measurements were carried out using a Gamry Reference 600+^{††} potentiostat/galvanostat. To verify the reproducibility of the results, all the electrochemical tests were repeated 2 to 3 times. The test matrix is shown in Table 4

Table 4. Experimental matrix for electrochemical tests

Total pressure (bar)	4.08
<i>p</i> CO ₂ (bar)	4
Solution	3.5 wt.% NaCl
Solution temperature	40 °C
Working electrode	UNS A91100 UNS A95052 UNS A91350 UNS A95356 UNS G10180

Surface Analysis

Typically, after 24 h of immersion in 3.5 wt. % NaCl saturated with CO₂, the samples were taken out, rinsed with isopropyl alcohol, dried and the exposed surface was characterized by a scanning electron microscopy (FEI Inspect-F^{††}) and an EDAX energy dispersive X-ray spectroscopy (EDS) system. Imaging was performed at an accelerating voltage of 15 kV using a secondary electron signal (SE) and base scattered electron (BSE) for the cross-section images. Chemical analysis of exposed surface was performed using EDS.

^{††} Trade name